Regioregular Polythiophene–Porphyirin Supramolecular Copolymers for Optoelectronic Applications

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Conjugated poly(3-hexylthiophene) copolymer derivatives containing 10% appended porphyrin moieties are prepared using a supramolecular approach toward applications in organic electronics. The self-assembled polythiophene–porphyrin copolymers are synthesized by coordination of the porphyrinato central zinc ions to the imidazole-functionalized polythiophene side chains. Evidence for the self-assembly process is provided by 1H NMR spectroscopy, single crystal X-ray diffraction, and optical absorption studies on model compounds. The polythiophene–porphyrin copolymers show an extended absorption window in the region of 420–650 nm due to the contribution of the porphyrin. Photoluminescence studies indicate concentration-dependent energy transfer from P3HT to the porphyrin. Preliminary photovoltaic studies are performed by combining the polythiophene–porphyrin copolymers with PC61BM in the photoactive layer of bulk heterojunction organic solar cells.

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1. Introduction

Polymer bulk-heterojunction (BHJ) solar cells have attracted considerable interest over the last decade due to their light weight, low-cost production and compatibility with flexible substrates.\[^1\] Even though power conversion efficiencies (PCEs) have recently increased up to 10% and their energy payback time (EPBT) is estimated to be 1.3 years,\[^1b,c,2\] further improvements are needed to extend their applicability compared to the traditional silicon-based solar cells.\[^3\] As a result, tremendous efforts have been made to improve the PCEs of polymer solar cells, as well as to understand the physical processes governing the operation of these devices.\[^4\]

BHJ polymer solar cells based on poly(3-hexylthiophene) (P3HT) as the electron donor material and [6,6]-phenyl-C\(_{61}\)-butyric acid methyl ester (PC\(_{61}\)BM) as the electron acceptor have been extensively studied leading to PCEs of about 5%.\[^5\] The P3HT:PC\(_{61}\)BM blend system is well-understood and exhibits good processability.\[^6\] The modest PCE of P3HT-based solar cells can be attributed to the weak absorption of P3HT in parts of the visible region and the near-infrared region of the solar spectrum.\[^7\] To overcome the absorption limitations, low bandgap (<1.8 eV) materials are required for a broader coverage of the solar spectrum.

A popular and successful strategy to achieve this purpose consists of developing conjugated polymers with alternating electron donor and acceptor segments, resulting in an extension of the absorption band to higher wavelengths due to intramolecular charge transfer (ICT) effects.\[^8\] Nevertheless, this ICT effect is inevitably associated with a weakened absorption of the short-wavelength photons. An alternative strategy increasingly being explored to extend the absorption profile of the active layer from the visible to near-infrared region relies on exploiting the concept of tandem solar cells, wherein materials with different bandgaps and absorption can be coupled.\[^9\] However, their multilayer architecture and technologically associated challenges are major drawbacks compared to the simple single-step processing of the photoactive layer in single junction BHJ solar cells.\[^9\]

Another approach consists of combining two electron donor materials in the photoactive layer, for example, a polymer and a molecular dye having different absorption spectra, in combination with a fullerene acceptor.\[^10\] In such ternary blends, the energy offsets between the two electron donor materials must be carefully matched with the electron acceptor to allow for efficient charge separation. In addition, good miscibility of the three components is a must to control the nanoscale morphology of the ternary photoactive layer and thus, the photoinduced charge transfer at the donor–acceptor interfaces.\[^10c,d\] To overcome this problem, the dye can be directly incorporated in or onto the polymer chain.\[^11,12\] Along this line, Torres and co-workers have reported the “click” functionalization of P3HT and poly(2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene) with phthalocyanines, leading to a broadened absorption window.\[^12a\] Unfortunately, the low solubility of the resulting polymers induced poor nanoscale organization in the photoactive layer, not appropriate for effective charge transport, thus, resulting in a rather disappointing PCE.\[^11a\]

