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**ESCUELA TÉCNICA SUPERIOR
DE INGENIEROS DE TELECOMUNICACIÓN**

**Conjugated Polymer Blends for Optical
Gain Applications**

TESIS DOCTORAL / Ph.D. THESIS

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Abbreviations

AFM	Atomic Force Microscopy
ASE	Amplified Spontaneous Emission
BBO	Barium Borate
BT	2,1,3-Benzothiadiazol
CdA	Cellulose Diacetate
CPs	Conjugated Polymers
CT	Charge Transfer
DFB	Distributed Feedback
DSC	Differential Scanning Calorimetry
EBSA	4-Ethylbenzenesulfonic Acid
F8	9,9-dioctylfluorene
F8BT	Poly(9,9-dioctylfluorene-alt-benzothiadiazole)
FRET	Förster Resonant Energy Transfer
FWHM	Full-Width-Half-Maximum
GAFF	General AMBER Force Field
GISAXS	Grazing Incidence Small Angle X-ray Scattering
GIWAXS	Grazing Incidence Wide Angle X-ray Scattering
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
Mn/Mw	Number / Weight-average Molecular Weight
NIL	Nanoimprint Lithography
OPO	Optical Parametric Oscillator
P3HT	Poly(3-hexylthiophene)
PA	Photoinduced Absorption
PB	Photobleach
PCBM	Phenyl-C61-butyric acid methyl ester
PCE	Power Conversion Efficiency

PDI	Polydispersity Index
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate)
PL	Photoluminescence
PLE	Photoluminescence Excitation
PLEDs	Polymer Light-emitting Diodes
PLQE	Photoluminescence Quantum Efficiency
PMMA	Poly(methyl methacrylate)
PMT	Photomultiplier
PS	Polystyrene
QMD	Quantum Molecular Dynamics
SE	Stimulated Emission
SEC	Size Exclusion Chromatography
T3	Terthienyl
TCSPC	Time-correlated Single Photon Counting
TDDFT	Time Dependent Density Functional Theory
TVA	Toluene Vapor Annealing

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Abstract

Conjugated polymers are organic semiconductors which can be processed into thin films following room temperature solution-based methods. Among the wide conjugated polymer family, poly(3-hexylthiophene) (P3HT), has been widely regarded as an archetypical semiconducting electron-donor in bulk heterojunction solar cells, mainly due to its notable exciton and charge transport properties. Conversely, its applications in photonic/lighting devices received little interest owing to its low emission quantum yield in the solid state, related to its large tendency to self-organize into aggregates with highly non-emissive character even upon blending P3HT in a large variety of matrices. Intriguingly, the use of poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT), as host matrix for P3HT leads to blend films with efficient red photoluminescence properties. In this thesis, we shed light into the structure-property relationships of these highly promising conjugated polymer blends. We present experimental and theoretical evidences pointing to the formation of *F8BT:P3HT complexes* involving strong ground state electronic interactions delocalized across adjacent P3HT and F8BT chromophores, accompanied by a large miscibility in blend. Emission in the solid state is entirely ascribed to *F8BT:P3HT complexes* due to the assistance of a highly efficient Förster resonance energy transfer (FRET) process from F8BT chains to *F8BT:P3HT complexes*. Concomitantly, blends experience a significant improvement in photoluminescence quantum efficiency (PLQE) with maxima values approaching 25% (almost a seven-fold efficiency enhancement with respect to neat/aggregated P3HT) and exhibit high optical gain properties in the red part of the spectrum. Accordingly, we investigate the application of F8BT:P3HT blends as emissive media in both polymer light-emitting diodes (PLEDs) and optically pumped lasers with distributed feedback (DFB) structures. Our results open up new prospects for improved photonic properties through appropriate control of inter-chain interactions.

Keywords: Conjugated polymer; Lasers; Structure-property relationships; Blends; Energy transfer; Complex; PLEDs; Distributed feedback.

Resumen

Los polímeros conjugados son semiconductores orgánicos que pueden ser procesados en capas finas a partir de disolución a temperatura ambiente. Entre la amplia familia de polímeros conjugados, poly(3-hexylthiophene) (P3HT) está considerado como un prototipo de polímero donador de electrones, de uso extendido en células solares orgánicas debido fundamentalmente a sus notables propiedades de transporte de carga y excitones. Por otro lado, su aplicación en diodos emisores de luz y dispositivos fotónicos ha recibido poco interés debido principalmente a su bajo rendimiento cuántico de emisión en estado sólido, motivado por la tendencia que tienen las cadenas de P3HT a auto-ensamblarse en agregados tipo H de naturaleza no fluorescente. Esta tendencia a la agregación es visible incluso dispersando P3HT en pequeñas concentraciones en una amplia gama de matrices, (Figura 1(a)). Sorprendentemente, poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT) ha demostrado ser hasta ahora la única matriz que permite aparentemente preservar la emisión de P3HT en estado sólido, habiendo sido demostrados dispositivos optoelectrónicos basados en capas finas mezcla de F8BT y P3HT, tales como diodos emisores de luz y láseres bombeados ópticamente.[1][2] Debida a la mencionada naturaleza agregada de P3HT, la emisión en estado sólido de mezclas de F8BT:P3HT no tiene hasta ahora precedentes. El fenómeno ha sido vagamente atribuido a emisión de cadenas de P3HT aisladas en la matriz de F8BT aunque no ha habido estudios que hayan profundizado en detalle en la naturaleza real de la emisión ni en la relación entre estructura química / morfológica y emisión de esta peculiar mezcla de polímeros. En esta tesis arrojamos luz sobre la intrigantes nanoestructura y las propiedades de emisión de estas mezclas. Nuestros resultados confirman que la emisión de las mezclas no es debida a cadenas aisladas de P3HT en la matriz de F8BT, sino a la formación de un complejo F8BT:P3HT que da lugar a una fuerte interacción en el estado electrónico fundamental caracterizado por deslocalización electrónica en cadenas adyacentes de F8BT y P3HT. Las topografías de las capas de F8BT:P3HT son muy homogéneas y presentamos pruebas espectroscópicas, microscópicas y

calorimétricas que apuntan a una ausencia de cristalización de P3HT en las mezclas, tal y como se ilustra en el sketch de la Figura 1(b). La emisión en estado sólido está enteramente atribuida a complejos F8BT:P3HT. La ausencia de emisión prístina de F8BT es debida a la presencia de una fuerte interacción de tipo Förster (FRET) entre cromóforos de F8BT y complejos F8BT:P3HT. Las mezclas resultantes presentan un rendimiento cuántico de emisión siete veces mayor respecto a P3HT puro, además de notables propiedades de ganancia óptica. En consecuencia, investigamos la aplicación de estas mezclas como medio emisor tanto en diodos emisores de luz como en láseres bombeados ópticamente a través del desarrollo de estructuras de retroalimentación distribuida (DFB).

Figura 1. Absorción de mezclas de (a) poly(methyl methacrylate) (PMMA) y P3HT y (b) F8BT y P3HT en diferentes concentraciones de P3HT. Los esquemas de la dispersión de los polímeros en las mezclas aparecen insertados en los recuadros.

Los resultados de esta tesis se organizan de la siguiente manera:

En el Capítulo 3 exponemos un estudio exhaustivo con métodos experimentales y teóricos de la fotofísica en mezclas de F8BT y P3HT en disolución. Los espectros de absorción y emisión en dispersiones de tolueno indican la presencia de complejos F8BT:P3HT, incluso en condiciones de muy baja concentración de polímero en disolución, en claro contraste con las dispersiones en cloroformo donde la interacción

entre los dos polímeros desaparece, (Figura 2(a-d)). Los cálculos obtenidos a través de métodos computacionales confirman la naturaleza híbrida de los estados electrónicos en dichos complejos. Realizamos un estudio cuantitativo de las condiciones de equilibrio termodinámico subyacentes en las dispersiones a través de valoraciones analíticas combinadas con UV-Vis. Dicho estudio nos permite obtener constantes de asociación K_{eq} en el rango entre 10^4 y 10^5 dependiendo de las condiciones, observando un claro aumento de la constante de asociación con la temperatura, lo cual nos permite confirmar su naturaleza endotérmica. La formación de los complejos F8BT:P3HT es además fuertemente dependiente de la polaridad del disolvente y la longitud de las cadenas de polímero. La característica huella espectral de los complejos (absorción y emisión) es individualizada.

Figura 2. Absorción de F8BT:P3HT en dispersiones en (a) cloroformo y (b) tolueno en distintas concentraciones de P3HT. Fotoluminiscencia de 100% P3HT (triángulos vacíos) y de una dispersión molar de 75% P3HT en F8BT (círculos vacíos) en (c) cloroformo y (d) tolueno. La energía de excitación es 2.4 eV. Las líneas continuas representan ajustes de Frank-Condon en 100% P3HT (negro) y 75% P3HT (rojo). La concentración total de P3HT y F8BT en disolución es de 0.001 mg ml^{-1} ($\sim 0.001 \text{ M}$ monomérico).

En el Capítulo 4, investigamos la fotofísica de capas finas de F8BT:P3HT. En línea con los resultados en disoluciones, la presencia de complejos F8BT:P3HT es claramente distinguible en los espectros de absorción y fotoluminiscencia en capas finas. Observamos una miscibilidad inusualmente grande y obstaculización de la cristalización de P3HT, tal como lo avala la espectroscopia Raman, la microscopía de fuerza atómica (AFM) y la calorimetría de barrido diferencial (DSC). Las cadenas de P3HT adoptan en las mezclas sólidas una conformación con bajo grado de planarización, caracterizada por una longitud de conjugación relativamente corta y una distribución más amplia de las conformaciones de la cadena. Estas propiedades imprevistas de la estructura allanan el camino para el uso de P3HT en aplicaciones fotónicas y de iluminación a través del control apropiado de las interacciones entre cadenas de P3HT. Además, estudiamos la evolución de la nanoestructura de las capas de F8BT:P3HT bajo dos protocolos de recocido posterior al procesamiento en capa: el recocido térmico y el recocido en vapor de tolueno. La redistribución de P3HT y el desmezclado local en muestras recocidas con alto dopaje de P3HT se infieren en los espectros de absorción, fotoluminiscencia, Raman y dispersión de rayos X de ángulo amplio con incidencia rasante.

En el Capítulo 5, arrojamamos luz sobre la interacción FRET entre cadenas de F8BT y complejos F8BT:P3HT en capas finas mediante espectroscopia de absorción transitoria de femtosegundos, observando una transferencia de energía muy eficiente a bajos niveles de dopaje y tasas de transferencia (tiempos) que alcanzan 1.8 ps^{-1} . (0.55 ps) a dopajes de 70% de fracción molar de P3HT. Las propiedades de ganancia óptica de las mezclas se investigan mediante mediciones de emisión espontánea amplificada (ASE), que demuestran una ganancia óptica eficiente en la región espectral del rojo adscrita a los complejos F8BT: P3HT. Además, los valores de umbral de ASE de las capas de F8BT: P3HT se evalúan a partir de dos esquemas de foto-excitación diferentes: foto-excitación de complejos (2.3 eV) y foto-excitación de F8BT (2.7 eV), (Figura 3 (a)). Los dos esquemas dan lugar a ASE en los complejos, bien por excitación directa de los mismos (ASE directo) o bien por excitación de F8BT y transferencia de energía a los complejos (ASE indirecto). En el régimen de baja

concentración de P3HT, observamos grandes diferencias de un orden de magnitud en el umbral de ASE a favor del ASE indirecto, diferencias que se reducen a medida que la concentración de P3HT aumenta. Las eficiencias de ASE obtenidas contabilizando la densidad de fotones absorbidos en condiciones de umbral de ASE indican sin embargo la presencia de pérdidas de excitones en ASE indirecto respecto a ASE directo, (Figura 3 (b)). En las mezclas con las tasas más altas tasa de FRET, las pérdidas de excitones adicionales representan aproximadamente el 20% de la población total de excitones cosechados, pérdidas que probablemente se atribuyen a la fenómenos de aniquilación exciton - exciton. A pesar de las pérdidas observadas, los valores de umbral de ASE más bajos se logran con el ASE indirecto.

Figura 3. (a) Valores de umbral ASE en capas mezcla de F8BT:P3HT en función de la concentración molar de P3HT bajo foto-excitación con 2.7 eV (círculos rellenos) y 2.3 eV (triángulos rellenos). (b) El número de fotones absorbidos a 2.7 eV (cuadrados vacíos) y 2.3 eV (círculos vacíos) y la eficiencia de ASE indirecto (triángulos rellenos) en función de la concentración molar de P3HT.

En el Capítulo 6, investigamos la aplicación de las mezclas F8BT:P3HT como medios emisivos tanto en láseres tipo DFB como en diodos emisores de luz. Los diodos emisores de luz con un 35% de P3HT exhiben la luminancia más alta (además del rendimiento cuántico de fotoluminiscencia más alto) con un color de emisión casi en el rango rojo puro (CIE $x = 0,64$, $y = 0,36$). Desarrollamos cavidades láser DFB altamente transparentes y flexibles adoptando diacetato de celulosa (CdA) como sustrato flexible con nanoestructuras de rejilla impresas en la superficie mediante litografía de nanoimpresión (NIL). Formamos capas finas de F8BT: P3HT de excelente calidad óptica a través de spincoating en sustratos de CdA corrugados con períodos de rejilla predeterminados, dando lugar a láseres DFB con emisión de superficie en el rojo y bajo umbral ($6.63 \cdot 10^{-3} \text{ mJ cm}^{-2}$). La Figura 4 muestra las características de emisión de un láser de F8BT:P3HT con la estructura DFB en un recuadro. La energía de emisión (longitud de onda) puede ajustarse en un rango de 0.1 eV (34 nm) variando el grosor de la película.

Figura 4. Espectros de emisión de un láser DFB de una mezcla F8BT:P3HT con un 45% de concentración de P3HT por encima (línea continua) y por debajo (línea de puntos) del umbral de emisión láser. La foto-excitación se llevó a cabo con impulsos de luz con las siguientes características: 450 nm de longitud de onda, 4 ns de duración y 10 Hz de frecuencia de repetición. El espesor de la película de la mezcla de F8BT: P3HT al 45% fue de 180 nm. La estructura DFB se muestra esquemáticamente en el recuadro.

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Chapter 1. Introduction

1.1 Background

1.1.1 Conjugated polymers

Conjugated polymers (CPs) are linear hydrocarbon chains characterized by the repetition of chemical units (monomers) which are chemically linked by alternating single and double carbon-carbon bonds along the polymer backbone. They combine novel optoelectronic properties, excellent mechanical features (light-weight, ductility and tenacity) and simple cost-effective processing, being investigated as attractive alternatives to inorganic semiconductors. The distinctive semiconducting properties of CPs arise from the alternating single and double bonds through the sp^2 hybridized carbon atoms, leading to a π -electron cloud delocalized along the polymer chain, which is the so-called π -conjugation. Figure 1.1(a) depicts the sp^2 hybridization of carbon, which primarily has the outermost electrons in $2s^2 2p^2$ configuration. One of the two electrons in the $2s$ orbital is promoted to the empty $2p_z$ orbital enabling each orbital in the outer shell to be occupied with a single electron ($2s^1 2p^3$); simultaneously the $2s$, $2p_x$ and $2p_y$ orbitals mix together to generate three identical sp^2 hybrid orbitals. Each sp^2 orbital is composed of $1/3$ s and $2/3$ p , located in the (x, y) plane with coplanar angle 120° . The remaining non-hybridized $2p_z$ orbital lies alone perpendicular to the (x, y) plane. Figure 1.1(b) elucidates the bonding via sp^2 hybridized carbons. Two sp^2 orbitals of adjacent atoms arranged *head-to-head* overlap spatially to form a strong σ -bond. Likewise, the $2p_z$ orbitals of both atoms overlap spatially in a *shoulder-to-shoulder* manner to yield a delocalized π -bond above and below the molecular plane. One simple example of π -conjugation is benzene, as depicted in Figure 1.1(c). Each carbon of sp^2 hybridization forms three σ -bonds with two neighboring carbons and one hydrogen atom. The overlap of non-hybridized $2p_z$ orbitals form a π -bonding ring across the σ -bond plane, enabling π -electrons to be delocalized along the molecule.

Figure 1.1. Schematic illustration of π -conjugation. (a) sp^2 hybridization of carbon. (b) The formation of σ - and π -bonding via sp^2 hybridized carbon atoms. (c) The chemical structure, spatial distributions of σ - and π -bonds in benzene (After Haken et al. [1]).

Symmetric and antisymmetric combinations of the two $2p_z$ atomic orbitals can produce two molecular orbitals, namely π bonding and π^* antibonding orbitals respectively. Among them, the π -bonding orbital has a lower energy associated, being denoted as highest occupied molecular orbital (HOMO), whereas the π^* -antibonding orbital leads to an upper energy level which is referred as the lowest unoccupied molecular orbital (LUMO). The HOMO-LUMO gap is also called optical band gap. The extension of the π -orbital delocalization effectively reduces the optical band gap. In practice, CPs chains are highly disorder strands far from being planar. The rotational freedom around the single bonds leads to a wide distribution of torsional angles which limits the conjugation to rods (chromophores) composed of a limited number of monomers. A direct consequence of the amorphous nature of CPs is that chains adopt a wide range of conformations, therefore leading to a distribution of band gap energies (colors). From the knowledge of Huckle theory and particle-in-a-box principle, which govern the relation between conjugation length and HOMO-LUMO energy difference, the energy bandgap of a given chromophore is

inversely proportional to the number of monomers over which the chromophore is delocalized.

1.1.2 Absorption and fluorescence in CPs

The photophysical processes that occur in CPs following the absorption of light are illustrated by the Perrin-Jablonski diagram in Figure 1.2. Absorption of a photon allows an electron to promote from the ground (S_0) to a singlet excited state S_1 or S_2 with same spin number (the total spin $S = 0$). Following absorption to S_2 , the excited chromophore rapidly relaxes to S_1 via internal conversion, a process that typically occurs on sub-picosecond timescales. During this event the excess of energy deposited is transferred into vibrational modes of the polymer backbone being dissipated as heat. Following this process, several competing processes may start from S_1 . Due to the much larger energy gap between S_1 and S_0 , internal conversion from S_1 to S_0 is less efficient compared to that of S_2 to S_1 . Emission of photons (fluorescence) thus can compete with non-radiative decay, occurring from the lowest vibrational level of S_1 to S_0 (Kasha's rule) with lifetime in the *ps* to *ns* range. Another possible non-radiative de-excitation process involves intersystem crossing from S_1 to the lowest triplet T_1 energy level, a process which is accompanied by spin flip ($S = 1$). Radiative deactivation from T_1 to S_0 (also known as phosphorescence) would require spin inversion, which can be favored through strengthening of the spin-orbit coupling being achieved for instance by introducing heavy atoms in the aromatic structure. Phosphorescence has a much longer lifetime than fluorescence (from μs to *ms*) and is generally shifted to lower energies with respect to fluorescence. Alternatively T_1 may decay non-radiatively to S_0 via phonon emission.

Figure 1.2. Perrin-Jablonski diagram. S_0 , S_1 and S_2 denote the ground, first and second excited singlet states; T_1 denotes the lowest triplet state. Each electronic state is associated with a manifold of vibrational levels due to electron-phonon coupling. Absorption (Abs) are represented by purple arrows, fluorescence (FL) and phosphorescence (PH) by blue arrows, internal conversion (IC) and intersystem crossing (ISC) by green arrows, and thermal relaxation (TR) by red wavy arrows.

The energy and intensity distribution of the vibronic bands seen in the absorption and fluorescence spectra can be further described by the Franck-Condon principle, Figure 1.3. The ground singlet state S_0 and the first excited singlet state S_1 have different equilibrium positions with minima potential displacement. The $S_0 \rightarrow S_1$ transitions are represented by vertical arrows since absorption takes place three orders of magnitude faster (about femtoseconds) compared to vibrational relaxations of the molecule. According to the Franck-Condon principle, there is no displacement of the nuclei (stationary) during an electronic transition. Absorption starts mostly from the lowest vibrational level of the ground state to different vibrational levels of the first excited state. This is because at room temperature thermal energy ($kT \approx 0.026$ eV) is not adequate to overcome the energy of phonons coupled to the electronic states (0.15-0.2 eV). Transitions to higher vibrational levels lead to peaks in the higher energy part of the absorption spectrum. Fluorescence has reversed transitions from the lowest vibrational level of S_1 to different vibrational levels of S_0 state (Kasha's rule), regardless of the excitation wavelength. Transitions to higher vibrational levels of S_0 appear as peaks shifted towards the lower energy part of the emission spectrum.

The relative intensities of the vibronic progressions are determined by the Franck-Condon factor, which describes the probability associated to the different transitions through the wavefunction overlap integral of the initial and final states. The most likely transition is the one that has the largest vibrational overlap integral, (for instance $0 \rightarrow 2$ transitions in Figure 1.3 for both absorption and fluorescence). The transition intensities are given by

$$I_{0-m} \sim \frac{(\hbar\omega)^3 n^3}{m!} S^m e^{-S} \quad \{1.1\}$$

where $\hbar\omega$ refers to the photon energy, n stands for the refractive index of the medium, m denotes the vibronic levels and S is the Huang-Rhys factor, which is in turn defined as

$$S = \frac{k(\Delta Q)^2}{2\hbar\omega} \quad \{1.2\}$$

where k is the force constant, ΔQ accounts for the discrepancy of nuclear configuration coordinates between S_0 and S_1 , and ω is the angular frequency of the phonon mode of energy $\hbar\omega$.

Due to the similarity of vibrational energy spacing in S_0 and S_1 , the emission spectrum often appears to be the mirror image of the absorption spectrum of $S_0 \rightarrow S_1$ (with symmetrical vibronic structure). However, the dissipation of energy by internal conversion or thermal relaxation (or energy migration) in the excited state enables a red-shift of the emission spectrum. The resulting separation between the maximum of the absorption and the most intense emission band is called the Stokes shift. In practice, the amorphous nature of CPs leads to a large statistical distribution of conjugation lengths, which is in turn reflected into inhomogeneous broadening and softening of the vibronic replica in the absorption and fluorescence spectra. This phenomenon manifests less in the fluorescence than in the absorption spectrum since fluorescence proceeds mainly from chromophores with lower energies associated, which narrows down the statistical sampling. Consequently, CPs often exhibit broad absorption bands and vibronically resolved fluorescence spectra.

Figure 1.3. Top: Franck-Condon principle energy diagram corresponding to the ground state and the first excited state. Vibrational levels are favored when they correspond to a minimal change in the nuclear coordinates. The most favoring transitions are shown as $0 \rightarrow 2$. Bottom: The corresponding absorption and fluorescence spectra.