In this context, porphyrins have attracted increasing interest due to their unique optical absorption and (photo)chemical stability, which can be tuned by modification of the molecular structure.\[^13,14\] Porphyrins are also known to strongly interact with fullerenes with an interaction energy (\(\Delta E_{\text{int}}\)) reported to be in the range of −16 to −18 kcal mol\(^{-1}\).\[^15\] In this case, supramolecular complexes showing an ultrafast photoinduced electron transfer from the porphyrin to the fullerene are formed.\[^16\] As a result, porphyrin-containing conjugated polymers have been widely studied for applications in polymer solar cells.\[^12,17\] Unfortunately, although porphyrin-containing conjugated polymers exhibit broadened absorption spectra, significant enhancement of the PCE has not been reached to date.\[^12,17\] Low short-circuit current densities (\(J_{\text{sc}}\)) and fill factors (FF) were obtained, which is mainly attributed to the non-optimal morphology of the active layer.\[^17a,b\] Indeed, porphyrins can alter the morphology of thin polymer films by weakening the intermolecular interactions between the polymer chains and by their propensity to undergo self-aggregation, which disturbs the supramolecular arrangement in the solid films.\[^17a,b\] In addition, developing new porphyrin-containing conjugated polymers requires tedious and challenging syntheses.

In this paper, two porphyrin-containing P3HT-type conjugated copolymers were synthesized by a simple supramolecular approach based on the coordination of the central zinc ions of simple metalloporphyrins to a polythiophene copolymer bearing imidazole ligands (Figure 1). This coordination strategy has been successfully utilized...
previously to synthesize porphyrin–fullerene dyads to probe light-induced electron and energy transfer. To reach a compromise between the solubility of the material and enhanced absorption, the molar content of porphyrin units has been set to around 10%. Two different porphyrin compounds (1Zn and 2Zn) were attached to the side chains of the polythiophene backbone. The choice of 2Zn was motivated by the improved charge separation and relatively slower charge recombination observed in fluorinated zinc porphyrin–fullerene supramolecular dyads in comparison with (5,10,15,20-tetrakis(phenyl)porphyrinato)zinc(II) (TPP)Zn, which is expected to be beneficial for photovoltaic applications. The synthesized polymers were found to be soluble in organic solvents and were fully characterized. Preliminary photovoltaic studies were performed combining the supramolecular polymers with PC61BM in BHJ solar cells.

2. Experimental Section

2.1. Materials and Characterization

All reactions were carried out under argon using standard high-vacuum and Schlenk techniques. Dry tetrahydrofuran (THF) and toluene were distilled under argon over Na/benzophenone and over Na, respectively. Chemicals were obtained from Alfa-Aesar, Sigma-Aldrich, and Acros and used without further purification. 3-Bromoheptylthiophene, 2,5-dibromo-3-(6′-bromohexyl)thiophene, 2-bromo-3-hexyl-5-iodothiophene, (5,10,15,20-tetrakis(p-toly)porphyrinato)zinc(II) (1Zn), and (5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato)zinc(II) (2Zn) complexes were prepared according to methods reported in the literature. All NMR spectra were acquired with Bruker Avance 300 and 600 spectrometers, using the solvent as the chemical shift standard. All chemical shifts and coupling constants are reported in ppm and Hz, respectively. Number-averaged (Mn) and weight-averaged (Mw) molecular weights and the molecular weight distribution (Đ) of P3HT-r-P3HTBr were measured using size exclusion chromatography (SEC) on a Polymer Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic HPLC pump LC 1120 (flow rate of 1 mL min⁻¹), a Marathon autosampler (loop volume of 200 mL, solution concentration of 1 mg mL⁻¹), a PL-DRI refractive index detector, and three columns: a PL gel 10 mm guard column and two PL gel Mixed-B 10 mm columns (linear columns for the separation of molecular weight polystyrene standards ranging from 500 to 10⁶ Da). The eluent used was THF at a flow rate of 1 mL min⁻¹ at 35 °C. Polystyrene standards were used to calibrate the SEC.