1.1.3 Ground state charge transfer in CPs

Charge transfer (CT) interactions are formed by transferring a fraction of electron charge from a donor to an acceptor site, resulting in a net electrostatic attraction which stabilizes the CT complex. The term electron donor and acceptor refers to different molecules or different parts of a large molecule or a polymer chain. Donor-acceptor association in the ground state gives rise to a ground state CT complex with reorganized molecular levels. The reorganization energy depends on the difference between the acceptor electron affinity (the released energy after an electron filling the LUMO) and the donor ionization potential (the energy required to remove an electron

from the HOMO), adjusted by the resulting electrostatic attraction between donor and acceptor as well as some other resonance contributions. Ground state CT complexes have associated new bands in the absorption and PL spectra. These characteristic bands are referred as CT bands.

In the last decade, ground state CT interactions have been intensively identified in a variety of conjugated polymer based blends.[2][3] Among these, pronounced ground state charge-transfer was found in blends of P3HT with one of the strongest organic acceptor, F₄-TCNQ.[4][5][6] Additionally, evidences for weak CT complexes were reported in CP-fullerene blends.[7][8] Owing to the large delocalization of excited states in conjugated polymer chains, the corresponding charge-transfer complexes exhibit a number of fascinating features with respect to their small-molecule counterparts. The presence of such polymer complexes can modify the blend properties by the way of extending the emission region, altering the blend morphology to facilitate intermixing or enhancing its photo-oxidation stability.

1.1.4 Förster resonance energy transfer in CPs

Förster resonance energy transfer (FRET) is a photophysical interaction which consists on the non-radiative transfer of a photoexcitation from one chromophore (host) to another (guest) of lower energy, provided that the emission spectrum of the host partially overlaps with the absorption spectrum of the guest. The host and the guest chromophores can be located in a single polymer chain, given the energy landscape associated to disorder in CPs, or alternatively in two different polymer chains. In the latter case, the two polymer chains can be identical (homotransfer) or chemically different (heterotransfer). The Förster transfer relies on dipole-dipole electrostatic interactions, without the interplay of emitted photons during the process. The FRET rate is expressed by

$$k_T = \frac{1}{\tau_H^0} \left[\frac{R_0}{r} \right]^6 \quad \{1.3\}$$

where τ_H^0 denotes the fluorescence lifetime of the host in the absence of energy transfer, r is the average distance between host and guest chromophores, and R_0 is the Förster radius defined as the distance at which the probability of energy transfer

equals the probability of exciton host decay ($k_T = \frac{1}{\tau_D^0}$). The characteristic r^{-6} dependence of the FRET rate implies a very efficient interaction at short distances (with FRET lifetimes down to few picoseconds) [9], becoming predominant compared to spontaneous host decay (typically in the 100 ps - 1 ns range) [9][10], but being rapidly attenuated as the distance increases. R_0 stands therefore for the strength of the FRET interaction, which can be calculated from:

$$R_0^6 = \frac{9000(\ln 10)\kappa^2\phi_H^0}{128\pi^5 N_A n^4} \int_0^\infty I_H(\lambda)\varepsilon_G(\lambda)\lambda^4 d\lambda \quad \{1.4\}$$

where κ^2 is a factor that accounts for the relative orientation of host and guest transition dipoles, ϕ_H^0 is the quantum yield of the host without energy transfer, n is the refractive index, N_A is Avogadro's number, $I_H(\lambda)$ is the normalized fluorescence intensity of the host and $\varepsilon_G(\lambda)$ is the molar extinction coefficient of the guest. The integral term clearly illustrates how R_0 is primarily dependent on the spectral overlap between the fluorescence of the host and the absorption of the guest. Values of R_0 in conjugated host:guest systems typically range within 10-80 Å.[9][11][12] For instance, the Förster radius associated to poly(9,9-dioctylfluorene):tetraphenylporphyrin host:guest mixtures was found to be 48 Å.[11] In summary, the efficiency of FRET is determined by the separation between the host and guest, and also the extent of spectral overlap. Given the large spectral gap between the host absorption and guest emission, FRET also contributes to minimize losses due to fluorescence re-absorption. Such losses are important in undoped molecular systems, particularly in those with low Stokes shift associated.

1.1.5 Optical gain in CPs

Optical gain takes place when the photons incident onto a given medium are amplified, i.e. the number of outgoing photons that leave the medium is larger than the total number of incoming photons. This condition typically occurs due to a process called stimulated emission (SE). When light impinges a medium where some electrons occupy upper energy levels, (promoted either by an optical or electrical excitation), incident photons with a particular frequency can stimulate the radiative relaxation of the excited electrons to the ground states, leading to the emission of photons with

frequency, phase and direction identical to the incoming photons. In this case, the incident photon stimulates the emission of a second photon and the light is thus coherently amplified. The coherent nature of stimulated emission is in sharp contrast with spontaneous emission (fluorescence or phosphorescence), where clear de-phasing between absorbed and emitted light occurs. On the other hand, incoming photons can be absorbed by the medium to promote electronic transitions from the ground to excited states, i.e. the opposed process to SE nevertheless governed with same cross sections. The respective rates of SE and absorption at a given energy are given by:

$$\left(\frac{\partial N_1}{\partial t}\right)_{SE} = B_{21}\rho(\nu)N_2 = -\left(\frac{\partial N_2}{\partial t}\right)_{SE} \quad \{1.5\}$$

$$\left(\frac{\partial N_1}{\partial t}\right)_{Abs} = -B_{12}\rho(\nu)N_1 = -\left(\frac{\partial N_2}{\partial t}\right)_{Abs} \quad \{1.6\}$$

where N_1 and N_2 are the number of electrons in the ground and excited states; B_{21} and B_{12} are known as the Einstein B coefficients, accounting for the transition between ground and excited states for SE (downwards) and absorption (upwards), $B_{21} = B_{12}$ and $\rho(\nu)$ is the density of the incident photons at frequency ν . Their relative rate thus depends on the ratio of the number of electrons in the ground state and in the excited state. By adding {1.5} and {1.6}, the net rate of competing SE and absorption is given by

$$\frac{\partial N_1}{\partial t} = B_{21}\rho(\nu)(N_2 - N_1) = -\frac{\partial N_2}{\partial t} \quad \{1.7\}$$

In thermal equilibrium, absorption exceeds SE since the ground state has a larger population with respect to the excited state ($N_1 > N_2$). In order to achieve dominant SE and concomitant net optical gain, a larger population in excited than in ground states is required ($N_2 > N_1$). Such condition, known as population inversion, is necessary to achieve laser action in a given medium. The optical gain coefficient (g) is expressed as the product of the SE cross section (σ) and the population difference ($N_2 - N_1$):

$$g = \sigma(N_2 - N_1) \quad \{1.8\}$$

In practice, population inversion could be realized in a system with at least three or

four energy levels, such is the case in CPs.

Due to the intrinsic electron-phonon coupling of CPs, most of them behave as four-level amplifying system thanks to vibronic splitting, (Figure 1.4). Absorption of light, (transition **a**), excites a chromophore from the lowest vibrational level of S_0 (L1) to a higher level of S_1 (L4), and it then rapidly relaxes to the lowest vibrational level of S_1 (L3), (transition **b**). Emission of light, (transition **c**), subsequently occurs by radiative relaxation into a vibrationally excited level of S_0 (L2), followed by a fast return to L1 (transition **d**). This diagram also explains why the laser emission spectral range is located in the lower energy part of the PL spectrum. Since the lifetime of transition **c** is much longer compared to transition **a**, **b** and **d**, there can be a population inversion readily formed between L3 and L2, even under the condition of low excitation density. Therefore, CPs are optical gain media with characteristic low population inversion thresholds.

Figure 1.4. Four-level laser system characteristic of CPs. S_0 , S_1 denote the ground state and the first excited singlet state. Transition **a** stands for absorption, **c** is radiative relaxation, **b** and **d** are non-radiative vibrational relaxations. L1, L2, L3 and L4 are the relevant energy levels.

In addition to the inherent four-level amplifying system, CPs exhibit several attractive attributes that are relevant to efficient optical gain and lasers. First, CPs have large absorption coefficients evidenced by a thin film of 100 nm thickness being capable of absorbing 90% of the incident light at the absorption peak.[13] The strong absorption indicates a high SE cross section. The characteristic broad PL spectra of CPs translate into wide optical gain windows, enabling to tune SE over a significant spectral range by varying film thicknesses.[14][15] Furthermore, some CPs exhibit high PL quantum

yields (up to 70%), a must condition to achieve efficient lasing.[16] On the negative side, strong inter-chain interactions leading to backbone π - π stacking [17] or inter-chain polaron absorption [18] can be detrimental for lasing. Hitherto, considerable efforts have been done to control intermolecular interactions, by adding for instance bulky side groups to the polymer backbones or by blending CPs in a host matrix to dilute polymer chains.

1.1.6 Host-guest CP blends

Solid host-guest dispersions of CPs can be easily obtained by solution-based methods such as spincoating, dip-coating, spray coating, etc... Such blends offer many opportunities for tuning the electrical, optical, and morphological properties of the pristine polymers. In particular, CP blends containing polymers which are coupled by FRET have been widely exploited for lighting and optical gain applications.[19][20] In a FRET coupled polymer blend we define the CP of higher bandgap with predominant concentration in the blend as host, whereas the low bandgap CP present in low concentrations is denoted as guest. FRET enables to tune spectrally the emission away from the host absorption at very low guest contents, thus reducing self-absorption effects and consequently enhancing emission efficiencies and device performances.[21] Concomitantly, upon effective dilution of the guest species, fluorescence quenching due to inter-chain interactions is suppressed. Also, FRET can be used to tune the emission color by changing the nature or the concentration of the guest polymer.[22][23] The blend film morphology is of paramount importance, yet the required optimized morphologies can be very different depending on the applications. Large degree of CP mixing at the nanoscale level is required in order to optimize host:guest interactions and achieve efficient polymer lasers. On the contrary, blends for solar cell applications must exhibit certain degree of phase separation with controlled characteristic domain size to achieve both efficient charge photogeneration and balanced charge transport. In practice this latter morphology condition is easier to achieve since most CPs blends exhibit low solubility and tend to phase separate in the solid state.[24] This is because polymers have low entropy of mixing (ΔS) due to their

intrinsic high disorder caused by high molecular weights which cannot overcome the positive enthalpy of mixing (ΔH) leading to a positive change in the Gibbs free energy of mixing ($\Delta G = \Delta H - T \cdot \Delta S$) at room temperature. Thus, mixing of polymers in film is typically not thermodynamically favorable. However, the formation of the blend films deposited from well mixed blend solutions is a kinetic process which involves solvent evaporation. By varying the employed solvent (boiling point) and evaporation speed, it is possible to achieve film structures from homogeneous surface topography to de-mixed domains of the two components.[25] Moreover, there are a few examples of miscible polymer blends, where miscibility is the result of certain specific interactions between polymers such as hydrogen bonds or electrostatic attractions,[26][27][28] to reduce the mixing energy. The miscibility of such blends exhibits a dependence on temperature and blend composition.[29]

1.2 Conjugated polymers relevant to this thesis

1.2.1 Poly(3-hexylthiophene) (P3HT)

P3HT is a conjugated polymer that has been widely regarded as an archetypical electron-donor in bulk heterojunction solar cells [30], mainly due to its notable exciton and charge transport properties in the solid state. The chemical structure of P3HT is depicted in the inset of Figure 1.6. The P3HT repetition unit is constituted by a thiophene ring with a hexyl side chain at the 3-position, which is attached to confer solubility to the polymer in organic solvents and also to increase intermolecular spacing, of benefit for some specific applications. The relative arrangements of the hexyl side chains in adjacent thiophene rings can be head-to-head, head-to-tail or tail-to-tail (see Figure 1.5).

Figure 1.5. Head-to-tail (H-T), head-to-head (H-H), and tail-to-tail (T-T) attachments of P3HT monomers. The head and tail are defined as the C atom at the 2-position and 5-position of the thiophene ring, respectively. R represents the hexyl side chain at the 3-position.

Regioregular P3HT is predominantly conformed by stereoregular head-to-tail attachments with hexyl side-chains alternatively distributed along the chain. This particular arrangement provides lower inter-thiophene torsional angles and concomitant enhanced backbone planarity in contrast to other possible arrangements.[31] The percentage of P3HT regioregularity depends on the fraction of head-to-tail attachments in the polymer chain. Unless specified differently in this thesis, hereafter P3HT refers always to regioregular P3HT. The chains have a large tendency to stack in film thereby facilitating P3HT crystallization. The nanostructure of P3HT films is characterized by regions where polymer chains closely π -stack in one direction, (~ 3.8 Å inter-chain distance as determined by X-ray studies) [32], with side chains interlocked (~ 16.5 Å inter-chain separation) in the other direction forming 2D crystalline lamellae.[33] These microcrystalline domains, usually embedded in amorphous P3HT matrix, are responsible for peculiar optoelectronic properties, allowing for two-dimensional charge transport involving intra-chain and inter-chain (along the π -stacking direction) charge diffusion, which manifest for instance, in high field-effect mobilities of the order of $0.1 \text{ cm}^2 (\text{Vs})^{-1}$ [3].

The semi-crystalline nature of P3HT leads to distinctive features in the absorption and PL spectra as shown in Figure 1.6 (a-b). The optical spectra of P3HT in solution are characterized by a broad absorption band (peak at 2.7 eV), and a PL spectrum with peaks at 2.01 eV and 2.16 eV, Figure 1.6 (a), assigned to isolated intra-chain P3HT excitons.[34][35] Films of P3HT show in turn a well-structured bathochromic-shifted absorption spectrum, (Figure 1.6 (b)), with new emerging peaks at lower energies

attributed to weakly interacting H-aggregates.[34] Strong π - π stacking within the lamellae leads to enhanced chain planarity translated into a lower bandgap. The average conjugation length of P3HT is typically 7-10 monomers according to previous reports.[36] The high energy part (above 2.3 eV) of the absorption spectrum has predominant contributions from disorder P3HT regions.[34] The distinctive signatures of aggregates in the absorption spectra have been utilized to determine the relative concentration of aggregates in thin films, the latter being dependent on the specific polymer characteristics (molecular weight, degree of regioregularity) as well as on film processing conditions (solvent, evaporation speed, and annealing) [37]. The photoluminescence spectrum of P3HT films is located in the red spectral range and it is in turn exclusively assigned to weakly emissive aggregates, as confirmed by time-resolved and low temperature PL experiments.[34][38] The same results are found upon selective photoexcitation of the amorphous areas due to efficient funneling of excitons from disordered into aggregate-rich areas in ~ 3 ps, as measured with pump-probe experiments.[39] The emission quantum yield of P3HT aggregates is very low, it scarcely reaches 4% [40], which limits the application of P3HT to photonic/lighting devices. Furthermore, the spectroscopic aggregate signatures are preserved even upon dispersing P3HT chains in a wide variety of matrices, such as for instance poly(methyl methacrylate) (PMMA) [41], polystyrene (PS) [42] or phenyl-C61-butyric acid methyl ester (PCBM) [43], even at low P3HT contents. It has been recently shown by Sepe et al. that lamellar crystallization of P3HT remains unperturbed in some polymer matrices, the latter being segregated as amorphous domains that fill P3HT inter-lamellar space.[44]

Figure 1.6. Normalized absorption and PL spectra of P3HT in (a) highly diluted solution, and (b) thin films spun from toluene. The chemical structure of P3HT is shown as an inset in (b).

1.2.2 Poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT)

The chemical structure of F8BT is depicted in Figure 1.7 (a). It is a fluorene-based conjugated copolymer with alternating 9,9-dioctylfluorene (F8) and benzothiadiazole (BT) units. F8BT has been widely applied as active component in light-emitting diodes [45][46], field-effect transistors [47] and photovoltaic cells [48][49], owing to its highly luminescent properties (PL quantum yields $\sim 60\%$) [10] and notable charge (electron) mobilities. The F8BT polymer chain conformation and packing structure in films have been previously characterized.[50] Regarding F8BT chain conformation, Donley et al. proposed that the adjacent F8 and BT units are twisted with large torsion angles, as supported by Raman studies and quantum chemical calculations.[50] In thin films, F8BT chains have a tendency to form some ordered regions with respect to the

majority of amorphous matrix. In these ordered F8BT, the chains π -stack in the direction normal to the substrate with inter-chain distance of 4.18 Å as determined by X-ray measurements [50], shown in Figure 1.7 (b). For in-plane packing a great amount of BT units in neighboring chains are adjacent to one another, as shown in Figure 1.7 (c). Owing to strong electron localization on the BT units [51], inter-chain electron transport along adjacent BT units is promoted, resulting in a relatively high electron field-effect mobilities of the order of $10^{-3} \text{ cm}^2 (\text{Vs})^{-1}$. [50][47] Upon annealing, the in-plane arrangement of F8BT chains changes into a new configuration where the F8-BT torsion angles are reduced and the BT units in neighboring chains are kept further apart ($\sim 5.3 \text{ Å}$ inter-chain spacing) [50], (Figure 1.7 (d)). Accordingly, a concomitant reduction in electron field-effect mobilities in F8BT annealed films is followed. Similar chain packing behavior and charge transport effects are observed upon reducing F8BT molecular weights.

Figure 1.7. (a) The chemical structure of F8BT. (b) The orientation of F8BT chains with respect to the substrate with the π -stacking direction represented by the arrow. Here the F8 and BT units within a single chain are considered as coplanar for simplicity. (c-d) Schematics of F8BT in-plane packing structures in pristine and annealed (or low molecular weight) films, respectively. (Figure 1.7 (b-d) after Donley et al. [50]).

F8BT has demonstrated to be an efficient optical gain medium in optically pumped lasers and waveguides.[10][52] It exhibits a SE cross section of $7 \times 10^{-16} \text{ cm}^2$ and a high net gain of 22 cm^{-1} in thin film [10]. The absorption spectrum of F8BT film is characterized by a strong absorption band at 2.7 eV, and the PL spectrum shows two main emission peaks at 2.3 eV (0-0) and 2.2 eV (0-1) in the green-yellow spectral range, (Figure 1.8). The lasing wavelength coincides with the 0-1 vibronic peak of the PL spectrum and can be tuned in the 2.2 - 2.1 eV range.[52] Furthermore, F8BT has been employed as host matrix in FRET coupled host:guest CP blends for the development of efficient red lasers with reduced optical pumping thresholds and optical losses.[53][54]

Figure 1.8. Normalized absorption and PL spectra of F8BT in thin film spun from toluene.

1.3 Scope of the thesis

The applications of P3HT in photonic and display devices received little interest owing to its low emission quantum yield in the solid state, related to its large tendency to self-organize into crystalline lamellae with highly non-emissive character. The strong inter-chain interactions due to aggregation cannot be alleviated by blending P3HT in a wide range of passive and emissive polymer matrices even at the lowest contents. Intriguingly, the use of F8BT as host matrix for P3HT chains in blends has shown to be accompanied with efficient red emission properties which have been previously exploited for the development of efficient organic light-emitting diodes

(PLEDs) and optically pumped lasers.[40][54] Owing to the large tendency of P3HT to self-organize into aggregates even in matrix, this result is completely unprecedented. The effect has been vaguely ascribed to emission from isolated P3HT strands in F8BT but no further studies have focused on exploring the real nature of the emission and the structure-property relationships of these highly interesting blends in more detail. In this thesis, we shed light into the intriguing nanostructure and emission properties of these blends. In contrast to the general understanding, our results support that the efficient solid state red emission in F8BT:P3HT blends is not related to emission of P3HT single chains effectively dispersed in F8BT but due to the formation of *F8BT:P3HT complexes* involving strong ground state interactions and electronic delocalization across adjacent P3HT and F8BT chromophores. Remarkably, we find that F8BT:P3HT blend topographies are highly homogeneous and P3HT crystallization is apparently absent. Emission in the solid state is entirely ascribed to *F8BT:P3HT complexes* enabled by a highly efficient FRET from F8BT to *F8BT:P3HT complexes*. Blends possess notable PL quantum yields approaching 25% (almost a seven-fold efficiency enhancement with respect to neat P3HT) and high optical gain properties in the red part of the spectrum. Accordingly, we investigate the application of F8BT:P3HT blends as emissive media in both PLEDs and optically pumped lasers with distributed feedback (DFB) structures. The thesis is organized as follows:

In Chapter 2, we provide a description of the materials, sample preparation methods as well as the characterization techniques employed in this thesis.

In Chapter 3, we perform a comprehensive experimental and theoretical investigation on the photophysics of mixtures of F8BT and P3HT in solution. We demonstrate that ground state *F8BT:P3HT complexes* form even under very high dilution conditions. The underlying equilibria and thermodynamic conditions of the complexation are quantitatively determined by titration experiments. *F8BT:P3HT complex* formation is observed to be strongly dependent on solvent polarity and polymer chain length. Moreover, the characteristic absorption and fluorescence spectra of the *F8BT:P3HT complexes* are singled out. Quantum chemical calculations allow us to unravel the

hybrid electronic nature of such complexes.

In Chapter 4, we investigate the photophysics of F8BT:P3HT blend films. In line with the results in solution mixtures, the presence of *F8BT:P3HT complexes* are clearly distinctive in the absorption and PL spectra in blend films. We observe a large degree of miscibility in blends and hindering of P3HT crystallization, as supported by Raman spectroscopy, atomic force microscopy (AFM) and differential scanning calorimetry (DSC). Comparative studies substituting F8BT by a 3-units oligomer or by PMMA are performed to elucidate the role of F8BT molecular weight on blend morphology and optical properties. Furthermore, we study the evolution of F8BT:P3HT film nanostructure under two post-processing annealing protocols, thermal annealing and toluene vapor annealing, by adoption of absorption, photoluminescence, Raman and grazing incident wide angle X-ray scattering.

In Chapter 5, we shed light into the efficient FRET interaction between F8BT and *F8BT:P3HT complexes* in blends by aid of femtosecond transient absorption spectroscopy. The optical gain properties of blends are investigated by amplified spontaneous emission (ASE) measurements, demonstrating efficient optical gain in the red spectral region attributed to *F8BT:P3HT complexes*. Upon direct photoexcitation of F8BT or *F8BT:P3HT complexes* we quantitatively determine the FRET contribution to ASE as well as competing exciton losses in blends. The corresponding density of absorbed photons at threshold conditions obtained following direct F8BT or *F8BT:P3HT complexes* pumping are compared to determine the respective ASE efficiencies.

In Chapter 6, PLEDs and DFB lasers based on F8BT:P3HT blends are fabricated. We develop highly transparent and flexible DFB laser cavities adopting cellulose diacetate (CdA) as flexible substrate with grating nanostructures imprinted on the surface. F8BT:P3HT blend films are spin-coated on the corrugated CdA substrates with pre-determined grating periods, giving rise to low-threshold surface-emitting DFB lasers with red emission.

Finally, in Chapter 7, conclusions and future outlooks are presented.

Chapter 2. Experimental Methods

2.1 Materials

This section concisely describes the characteristics of the materials investigated in this thesis, comprising light-emitting π -conjugated materials, the optically passive polymer matrix, and materials for electrical devices and photonic cavities. All the materials were used as received.

2.1.1 Light-emitting π -conjugated materials

2.1.1.1 Poly(3-hexylthiophene) (P3HT) and terthiophene (T3)

P3HT was purchased from BASF (Sepiolid P200). The relevant molecular weights (M_n and M_w) and polydispersity index (PDI) are 14.0 kg mol^{-1} , 34.6 kg mol^{-1} and $\text{PDI} = 2.48$, respectively. The regioregularity (ratio of head-to-tail to head-to-head conformers) is exceeding 98%. Terthienyl (T3) is a three units oligothiophene ($M_n = 0.248 \text{ kg mol}^{-1}$) supplied by the group of Dr. Mariacecilia Pasini at Istituto per lo Studio delle Macromolecole, (Consiglio Nazionale delle Ricerche) (Italy). The chemical structures of P3HT and T3 are displayed in Figure 2.1(a-b).

Figure 2.1. Chemical structures of (a) P3HT and (b) T3.

2.1.1.2 Poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT)

Five batches of F8BT with different molecular weights are classified and named (from high to low molecular weight) as H1-F8BT, H2-F8BT, L1-F8BT, L2-F8BT and

L3-F8BT, respectively. Their associative molecular weights (M_n , M_w , PDI) are determined with Size Exclusion Chromatography (SEC) and summarized in Table 2.1. Herein, H1-F8BT and H2-F8BT were provided by American Dye Source and Solaris, respectively. The low-molecular-weight F8BTs were delivered by the group of Prof. Jorge Morgado at the University of Lisbon, (Portugal). Figure 2.2 shows the chemical structure of F8BT.

Name	Molecular weights (M_n , M_w , PDI)
H1-F8BT	33.0 kg mol ⁻¹ , 217.8 kg mol ⁻¹ , 6.6
H2-F8BT	8.4 kg mol ⁻¹ , 16.8 kg mol ⁻¹ , 2
L1-F8BT	8.0 kg mol ⁻¹ , 15 kg mol ⁻¹ , 1.9
L2-F8BT	1.8 kg mol ⁻¹ , 2.3 kg mol ⁻¹ , 1.3
L3-F8BT	1.5 kg mol ⁻¹ , -, -

Table 2.1. Molecular weights of F8BTs.

Figure 2.2. Chemical structure of F8BT.

2.1.2 Optically passive polymer matrix

2.1.2.1 Poly(methyl methacrylate) (PMMA)

PMMA with chemical structure as depicted in Figure 2.3 was supplied by Sigma Aldrich. The molecular weights (M_n and M_w) and polydispersity index (PDI) of PMMA are 10.4 kg mol⁻¹, 10.9 kg mol⁻¹, PDI = 1.05, respectively.

Figure 2.3. Chemical structure of PMMA.

2.1.3 Materials for electrical devices and photonic cavities

2.1.3.1 Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)

PEDOT:PSS is used as hole-injecting material in the fabrication of polymer light-emitting diodes, (Figure 2.4(a-b)). PEDOT:PSS was provided by Sigma Aldrich. The PEDOT content is 0.5 wt.% and PSS content is 0.8 wt.%. The conductivity is 1 S cm^{-1} and the resistivity is $200 \text{ } \Omega \text{ sq}^{-1}$.

Figure 2.4. Chemical structures of (a) PEDOT and (b) PSS.

2.1.3.2 Cellulose diacetate (CdA)

CdA is selected as substrate to fabricate flexible all-polymer DFB lasers, Figure 2.5. CdA foil (refractive index $n=1.49$) of $300 \text{ } \mu\text{m}$ thickness with flat surface was provided by Clarifoil, Celanase, UK.

Figure 2.5. Chemical structure of CdA.

2.2 Methods

In this section, we primarily address the protocols for preparation of samples, either

polymer solution mixtures or blend films, as well as the characterization techniques employed to investigate the optical and morphological properties of the samples.

2.2.1 Sample preparation

2.2.1.1 Polymer mixtures in solution

For solution measurements, binary polymer mixtures with 10^{-3} - 10^{-1} mg ml⁻¹ total polymer concentration were typically prepared upon mixing separated master solutions of each polymer (bearing both same polymer weight per volume) in different weight ratios, and stirring moderately for hours at 50°C. In some cases, mixtures of solvents in different volume ratio were employed to study the effects of solvent polarity on absorption and photoluminescence, (see Chapter 3.1.2). Spectroscopic characterization in solution involved the use of 1 mm optical path quartz cuvettes.

2.2.1.2 Spin-coated blend films

For thin film deposition, mixed solutions of both compounds were normally prepared in different weight ratios at a total polymer concentration of 20 mg ml⁻¹ (from toluene) or 15 mg ml⁻¹ (from chloroform). After vigorous stirring at 60°C (for toluene) or 50°C (for chloroform) overnight, the solutions were subsequently spin-coated on pre-cleaned quartz substrates at 2000 rpm for 1 minute, with the acceleration set at 12000 rpm s⁻¹, (Laurell WS-400A-6TFM/LITE Spincoater). The thickness of F8BT:P3HT blend films, measured by a Bruker Dektak profilometer, varied from 90 to 100 nm depending on the blend composition.

2.2.2 Relevant characterization techniques

In the following we describe all the experimental setups employed to characterize the samples in this thesis. All the experimental characterization was carried out at IMDEA Nanociencia unless specified differently.

2.2.2.1 Steady state absorption spectroscopy

Absorption measurements in solutions and films were normally performed on a Cary 50 UV-Vis spectrophotometer (Varian/Agilent), equipped with a xenon pulsed lamp, a

double beam Czerny-Turner monochromator and dual silicon photodiodes. The monochromator grating ranged from 190-1100 nm with 1.5 nm fixed spectral bandwidth. A baseline correction was recorded before the sample measurement by using a quartz cuvette filled with same solvent (for solution characterization) or a clean quartz substrate (for film characterization). Typical absorbance values from dilute solutions (10^{-3} - 10^{-1} mg ml⁻¹) measured using a 1 mm quartz cuvette ranged between 0.01 and 1. Temperature-controlled UV-Vis titration experiments of F8BT:P3HT, (refer to Chapter 3.4), were carried out on a Cary 5000 UV-Vis-NIR spectrophotometer (Varian/Agilent), equipped with a Cary 6 x 6 Peltier-Thermostatted Multicell holder in conjunction with temperature probe and controller. The temperature can be measured in the range from -10 to 100 °C with a ± 0.3 °C temperature accuracy.

2.2.2.2 Steady state photoluminescence (PL) and photoluminescence excitation (PLE) spectroscopy

PL and PLE measurements in solutions and films were carried out with a FluoroMax-4 spectrofluorometer (Horiba). The FluoroMax-4 comprises a continuous Xenon arc-lamp, two Czerny-Turner monochromators for excitation and emission, a photomultiplier (PMT) and a reference silicon photodiode. The gratings in both monochromators contain 1200 grooves mm⁻¹ with blaze wavelengths at 330 nm (excitation) and 500 nm (emission). The typical slit width set at 0.5 mm corresponds to 2 nm spectral resolution. PL spectra were measured by setting the excitation grating at a fixed excitation wavelength and scanning the detection grating, while PLE detected at the maximum of emission involved the opposite operating configuration. In both types of measurements, the fluorescence intensity was optimized to be in the 10^5 - 10^6 counts s⁻¹ range, which provides enough signal-to-noise while keeping below the saturation of the photomultiplier. Optimization involved adjusting the excitation incident angle respect to the sample (cuvette or substrate) as well as adjustment of the slit widths whilst maintaining sharp-enough spectral resolution.

2.2.2.3 Femtosecond pump-probe transient absorption spectroscopy

The energy transfer dynamics in F8BT:P3HT blends were studied with adoption of pump-probe transient absorption experiments. Figure 2.6 depicts the experimental set-up. A Clark MXR femtosecond laser equipped with a regenerative amplifier (CPA-2101) was used as primary source delivering 120 fs pulses at 775 nm and 1 KHz repetition rate. The primary beam was split into pump and probe beams by a 20:80 R:T beam splitter, (see the red arrows in Figure 2.6). The beam with lowest fraction of energy (pump) was then sent onto a 0.5 mm thick β -Barium Borate (BBO) crystal to obtain second harmonic generation (387.5 nm), (see the blue arrows in Figure 2.6). This process led to conversion of approximately 30% of fundamental photons, the residual 70% being notch filtered after passing through the crystal. Afterwards, the pump beam was sent onto a computer assisted delay line to control the time arrival of the pump to the sample, mechanically chopped at 500 Hz, (i.e. one pump pulse every two was blocked), and subsequently focused onto the sample, (typical fluences were in the 0.01 - 0.1 mJ cm⁻² range). The fraction of photons transmitted through the beam splitter (probe) was focused on a 2 mm sapphire plate to generate a supercontinuum from 420-1600 nm by self-phase modulation. The supercontinuum beam was collimated and focused with a pair of spherical concave mirrors on the sample on a spot spatially overlapped with the pump beam, (see the grey lines in Figure 2.6). A fraction of the probe was ultimately split off before passing through the sample which aimed as reference beam. A prism spectrometer, (Ingenieurbüro Stresing), equipped with two double superposed Si-InGaAs array detectors for VIS and NIR operating at single shot was employed to monitor the transmitted probe light through the sample (signal beam) and the reference beam. Both channels allowed for single-shot acquisition of pump-induced changes in the absorbance of the sample at fixed delay times. The temporal evolution of these changes was recorded by controlling the time delay between pump and probe pulses. This required synchronization of the signal acquisition with the motorized delay stage. Measurements were performed with pump-probe polarization at magic angle (approximately 54.7°). Samples were placed on a vacuum chamber (10⁻² mbar) during measurements.

Figure 2.6. Schematic representation of femtosecond pump-probe spectroscopy experimental setup.

The pump pulse is absorbed by the sample generating excited states. Then the delayed probe pulse impinges on the sample and tracks the pump-induced changes. The measured pump-induced change in probe transmission (ΔT) normalized by the transmission of reference probe (T) describes all possible electronic transitions between i and j and is given by

$$\frac{\Delta T}{T} = -\sum_{i,j} \sigma_{ij}(\omega) \Delta N_j d \quad \{2.1\}$$

where $\sigma_{ij}(\omega)$ is the cross section of transition $i \rightarrow j$ at the ω photon energy, ΔN_j is the population change in j , and d is the sample thickness. This equation is derived from the Lamber-Beer law in the small signal limit. $\Delta T/T$ depends on the excitation energy and evolves with time as the population changes. The different ways in which the probe interacts with the pumped sample are depicted in Figure 2.7. When the probe energy is resonant with ground state absorption ($S_0 \rightarrow S_n$), an increase in transmission is followed thanks to the partial depletion of ground states. This effect is known as photobleaching (PB) and it is responsible for a positive $\Delta T/T$ band which barely resembles the absorption spectrum. When the probe energy is resonant with excited state absorption, ($S_1 \rightarrow S_n$, $T_1 \rightarrow T_n$ or $D_0 \rightarrow D_n$ corresponding to the singlet, triplet

and polaron manifolds respectively), probe photons are absorbed by the sample and thus, the transmission of the probe is reduced. This effect is known as photoinduced absorption (PA) and has negative $\Delta T/T$ bands associated. Finally, if the incoming probe photons are resonant with the transition $S_1 \rightarrow S_0$, stimulated emission (SE) may occur giving rise to a positive $\Delta T/T$ band due to more outgoing photons.

Figure 2.7. Schematic diagram of energy levels and transitions monitored with pump-probe. S, T and D refer to singlet, triplet and polarons, respectively. (After Cabanillas-Gonzalez et al. [55])

2.2.2.4 Amplified spontaneous emission (ASE)

The optical gain properties of F8BT:P3HT blends were studied by ASE measurements, (set-up depicted in Figure 2.8). The photoexcitation was provided by a Q-switched Nd:YAG laser which pumped a β -BBO optical parametric oscillator (OPO), delivering pulses of 5 ns at 10 Hz repetition rate. The pump wavelengths were selected at 450 nm and 530 nm, coinciding with the F8BT and P3HT absorption maxima respectively. The excitation fluence incident on the sample was adjusted by inserting neutral density filters into the beam path. A cylindrical lens and a variable slit were used to shape the laser beam into a narrow 400 $\mu\text{m} \times 4$ mm stripe on the sample. At sufficient excitation densities, the emitted photons were amplified by means of stimulated emission. The output signal was collected and sent in free-space configuration to a SP-2500 Princeton Instruments spectrometer (Acton Research) equipped with a liquid N₂ cooled deep-depleted CCD. In addition, for F8BT:P3HT based DFB laser measurements, the pump pulse of 4 ns at 450 nm and 10 Hz was focused using a 30 mm focal length spherical lens with the sample placed out of focus, and the emission was collected perpendicular to the DFB surface.

Figure 2.8. Schematic representation of ASE spectroscopy experimental setup.

2.2.2.5 PL lifetime

PL decay measurements were carried out with time-correlated single photon counting (TCSPC) technique. The excitation was provided by a 405 nm picosecond pulsed diode laser (LDH-D-C-405, PicoQuant) of approximately 80 ps pulse duration and 2 - 40 MHz repetition rate. Samples were typically measured in air conditions. The emission was dispersed with a SP-2500 spectrometer (Acton Research). Acquisition involved single channel photon detection with a PMA-06 (Hamamatsu) photomultiplier connected to a HydraHarp-400 (PicoQuant) time interval analyzer. The decay time fitting procedure was performed by deconvolution of the instrumental response function using a commercial Fluofit software.

2.2.2.6 Photoluminescence quantum efficiency (PLQE)

PLQE values were provided by the group of Prof. Ruidong Xia (Nanjing University of Posts and Telecommunications, China). The measurements were performed with an integrated sphere equipped with a FLSP920 lifetime spectrometer (Edinburgh Instruments) and a 375 nm picosecond laser diode with typical pulse width of 55 ps at 20 MHz repetition frequency. Samples were placed in air conditions during measurements.

2.2.2.7 Raman spectroscopy

Polymer backbone chain conformations were probed with Raman spectroscopy. The measurements were performed with a Senterra II Raman microscope (Bruker), which combines a Raman spectrometer equipped with 532, 633 and 785 nm laser lines and a confocal microscope module (Olympus BX51). The sample was positioned on the stage and excitation was focused with a 20X objective on a spot of c.a. 100 μm^2 . In this thesis all Raman spectra were acquired with a 785 nm excitation, (non-resonant Raman), with 10 mW laser power, 5 s of integration time and a spectral resolution in the 9-15 cm^{-1} . Each Raman spectrum was the result of an average from four consecutive measurements at different positions on the sample. Background was removed with a mathematical tool available on the software (OPUS) acquisition. The Raman signals from quartz substrates and respective matrix were subtracted from the spectra for analysis. The position and full width at half maximum of Raman peaks were obtained by fitting the spectra with Gaussian functions.

2.2.2.8 Atomic force microscopy (AFM)

AFM topography images of P3HT in different matrices were measured using a JPK NanoWizard II AFM working in contact or tapping mode, coupled to a Nikon Eclipse Ti-U inverted optical microscope. Standard Olympus silicon nitride cantilevers of 0.05 N m^{-1} spring constant and 18 kHz resonant frequency were employed in air conditions. JPK SPM data processing software was used for image analysis

2.2.2.9 Differential scanning calorimetry (DSC)

DSC thermal analysis was carried out at Chalmers University (Sweden) in collaboration with Prof. Christian Muller. A Mettler DSC2 calorimeter equipped with a HSS7 sensor and a TC-125MT intra-cooler was employed. DSC heating and cooling thermograms were recorded under nitrogen at a scan rate of 10 $^{\circ}\text{C min}^{-1}$. Peak temperatures were reported for glass transition, melting, crystallization and cold-crystallization.

2.2.2.10 Grazing incidence small / wide angle X-ray scattering (GISAXS / GIWAXS)

GISAXS and GIWAXS have been effectively used to characterize nanostructured surfaces and thin films, benefiting from the surface sensitivity of grazing incidence

X-ray diffraction [56]. They allow probing nanostructures in large areas due to the elongated footprint of the X-ray beam. GIWAXS is especially adapted for identifying surface and thin film morphology on atomic scale, corresponding to the larger scattering angles with respect to GISAXS. In this thesis, we employed GIWAXS to study the crystallinity evolution of F8BT:P3HT blend thin films upon vapor annealing (see Chapter 4.3.2), and GISAXS to characterize the periodic nanostructures of CdA gratings in DFB lasers (see Chapter 6.2.3). The measurements were both performed at the BM26 - DUBBLE Dutch - Belgian beamline at European Synchrotron Research Facility [57]. The energy of X-ray beam was fixed at 12 KeV (1.03 Å). The slits allowed a beam size (horizontal x vertical) of 1.3 x 0.3 mm. A nominal incidence angle of the beam with respect to the sample surface $\alpha_i = 0.35^\circ$ was applied, enabling to average the recorded information over an area of c.a. 70 mm². For GISAXS experiments, a distance between sample and detector of 7322 mm was estimated using a rat tail sample as standard calibration. The 2D scattering patterns from the sample were recorded by a Pilatus1M detector with 172 µm pixel size. In order to verify the periodicity of the gratings and the quality of the polymer replica, sample alignment was required to render the grating lines parallel to the X-ray beam. Compared to GISAXS setup, a FReLoN 2k CCD detector (pixel size 46.4 x 46.4 µm²) was placed in a close distance to the sample enabling the sufficient recording of X-ray scattering at wide angles. The distance between sample and detector in GIWAXS setup was 132 mm, determined with calibration of Al₂O₃ standard. 1D curves of GISAXS and GIWAXS were analyzed by using the FIT2D software.

Chapter 3. Strong Polymer Interactions in Dilute Solutions of F8BT and P3HT.

In this chapter, we identify and characterize the strong F8BT:P3HT ground state charge-transfer interaction present in diluted (10^{-3} - 10^{-1} mM) solutions of F8BT and P3HT. A comprehensive experimental and theoretical investigation has been undertaken on F8BT and P3HT mixtures in two solvents: toluene and chloroform. Unless specified differently, the data displayed in this chapter refers to high molecular weight F8BT, (H1-F8BT) and regioregular P3HT. The study was further extended to investigate analogous interactions in mixtures containing oligomeric compounds, (namely Ln-F8BT and Tn). Hereby, the significant impacts of solvent polarity and polymer chain length on complex formation were highlighted. Furthermore, we quantitatively studied the underlying equilibria and thermodynamics of *F8BT:P3HT complex* in toluene by deployment of absorption measurements in titrated solutions. The absorption spectrum of the *F8BT:P3HT complex* was singled out with photoluminescence excitation and doping induced absorption.

3.1 Optical spectra of F8BT:P3HT mixtures in solution

3.1.1 Absorption and PL

The absorption spectra of F8BT:P3HT mixtures in toluene with P3HT monomer molar concentration comprised between 15% and 70%, (Figure 3.1(a)), are characterized by a broad absorption band centered at around 2.7 eV ascribed to F8BT, (dashed green spectrum in Figure 3.1(a)), which progressively shifts to 2.6 eV as the P3HT concentration is raised. Additionally, a shoulder located around 2.2 eV arises and becomes more prominent with P3HT content. An opposed behavior is found in the high concentration regime (80% to 95%). A gradual blueshift of the main absorption band concomitant with a reduction of the satellite shoulder is observed upon adding P3HT, (Figure 3.1(b)). Based on the absorption spectra of F8BT and P3HT (dashed green line in Figure 3.1(a) and dashed red line in Figure 3.1(b) respectively), we conclude that the 2.2 eV shoulder cannot be ascribed to single spectral contribution. Further insights into the origin of the 2.2 eV shoulder are provided by the ratio between the absorption peaks

at 2.2 and 2.7 eV as function of concentration, (Figure 3.1(c)). The ratio increases gradually achieving a maximum value at concentrations in the 45% - 70% range, i.e. for medium P3HT content, followed by a progressive decrease at higher P3HT content. It thus appears clear that the 2.2 eV absorption peak is associated to a new electronic state related to the presence of F8BT and P3HT moieties.

Figure 3.1. Absorption of F8BT:P3HT toluene solutions with (a) low and (b) high P3HT molar content. The 0 and 100% spectra are shown as dashed green and red lines respectively whereas mixtures with low and high P3HT content appear as solid green and red lines. In both cases the increasing transparency indicates a higher P3HT content. The total polymer concentration is 0.1 mg ml⁻¹ (~0.1 mM monomer concentration). (c) Absorption ratio at 2.2 and 2.7 eV in F8BT:P3HT toluene solutions. (d) Photoluminescence of 100% P3HT (open triangles) and a 75% F8BT:P3HT mixture (open circles) in toluene solutions. Excitation energy was 2.4 eV.

Figure 3.1(d) depicts the PL spectra of a pristine P3HT and a 75% F8BT:P3HT toluene solution upon photoexcitation with 2.4 eV, i.e. close to the 2.2 eV shoulder. The PL spectrum of pristine P3HT has a main peak at 2.17 eV (0-0), with satellite replica at

1.99 (0-1) and 1.81 eV (0-2). The PL spectrum of the 75% mixture is in turn strikingly different, bearing a more pronounced vibronic progression with peaks at lower energies: 2.04 (0-0), 1.87 (0-1) and 1.70 eV (0-2). We exclude here any F8BT contribution to the PL spectrum of the mixture owing to its negligible absorption at 2.4 eV, (see dashed green line in Figure 3.1(a)). Similar to absorption, the PL of F8BT:P3HT solutions cannot be ascribed to single component (F8BT or P3HT) contribution, but it is correlated to a new electronic state associated to F8BT and P3HT.

3.1.2 Influence of solvent polarity.

The effect of solvent polarity on the optical spectra was investigated by substituting a low polar solvent as toluene (0.36 Debye) by chloroform (1.04 Debye). In contrast with toluene mixtures, the absorption spectra in chloroform are given by spectral superposition of F8BT and P3HT in different statistical weights, leading to an absorption spectrum with a maximum around 2.7 eV and a progressive broadening with increasing P3HT content, (Figure 3.2(a-b)). The optical transition at 2.2 eV observed in toluene is absent in chloroform. These differences in absorption have a clear correspondence in the PL spectra.

Figure 3.2. Absorption of F8BT:P3HT in (a) chloroform and (b) toluene solutions with different P3HT molar content. The 0 and 100% spectra are shown as dashed green and red lines respectively whereas mixtures with low and high P3HT content appear as solid green and red lines. In both cases the increasing transparency of the color line indicates a higher P3HT content. The total polymer concentration is 0.1 mg ml^{-1} ($\sim 0.1 \text{ mM}$ monomer concentration).

Figure 3.3(a-b) depicts the PL spectra of a 75% F8BT:P3HT mixture in chloroform and toluene respectively upon 2.4 eV photoexcitation. Whilst the PL spectrum of the chloroform mixture resembles P3HT, the PL spectrum in toluene is clearly different featuring better resolved vibronic bands with energy displacements ($\sim 0.12 \text{ eV}$) that are too large to be simply attributed to a dielectric shifts.[58]

Figure 3.3. Photoluminescence of 100% P3HT (open triangles) and a 75% F8BT:P3HT mixture (open circles) in (a) chloroform and (b) toluene solutions. Excitation energy was 2.4 eV. Straight lines stand for Frank-Condon fits of the 100% (black) and 75% (red) P3HT spectra. The total concentration of P3HT and F8BT in solution is 0.001 mg ml^{-1} ($\sim 0.001 \text{ mM}$ monomer concentration).