Crystal evaluation and data collection were performed on a Rigaku-Oxford Diffraction Gemini-S diffractometer with sealed-tube Mo Kα radiation using the CrysAlis Pro program (Agilent, 2012). This program was also used for the integration of the frames using default parameters, correction for Lorentz and polarization effects, and for empirical absorption correction using spherical harmonics with symmetry-equivalent and redundant data. All structures were solved using the ab initio iterative charge flipping method with parameters described elsewhere using the Superflip program and they were refined using full-matrix least-squares procedures as implemented in CRYSTALS on all independent reflections with I > 2σ(I). Crystals of TIm-2Zn proved to be very weakly scattering. The data collection strategy was therefore set up so as to have good data until 1.0 Å resolution only by counting 350 s per frame, and with the generator power at maximum values.
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ppm. 13C{1H} NMR (75 MHz, CDCl3, δ) at a rate of 20 °C min−1 under an inert atmosphere (nitrogen). Differential scanning calorimetry (DSC) characterization was performed using a DSC instrument Q200 under an atmosphere of nitrogen at a heating/cooling rate of 10 °C min−1. All DSC analyses were performed using an aluminum pan with a sample of ~5-10 mg. UV–vis absorption and fluorescence spectra were recorded at room temperature on a Shimadzu UV2401 PC UV–vis scanning spectrometer and a Fluorolog-3 (Horiba Jobin Yvon) spectrophotometer, respectively. Emission and excitation spectra were corrected for the wavelength response of the system using correction factors supplied by the manufacturer. Atomic force microscopy (AFM) measurements were performed using a Nanoscope III microscope (from Bruker Nano) in tapping-mode at room temperature under ambient conditions. The silicon cantilevers used were NCHV tips with nominal resonance frequency of 320 kHz. All raw AFM images were visualized and analyzed using the Nanoscope analysis software.

2.2. Synthetic Procedures

3-(6′-(1′-Imidazolyl)-Hexyl)Thiophene (TIm): Dry THF (10 mL) was added to sodium hydride (60% in oil; 268 mg, 6.69 mmol). A solution of imidazole (414 mg, 6.08 mmol) in THF (10 mL) was added dropwise to this suspension at 0 °C and 1409857 (d, 3JH-H = 7.5 Hz, 2H, ThCH2) 1.82 (m, 2H, NCH2) 1.31 (m, 2H, CH2), 0.87 (m, 4H, CH2), 0.51 (m, 2H, CH2) ppm. MS (ESI): m/z = 966.2 [M+H]+. UV–vis (toluene): λmax (ε) = 432 (538000), 566 (215000), 610 (13800) nm. TIm-2Zn: Yield: 96% (61 mg). 1H NMR (300 MHz, CDCl3, δ): 8.90 (s, 8H, PyrH), 7.20 (m, 1H, ThH), 6.79 (m, 2H, ThH), 4.94 (m, 1H, ImH), 4.45 (m, 1H, ImH), 2.40 (m, 1H, ImH), 1.85 (m, 3JH-H = 7.5 Hz, 2H, ThCH2), 1.26 (m, 2H, NCH2), 0.81 (m, 2H, CH2), 0.65 (m, 4H, CH2), 0.28 (m, 2H, CH2) ppm. 13C{1H} NMR (282 MHz, CDCl3, δ): −136.2, −137.9, −152.7, −161.9, −162.7 ppm. M5 (Maldi-ToF): m/z = 1270.2 [M]+. UV–vis (toluene): λmax (ε) = 423 (435000), 558 (22000), 593 (1500) nm.