In order to establish a quantitative comparison in both solvents, the PL spectra were fitted with a Gaussian superposition of vibronic sidebands with relative intensities given by a Frank-Condon progression [59][60]:

$$I_{0-m} \sim \frac{(\hbar\omega)^3 n^3}{m!} S^m e^{-S} \quad \{3.1\}$$

where $\hbar\omega$ refers to the photon energy, n stands for the refractive index of the medium, m denotes the vibronic levels and S is the Huang-Rhys factor, which accounts for the magnitude of the coupling between the 0- m electronic transition and the phonon mode.

We assumed for all fits predominant coupling to one single phonon mode with Δ associated energy, (the dominant Raman mode of P3HT located at 1445 cm^{-1} (0.18 eV) corresponding to C=C stretching) [61]. The Frank-Condon progression was spectrally convoluted with a Gaussian band of w energy linewidth. A summary of fit parameters is found in Table 3.1.

	0-0 energy (eV)	Δ (eV)	S	w (eV)
P3HT (chloroform)	2.16	0.18	0.93	0.08
P3HT (toluene)	2.17	0.18	0.96	0.08
75:25 (chloroform)	2.17	0.18	0.85	0.08
75:25 (toluene)	2.04	0.17	0.80	0.06

Table 3.1. Parameters extracted from Frank-Condon fits.

From the fit parameters and the similar values found for the 0-0 emission, Δ , and w we infer a clear correlation between the PL spectra of P3HT and 75% F8BT:P3HT mixtures in chloroform. Conversely, the discrepancy found between the P3HT and 75% F8BT:P3HT mixtures in toluene implies that emission cannot be ascribed to P3HT strands. Note that the excitation energy employed (2.4 eV) is located close to the low-energy absorption shoulder observed in toluene solutions at 2.2 eV, so that we ascribe the distinctive absorption and emission features in toluene to common species. Owing to the cooperative role of P3HT and F8BT on the stabilization of the low energy absorption band in toluene, we infer the presence of a *F8BT:P3HT complex*, which involves π - π interactions between P3HT and F8BT chromophores, giving rise to a new electronic state. The dependence of the optical spectra on solvent polarity underlines the role that polar interactions play on the stabilization of the *F8BT:P3HT complex*.

Figure 3.4. (a) Absorption spectra of 75% F8BT:P3HT in solvent mixtures with varying toluene : chloroform volume ratios: 0:1 (black), 0.2:0.8 (red), 0.4:0.6 (blue), 0.6:0.4 (magenta), 0.8:0.2 (dark yellow) and 1:0 (green). (b) PL spectra of same mixtures upon excitation with 2.4 eV. The total concentration of P3HT and F8BT in solution is 0.001 mg ml^{-1} ($\sim 0.001 \text{ mM}$ monomer concentration).

In order to further highlight the interplay of polymer / polymer and polymer / solvent interactions in the absorption and emission properties of F8BT:P3HT solutions, we investigated solvent mixtures of toluene and chloroform in different volume ratios, (Figure 3.4(a-b)). Clearly, both absorption and PL spectra are gradually tuned with solvent polarity. The concentration of *F8BT:P3HT complex* rises as the toluene content increases. Concomitant with the gradual increase in absorption, the PL spectra of mixtures evolves from P3HT towards the sharp emission observed in toluene solutions. These results demonstrate that the emission properties in solution can be partially tuned through appropriate control of the solvent polarity. We shed more light into the

intriguing absorption and emission features of F8BT:P3HT complexes in toluene solutions in the next section.

3.2 Determination of the *F8BT:P3HT complex* absorption

In this section, we try to single out the absorption spectrum of the *F8BT:P3HT complex* in low doping dilute mixtures by two spectroscopic approaches: doping induced absorption and photoluminescence excitation.

3.2.1 Doping induced absorption

3.2.1.1 The derivation of *F8BT:P3HT complex* absorption

Upon addition of a very small amount of P3HT into dilute F8BT toluene solution, the process sketched below as {3.2} takes place provided that all the added P3HT chains associate to F8BT in the equilibrated mixture:

The initial monomer molar concentrations of F8BT and P3HT (x and y respectively) yield a y concentration of *F8BT:P3HT complexes* and a $(x - y)$ F8BT concentration in equilibrium, assuming monovalent 1:1 interactions in *F8BT:P3HT complex*, (the validity of this assumption will be confirmed in section 3.4).

Subsequently, the derivation of the absorption of *F8BT:P3HT complex* is interpreted on the basis of Lambert-Beer Law,

$$A = \sum \varepsilon_i c_i b \quad \{3.3\}$$

where ε_i is the molar extinction coefficient expressed in $\text{M}^{-1}\text{cm}^{-1}$, the concentration c_i is expressed in M and the optical path length b in cm. Accordingly, the absorbance values before (A^0) and after (A^f) P3HT addition are given by {3.4} and {3.5} respectively:

$$A^0 = A(\text{F8BT}) = x b \varepsilon_{\text{F8BT}} \quad \{3.4\}$$

$$A^f = A(\text{F8BT:P3HT}) + (x - y) b \varepsilon_{\text{F8BT}} \quad \{3.5\}$$

Then subtraction of {3.4} from {3.5}, gives rise to the doping induced absorption difference:

$$A^f - A^0 = A(\text{F8BT:P3HT}) - y b \varepsilon_{\text{F8BT}} \quad \{3.6\}$$

Combining {3.4} and {3.6}, the absorption of the complex is obtained as:

$$A(F8BT:P3HT) = (A^f - A^0) + \frac{y}{x}A^0 \quad \{3.7\}$$

where $\frac{y}{x}$ is the molar ratio of total monomer concentration of P3HT and F8BT and also stands for the fraction of associated F8BT to the total F8BT molar content. Therefore, the absorption of *F8BT:P3HT complex* could be estimated from the absorption before and after P3HT doping as well as the molar concentration ratio of P3HT and F8BT. We must remind again that this method relies on two approximations. First the F8BT:P3HT association ratio is 1:1. Second, there are no unassociated P3HT chromophores in mixtures with low P3HT fraction content. Such assumption seems to be supported by the absence of distinctive P3HT absorption and emission features in solution at low P3HT fraction, (see Figure 3.1).

3.2.1.2 Experimental determination of *F8BT:P3HT complex* absorption

In order to facilitate the measurements and simultaneously avoid solvent dilution effects on the absorption spectra, we carried out controlled experiments on pure F8BT solutions, i.e. measuring the absorption of a F8BT solution before and after adding a small toluene volume analogue to the one employed for P3HT doping. The contribution from dilution induced by the excess of toluene added to the initial F8BT solution (5%) is almost insignificant. Anyhow, the diluted F8BT absorption was directly compared with the P3HT doped spectra to visualize directly the effect caused by F8BT:P3HT association on the absorption spectrum. Details on the F8BT and P3HT solutions employed to prepare the mixture and the controlled F8BT sample (e.g. volume, molar concentration, molar ratio, etc.) are given in the caption of Figure 3.5. Figure 3.5(a) depicts the effect of doping a F8BT solution with a small volume of P3HT solution (25% approximate F8BT:P3HT fraction in the final mixture). The absorption spectra before (A^0 , black straight line) and after (A^f , blue straight line) adding P3HT are shown. As a result of P3HT doping, the main F8BT absorption band experiences an increase of 8% along with a slight bathochromic shift and a raise of the satellite shoulder at 2.2 eV. According to {3.7}, the absorption of *F8BT:P3HT*

complex (red straight line) was obtained from doping induced difference in absorption ($A^f - A^0$, dashed pink line) plus the absorption of F8BT multiplied by the relative molar ratio of P3HT and F8BT ($25 * A^0/75$). For comparison purposes, the experiment was repeated with a different P3HT dopant content (15% approximate F8BT:P3HT fraction in the final mixture) following the same approach. The resulting absorption spectrum of *F8BT:P3HT complex* obtained from these two independent doping experiments are shown in Figure 3.5(b). Note that they almost look alike. The increase in absorption at longer wavelengths indicates that the optical band gap (E_g) of *F8BT:P3HT complex* is considerably lower respect to the pristine polymers.

Figure 3.5. (a) Doping induced absorption change of a 25% F8BT:P3HT mixture in toluene. (b) Absorption spectra of *F8BT:P3HT complex* determined from 25% and 15% F8BT:P3HT toluene solutions. For 25% (15%) F8BT:P3HT system, the mixture solution comprised 0.1 mM F8BT of 300 μ L and 0.5 mM P3HT of 20 (10) μ L, and the controlled F8BT solution consisted of 0.1 mM F8BT of 300 μ L and the solvent toluene of 20 (10) μ L. The stabilization time for doping was 2 min.

3.2.2 PLE

PLE can be understood as “fluorescence detected absorption”, since it measures the fluorescence intensity at a particular wavelength upon scanning of the excitation wavelength. Accordingly, we attempted to single out the absorption characteristics of the *F8BT:P3HT complex* in diluted F8BT and P3HT mixtures with the assistance of PLE.

Firstly, we monitored the PL spectra of the 15% and 25% diluted mixtures upon photoexcitation with 3.07 eV (405 nm, the main absorption peak of F8BT) as shown in Figure 3.6(a). The PL spectra of mixtures are composed of a main emission band centered at 2.35 eV (530 nm) ascribed to F8BT and a weak emission feature at the PL tail which is tentatively attributed to *F8BT:P3HT complex*. As the P3HT content increases from 15% to 25%, there is a reduction of F8BT emission and a concomitant growth of the low energy band in line with the assignment of the latter to *F8BT:P3HT complexes*. Next, we tried to understand whether F8BT:P3HT emission was associated to direct photoexcitation of the *complex* or mediated via energy transfer from F8BT. Accordingly, we performed PL decay measurements in 15% and 25% diluted mixtures detecting at the peak of F8BT, i.e. 2.35 eV. The results (displayed in Figure 3.6(b)) show that the lifetime of F8BT excitons is independent of P3HT doping as far as the total polymer concentration is kept at a concentration value of 0.1mM. Therefore, there is no obvious energy transfer from F8BT to *F8BT:P3HT complex* in the studied mixtures, confirming that the low energy emission band yields from direct photoexcitation of *F8BT:P3HT complexes* in solution. Based on this scenario, it is possible to retrace the *F8BT:P3HT complex* absorption with PLE measurements detecting at the tail of the PL spectrum.

We carried out PLE in 15% and 25% F8BT:P3HT mixtures detecting at 1.78 eV (700 nm). The resulting excitation spectra are found in Figure 3.6(c). Compared to 25% F8BT:P3HT, the PLE spectrum obtained in 15% F8BT:P3HT exhibits an enhancement at the higher energy spectral part and a reduced low energy band. This phenomenon is probably due to contribution from the F8BT PL tail which is weak but non negligible at the detected PLE energy, leading to overestimation of the absorption

in the F8BT absorption spectral part and underestimation in the low energy part.

Figure 3.6. (a) PL spectra of F8BT (black), 15% (blue) and 25% (red) F8BT:P3HT toluene solutions upon excitation with 3.07 eV (405 nm). (b) PL lifetime of F8BT (black), 15% (blue) and 25% (red) F8BT:P3HT toluene solutions detected at 2.35 eV (530 nm, F8BT dominant emission). (c) PLE spectra of *F8BT:P3HT* complex obtained from 15% (blue) and 25% (red) F8BT:P3HT detected at 1.78 eV (700 nm). As 3.2.1, 15% (25%) F8BT:P3HT mixture solution comprised 0.1 mM F8BT of 300 μ L and 0.5 mM P3HT of 10 (20) μ L.

To sum up, we studied the absorption features of *F8BT:P3HT complex* upon two low doping (15% and 25%) F8BT:P3HT mixtures by doping induced absorption and PLE. The absorption of *F8BT:P3HT complex* obtained following the two methods (Figure 3.7), are very similar. Generally speaking, the complex absorption spectrum determined by PLE exhibits slightly stronger contributions in the higher energy part of the spectrum. This effect is likely attributed to an experimental artefact caused by an effect known as the inner filter effect.

Figure 3.7. Absorption spectra of the *F8BT:P3HT complex* determined in a 25% F8BT:P3HT toluene solution from doping induced absorption (red line) and PLE experiments (blue line). The mixture solution comprised 0.1 mM F8BT of 300 μ L and 0.5 mM P3HT of 20 μ L.

3.3 Optical spectra of F8BT:P3HT oligomer mixtures in solution

Oligomers are model compounds which have been frequently studied as a useful approach in the understanding of the optical and photophysical properties of the related polymers since their lower monomer numbers allow for simpler modelling implementation. Accordingly, we extended the absorption and photoluminescence studies to mixtures of F8BT and P3HT oligomers in toluene and investigated the presence of cross interactions. It is noteworthy to remind here the nomenclature employed to distinguish different molecular weights. All the data discussed so far in this chapter was obtained with 33 kg mol⁻¹ (Mn) molecular weight F8BT (H1-F8BT). F8BT with molecular weights (Mn) 8.4 kg mol⁻¹, 8.0 kg mol⁻¹ and 1.8 kg mol⁻¹ will be

referred in the following as H2-F8BT, L1-F8BT and L2-F8BT respectively, (refer to experimental chapter 2.1.1.2 for more detailed information). Likewise two batches of P3HTs (M_n) were investigated: 14.0 kg mol^{-1} (P3HT) and $0.248 \text{ kg mol}^{-1}$ (T3).

First, oligomeric mixtures involving L2-F8BT and T3 were investigated. The absorption spectra of L2-F8BT, T3 and a 75% mixture in toluene are provided in Figure 3.8(a). The absorption spectrum of the mixture can be perfectly reproduced by a linear combination of L2-F8BT and T3 contributions. Furthermore, the PL spectrum upon photoexcitation at 2.8 eV (440 nm) resembles L2-F8BT emission (Figure 3.8(b)), further evidencing that PL arises from individual L2-F8BT contribution without any indication of L2-F8BT:T3 interaction. We did not find any evidences from PL contributions other than L2-F8BT and T3 upon changing photoexcitation.

Next, the study was further complemented with mixtures of oligomeric F8BT and high molecular weight P3HT. In contrast with H1-F8BT, mixing L1-F8BT or L2-F8BT with P3HT in toluene does not result into lower energy optical transitions in absorption and PL spectra. Figure 3.8(c-d) depict the absorption and photoluminescence features of L1-F8BT:P3HT toluene mixtures. The absorption spectrum of a 75% mixture is given again by single spectral superposition of L1-F8BT and P3HT spectra. Additionally, the PL spectrum of the mixture upon photoexcitation at the absorption tail (2.4 eV, 520 nm) resembles P3HT emission. Therefore, taking into account all these observations we can conclude that there are no evidences for strong inter-chain interactions in oligomeric F8BT:P3HT dispersions.

Figure 3.8. (a) Absorption of L2-F8BT:T3 toluene solutions with different T3 molar content: 0% (dashed green), 100% (dashed red), and a 75% mixture (solid red). The dashed blue line corresponds to a fit that reproduces the 75% absorption as a linear combination of L2-F8BT and T3 components. (b) Photoluminescence of 0% (dashed green) and 75% (solid red) L2-F8BT:T3 toluene mixtures upon excitation with 2.8 eV (440 nm). (c) Absorption of L1-F8BT:P3HT toluene solutions with varying P3HT molar concentrations: 0% (dashed green), 100% (dashed red), and a 75% mixture (solid red). The dashed blue line corresponds to a fit that reproduces the 75% absorption spectrum by single spectral superposition of L1-F8BT and P3HT spectra. (d) Photoluminescence of 100% (dashed red) and 75% (solid red) L1-F8BT:P3HT toluene mixtures pumped with 2.4 eV (520 nm). The total concentration is 0.001 mg ml⁻¹.

Nevertheless, similar to H1-F8BT:P3HT in toluene solutions, the characteristic absorption shoulder of *F8BT:P3HT complex* appears in H2-F8BT:P3HT mixtures and becomes more prominent with P3HT content. On the other hand, the spectra of these two mixtures are not identical. The main absorption band experiences a larger red-shift for the same P3HT doping range in H1-F8BT:P3HT respect to

H2-F8BT:P3HT, (Figure 3.9(a-b)). Likewise the shoulder at 2.2 eV is more pronounced in H1-F8BT:P3HT which could indicate that the strongest F8BT:P3HT interactions are present in mixtures with the highest F8BT molecular weight.

Figure 3.9. Absorption of (a) H2-F8BT:P3HT and (b) H1-F8BT:P3HT toluene solutions with varying P3HT molar concentrations. The 0 and 100% spectra are shown as dashed green and red lines respectively whereas mixtures with low and high P3HT content appear as solid green and red lines. The increasing transparency indicates a higher P3HT content. The total concentration is 0.1 mg ml⁻¹ (~0.1 mM monomer concentration).

In summary, F8BT:P3HT interactions are absent in mixtures containing oligomers implying that the chain lengths of both polymers play a crucial role on the formation and stabilization of the *F8BT:P3HT complexes*. Next we try to quantify in detail the strength of F8BT:P3HT interactions and the thermodynamic conditions which favor them.

3.4 Quantitative analysis of F8BT:P3HT binding interactions

The most common approach for quantifying supramolecular interactions is the titration method, the guest molecular compound being gradually added to solution of the host while simultaneously monitoring the changes in some physical property through NMR, UV-Vis or other techniques.[62][63] In this section, we quantitatively study the underlying equilibria of H1-F8BT:P3HT (hereafter simply referred as F8BT:P3HT) interactions at varied temperatures by adoption of the titration method. This will allow us to determine a range of associated physical constants such as stoichiometry ratio, binding constants, and thermodynamical conditions (ΔH and ΔS).

3.4.1 The underlying equilibria and association constants

To start with, let us briefly look at how the typical equilibria and the relevant association constants are defined in supramolecular chemistry. Host-guest interaction usually based on simultaneous non-covalent binding is a reversible association / dissociation reaction. For a general reaction yielding any $m \times \text{host} \cdot n \times \text{guest}$ complex in a given solvent at a certain temperature [64]:

The thermodynamic association constant at equilibrium can be defined by:

$$\beta_{mn} = \frac{[H_m G_n]}{[H]^m [G]^n} \quad \{3.9\}$$

When $m=n=1$, we achieve at the simple 1:1 equilibria,

$$K_{eq} = \frac{[HG]}{[H][G]} \quad \{3.10\}$$

While for multivalent interactions, the complex is considered to form stepwise. For instance, in the case of $m=1$, $n=2$, two guests bound to a host, the stepwise constants K_1 , K_2 and the overall constant β_{12} are described as

$$\begin{aligned} K_1 &= \frac{[HG]}{[H][G]} \\ K_2 &= \frac{[HG_2]}{[HG][G]} \\ \beta_{12} &= \frac{[HG_2]}{[H][G]^2} = K_1 K_2 \end{aligned} \quad \{3.11\}$$

Association constants are often reported as $\log K$, since magnitudes of them can vary widely. Then coming back to F8BT:P3HT interactions, can we determine the binding constant in F8BT:P3HT? This question will be addressed in the following section.

3.4.2 UV-Vis titration experiments

Temperature-controlled UV-Vis spectroscopy was applied to follow the course of F8BT:P3HT titration. The titration method briefly consisted on the preparation of a F8BT *host* solution in toluene with 0.1 mM F8BT monomer concentration ($[F8BT]_0$) and a separate *guest* toluene solution composed of a mixture of 1 mM P3HT in 0.1 mM F8BT and subsequent adding different volumes of *guest* to *host* solutions. Given that the F8BT monomer concentration in *host* and *guest* solution was the same, the total F8BT concentration upon subsequent addition of *guest* into *host* solution remained constant whilst P3HT content in the titrated solution ($[P3HT]_0$) increased proportionally. Absorption spectra were measured systematically after addition of *guest* solution in steps of 0.1 $[P3HT]_0/[F8BT]_0$ equivalents up to a total P3HT content of 3 $[P3HT]_0/[F8BT]_0$ equivalents (75% mole fraction). The total component concentrations ($[F8BT]_0$ and $[P3HT]_0$) and the corresponding volume of *guest* solution added for each sample are shown in Table 3.2. Each spectrum was acquired 2 minutes after addition in order to achieve complete equilibrium. The spectra set from titration at 298 K are depicted in Figure 3.10. In accordance with our previous findings, P3HT addition results in the formation of a shoulder at lower energies and a red shift of the main absorption band from 2.73 eV to 2.67 eV (from 455 nm to 465 nm), which is unambiguously indicative of the complex. The evolution of these complex-driven features can be correlated with appropriate binding models to quantify F8BT:P3HT interactions.

Figure 3.10. Titrated absorption spectra of F8BT:P3HT in toluene measured as a function of *guest* addition at 298K.

Addition	<i>Guest</i> added (μL)	Volume (μL)	[F8BT] ₀ (mM)	[P3HT] ₀ (mM)	[P3HT] ₀ /[F8BT] ₀
0	0	260	0.1	0	0
1	2.9	262.9	0.1	0.01	0.1
2	2.9	265.8	0.1	0.02	0.2
3	3.0	268.8	0.1	0.03	0.3
4	3.0	271.7	0.1	0.04	0.4
5	3.0	274.8	0.1	0.05	0.5
6	3.1	277.8	0.1	0.06	0.6
7	3.1	280.9	0.1	0.07	0.7
8	3.1	284.0	0.1	0.08	0.8
9	3.2	287.2	0.1	0.09	0.9
10	3.2	290.4	0.1	0.1	1
11	3.2	293.6	0.1	0.11	1.1
12	3.3	296.9	0.1	0.12	1.2
13	3.3	300.2	0.1	0.13	1.3
14	3.3	303.5	0.1	0.14	1.4
15	3.4	306.9	0.1	0.15	1.5
16	3.4	310.3	0.1	0.16	1.6

17	3.4	313.7	0.1	0.17	1.7
18	3.5	317.2	0.1	0.18	1.8
19	3.5	320.7	0.1	0.19	1.9
20	3.6	324.3	0.1	0.2	2
21	3.6	327.9	0.1	0.21	2.1
22	3.6	331.5	0.1	0.22	2.2
23	3.7	335.2	0.1	0.23	2.3
24	3.7	339.0	0.1	0.24	2.4
25	3.8	342.7	0.1	0.25	2.5
26	3.8	346.5	0.1	0.26	2.6
27	3.9	350.4	0.1	0.27	2.7
28	3.9	354.3	0.1	0.28	2.8
29	3.9	358.2	0.1	0.29	2.9
30	4	362.2	0.1	0.3	3

Table 3.2. Additions of titration experiments and the total concentrations of F8BT and P3HT following each addition.

3.4.3 Binding model analysis

The absorption spectra obtained from F8BT:P3HT titration were fitted with the aid of a ReactLabTM EQUILIBRIA (Jplus Consulting) software [65], which provides different binding models for global analysis. After populating the data of the titration absorption spectra and the total component concentrations for each solution, the next crucial step is to define the binding reaction model, namely, the values of m and n constants in {3.8}. Generally, it is suggested to start from an assumption of 1:1 equilibria prior to other sensible stoichiometries.[66][67] In our case, we already demonstrated that the absorption shoulder at 2.2 eV associated to the *F8BT:P3HT complex* reaches a maximum at a value close to 50% P3HT molar content (see Figure 3.1(c) in section 3.1.1.) Thus, 1:1 complexation was here considered to be a sound starting point. Entering an initial guess of binding model (binding ratio and association constant), the final fit was updated with minimum residual by the compilation of assumed model

and comparison with real scenario. The simulation results comprised of an equilibrium constant (expressed as its log value) as well as the corresponding concentration profiles and absorption spectra of all the species. Apart from 1:1 stoichiometry ratio, we also inspected carefully more complex multivalent interactions such as 1:2, 1:3, 2:1, 2:3, 3:1 and 3:2 (see {3.9} and {3.11}). From the evaluation of the results, the best agreement with the experimental data is overwhelmingly attributed to 1:1 ratio for all tested temperatures. In Figure 3.11, the results of the global fit analysis are shown. Figure 3.11(a) depicts the simulated absorption spectra of F8BT, P3HT and *F8BT:P3HT complex*, whereas Figure 3.11(b) provides their corresponding equilibrium component concentrations ([F8BT], [P3HT] and [F8BT:P3HT]). We must notice here that a slight discrepancy appears when comparing the simulated (solid red line in Figure 3.11(a)) and experimental P3HT absorption spectra (dashed red line in Figure 3.11(a)): the simulated P3HT spectrum possesses a shoulder at 2.2 eV and the main absorption band is shifted to lower energies. Hitherto, we consider our approximation reasonable on the basis that it accurately reproduces all the titrated spectra as well as the absorption of F8BT with very good agreement, (solid green line in Figure 3.11(a). The predicted absorption spectrum of the *F8BT:P3HT complex*, (depicted as solid blue line in Figure 3.11(a)), is composed of a broad absorption band centered at 2.67 eV (465 nm) and a satellite shoulder located around 2.2 eV, which is very similar to the complex spectrum previously determined from doping induced absorption in section 3.2.1.2 (dashed blue line in Figure 3.11(a)). From Figure 3.11(b) we can see that F8BT and *F8BT:P3HT complex* concentration profiles are mirror images, pointing to a direct correlation between a reduction of free F8BT chromophores and an increase of complexes in solution. The concentration of complexes ([F8BT:P3HT]) rises steeply until it reaches an inflection point at 1:1 of [P3HT]₀/[F8BT]₀. At this point, there is an equal low concentration of free F8BT and P3HT chromophores ([F8BT] and [P3HT]).

Figure 3.11. Simulated UV-Vis titrations for F8BT: P3HT 1:1 equilibria in toluene. (a) Simulated absorption spectra of F8BT (green), P3HT (red) and *F8BT:P3HT complex* (blue). The dashed black and red lines correspond to experimental absorption spectra of F8BT and P3HT respectively, and the dashed blue line represents absorption of *F8BT:P3HT complex* determined from doping induced absorption. They are all normalized to their simulated spectra. (b) Concentration profiles of F8BT (green), P3HT (red) and *F8BT:P3HT complex* (blue) upon titration.

3.4.4 Energetics of F8BT:P3HT interactions

Similar titration experiments were carried out at different temperatures (283K, 288K, and 318K) and compared with 298 K. Table 3.3 shows the temperature dependence of association constants (K_{eq}) determined for F8BT:P3HT 1:1 equilibria. Titration experiments were repeated three times for each temperature and the K_{eq} values averaged. The K_{eq} values at 298K and 318K range from 4×10^4 to almost 10^5 , suggesting that the formation of *F8BT:P3HT complex* in toluene is very favorable. Furthermore, the interactions occur more preferably at higher temperatures, with K_{eq}

increasing by almost two orders of magnitude as temperature is increased from 283K to 318K, proposing that the association of F8BT and P3HT is an endothermic process.

T (K)	$\log K_{eq} (K_{eq})$	σ
283	3.90 (7943)	0.0318
288	3.87 (7413)	0.0184
298	4.64 (43651)	0.284
318	4.97 (93325)	0.219

Table 3.3. Temperature dependence of association constants along with standard deviations for F8BT:P3HT 1:1 equilibria in toluene.

The thermodynamical magnitudes associated to the complexation were obtained with a Van't Hoff plot (Figure 3.12). It is observed that the natural logarithm of association constants have a linear dependence on the reciprocal of test temperatures, defined by the Van't Hoff equation [62]:

$$\ln K_{eq} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad \{3.12\}$$

Where ΔH (KJ mol⁻¹) and ΔS (J mol⁻¹K⁻¹) denote the enthalpy and entropy changes, R is gas constant (8.314 J mol⁻¹K⁻¹), and T (K) is absolute temperature. By inspection of the slope and intercept with Y-axis of the fitted straight line ($y=-6952.6x+33.482$, $R^2=0.8942$), the variations of enthalpy and entropy could be obtained as:

$$\Delta H = -R * \text{slope} = 57.8 \text{ KJ mol}^{-1}$$

$$\Delta S = R * \text{intercept} = 278.4 \text{ J mol}^{-1}\text{K}^{-1}$$

Accordingly, the interaction Gibbs free energy is $\Delta G = \Delta H - T * \Delta S < 0$ at the tested temperatures. Since the changes of enthalpy and entropy are both positive, the spontaneous complexation of P3HT and F8BT in toluene solution is an entropy-driven process. Previous studies on entropy driven host-guest encapsulations in inorganic or organic solvents have interpreted that the large entropy gain arising from desolvation

of the host interior cavity and of the guest surface compensates for the enthalpic cost.[68][69] Likewise, as two single P3HT and F8BT chains encounter to form complex, abundant toluene molecules surrounding the polymer chains are liberated to the bulk solvent, giving rise to the observed increase in entropy. This brings another insight towards the molecular weight dependence since longer chains will lead to larger desolvated volumes, which may explain why we observe strong host:guest association only with high molecular weight polymers. Additionally, in contrast to chloroform, the nonpolar nature of toluene molecules implies that they are significantly free of interaction and thus would not interfere with hydrophobic interactions between P3HT and F8BT chains. However, entropy driven process in the complexation of conjugated polymers in dilute organic solvent is rarely seen and can only be explained by strong specific affinities between P3HT and F8BT moieties. Next, we will address such specific interactions.

Figure 3.12. Van't Hoff plot.

3.5 Modelling F8BT:P3HT interactions in solution

In this section, molecular dynamics simulations followed by density functional theory calculations were performed on F8BT:P3HT toluene and chloroform models. The relevant work has been done in collaboration with Dr. Belen Nieto and Prof. Emilio M. Pérez from IMDEA Nanociencia.

3.5.1 Quantum molecular dynamics (QMD)

With the aim of better understanding the differences in association affinities between P3HT and F8BT from toluene and chloroform, we carried out QMD simulations on these two models. It is noted that the QMD simulations were executed using the AMBER12 force field [70], which accounted for dispersion interactions. The corresponding values for the parameters not included in this force field, such as missing bonds, angle torsions, and Van Der Waals forces, were transferred from the general AMBER force field (GAFF) [71].

The initial structures of individual P3HT and F8BT determined in vacuum are depicted in Figure 3.13, along with the number of containing monomers and the total length. Then the structures were heated slowly from 0 K to 300 K during a period of 0.5 ns. Subsequently, we carried out QMD simulations of 5.0 ns (2 fs time step) in NVT ensemble (constant-volume-constant-temperature) to monitor the balance phases of F8BT:P3HT in chloroform and toluene with adoption of continuum solvation models. The evolution of calculated potential energies for F8BT:P3HT chloroform and toluene models are shown in Figure 3.14. It is observed that for both systems the energies increase speedily during the first 500 fs, which are related to the heating process, whilst afterwards the energies almost remain constant. The equilibria is reached at about 2 ns. After this time interval we do not see any variation in the total energies of the two systems.

Figure 3.13. Initial structures of P3HT and F8BT for QMD simulations. Color code: green carbon atoms belong to P3HT, red carbon atoms belong to F8BT, blue for nitrogen atoms and yellow for sulfur atoms.

Figure 3.14. Stabilization energy of F8BT:P3HT in chloroform (black line) and toluene (red line).

Next, we select a range of representative snapshots of F8BT:P3HT chloroform and toluene models respectively, displayed in Figure 3.15(a-f). From the images in chloroform we discover that the most stable arrangements provoke a perpendicular interaction between the respective aromatic moieties of F8BT and P3HT, and they are kept together by the interactions between the aliphatic chains and the aromatic moieties. Meanwhile interestingly, for F8BT:P3HT toluene model, there are some certain degrees of π - π interactions observed between the aromatic moieties of F8BT and P3HT in all studied snapshots. The polymer chains in toluene intertwine to form

an analogous heterogeneous double helix rather than more separated assembly in chloroform, which favors cofacial π - π interactions.

Figure 3.15. Selected QMD snapshots of F8BT:P3HT assembly in chloroform at a) 3.5, c) 4.5, e) 5.5 ns time step and in toluene at b) 3.5, d) 4.5, f) 5.5 ns time step. Color code: green carbon atoms belong to P3HT, red carbon atoms belong to F8BT, blue for nitrogen atoms and yellow for sulfur atoms.

3.5.2 Time dependent density functional theory (TDDFT)

In order to further explore the role of the different F8BT:P3HT interactions on their absorption behaviors, we adopted TDDFT calculations on these two assemblies. To perform TDDFT calculations as practically feasible, the number of atoms involved requires to be minimized. For this reason, we selected the significative F8BT:P3HT segments from QMD optimization for both models, Figure 3.16(a-b). The corresponding theoretical absorption spectra are very well reproduced by TDDFT, Figure 3.16(c), compared to our absorption results of polymer mixtures in 3.1.1. Remarkably, the TDDFT calculations predict the existence of an additional band at 2.4 eV for optimized F8BT:P3HT toluene model, which is reminiscent of the characteristic low energy band of *F8BT:P3HT complex*.

Figure 3.16. Optimized F8BT:P3HT structures (a) in chloroform and (b) in toluene for TDDFT calculations. Color code: green carbon atoms belong to P3HT, red carbon atoms belong to F8BT, blue for nitrogen and yellow for sulfur. (c) Theoretical UV-Vis spectra of the two models, black for chloroform and red for toluene. The energies and oscillator strengths calculated for the electronic transitions are included as bars. Level of calculations: TDDFT/CAM-B3LYP/3-21g*.

The electronic transition computed at 2.4 eV (with oscillator strength $f = 0.0597$) corresponds to the excitation from the ground state to the first singlet excited state ($S_0 \rightarrow S_1$). A further explanation of the nature of this transition can be achieved by analyzing the molecular orbitals. As a result, the electronic transition can be described as HOMO $\rightarrow$ LUMO (62%) and HOMO $\rightarrow$ LUMO+1 (31%) one-electron promotions. From Figure 3.17, it can be seen that the HOMO is localized in the conjugated terthiophene skeleton whereas the LUMO and LUMO+1 are centered in the F8BT moieties, confirming the charge transfer (CT) nature of this transition. Hence, the characteristic absorption band of *F8BT:P3HT complex* is referred to as CT band, P3HT acting as an electron donor and F8BT as an electron acceptor. Previous studies on oligomers with alternating thiophene-benzothiadiazole groups have demonstrated how the donor (acceptor) nature of thiophene (benzothiadiazole) groups results in the formation of an intra-molecular charge transfer state.[72] Likewise, predominance of polymer / polymer over polymer / solvent interactions in F8BT:P3HT solutions could

favor the formation of inter-chain charge transfer states delocalized across adjacent P3HT and F8BT chromophores.

Figure 3.17. Molecular orbital topologies calculated for ($S_0 \rightarrow S_1$) mono electronic transition for *F8BT:P3HT* complex in toluene (HOMO $\rightarrow$ LUMO (62%), HOMO $\rightarrow$ LUMO+1 (31%)). Color code: grey for carbon atoms, blue for nitrogen and yellow for sulfur.

3.6 Conclusions

In contrast to F8BT:P3HT mixtures in chloroform, the distinctive absorption and photoluminescence features of F8BT:P3HT toluene solutions implied the presence of *F8BT:P3HT* complexes involving the formation of a ground state charge transfer interaction delocalized across adjacent P3HT and F8BT chromophores. This was further substantiated by QMD simulations together with TDDFT theoretical calculations. The absorption signature band of complex corresponding to the lowest vertical one-electron electronic transition shows a clear HOMO to LUMO charge-transfer character.

Furthermore, the underlying equilibria of the formation of *F8BT:P3HT* complex were quantitatively studied by UV-Vis titration method with association constants K_{eq} in the range of 10^4 - 10^5 for 1:1 F8BT:P3HT complexation at varying temperatures, confirming the presence of strong charge transfer inter-chain interactions. Moreover, the thermodynamics demonstrated that F8BT:P3HT association is an endothermic process using entropy as driving force.

Owing to the absence of such interactions in F8BT:P3HT oligomeric models, polymer chain length is believed to play a significant role on the complexation. The formation of *F8BT:P3HT* complexes also is strongly dependent on solvent polarity and

temperature. From the characteristic absorption and fluorescence spectra of F8BT:P3HT we envisage such polymer-based charge transfer complexation as an effective way to tune the absorption and emission of the conjugated polymer F8BT, which could be applied in light emitting devices or to enhance light harvesting at lower energies of the spectrum. We will focus in this thesis on the emission applications of *F8BT:P3HT complexes*.

Chapter 4. Monitoring Polymer Interactions in F8BT:P3HT Thin Films

In this Chapter, we study the miscibility, nanostructure and optical properties of F8BT:P3HT in the solid state. The correlation between the optical properties of F8BT:P3HT blends, P3HT chain conformation and film nanostructure was investigated by means of Raman spectroscopy, atomic force microscopy (AFM) and differential scanning calorimetry (DSC). Comparative studies on F8BT:P3HT, L3-F8BT:P3HT and PMMA:P3HT blends were performed to elucidate the role of F8BT molecular weight on blend morphology and optical properties. Furthermore, the study was complemented with the evolution of film nanostructure under two post-processing annealing protocols: thermal annealing and toluene vapor annealing. Using this information, we obtain an overall description of the intriguing nanomorphology of F8BT:P3HT films. We verify the persistence of a strong F8BT:P3HT ground state charge-transfer interaction previously identified in solution, in contrast with large P3HT crystallization observed in PMMA and L3-F8BT solid state matrices.

4.1 Optical spectra of F8BT:P3HT blend films

In this section, we investigated the absorption and emission properties of F8BT:P3HT blend films together with two controlled blends composed of P3HT dispersed in PMMA and in L3-F8BT respectively. We performed Raman spectroscopy as probe for the different P3HT chain conformation in the matrices and studied the induced film nanostructures by AFM.

4.1.1 Absorption and PL

Blend films of P3HT in PMMA, F8BT and L3-F8BT were processed by spin-coating toluene mixtures with P3HT monomer molar concentration comprised between 15% and 70%. The resulting absorption spectra are displayed in Figure 4.1(a-c). The absorption spectra of PMMA:P3HT films, (Figure 4.1(a)), preserve the absorption spectral shape of a pristine P3HT film, (dashed black line in Figure 4.1(b)), being

composed of well-structured spectrum with a S_1-S_0 0-0 feature at 2.05 eV and vibrational satellite peaks at 2.25 eV and 2.37 eV, which are characteristics of lamellar crystalline P3HT aggregates.[73][37] As described in the Introduction chapter, P3HT aggregates are clearly visible upon dispersing P3HT into a wide range of polymer matrices already at low content levels. Remarkably, the absorption spectra of F8BT:P3HT blend films, (Figure 4.1(b)), are characterized instead by a broad absorption band attributed to F8BT, (main peak 2.7 eV, dashed grey line in Figure 4.1(b)), and an additional shoulder located at around 2.2 eV, which resemble the absorption of F8BT:P3HT solution mixtures. The absence of P3HT aggregate features is evident for molar ratios up to 70%, manifesting that the strength of the F8BT:P3HT interaction is capable to hinder P3HT nucleation to a large extent during film formation. It is noteworthy to mention that the choice of solvent employed for the precursor solutions had no substantial effect on the absorption spectra of F8BT:P3HT blend films. Samples processed from toluene or chloroform had identical absorption spectra, (data not shown), even though the larger polarity of the latter solvent led to hindrance of F8BT:P3HT interactions in solution, as demonstrated in the previous chapter. Thus, this observations point towards a recovery of the F8BT:P3HT interactions upon chloroform removal during film formation. Substitution of F8BT by L3-F8BT as matrix for P3HT has also interesting implications. In contrast with F8BT:P3HT, the absorption spectra of L3-F8BT:P3HT possess the characteristic spectral features of P3HT aggregates even at low P3HT content, (Figure 4.1(c)). Additionally, the absorption spectra are composed by a clear superposition of L3-F8BT and P3HT absorption spectra without additional features (absence of shoulder at 2.2 eV), which rules out the presence of L3-F8BT:P3HT ground state interactions. The lack of interactions in L3-F8BT:P3HT films, inherited from oligomeric solution mixtures, highlights once again the crucial role of polymer chain lengths on complexation.

Figure 4.1. Absorption of (a) PMMA:P3HT, (b) F8BT:P3HT, and (c) L3-F8BT:P3HT blend films spun from toluene comprising 15% (dark yellow), 45% (red) and 70% (blue) P3HT monomer molar content. The pristine F8BT and P3HT absorption spectra are shown as dashed grey and black lines in (b) respectively. (d) PL of a 45% F8BT:P3HT film (red squares) and a 75% F8BT:P3HT solution (blue circles) with their Frank-Condon fits (red and blue lines respectively). Excitation energy was 2.4 eV. PL of pristine F8BT and P3HT films are shown as grey diamonds and black triangles respectively.

Figure 4.1(d) depicts the PL spectrum of a 45% F8BT:P3HT blend film together with pristine polymers. The PL of the 45% F8BT:P3HT, (red squares in Figure 4.1(d)), has comparably pronounced vibronic progressions with respect to the PL of a 75% mixture in toluene, (blue circles in Figure 4.1(d)). A more straightforward comparison in film and solution by Frank-Condon analysis is given in Table 4.1. From the very similar Δ , w and 0-0 energy values in toluene solution and film, (the 30 meV shift in the 0-0 transition likely stems from the change in dielectric constant from solution to film) [74], we confirm that the emission in blend films also arises from *F8BT:P3HT* complexes. It is remarked that self-absorption effects of the studied film may cause a slight reduction

of the 0-0 intensity, which could explain the discrepancy when comparing the Huang-Rhys factor values in film and solution. Also note that there is a lack of spectral differences upon exciting at the absorption shoulder (2.4 eV) or at the maximum of F8BT absorption (2.7 eV), due to the interplay of an efficient Förster resonant energy transfer from F8BT to *F8BT:P3HT complexes*. The relevant studies concerning energy transfer processes in film will be the subject of the next chapter.

	0-0 energy (eV)	Δ (eV)	S	w (eV)
45% (film)	2.01	0.16	0.95	0.06
75% (toluene)	2.04	0.17	0.80	0.06

Table 4.1. Parameters extracted from Frank-Condon fits for F8BT:P3HT in film and solution.

Consequently, F8BT:P3HT complexation is retained in the solid state, prevailing over P3HT aggregation during film formation. As known, the nanostructures of pristine regioregular P3HT films are characterized by regions where polymer chains planarize and π -stack into 2D crystalline lamellae.[33] Such a planarization has a clear effect in the Raman spectrum of P3HT. Next, we will address changes in chain conformation and film nanostructure in the studied blends.

4.1.2 Raman

In order to gain further insights on P3HT chain conformation in blends, films of P3HT pristine and blended with F8BT, PMMA and L3-F8BT were studied by Raman spectroscopy. Figure 4.2(a) displays the Raman spectrum of pristine P3HT excited at 785 nm. Among the different Raman modes observed, we particularly focus on the two intense peaks located at ~ 1445 and ~ 1381 cm^{-1} wavenumbers associated with the symmetric C=C and inter-ring C-C stretch modes of the P3HT backbone respectively.[75] As demonstrated on previous reports, these two modes are sensitive probes for polymer backbone conformation and molecular order of P3HT in film.[76][77] Furthermore, the Raman signals from the matrices investigated here in this fingerprint range are almost negligible with respect to P3HT. As displayed in

Figure 4.2(a-c), the Raman contribution from P3HT outweighs F8BT and PMMA in the 1350 -1500 cm^{-1} spectral region.

Figure 4.2. Raman spectra of pristine (a) P3HT (red), (b) F8BT (dark yellow) and (c) PMMA (blue) thin films on quartz with ca. 100 nm nominal thickness upon photoexcitation at 785 nm. The Raman signal from blank quartz is also included as black line in (c).

Figure 4.3(a-b) shows the C=C and C-C Raman modes of P3HT dispersed in F8BT, PMMA and L3-F8BT under non-resonant condition (785 nm excitation) with 45%

and 70% P3HT concentration respectively. Note that as already mentioned, the contributions from matrices in this spectral range are weak and have been removed. A summary of the peak position, full-width-half-maximum (FWHM) values and relative C-C to C=C Raman intensity values ($I_{C-C}/I_{C=C}$) of blends and pristine P3HT is shown in Table 4.2. The relative intensities were calculated by integrating the peak areas of the C-C to C=C modes. Several important differences are discerned when comparing the values from F8BT:P3HT and PMMA:P3HT blends.

Firstly, the C=C stretching modes in PMMA:P3HT blends appear centered at 1446 cm^{-1} , (characteristic of P3HT crystalline phase), whilst a $6\text{-}7\text{ cm}^{-1}$ shift to longer wavenumbers is found in F8BT:P3HT blends. The FWHM values of the C=C stretch mode also differ (26 cm^{-1} in PMMA and 32 cm^{-1} in F8BT blends). Moreover, the $I_{C-C}/I_{C=C}$ ratios of PMMA blends (0.25) are significantly larger than those found for F8BT blends, (0.16 (0.09) for 45% (70%) samples).

Previous Raman studies on ordered and disordered P3HT phases have identified that in general the C=C mode peak of ordered P3HT shows a large shift to lower wavenumbers with a much narrower FWHM and an increased intensity ratio $I_{C-C}/I_{C=C}$ value.[78][61] *Tsoi et al.* performed Raman simulations of the two modes based on density functional theory in regioregular P3HT oligomers with different chain length and inter-ring dihedral angle (degree of planarity).[61] It was found that the C=C mode significantly shifts to lower wavenumbers concomitant with enhanced $I_{C-C}/I_{C=C}$ values for longer conjugation lengths or/and more planar backbone, in good agreement with the experimental results. On the basis of all these observations, we infer that P3HT chain conformations in the F8BT matrix are characterized by a less extended π -delocalization and wider statistical distribution of conjugation lengths as opposed to P3HT in PMMA. This scenario is consistent with F8BT enabling high dilution of amorphaously dispersed P3HT chains in contrast with a larger chain planarization associated to P3HT crystallinity in PMMA. The Raman conclusions in F8BT:P3HT blends are also in line with quantum molecular dynamics simulations on *F8BT:P3HT complexes* in toluene described in the previous chapter, where P3HT and F8BT chains were found to intertwine to form an analogous double helical structure

accompanied by certain degree of π - π interaction.

Then we turn our attention to L3-F8BT:P3HT blends. The Raman peak of the C=C mode in the L3-F8BT:P3HT blend film (1445 cm^{-1}) has almost the same position as that of PMMA:P3HT blends and pristine P3HT film (1446 cm^{-1}). There are only small variations on the FWHM of C=C mode ($27\text{ (28) vs }26\text{ cm}^{-1}$) and $I_{\text{C-C}}/I_{\text{C=C}}$ values ($0.24\text{ (0.22) vs }0.25$) when we compare L3-F8BT and PMMA blend films with 45% (70%) P3HT content. These observations indicate that P3HT chain conformations in an L3-F8BT matrix exhibit some minor local disorder despite predominance of crystalline P3HT. The predominant P3HT crystallinity in L3-F8BT:P3HT inferred from Raman is well correlated with the aggregate absorption features observed in the same blends.

Figure 4.3. Normalized Raman spectra (C=C and C-C modes) of PMMA:P3HT (red, solid), F8BT:P3HT (black, dotted) and L3-F8BT:P3HT (blue, dashed) blend films with (a) 45% and (b) 70% P3HT content upon photoexcitation at 785 nm respectively.

	C=C mode (cm ⁻¹)	C-C mode (cm ⁻¹)	FWHM _{C=C} (cm ⁻¹)	I _{C-C} /I _{C=C}
<i>P3HT</i>	1446	1381	24	0.25
<i>PMMA:P3HT</i> (45%)	1446	1381	26	0.25
<i>F8BT:P3HT</i> (45%)	1452	1379	32	0.16
<i>L3-F8BT:P3HT</i> (45%)	1445	1380	27	0.24
<i>PMMA:P3HT</i> (70%)	1446	1380	26	0.25
<i>F8BT:P3HT</i> (70%)	1453	1376	32	0.09
<i>L3-F8BT:P3HT</i> (70%)	1445	1380	28	0.22

Table 4.2. Summary of parameters obtained from fits of the Raman spectra.

4.1.3 AFM

Additional insights into surface topography and nanostructure of blends are provided by AFM images in contact mode depicted in Figure 4.4(a-f). The rougher topographies of 45% PMMA:P3HT and L3-F8BT:P3HT with respect to 45% F8BT:P3HT blends indicate de-mixing in the formers, (Figure 4.4(b-c)). The roughness and domain size increases with P3HT content, as can be seen for the 70% PMMA and L3-F8BT blends, (Figure 4.4(e-f). Conversely, 45% and 70% F8BT:P3HT blends exhibit a large degree of mixing and lack of phase separation, (Figure 4.4(a) and (d)), which confirms the tendency to form highly homogeneous films lacking of P3HT crystals.

Figure 4.4. AFM topography images of (a) 45% F8BT:P3HT, (b) 45% PMMA:P3HT, (c) 45% L3-F8BT:P3HT, (d) 70% F8BT:P3HT, (e) 70% PMMA:P3HT and (f) 70% L3-F8BT:P3HT blend films.

In the next section, we carried out thermal analysis in order to investigate the phase behavior of F8BT:P3HT blends in more detail.

4.2 Thermal analysis of blends: tracing F8BT:P3HT solid state miscibility

4.2.1 DSC thermograms and crystallization enthalpy analysis

Firstly, we will discuss the DSC thermograms of pristine P3HT and F8BT upon heating

- cooling cycles, (Figure 4.5(a)). Regioregular P3HT is a semi-crystalline polymer: we observe a distinct melting temperature $T_m \sim 230$ °C upon heating and a crystallization temperature $T_c \sim 196$ °C upon cooling, as already described in the literature.[79] F8BT can also organize into semi-crystalline structures. The heating thermogram of F8BT exhibits a number of transitions in agreement with previous findings: (1) a glass transition temperature $T_g \sim 120$ °C from the glassy to rubbery state, (2) a cold crystallization temperature $T_c \sim 135$ °C, (3) a melting temperature $T_m \sim 223$ °C, and (4) a transition temperature from broad liquid-crystalline to isotropic solution $T_{lc} \sim 270$ °C. [50] [80] [81] In contrast, the F8BT cooling thermogram only displays a glass transition $T_g \sim 110$ °C, indicating that the solid-state structure of this polymer develops more slowly.

Because of the similar melting temperatures of the two polymers we focused our analysis on the crystallization exotherms of F8BT:P3HT blends observed during cooling, (shadowed dips in Figure 4.5(b)), which we purely ascribe to crystallization of the P3HT fraction. Remarkably, absence of P3HT crystallization is observed for P3HT molar content in F8BT up to 70%. The normalized crystallization enthalpies ($\Delta H_c / f_{P3HT}$) are obtained by integration of the shadowed peak on the corresponding thermogram and subsequent normalization by the P3HT weight fraction contained on the sample (f_{P3HT}). For neat P3HT we find the corresponding value is ~ 19.5 J g⁻¹. The $\Delta H_c / f_{P3HT}$ values in F8BT:P3HT blends rapidly decrease as the P3HT content in blend is reduced reaching a value of only $\Delta H_c / f_{P3HT} \sim 8$ J g⁻¹ in 45% F8BT:P3HT, (Figure 4.5(c)). This observation clearly indicates that in F8BT-rich blends P3HT crystallization is strongly inhibited.

Figure 4.5. (a) DSC thermograms of pristine P3HT and F8BT upon heating and cooling scans recorded under nitrogen at a scan rate of $10\text{ }^{\circ}\text{C min}^{-1}$. The observed melting and crystallization peaks are marked with red and blue patterns. (b) DSC cooling thermograms of F8BT:P3HT blends solidified from toluene with P3HT molar contents. (c) The corresponding crystallization exotherm enthalpies ΔH_c of F8BT:P3HT blends observed between 200–180 $^{\circ}\text{C}$, normalized by the P3HT weight fraction f_{P3HT} .

4.2.2 Variable-temperature optical microscopy

In order to visualize polymer miscibility, we carried out a simple experiment consisting of annealing a F8BT film to the liquid-crystalline phase at 250 °C on top of which we deposited some grains of P3HT and subsequently cooled down. At 250 °C we rapidly observe the appearance of a yellow halo around the molten P3HT grains, which suggests that P3HT diffuses into the F8BT film, (Figure 4.6). Evidently, the two polymers are partially miscible in the molten state. This homogeneous solution of the two polymers is frozen in upon cooling down to the glass transition temperature of F8BT ($T_g \sim 110$ °C). No further development of the solid-state nanostructure occurred upon reaching room temperature. Based on these observations we conclude that P3HT crystallization is suppressed in F8BT:P3HT blend films likely because P3HT remains dissolved in the high- T_g F8BT matrix, which itself does not undergo crystallization during cooling.

Figure 4.6. Cross-polarized optical microscope image of a F8BT film casted from 5 mg ml⁻¹ toluene solution with a P3HT grain placed on top during annealing at 250 °C for 5 min and upon subsequent cooling down to room temperature. Note that the sample was placed between the crossed polarizers enabling the contrast between isotropic molten P3HT (dark black) and anisotropic liquid-crystalline F8BT film (bright blue, birefringence).

The miscibility observed in the mixture is in line with recent investigations on the stability of F8BT/P3HT bilayers with X-ray reflectivity.[82] Zawodzki et al. reported

a progressive increase in interface roughness and drop of power conversion efficiency (PCE) values in solar cells based on F8BT/P3HT bilayers upon soft annealing at temperatures well below the glass transition. The absence of any induced crystallinity confirmed that the increase in roughness at the interface was not related to ordering of the polymer layers, but to inter-diffusion between the two phases. On account of the discussed mixing tendency, it is not surprising that the performance of solar cells based on mixtures of F8BT:P3HT are rather modest.[49] Blend phase separation is crucial in bulk-heterojunction solar cells in order to create an interface for both efficient exciton dissociation and efficient hole and electron transport to the electrodes. F8BT:P3HT blends clearly do not fulfil these conditions. Interestingly, it has been reported that adding 4-ethylbenzenesulfonic acid (EBSA) to F8BT:P3HT blends leads to enhanced phase separation accompanied by an increase in electron mobility and in turn, a 3-fold enhancement in PCE with respect to un-doped mixtures.[83] Doping with EBSA results in formation of F8BT-EBSA complexes bound by electrostatic interaction at the sulfur atom of the benzothiadiazole (BT) unit, which would in principle jeopardize F8BT:P3HT interactions leading to the observed morphology changes. Therefore, we conclude that the unusual miscibility found in F8BT:P3HT blends is favored by formation of inter-chain complexes delocalized across adjacent P3HT and F8BT chromophores which already form in the precursor solutions. Moreover, F8BT molecular packing in pristine films is influenced by the strong repulsion between BT units of neighbor chains.[50] Association between F8BT and P3HT could be a way to minimize repulsion between BT units and achieve a lower energy configuration.

4.3 Temperature and vapor annealing of blend films

Many polymer:polymer blends are immiscible partially because their high molecular weights contribute to decrease their effective entropy of mixing. Despite the existence of immiscibility, some as-spun films from polymer blends could have homogeneous surface topography due to a fast quench through solvent removal, which suppress surface phase separation and component crystallization. Indeed, these as-spun films

are remained in a thermodynamical pseudo-equilibrium. Post-deposition methods such as temperature or vapor annealing may assist in breaking this metastable equilibrium by providing significant mobility of polymer chain segments, thereby further altering the nanostructure of polymer blends.[84][85] In this regard, we examined the impact of annealing on the miscibility of P3HT in F8BT blends under temperature and organic vapor conditions.

4.3.1 Thermal annealing

Absorption spectroscopy depicted in Figure 4.7(a-c) was used as sensitive probe to investigate whether P3HT ordering in blends develops with temperature. F8BT:P3HT blend films with 45%, 70% and 80% P3HT molar contents were thermally annealed in N₂ atmosphere at 160 and 200 °C temperatures, i.e. well above F8BT glass transition. We observed no significant changes in the absorption spectra of 45% and 70% blends at such high annealing temperatures, Figure 4.7(a-b). The absence of P3HT crystallization and lack of reorganization upon annealing is in agreement with the results reported by *McNeill et al.*[84] Remarkably, the vibrational shoulders characteristic of crystalline P3HT appear for 80% annealed film and become more defined at higher temperature, Figure 4.7(c), indicating increased P3HT ordering and larger coherent length of the crystallites. Moreover, the lack of evidences for crystallization in blends upon annealing above the glass transition temperature is concomitant with our DSC results, pointing towards a large miscibility of P3HT in F8BT-rich blends corresponding to relatively lower crystallization enthalpy. For P3HT doping more than 80%, the frozen P3HT chains are aroused by temperature leading to the formation of aggregates as a result of P3HT nucleation.

Figure 4.7. Absorption spectra of F8BT:P3HT spin-coated and thermally annealed films with (a) 45%, (b) 70% and (c) 80% P3HT molar content. The annealed films were prepared by heating the respective as-spun films at 160 and 200 °C under nitrogen for 40 minutes and then cooling down slowly.

4.3.2 Toluene vapor annealing (TVA)

4.3.2.1 Absorption and PL

First, we studied the absorption and emission properties of F8BT:P3HT blends upon toluene annealing. Figure 4.8(a-b) depicts the absorption and PL spectra of a 75% F8BT:P3HT blend exposed to toluene for time periods from 15 min up to 4h, respectively. Upon annealing, the absorption spectra of blends showed enhanced vibronic shoulders at the absorption tail, pointing to increased ordering of the P3HT phase. Meanwhile, there are no significant differences between the PL of as-spun and annealed films, indicating an overwhelming PL contribution of *F8BT:P3HT complexes* over P3HT aggregates in annealed films.

Figure 4.8. (a) Absorption and (b) PL spectra of a 75% F8BT:P3HT spin-coated (black) and toluene vapor annealed films upon 15min (red), 1h (blue) and 4h (green). Excitation energy was 2.7 eV. The annealed films were prepared by placing as-spun thin films in a closed recipient containing a petri dish full of toluene.

4.3.2.2 Raman

Raman spectroscopy was employed to monitor the conformational evolution of

polymer chains. Figure 4.9 shows the Raman spectra of 75% F8BT:P3HT as-spun and annealed films upon 785 nm excitation, their peak positions, FWHMs of the C=C Raman mode and C-C to C=C Raman intensity ratios ($I_{C-C}/I_{C=C}$) being summarized in Table 4.3. As vapor annealing time increases, the C=C Raman mode gradually shifts to lower wavenumbers (from 1450 to 1448 cm^{-1}) and the FWHM value drops (from 31 to 28 cm^{-1}) concomitant with an enhancement of the $I_{C-C}/I_{C=C}$ value (from 0.12 to 0.19). These observations point towards an increase in conjugation length of P3HT chains upon vapor exposure. Film swelling leads to partial nucleation of P3HT chains into aggregates, where chains adopt more planar conformations resulting in the observed conjugation length enhancement.

Figure 4.9. Normalized Raman spectra of a 75% F8BT:P3HT spin-coated (black) and annealed films after exposure to toluene vapor for 15 min (red), 1h (blue) and 4h (green).

	C=C mode (cm ⁻¹)	C-C mode (cm ⁻¹)	FWHM _{C=C} (cm ⁻¹)	I _{C-C} /I _{C=C}
<i>As-cast</i>	1450	1376	31	0.12
<i>TVA 15min</i>	1449	1378	30	0.18
<i>TVA 1h</i>	1448	1378	30	0.18
<i>TVA 4h</i>	1448	1379	28	0.19

Table 4.3. Summary of parameters obtained from fits of the Raman spectra.

4.3.2.3 GIWAXS

GIWAXS has been effectively applied to study the crystallinity of polymer thin films, benefiting from the surface sensitivity of grazing incidence diffraction and the accessible atomic scale at wide-angle scattering.[86] The GIWAXS scattering patterns of F8BT:P3HT pristine as well as annealed films are presented in one-dimensional and two-dimensional forms, respectively. The recorded 2D pattern provides information about crystalline structure and sample orientation, while the 1D curve represents the integrated intensity as a function of the scattering vector of the meridional or in-plane region of the 2D pattern. The resulting 1D curves are plotted as a function of the q scattering vector, which is related to d (inter-planar distance) according to Bragg's law ($n\lambda = 2d\sin\theta$).

$$q = \frac{4\pi\sin\theta}{\lambda} = \frac{2\pi}{d} \quad \{4.1\}$$

Here θ is the scattering angle and λ is the incident wavelength. From {4.1}, we infer that the larger q values correspond to the smaller d at larger scattering angles.

Figure 4.10(a) and Figure 4.11(a-b) depict 1D and 2D GIWAXS patterns of semicrystalline P3HT and F8BT on quartz substrates respectively. The neat P3HT spin-coated thin film processed from toluene (red line in Figure 4.10(a)) shows characteristic scattering from the (100) peak at $q \sim 0.38 \text{ \AA}^{-1}$ and the (010) peak at $q \sim 1.6 \text{ \AA}^{-1}$. The (100) peak originates from P3HT lamellar stacking in the vertical

direction with inter-chain spacing $d \sim 16.5 \text{ \AA}$, as it can be deduced from the strong scattering centered on the meridional region of the corresponding 2D pattern (Figure 4.11(a)).[87] Likewise, the (010) peak is ascribed to π - π stacking ($d \sim 3.9 \text{ \AA}$) parallel to the substrate.[87] The (001) peak at $q \sim 0.39 \text{ \AA}^{-1}$ ($d \sim 16.2 \text{ \AA}$) and (004) peak at $q \sim 1.52 \text{ \AA}^{-1}$ ($d \sim 4.13 \text{ \AA}$) observed from the scattering of the semicrystalline F8BT (green line in Figure 4.10(a)) are responsible for π - π stacking in the normal direction with respect to the thin film plane [50], as evidenced by the presence of meridional spot in the 2D pattern, Figure 4.11(b).

Next, we compare the scattering patterns and peaks of 75% F8BT:P3HT blend films processed following three different methods: spincoating, spincoating followed by subsequent vapor annealing, and dropcasting. The 1D GIWAXS curve of spincoated blend (black line in Figure 4.10(b)), shows absence of crystallinity from any single component. In contrast, the dropcasted film (blue line in Figure 4.10(b)) shows the presence of semicrystalline structures reflected from the noticeable scattering peak at $q \sim 0.35 \text{ \AA}^{-1}$ ($d \sim 17.9 \text{ \AA}$), which corresponds to the strong inner scattering ring of the 2D pattern, (Figure 4.11(f)). It is not possible to undoubtedly ascribe it to P3HT or F8BT since the characteristic d-spacings of both polymers are fairly similar. Dropcasting enables the polymers to arrange in a lower free-energy configuration owing to the high boiling temperature of toluene and much slower evaporation rate compared to spincoating, thus favoring crystallization. Similar behavior occurs upon vapor annealing; the characteristic peak at $q \sim 0.35 \text{ \AA}^{-1}$ arises and becomes more prominent with time as evidenced by the increased scattering intensity as well as reduced FWHM, (Figure 4.10(b)). Accordingly, the corresponding inner ring of 2D patterns becomes more intense as a function of annealing time, (Figure 4.11(d-f)). Reorganization is however more clear in the dropcasted film since this fabrication method enables the larger interactions of polymers with solvent. Although the semicrystalline features cannot be unambiguously distinguished from P3HT or F8BT as previously mentioned, we speculate that they might be more probably related to P3HT crystallization based on our observations from absorption and Raman spectra. It is clear that toluene annealing leads to increased ordering and local de-mixing of the

F8BT and P3HT components.

Figure 4.10. 1D GIWAXS curves of (a) semicrystalline P3HT and F8BT films deposited on quartz, (b) 75% F8BT:P3HT dropcasted film (on quartz), spincoated film (on silicon), and toluene vapor annealed films (on quartz). The scattered intensity presented with arbitrary units has been separated for clarity. The region selected for integration is from $q \sim 0.2$ to $2.5 \text{ \AA}^{-1}$.

Figure 4.11. 2D GIWAXS patterns of (a) P3HT, (b) F8BT, (c) quartz, F8BT:P3HT toluene vapor annealed films for (d) 1h, (e) 4h and (f) F8BT:P3HT dropcasted film.

Consequently, based on all these observations, P3HT reorganization and local de-mixing are found in high-doping F8BT blends upon thermal and toluene vapor annealing. High temperature and film swelling after exposed to vapor enable re-arrangement of the polymer chains into lower configuration energies, breaking the thermodynamical pseudo-equilibrium of F8BT:P3HT spincoated films. At low P3HT content though, the absence of P3HT aggregation and lack of reorganization upon thermal annealing is evident, suggesting that the P3HT dispersion in F8BT remains unperturbed.

4.4 Conclusions

We find evidence for an unusually large miscibility of P3HT in F8BT matrix, due to

the distinctive F8BT:P3HT interactions well described in solution which strongly hinder P3HT crystallization. In contrast with P3HT crystallization observed in PMMA and L3-F8BT blends, *F8BT:P3HT complexes* associated with ground state charge-transfer interactions are transferred from F8BT:P3HT solutions and preserved in the solid state. There is no evidence for de-mixing and reorganization of polymers in blend films. P3HT chains in F8BT matrix adopt a conformation with low degree of planarization, characterized by relatively short conjugation length and a wider distribution of chain conformations. These unforeseen structure properties pave the way for the use of regioregular P3HT in photonic and lighting applications through appropriate control of P3HT inter-chain interactions.

Furthermore, we study the evolution of F8BT:P3HT film nanostructure under two post-processing annealing protocols: thermal annealing and toluene vapor annealing. P3HT re-arrangement and local de-mixing are inferred in high-doping blends from absorption, photoluminescence, Raman and grazing angle X-ray scattering experiments. The miscibility of P3HT in F8BT blend films has a dependence on P3HT doping composition.

Chapter 5. Photophysics and Optical Gain Properties of F8BT:P3HT Blend Films

In this Chapter, we shed light into the efficient Förster resonant energy transfer (FRET) interaction between F8BT and *F8BT:P3HT complexes* in F8BT:P3HT blends by femtosecond transient absorption spectroscopy. The optical gain properties of blends were investigated by amplified spontaneous emission (ASE) measurements, demonstrating efficient optical gain in the red part of the spectrum attributed to *F8BT:P3HT complexes*. Furthermore, upon direct photoexcitation of F8BT or *F8BT:P3HT complexes* we quantitatively determined the FRET contribution to ASE as well as competing exciton losses in blends. The corresponding density of absorbed photons at threshold conditions obtained following direct F8BT or *F8BT:P3HT complexes* pumping were compared to determine the respective ASE efficiencies. We observe a reduction in ASE efficiency upon F8BT photoexcitation which in the best case, amounts to 20% respect to direct photoexcitation of *F8BT:P3HT complexes*, this loss being likely attributed to exciton - exciton annihilation in F8BT.

5.1 Preliminary evidences for FRET in F8BT:P3HT blends

Figure 5.1(a) depicts the absorption spectra of a set of F8BT:P3HT blends with different P3HT content. As already discussed in the previous two chapters, they are composed by two dominant contributions associated to F8BT chromophores and F8BT:P3HT ground state charge-transfer complexes. At low P3HT doping, the absorption spectra can be perfectly reconstructed with both F8BT and *F8BT:P3HT complex* spectral contributions, (Figure 5.1(b)).

The PL spectra of blends upon photoexcitation at the absorption peak of F8BT (2.7 eV, 460 nm) evolve from F8BT green-yellow emission (for low P3HT content) towards *F8BT:P3HT complex* emission with maximum peak at 2.0 eV, and satellite peaks at 1.8 and 1.7 eV (for medium / high P3HT content), (Figure 5.1(c)). The gradual quenching of F8BT fluorescence with P3HT doping and the concomitant augment of emission in the red part of the spectrum indicates the interplay of a FRET process between F8BT

chromophores and *F8BT:P3HT complexes*. Optimum Förster resonant conditions are supported by the spectral overlap between F8BT emission and *F8BT:P3HT complex* absorption (Figure 5.1(d)).[88] Moreover, residual F8BT emission is only observed at the lowest P3HT content levels (35% and less) thus confirming a highly efficient energy transfer in blends.

Figure 5.1. (a) Absorption of F8BT:P3HT blend films with 0% (dotted grey), 15% (red), 25% (blue), 45% (navy), 70% (dark yellow) and 100% (dashed black) monomer molar fraction of P3HT. (b) Spectral decomposition of the absorption spectrum of a 15% F8BT:P3HT blend film in F8BT (dotted grey) and *F8BT:P3HT complex* (dashed red) contributions. (c) PL spectra of blends containing 5% (red), 25% (blue), 35% (navy), 45% (pink) and 70% (dark yellow) P3HT molar contents as well as pristine F8BT (dotted grey) and P3HT (dashed black). Excitation energy was 2.7 eV for blends and 2.3 eV for P3HT. (d) Spectral overlap between PL of F8BT (black) and absorption of the *F8BT:P3HT complex* (red).

5.2 Photoluminescence quantum efficiency of F8BT:P3HT blends

Next, we evaluate the FRET efficiency in blends by performing photoluminescence

quantum efficiency (PLQE) measurements upon excitation with 2.7 eV, (Figure 5.2). Note that at 2.7 eV the photoexcitation is predominantly placed on F8BT and residual *F8BT:P3HT complex* absorption is only noticeable at high P3HT doping levels. PLQE here is defined as the ratio of the number of photons emitted (both by F8BT and/or *F8BT:P3HT complexes*) to the number of photons absorbed. A maximum PLQE value of 24% is found in 15% blends, this value remaining unaltered in the 15% - 45% concentration range. These values are considerably enhanced with respect to the PLQE reported in pristine regioregular P3HT (4%) [40] or regiorandom P3HT (8%) [89]. PLQE values subsequently drop for P3HT doping levels between 45% and 80% molar content, probably due to counter-balancing concentration quenching effects, in line with the decrease in PL quantum efficiency at high guest doping reported in polymer blends elsewhere.[88][90]

Figure 5.2. PLQE values of F8BT:P3HT blends upon photoexcitation with 2.7 eV as a function of P3HT molar content.

5.3 Femtosecond transient absorption spectroscopy in F8BT:P3HT blends

5.3.1 Energy transfer dynamics

Transient absorption studies in blends were carried out upon pumping with 3.2 eV (387 nm) and probing the spectral region from 2.5 (497 nm) down to 1.7 eV (730 nm). The transient absorption spectra at 0 and 4 ps delays in pristine F8BT and a 15% F8BT:P3HT blend are shown in Figure 5.3. The 0 ps differential absorption (ΔA)

spectrum of F8BT (Figure 5.3(a)) is characterized from high to low energies by a negative photobleach (PB) tail extending down to 2.4 eV, a stimulated emission (SE) band centered at 2.2 eV and a positive ΔA band between 2.0 and 1.7 eV associated to photoinduced absorption (PA), in agreement with previous reports.[91] Lack of spectral evolution is inferred from the 4 ps ΔA spectrum, (Figure 5.3(b)), except for a smoothing of the pronounced spectral dip at 2.4 eV. Silva et al. assigned this dip to sharp PA associated to polaron-pairs overlapping with PB.[91] Attenuation of the PA at 2.4 eV is likely caused by a change in the relative concentration of singlet excitons, (which dominates most of the pump-probe spectrum) respect to polaron-pairs. This effect is emphasized upon increasing the pump fluence and consequently the polaron-pair quantum yield.[92] The 0 ps ΔA spectrum of the F8BT:P3HT blend, (Figure 5.3(c)), preserves the spectral features characteristic of F8BT except for the absence of spectral dip at 2.4 eV, and a red-shift of the isosbestic point by about 20 meV. Note that the 3.2 eV pump pulse implies that photoexcitation is placed mainly (not exclusively) in F8BT chromophores, (refer for instance to the spectral decomposition of a 15% F8BT:P3HT blend absorption in Figure 5.1(c)). Thus, the subtle spectral differences observed in the 0 ps delay spectra of F8BT and blend could be associated to minor contributions from direct *F8BT:P3HT complex* photoexcitation. Focusing on the 4 ps delay spectrum of F8BT:P3HT (Figure 5.3(d)), the positive ΔA band (2.1 - 1.7 eV) ascribed to F8BT PA in the 0 ps spectrum is considerably reduced and overcome by negative ΔA in the 2.0 - 1.8 eV. This latter spectral region is in correspondence with the F8BT:P3HT PL in blends, so that we univocally assign it to SE from the exciton levels of *F8BT:P3HT complexes*. This delayed SE confirms the presence of a FRET mechanism from F8BT to *F8BT:P3HT complexes* and a significant exciton transfer at 4 ps delay.

Figure 5.3. (a-b) ΔA spectra of F8BT at 0 and 4 ps delay respectively. (c-d) ΔA spectra of a 15% F8BT:P3HT blend at 0 and 4 ps respectively. The horizontal line in each graph is the zero line and the 1% and 0.5% arrows correspond to ΔA scale values of 0.01 and 0.005.

5.3.2 Energy transfer rates

Additional insights into the FRET efficiency are displayed in Figure 5.4. The ΔA dynamics at 2.3 eV (F8BT SE) of 5%, 15% and 70% blends (from green to black signal) reflect acceleration with doping due to F8BT SE quenching. Concomitantly, build-up kinetics is seen at 2.1 eV associated to the appearance of the PB band of *F8BT:P3HT complexes*, (Figure 5.4(b-c)). Likewise, the ΔA dynamics at 1.8 eV of 5% and 15% blends (Figure 5.4(a)), show a change of sign as F8BT PA is gradually overcome by *F8BT:P3HT complex* SE due to energy transfer from F8BT. In 70% blends the transfer rate approaches the pulse duration and gradual population effects are no longer visible. Interestingly, the SE contribution at 1.8 eV is overwhelmed by a characteristic long-lived PA, absent in blends with low P3HT content. Global fit analysis involving three excited states associated to singlet excitons in F8BT (S_1^{F8BT}), *F8BT:P3HT complex* ($S_1^{F8BT:P3HT}$) and a longer-lived excited state associated to the complex

($X^{F8BT:P3HT}$) coupled by a sequential chain reaction ($S_I^{F8BT} \rightarrow S_I^{F8BT:P3HT} \rightarrow X^{F8BT:P3HT}$), was applied to fit the ΔA kinetics. Accurate fits of the highest concentrated samples (45% and 70%) required necessarily to invoke the long-lived $X^{F8BT:P3HT}$ state.

Figure 5.4. Pump-probe dynamics at (a) 1.8 eV, (b) 2.1 eV and (c) 2.3 eV of 5% (green), 15% (red) and 70% blends (black). Dashed lines stand for fits to kinetics. The horizontal line in (a-c) corresponds to the zero line. (d) FRET rates obtained from global fits as function of P3HT molar content.

Scheme 5.1. Global model proposed for F8BT:P3HT blends.

The kinetic model (Scheme 5.1) describes direct photoexcitation of F8BT and sequential population of *F8BT:P3HT* complex singlet exciton levels with the following rate equations:

$$\frac{dS_0^{F8BT}}{dt} = -g + k_{ET}S_1^{F8BT} \quad \{5.1\}$$

$$\frac{dS_1^{F8BT}}{dt} = g - k_{ET}S_1^{F8BT} \quad \{5.2\}$$

$$\frac{dS_1^{F8BT:P3HT}}{dt} = k_{ET}S_1^{F8BT} - k_1S_1^{F8BT:P3HT} \quad \{5.3\}$$

$$\frac{dX^{F8BT:P3HT}}{dt} = k_1S_1^{F8BT:P3HT} - k_xX^{F8BT:P3HT} \quad \{5.4\}$$

$$\frac{dS_0^{F8BT:P3HT}}{dt} = -k_{ET}S_1^{F8BT} + k_xX^{F8BT:P3HT} \quad \{5.5\}$$

where S_0^{F8BT} and $S_0^{F8BT:P3HT}$ denote the ground state of F8BT and *F8BT:P3HT complex* respectively; g , k_{ET} , k_1 and k_x represent the rates of pump-induced exciton generation, host:guest energy transfer, $S_1^{F8BT:P3HT}$ decay and $X^{F8BT:P3HT}$ decay, respectively. Table 5.1 displays the parameters obtained from the fits.

P3HT molar fraction	$k_{ET} (ps^{-1})$	$k_1(ps^{-1})$	$k_x (ps^{-1})$
5%	$4 \cdot 10^{-1}$	$8.3 \cdot 10^{-2}$	$2.4 \cdot 10^{-3}$
15%	1.3	$2.2 \cdot 10^{-1}$	$1.3 \cdot 10^{-3}$
45%	1.6	$9.4 \cdot 10^{-1}$	$2.8 \cdot 10^{-3}$
70%	1.8	$2.3 \cdot 10^{-1}$	$5.1 \cdot 10^{-4}$

Table 5.1. Decay rates extracted from global fit analysis of pump-probe data.

The FRET rate values estimated from the build-up of *F8BT:P3HT complex* exciton populations are illustrated in Figure 5.4(d). A low content of 15% P3HT in blend already suffices to achieve large host:guest interaction as reflected in a 1.3 ps^{-1} (0.77 ps) energy transfer rate (time). This observation is in line with the already noticeable concentration of complexes deduced from the absorption spectral decomposition shown in Figure 5.1. FRET rates reach a maximum value at c.a. 70% blend composition with a corresponding FRET rate (time) of 1.8 ps^{-1} (0.55 ps). This value confirms the strong FRET coupling present in F8BT:P3HT blends compared to other polymer:polymer blends.[9] The gradual rate increase and FRET rate saturation at high P3HT content (70%) is perfectly consistent with the large degree of miscibility of P3HT

and F8BT polymers. In conjugated polymer blends, FRET is often jeopardized by the appearance of polymer phase segregated domains and consequently a recovery of the host polymer emission at high guest content.[20] The presence of SE from *F8BT:P3HT complexes* in the red spectral region by aid of efficient energy transfer and the notable PLQE values in blends motivates our next investigations on F8BT:P3HT films as optical gain medium.

5.4 Amplified spontaneous emission upon selective photoexcitation

5.4.1 ASE spectra of F8BT:P3HT blends

The optical gain properties of F8BT:P3HT blends were studied by ASE measurements. Figure 5.5(a) depicts a set of PL spectra of a 35% F8BT:P3HT blend photoexcited at 2.7 eV (460 nm) with varying pump energy densities. ASE leads to spectral narrowing of the emission giving rise to a narrow peak centered at 1.9 eV for pump fluences above 0.04 mJcm⁻². [93] The spectral position of the ASE peak coincides with the 0-1 vibronic peak of the PL spectrum confirming that the polymer blend behaves as a four-level amplifying system. Lower ASE thresholds are expected in the 0-1 spectral region since ultrafast vibrational relaxation enables population inversion to be more efficiently achieved from the lowest vibrational level of the excited state to the vibrationally excited levels of the ground state. [94][10] The dependencies of both the ASE full-width-half-maximum (FWHM) and the output light intensity (integrated area under PL spectrum) with the pump fluence are shown in Figure 5.5(b). ASE gives rise to a soaring growth of the output intensity at the highest gain position and a dramatic collapse in the linewidth from 60 to less than 10 nm. Figure 5.5(c) displays the normalized ASE spectra of F8BT:P3HT blends with P3HT molar fraction comprised between 5% and 70%. As the P3HT fraction increases, a slight shift of the ASE peak from 1.9 eV to 1.85 eV appears, also seen in the PL spectra of blends, being caused by P3HT doping and the different dielectric constants of F8BT and P3HT. [54] The observation of ASE at 1.9 eV upon predominant F8BT pumping is a direct consequence of efficient exciton transfer from the F8BT exciton levels to *F8BT:P3HT complexes*. The losses from self-absorption are expected to be alleviated in 25% and 45%

blends, since their emission are efficiently shifted away from blend absorption. Likewise, the broad fluorescence backgrounds superposing with ASE in 5% and 15% blends are explained as due to incomplete FRET, consistent with our previous PL observations. Hitherto, the absence of F8BT ASE in blends, i.e. the lack of line narrowing around 2.2 eV characteristic of F8BT ASE [10], confirms that FRET competes effectively with F8BT stimulated emission even at the lowest 5% and 15% doping concentrations.

Figure 5.5. (a) ASE spectra and (b) corresponding values of FWHM (open circles, left ordinate) and integrated area (filled squares, right ordinate) as a function of input fluences, for 35% F8BT:P3HT blend film upon excitation with 2.7 eV. (c) ASE spectra of F8BT:P3HT blend films normalized at the peak with 5, 15, 25, 45 and 70% P3HT molar concentrations.

5.4.2 Efficiency of Förster-assisted optical gain

In order to shed light into the contribution of FRET on ASE, we evaluated and

compared the ASE threshold values obtained in blends upon two different pumping schemes: photoexcitation with 2.3 eV (direct pumping of *F8BT:P3HT complexes*) and photoexcitation with 2.7 eV (predominant pumping of F8BT exciton levels followed by FRET to *F8BT:P3HT complexes*). For comparative purposes, energy pulses employed for photoexcitation with 2.7 and 2.3 eV had same duration and were focused on approximately same areas.

First, Figure 5.6 (a) shows the ASE thresholds of blends upon 2.7 and 2.3 eV photoexcitation as a function of P3HT molar concentration. ASE threshold values are determined as the incident pump fluence at which the FWHM linewidth falls to half with respect to that of the PL spectrum obtained with the lowest pump fluences. The 2.3 eV-pumped ASE threshold value for the 0 - 25% P3HT content ratio exhibits a decreasing trend with P3HT concentration. This in other words means that less fluences are required to generate ASE as the P3HT doping rises, a behavior likely caused by the progressive absorption increase at 2.3 eV with P3HT content. Above 25%, the ASE threshold value saturates and eventually rises at P3HT doping above 45%. This latter effect is most likely due to concentration quenching, in line with the already discussed drop in PLQE in highly P3HT loaded blends. The 2.7 eV-pumped ASE thresholds follow a similar trend; in the low concentration regime the threshold values decrease due to the increased F8BT to *F8BT:P3HT complexes* energy transfer efficiency. The 2.7 eV-pumped ASE thresholds are mostly below those obtained with 2.3 eV photoexcitation, observing the larger differences at low doping concentrations (5% and 15%). For such low P3HT fractions, FRET contributes to reduce the ASE threshold by a factor of 3. The lowest ASE threshold values are found on 45% blends (0.05 and 0.06 mJcm⁻² for 2.7 and 2.3 eV excitation respectively). At those medium-high concentrations, the differences in ASE thresholds upon host / guest photoexcitation shrink owing to the enhanced blend absorption at 2.3 eV. Thus, FRET appears to be particularly effective to reduce thresholds in blends with very low guest content.

Based on the obtained threshold values we calculated the absorbed photon density at thresholds upon photoexcitation with 2.7 eV and 2.3 eV in order to compare the ASE efficiencies upon F8BT or *F8BT:P3HT complex* photopumping. Bearing this in mind,

we first define the total absorbed photon number (β) at threshold conditions upon photoexcitation with ω (eV) energy as:

$$\beta \sim \frac{SE_{th}A}{\omega\xi} \quad \{5.6\}$$

where E_{th} is the measured ASE fluence threshold (mJ cm^{-2}), S refers to the excitation area (cm^2), A stands for the absorbance value of blend at ω (eV) and ξ is the eV to mJ conversion constant ($1.6 \cdot 10^{-16} \text{ mJ eV}^{-1}$). The FRET-assisted ASE efficiency (Δ) is then defined as the ratio of the absorbed photon numbers at threshold upon 2.3 ($\beta_{2.3}$) and 2.7 eV ($\beta_{2.7}$) photoexcitation as:

$$\Delta (\%) = 100 * \frac{\beta_{2.3}}{\beta_{2.7}} \quad \{5.7\}$$

The dependencies of $\beta_{2.7}$, $\beta_{2.3}$ and Δ with P3HT molar concentration are shown in Figure 5.6(b). Interestingly, the $\beta_{2.7}$ values are above the $\beta_{2.3}$ for all concentrations, i.e. a larger number of absorbed photons to produce ASE is required when pumping F8BT than *F8BT:P3HT complexes*. This in other words suggests the presence of additional exciton de-activation pathways upon FRET-assisted respect to direct pumping of *F8BT:P3HT complexes*. These losses diminish with concentration; in a 70% blend for instance a Δ value of 80% is found, implying only a 20% difference upon both photoexcitation schemes. In the low doping regime, the progressive loss reduction upon increasing the P3HT molar fraction is concomitant with enhancement of FRET rate values and seems to suggest that in this regime F8BT exciton losses are mainly caused by incomplete energy transfer. This hypothesis is supported by the residual F8BT emission observed in blends with 5 - 35% P3HT content. At high doping levels however, the lack of residual F8BT emission points towards a different exciton loss mechanism competing with FRET-assisted *F8BT:P3HT complex* population. It has been previously shown that exciton - exciton annihilation is particularly pronounced in F8BT owing to the large spectral overlap between the F8BT PL and excited state absorption spectra, which yields to a large exciton - exciton interaction radius.[91] Therefore, in the high concentration regime, exciton - exciton annihilation in F8BT is likely to be the primary mechanism responsible for the different ASE efficiencies upon direct/indirect guest photoexcitation. At high P3HT content, competition between

FRET and F8BT exciton - exciton annihilation leads to 20% less of the total harvested F8BT excitons failing to contribute to ASE.

Figure 5.6. (a) ASE threshold values of F8BT:P3HT blend films as a function of P3HT molar concentration upon 2.7 eV (filled circles) and 2.3 eV (filled triangles) photoexcitation. (b) The absorbed photon number at 2.7 eV (open squares) and 2.3 eV (open circles) and the FRET to ASE efficiency (filled triangles) as function of P3HT molar concentration.

5.5 Conclusions

Concomitant with the large miscibility of P3HT in F8BT, an effective Förster resonant energy transfer occurs from F8BT to *F8BT:P3HT complexes*, leading to efficient red emission and optical gain properties in the latter as demonstrated by ASE measurements. The FRET dynamics are investigated with femtosecond transient absorption spectroscopy observing a very efficient energy transfer at low doping

levels and transfer rates (times) which reach 1.8 ps^{-1} (0.55 ps) at 70% P3HT molar content. Accordingly, the emission of F8BT:P3HT blends reach maxima PLQE values of 25% (almost a seven-fold efficiency enhancement with respect to neat / aggregated P3HT).

Furthermore, the ASE threshold values of F8BT:P3HT blends are assessed upon two different photoexcitation mechanisms: direct and FRET-assisted guest exciton generation. In the low guest concentration regime we observe large differences in the threshold values obtained upon these two photoexcitation schemes. Such differences are primarily caused by the large dilution and low absorption of guest in blends, leading to differences of one order of magnitude in favor of FRET-assisted ASE. The ASE efficiencies obtained by accounting for the relative host (guest) absorption in blends indicate however the presence of exciton losses when pumping F8BT respect to pumping *F8BT:P3HT complexes*. In blends with the highest FRET rates, additional exciton losses amount to approximately 20% of the total harvested exciton population being likely attributed to exciton - exciton annihilation. Despite the observed losses, we remark that the lower ASE thresholds values were achieved upon F8BT pumping and subsequent energy transfer to *F8BT:P3HT complexes*. Thus, the use of host:guest systems coupled by FRET is an attractive approach to achieve optical gain at low pumping thresholds. The long range nature of the FRET interaction enables efficient host-to-guest energy transfer at low guest doping levels and concomitant promotion of the guest emission properties due to dilution in the host matrix.[9] Our results demonstrate that these positive effects are not outbalanced by competing losses such as exciton - exciton annihilation in the host polymer. Yet, we conclude that excitonic losses in strongly coupled host:guest systems upon large fluence photoexcitation conditions are not negligible and their hindrance would lead to further performance improvements of optically pumped lasers and optical amplifiers. These observations are particularly relevant in polyfluorene based gain media, where excitonic losses upon high photoexcitation fluences are notorious.[95]

Chapter 6. F8BT:P3HT Device Applications

In this chapter, we investigate the application of F8BT:P3HT blends as emissive media in both electrically pumped light-emitting diodes and optically pumped lasers based on distributed feedback structures. This work is motivated by the already discussed high photoluminescence quantum yields and efficient optical gain properties exhibited by F8BT:P3HT blend films. We develop highly transparent and flexible DFB lasers adopting CdA foil as flexible substrate with grating nanostructures imprinted on the surface, instead of conventional quartz or SiO₂ based nanostructured surfaces.[96][97] F8BT:P3HT blend films were spin-coated on periodically corrugated CdA substrates with pre-determined grating periods, bringing about low-threshold surface-emitting DFB lasers for red emission. The DFB fabrication processes combine the convenience of the nanoimprinting method and simple solution processing of conjugated polymers, favoring its feasibility for scaled-up production at low cost.

6.1 PLEDs based on F8BT:P3HT blends

6.1.1 Device fabrication

PLEDs based on F8BT:P3HT, with sandwich structures as depicted in Figure 6.1, are in essence composed of F8BT:P3HT blends with different P3HT content as an emissive layer and PEDOT:PSS as a hole-injecting layer, sandwiched between transparent ITO anode and a thermally evaporated aluminum cathode. The ITO coated glass substrates were initially cleaned by three successive ultrasonic baths of acetone, water and isopropanol for each 10 minutes before drying under nitrogen. PEDOT:PSS solutions were then spin-coated onto ITO substrates at the speed of 3500 rpm for 1 minute, and subsequently annealed in air at 120 °C for 15 minutes. On top of the PEDOT:PSS layer (c.a. 60 nm thick), F8BT:P3HT toluene mixtures of 20 mg ml⁻¹ total polymer concentration were spin-coated at 2000 rpm for 1 minute. The thickness of F8BT:P3HT blend films varied from 90 to 100 nm depending on the blend composition. Finally, aluminum cathodes (50 nm) were deposited by thermal

evaporation in vacuum (5×10^{-6} torr), being the cathode shape delimited with a purposely designed shadow mask.

Figure 6.1. (a) PLED sandwich structure. (b) Energy level diagram of PLED device.

6.1.2 Device characterization

PLEDs based on F8BT:P3HT blends were fabricated with P3HT monomer molar concentration comprised between 15% and 70%. The corresponding electroluminescence (EL) spectra, shown in Figure 6.2(a), resemble the PL particularly at low P3HT doping (15% and 35%). The color coordinate (CIE), (Figure 6.2(b)), suggests that the emission is almost in the red range with little orange component. The current density-voltage curves of devices are displayed in Figure 6.2(c). As P3HT concentration is raised, the turn-on voltage tends to decrease from 4.1 to 3.0 V with a concomitant enhancement in the rectification ratio. This is likely due to the notable hole injection and transport properties of P3HT consequently lowering hole injection

barrier between PEDOT:PSS and F8BT:P3HT layers. However, the highest luminance behavior is found in 35% F8BT:P3HT blends (7.85 cd/m^2 at 450 mA/cm^2), (Figure 6.2(d)), concomitant with the highest PLQE value (24%) found for this composition, (c.f. PLQE measurements in Chapter 5). Note that PLEDs based on 15% blends have lower device luminance than PLEDs based on 35% blends despite having comparable PLQE values, which confirms that hole injection and transport in PLEDs with low P3HT content is an important limiting factor. In the opposite case, PLEDs with 70% P3HT content shows more saturated red EL and better current density-voltage characteristics, yet their luminance are extremely low because of their low PLQE (12%). The relevant parameters are summarized in Table 6.1. Therefore, the optimum PLED is obtained with 35% P3HT content, consistent with previous work on F8BT:P3HT PLEDs.[40] Kim et al. reported PLEDs with luminances above 2900 cd/m^2 for current densities above 600 mA/cm^2 , values which are much higher than our results. This is probably related to the use of LiF between cathode and emission layer which promotes electron injection and helps to prevent exciton quenching at the Al cathode.

Figure 6.2. PLED device performances of F8BT:P3HT blends with 15% (blue), 35% (red), 70% (cyan) and 100% (black) P3HT molar content: (a) electroluminescence spectra, (b) color coordinate (only for 35%), (c) current density-voltage characteristics and (d) luminance-current density characteristics. The dashed blue spectrum in (a) corresponds to the PL of 15% F8BT:P3HT, exemplifying the similarity between EL and PL blend spectra.

P3HT molar fraction	λ_{EL} (nm)	CIE (x, y)	Turn-on Voltage (V)	Luminance (cd/m^2) at $450 mA/cm^2$
15%	613	(0.63, 0.37)	4.1	2.65
35%	609	(0.64, 0.36)	5.0	7.85
70%	644	(0.65, 0.35)	3.0	0.04
100%	659	(0.67, 0.33)	3.4	0.36

Table 6.1. Parameters for PLED device performances.

6.2 All-polymer DFB lasers based on F8BT:P3HT blends

6.2.1 Introduction

6.2.1.1 The DFB principle

Optically pumped organic lasers have been intensively devised with different resonator geometries such as planar microcavities formed by stacks of alternating dielectric layers of different index, microrings, microspheres and distributed feedback geometries, benefiting in many cases from simple organic semiconductor solution processing.[98][99][100][101] Among all, DFB lasers are distinctive in that the resonators do not rely on either mirrors or total internal reflection for optical feedback, but alternatively impose periodic wavelength-scale diffractive structures functioned as Bragg gratings. The light waveguided in the gain layer is scattered by the periodic corrugations. If the periodic corrugation is appropriately designed, the scattered waves will constructively interfere with each other leading to a standing wave travelling back and forth along the layer. Given the implicit dependence of diffraction angle and wavelengths expressed by the Bragg law ({6.1}), for a given diffraction period only a discrete set of wavelengths will selectively respond to produce coherent emission in a reversed direction with respect to the incident light and thereby give rise to feedback of the optical field. These corresponding wavelengths are given by Bragg's condition at 90°.[102]

$$m\lambda = 2n_{\text{eff}}\Lambda \quad \{6.1\}$$

On the left-hand side, m is an integer number that denotes the diffraction order and λ is the emission wavelength; on the right-hand side, n_{eff} stands for the effective refractive index of the corrugated waveguide and Λ is the corrugation period. For first ($m=1$) and second ($m=2$) order diffraction, the light emitted respectively at wavelengths $\lambda = 2n_{\text{eff}}\Lambda$ and $\lambda = n_{\text{eff}}\Lambda$ propagates along the plane of the corrugated waveguide. DFB lasers with second-order grating structures ($\Lambda = \frac{\lambda}{n_{\text{eff}}}$) can pave an elegant way for surface laser emission, although they normally have higher thresholds than lasers with first-order gratings due to their outcoupling losses.[94] The implementation of DFBs based on second order diffraction is however simpler since

the separation between the grating lines is twice larger than for first-order diffraction, making them more accessible with nanopatterning techniques. In the past few decades, DFB laser cavities with 1D and more complex 2D or 3D feedback have been developed based on a large variety of organic semiconductors, including small molecules, conjugated polymers and host:guest energy transfer blends. [10][14][97][103] These reports have demonstrated that fine-design of DFB organic lasers translates into low-threshold surface emission and excellent wavelength selection properties. In this chapter section, 1D DFB lasers based on F8BT:P3HT blends were fabricated by imprinting linear gratings with 416 nm period on CdA substrates with nanoimprint lithography (NIL). The principle of NIL and the distinctive thermoplastic properties of CdA will be described in the following.

6.2.1.2 NIL

The preparation of periodic DFB nanostructures in polymer films can be readily achieved using NIL by simple replication of the original master grating onto the polymer surface upon applying temperature and pressure.[104] Standing out from other elaborated lithographic approaches like electron beam lithography (EBL), NIL not only can reproduce surface patterning at great precision down to sub-5 nm resolution [105], but also can achieve a volume production at low costs.

The NIL process generally starts with heating a polymer film above its T_g , where the polymer experiences a sharp decrease in viscosity from the glassy to rubbery state, as shown in Figure 6.3, accompanied by an enhanced flow behavior. Then a rigid master grating mold is pressed into the soften polymer surface to render the deformation. After molding, the temperature is cooled below T_g enabling the polymer back into the glassy state to maintain the deformation. Finally the pressure is released and the mold is separated from the patterned polymer. In this thesis, the grating nanostructures were imposed on CdA substrates rather than on the conjugated polymer layer itself to avoid the degradation of conjugated polymer gain media at high temperatures.

Figure 6.3. Typical behavior of the storage modulus of a polymer as a function of temperature during the NIL and demolding processes. T_g and T_m stand for the glass transition and melting temperatures respectively of the polymer. (After Chantiwas et al. [105])

6.2.1.3 CdA as substrate

CdA was employed in our DFB laser as flexible substrate. CdA is obtained from a renewable wood pulp, which is highly available and biodegradable. It benefits from a combination of excellent optical properties (large transparency even upon annealing, relatively low refractive index $n \sim 1.49$ beneficial for light confinement) and exceptional mechanical properties (thermoplastic, $T_g \sim 110^\circ\text{C}$) highly suitable for developing nanostructures using nanoimprinting. Furthermore, the compatibility of CdA substrates with the solvents employed for thin film processing was preliminarily characterized. Contact angle microscopy of toluene droplets on CdA revealed very low contact angles and high degree of wetting, comparable to other hydrophilic substrates of high affinity to toluene, (for instance quartz), Figure 6.4(a-b). Such high surface energy of the CdA substrate allows polymer-toluene solution to uniformly spread and to form a homogeneous polymer layer during spincoating. In view of all these distinctive characteristics, CdA appears as a material of interest for flexible optoelectronics.

Figure 6.4. The measured contact angles of toluene on (a) CdA and (b) quartz surfaces.

6.2.2 Fabrication of DFBs based on F8BT:P3HT blends on CdA substrates

The all-polymer DFB lasers were fabricated by spin-coating F8BT:P3HT blend films onto corrugated CdA substrates, where gratings were engraved by NIL using nanostructured Si molds. Here, a silicon master mold with $\Lambda = 416$ nm periodicity, fill-factor 50%, and 250 nm etch depth acquired from Lightsmyth Technologies Inc. was used. Before molding, the standard Si master mold was treated with a fluorosilane through vapor deposition of 1H,1H,2H,2H-perfluorodecyl trichlorosilane (Alfa Aesar, MA) as anti-adhesive coating to facilitate the demolding process. Then, the master mold was directly imprinted onto each CdA substrate by means of an Eitre 3 Nano Imprint Lithography System by Obducat. During the process, the Si mold / CdA substrate assembly was heated at 180 °C under an applied pressure of 40 bar for 300 s and after that, cooled down to 70 °C without releasing the pressure. A 45% F8BT:P3HT blend solution was prepared from toluene at a concentration of 20 mg/ml. The solution was filtered with a 0.22 μ m syringe filter and subsequently spin-coated at 2000 rpm for 1 minute on top of the imprinted CdA substrates ($n=1.49$) with grating period 416 nm (45% F8BT:P3HT, $n=1.95$). The used CdA substrate had 300 μ m thickness and the mean thickness for the F8BT:P3HT film was 180 nm.

6.2.3 Surface characterization of nanoimprinted CdA substrates

6.2.3.1 AFM

The surface topography of the grating pattern was first studied by non-contact AFM. Figure 6.5 illustrates a comparison between the master Si mold and the CdA replica comprising the AFM topography image and the corresponding grating depth profile. The images confirm that the period value approaches to the nominal value for both the mold and the replica by measuring the total length across 10 lines. Considering the specific shape of the measured profile caused by the shape of the AFM tip, the surface profiles indicate that the grating depth is well reproduced through imprinting, extracting a modulated depth of c.a. 250 nm. Thus, the surface morphology of the Si mold is replicated onto the CdA substrate with high fidelity.

Figure 6.5. AFM topography images with their respective profiles below of a 416 nm period grating in (a) Si and (b) CdA. The white line in each AFM image means the length across 10 lines, and the grating depth is measured along it.

6.2.3.2 GISAXS

Further insights into the periodicity of the gratings and the quality of the CdA replica are provided by GISAXS, which has demonstrated to be a powerful technique for the characterization of periodic surface structures prepared by a variety of methods [106][107]. The 2D diffraction patterns shown in Figure 6.6(a) present statistical information averaged over large areas (c.a. 70 mm²) covered by the elongated

footprint of the X-ray beam. The corresponding pattern obtained from the hard silicon gratings, in the top row, features a series of intense spots accompanied by a weak vertical scattering forming a semicircle, which are characteristic of gratings as observed at shallow incidence angles.[108][109] These spots are consecutive orders of the first scattered order located at the lowest horizontal scattering angle (ω) value and are related to the pitch length of the grating. The 2D pattern situated in the bottom row is acquired from nanoimprinted CdA. At first sight it is qualitatively different with respect to that of Si mold. The circular interference pattern vanishes and the dominant feature turns into vertical rod-like scattering maxima. This transition from semicircular spots to rod-like maxima has been verified by different authors as a consequence of the decrease in the coherence length of the scatters, i.e. the longitude of the grating lines.[106][109] Here two factors arising from the imprinting of CdA substrate maybe responsible for such a diminution: first and most likely, the lower planarity of the CdA sample compared to the Si master mold (the beam impinges the CdA sample at various angles at the same time depending on the local area) and second, the presence of small defects (some degree of discontinuity) along the grating lines.

Figure 6.6. (a) Characteristic 2D GISAXS patterns correspond to the Si grating (top row) and the CdA replica prepared by NIL (bottom row) with period of approximately 416 nm. α and ω represent the two main scattering angles for obtaining information about structural correlations in the vertical and horizontal directions respectively. (b) Integrated intensity curve along the vertical direction of the GISAXS pattern for both Si and CdA gratings. For clarity, only half of each curve is presented. The curves were shifted in order to correct the pixel position according to the origin ($\omega=0$), estimated by the symmetry of the reflections on both sides of the beam stop.

Figure 6.6(b) depicts the 1D curves by integration of the total intensity along the vertical direction using the scattering vector q_y , which probes the correlations existing in the horizontal plane [110], that is, the grating period under study. Despite the mentioned differences in the 2D patterns, the 1D profiles obtained from both the CdA replica and the Si mold display a fairly similar modulation, confirming the successful transfer of the grating lines from the Si mold to CdA. The values of the period (P) for

both Si and CdA gratings were calculated according to {6.2} and averaged from different reflection orders, as shown in Table 6.2.

$$P = 2\pi/q_y \quad \{6.2\}$$

There is minor variation in the periodicity between the Si mold and the CdA replica in line with the results from AFM, further evidencing a high accuracy of the performed imprinting process.

Sample	Period (nm)
Si	417±5
CdA	409±10

Table 6.2. Calculated period values from GISAXS measurements for both Si and CdA gratings.

6.2.4 Laser action on F8BT:P3HT DFBs

6.2.4.1 Transmission characteristics

CdA substrates with nanoimprinted gratings possess large transparency, as can be noticed by the high transmittance values in the visible range, (Figure 6.7). The dip in the transmittance spectrum is at the wavelength which accurately matches the grating period, evidencing the presence of periodic corrugation on the surface. There is also an attenuation of transmittance observed around the dip, as a result of diffuse scattering caused by the periodic nanostructures. The large compatibility of CdA with toluene-based solution processing is conducive to form homogeneous polymer layers coated onto the transparent corrugated gratings, with excellent optical quality. The inset in Figure 6.7 depicts a picture of a F8BT:P3HT coated CdA nanoimprinted substrate under UV light demonstrating a highly uniform polymer coating.

Figure 6.7. Transmittance spectra of a plain CdA (pink dashed line) and a nanoimprinted CdA substrate bearing a grating of 416 nm period (red solid line). The arrow points out to a transmittance dip located at around 416 nm. The inset is a picture of a 45% F8BT:P3HT spincoated film on nanoimprinted CdA under UV light.

6.2.4.2 Laser emission characteristics

Figure 6.8(a) shows the emission spectra of a 45% F8BT:P3HT blend deposited on nanoimprinted CdA (see schematic structure in the inset) photoexcited with 2.7 eV (450 nm, near the F8BT absorption maximum) with fluences below and above the threshold for laser action. At low photoexcitation fluences, the emission spectrum (dotted red line in Figure 6.8(a)) is broad and follows the PL, except for the presence of a stop-band manifested as a dip at around 1.83 eV (680 nm). Upon large photoexciting fluences laser action occurs, featuring a narrow single-mode surface emission with peak at 1.84 eV (676 nm) and FWHM linewidth of less than 1nm, as shown by red solid line in Figure 6.8(a). Accordingly, the output emission intensity experiences a sharp super-linear increase with the pumping fluence, Figure 6.8(b). The lasing threshold was determined by the abrupt change in the slopes of the output intensities, obtaining a value of $6.63 \times 10^{-3} \text{ mJ cm}^{-2}$. The novel all-polymer DFB exhibits comparable or even lower threshold value with respect to so far reported DFBs deployed on rigid substrates (quartz, SiO_2) with lasing emission in blue [10][111], green-yellow [52][112] and red [54][113] spectral ranges.

Figure 6.8. (a) Emission spectra of a 45% F8BT:P3HT DFB when operating above (solid line) and below (dotted line) the lasing threshold. Photoexcitation was carried out with 450 nm pulses of 4 ns duration delivered at 10 Hz repetition rates. The film thickness of the 45% F8BT:P3HT blend was 180 nm. (b) Output emission intensity as a function of the pumping fluence for a 45% F8BT:P3HT (red dots) DFB laser. Lines are guides for the eye to emphasize the abrupt slope change.

In addition, for a given grating period the lasing wavelength can be readily tuned by altering the thickness of the optical gain layer (i.e. the effective refractive index in {6.1}), through control of the solution concentration or the spin-coating speed. Figure 6.9 shows the shift of the laser spectrum of the F8BT:P3HT DFB upon increasing the polymer solution concentration, from 10 to 40 mg ml⁻¹, resulting in the adjustment of emission energy (wavelength) over a range of 0.1 eV (34 nm).

Figure 6.9. Tunability of lasing wavelength upon adjustment of film thickness of the gain layer. The DFB laser emission spectra of F8BT:P3HT (with 416 nm period grating) were achieved by optical pumping with 450 nm pulses of 4 ns at 10 Hz repetition rates. F8BT:P3HT blend films involved spincoating polymer solutions with, (from left to right), 10 mg ml⁻¹ (red solid line), 20 mg ml⁻¹ (red dashed line) and 40 mg ml⁻¹ (red dash dotted line) leading to F8BT:P3HT film thicknesses of 120, 180 and 260 nm respectively.

6.3 Conclusions

PLEDs and DFB lasers based on F8BT:P3HT blends were fabricated. The PLEDs with 35% P3HT exhibited the highest luminance, in line with also highest PLQE values. The emission color is very close to red with little orange component (CIE $x = 0.64$, $y = 0.36$). In addition, we develop highly transparent and flexible DFB laser cavities employing CdA as flexible substrate with grating nanostructures imprinted on the surface by NIL. The high accuracy of imprinted nanostructures with respect to Si mold is manifested by AFM and GISAXS measurements. F8BT:P3HT blend films are subsequently spin-coated on the corrugated CdA substrates with pre-determined grating periods, leading to red surface-emitting DFB lasers with excellent optical quality and low threshold ($6.63 \cdot 10^{-3}$ mJ cm⁻²). The emission energy (wavelength) can be tuned over a range of 0.1 eV (34 nm).

Chapter 7. Conclusions and Future Work

In this thesis we presented a comprehensive study of the intriguing nanostructure and emission properties of F8BT:P3HT blends. Our results support that the efficient solid state red emission in F8BT:P3HT blends is attributed to the formation of *F8BT:P3HT complexes* involving strong ground state interactions and electronic delocalization across adjacent P3HT and F8BT chromophores. The supremacy of *F8BT:P3HT complex* over bulk F8BT emission in blends stems from a strong FRET interaction between F8BT and *F8BT:P3HT complexes*. The large miscibility of P3HT in F8BT matrix is found to have a very important role in the host:guest interactions and emission properties, being dependent on temperature, polymer chain length and compositions.

In Chapter 3, we performed a combined experimental and theoretical investigation on the photophysics of mixtures of F8BT and P3HT in solution. In contrast to F8BT:P3HT mixtures in chloroform, the distinctive absorption and PL features of F8BT:P3HT mixtures in toluene indicate the presence of ground state *F8BT:P3HT complexes* even under highly diluted conditions. Quantum chemical calculations (QMD and TDDFT) confirmed the hybrid electronic nature of such complexes. The underlying equilibria and thermodynamic conditions of the complexation were studied with UV-Vis titration experiments, which allowed us to obtain association constants (K_{eq}) ranging from 10^4 to 10^5 for 1:1 monomer association. The increase in K_{eq} with temperature unraveled the endothermic nature of the F8BT:P3HT ground state interactions. In addition, *F8BT:P3HT complex* formation is observed to be strongly dependent on solvent polarity and polymer chain length. The characteristic absorption and fluorescence spectra of complexes were singled out.

In Chapter 4, we investigated the photophysics of F8BT:P3HT blend films. In accordance with the results in solution mixtures, the presence of *F8BT:P3HT complexes* were clearly distinguishable in the absorption and PL spectra in blend films. We observed an unusually large miscibility in blends and hindering of P3HT crystallization, as supported by Raman, AFM and DSC measurements. P3HT chains

in F8BT matrix adopted a conformation with low degree of planarization, characterized by relatively short conjugation length and a wider distribution of chain conformations. These unforeseen structure properties pave the way for the use of P3HT in photonic and lighting applications through appropriate control of P3HT inter-chain interactions. Furthermore, we studied the evolution of F8BT:P3HT film nanostructure under two post-processing annealing protocols: thermal annealing and toluene vapor annealing. P3HT re-arrangement and local de-mixing was inferred in highly doped blends from absorption, PL, Raman and GIWAXS experiments. At low P3HT content though, the absence of P3HT aggregation and lack of reorganization upon thermal annealing is evident, suggesting that the P3HT dispersion in F8BT remains unperturbed.

In Chapter 5, we shed light into the FRET interaction between F8BT and *F8BT:P3HT complexes* in blends by aid of femtosecond transient absorption spectroscopy, observing a very efficient energy transfer at low doping levels and transfer rates (times) which reached 1.8 ps^{-1} (0.55 ps) at 70% P3HT molar fraction. Accordingly, the emission of F8BT:P3HT blends experienced a significant improvement with PLQE values approaching 25% (almost a seven-fold efficiency enhancement with respect to pristine / aggregated P3HT). The optical gain properties of blends were investigated by ASE measurements, demonstrating efficient optical gain in the red spectral region ascribed to *F8BT:P3HT complexes*. Furthermore, the ASE threshold values of F8BT:P3HT blends were assessed upon two different photoexcitation mechanisms: direct and FRET-assisted guest exciton generation. In the low guest concentration regime we observe large differences of one order of magnitude in favor of FRET-assisted ASE, which shrunk at medium-high concentrations. The ASE efficiencies obtained by accounting for the relative host (guest) absorbed photon density at threshold conditions indicated however the presence of exciton losses when photoexcitation is placed in F8BT instead of in *F8BT:P3HT complexes*. In blends with the highest FRET rates, additional exciton losses amounted to approximately 20% of the total harvested exciton population, being these losses likely attributed to exciton - exciton annihilation. Despite the observed losses, we remark that the lower ASE

thresholds values were achieved upon F8BT photoexcitation and subsequent energy transfer to *F8BT:P3HT complexes*.

In Chapter 6, we investigated the application of F8BT:P3HT blends as emissive media in both PLEDs and DFB lasers. The PLEDs with 35% P3HT exhibited the highest luminance (also highest PLQE) with emission color almost in the red range (CIE $x = 0.64$, $y = 0.36$). We developed highly transparent and flexible DFB laser cavities adopting CdA as flexible substrate with grating nanostructures imprinted on the surface by NIL. F8BT:P3HT blend films were spin-coated on the corrugated CdA substrates with pre-determined grating periods, giving rise to red surface-emitting DFB lasers with excellent optical quality and low threshold ($6.63 \times 10^{-3} \text{ mJ cm}^{-2}$). The emission energy (wavelength) was adjusted over a range of 0.1 eV (34 nm) by varying the film thicknesses.

There are still open questions in this work which are worth to be addressed in future in order to provide a better understanding on the polymer arrangements in the complexes and the main driving force for the unusually high blend miscibility. Based on the quantum chemical calculations described in Chapter 3.5, we know that F8BT and P3HT chains in toluene tend to intertwine forming a sort of heterogeneous double helix configuration which favors π - π interactions between the co-facial aromatic moieties. This conformation is in sharp contrast with the perpendicular F8BT:P3HT moieties arrangement predicted in chloroform. An experimental evidence for these predicted arrangements could be provided by transmission electron microscopy, scanning tunneling microscopy or super-resolution fluorescence microscopy, and would be of great interest. As already mentioned, the complexation is likely influenced by polar interactions between F8BT and P3HT, particularly by the electron donor and electron acceptor nature of the thiophene and benzothiadiazole groups respectively, which meanwhile gives rise to the high miscibility in blends. Whether miscibility gives rise to complexations or the opposite is not clear and stands for a sort of “chicken-egg” relationship; more likely they both benefit from each other. It would be very interesting to examine similar mixtures, substituting F8BT for instance by other polymers such as F8TBT (with one thiophene before the benzothiadiazole unit),

or the addition of 4-ethylbenzenesulfonic acid (EBSA) to screen the polarity of the benzothiadiazole and evaluate any effect on F8BT:P3HT complexation. An interesting aspect still to be determined is the interplay of P3HT regioregularity on complexation. For this purpose regiorandom P3HT blended with F8BT could be inspected. Important differences with respect to regioregular P3HT could appear, since regiorandom P3HT has larger inter-thiophene torsional angles and decreased backbone planarity in solid state. Moreover, the dependences of blend miscibility on polymer chain length and temperature are quite intriguing. It is possibly worthy to study F8BT:P3HT oligomer blends at varying temperatures to see whether the associations could be achieved below room temperature. Concerning the application of F8BT:P3HT blends to polymer lasers, the excitonic losses in F8BT upon high photoexcitation fluences are not negligible. Given our present experience from our studies in F8BT:P3HT blends, the prospects of exploring novel polymer combinations containing separately benzothiadiazole and thiophene units could enable new miscible blends. In conclusion, this work will help chemists to design new miscible polymer combinations which could be very attractive for optoelectronics, particularly for polymer lasers and PLEDs.

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