Poly(3-Hexylthiophene-2,5-Diyl)-Ran-Poly[3-(6′-Bromohexyl)-Thiophene-2,5-Diyl] Random Copolymer (P3HT-r-P3HTr): To a solution of 3-hexylthiophene (826 mg, 87%). 1H NMR (300 MHz, CDCl3, δ): 7.14 (m, 1H, ImH), 7.14 (m, 1H, ThH), 6.97 (s, 1H, ImH), 6.85 (s, 1H, ThH), 6.82 (s, 1H, ThH), 6.80 (s, 1H, ThH), 3.78 (t, 3JH-H = 7.1 Hz, 2H, NCH2), 2.53 (t, 3JH-H = 7.3 Hz, 2H, ThCH2) 1.53 (m, 4H, CH2), 1.20 (m, 4H, CH2) ppm. 13C{1H} NMR (75 MHz, CDCl3, δ): 143.1, 137.4, 129.6, 128.5, 125.5, 120.3, 119.1, 47.2, 31.3, 30.6, 30.5, 30.4, 28.9, 26.6, ppm. MS (ESI): m/z = 235.1 [M-H]−.

Complexation Procedure of the Zinc Porphyrins with 3′-(6′-(1′-Imidazolyl)-Hexyl)Thiophene: To a solution of 3′-(6′-(1′-imidazolyl)-hexyl)thiophene (0.05 mmol) in chloroform (1 mL) was added a solution of zinc porphyrin 12n or 22n (0.05 mmol) in chloroform (4 mL). The reaction mixture was stirred at room temperature for 1 h and then, the solvent was removed by evaporation. The residue was recrystallized from a chloroform/n-hexane mixture affording the desired complexes TIm-1Zn and TIm-2Zn as purple crystals. TIm-1Zn: Yield: 98% (47 mg). 1H NMR (300 MHz, CDCl3, δ): 8.85 (s, 8H, PyrH), 8.08 (d, 3JH-H = 6.0 Hz, 8H, ArH), 7.51 (d, 3JH-H = 6.0 Hz, 8H, ArH), 7.19 (m, 1H, ThH), 6.78 (m, 2H, ThH), 5.18 (m, 1H, ImH), 3.17 (m, 1H, ImH), 2.64 (m, 12H, CH2), 2.42 (t, 3JH-H = 7.5 Hz, 2H, ThCH2), 1.82 (m, 2H, NCH2), 1.31 (m, 2H, CH2), 0.87 (m, 4H, CH2), 0.51 (m, 2H, CH2) ppm. MS (ESI): m/z = 966.2 [M+H]+. UV–vis (toluene): λmax (ε) = 432 (538000), 566 (215000), 610 (13800) nm.

Poly(3-Hexylthiophene-2,5-Diyl)-Ran-Poly[3-(6′-Bromohexyl)-Thiophene-2,5-Diyl] Random Copolymer (P3HT-r-P3HTBr): Two random-bottled flask (100 mL) were dried by heating under reduced pressure and cooled to room temperature. 2-Bromo-3-hexyl-5-iodothiophene (0.68 g, 1.82 mmol) and 2,5-dibromo-3-(6′-bromothiophene)thiophene (0.10 g, 0.25 mmol) were dried by three successive azeotropic distillations with toluene and then, dried THF (10 mL) was added. One equivalent of 2BuMgCl (2 m in THF) was added to those solutions via a syringe, and the mixtures were stirred at 0 °C for 30 min (solutions A and B). Solutions A and B were brought together and then, added in one portion to the Ni(dppp)Cl2 catalyst (8 mg) in THF (10 mL) and the resulting solution was stirred overnight. The reaction was quenched quickly by pouring HCl aq. (5 mL) into the solution and stirring for 0.5 h. Then, the mixture was precipitated in cold MeOH and filtered. The product was washed with MeOH and n-hexane to afford a red solid of P3HT-r-P3HTBr (90/10). Yield: 82% (0.99 g). 1H NMR (600 MHz, CDCl3, δ): 6.98 (s, 2H, Th), 3.42 (t, 2H, CH2–Br, 3JH-H = 6.7 Hz), 2.80 (t, 4H, CH2–Th, 3JH-H = 7.9 Hz), 1.62 (m, 16H, CH2), 0.90 (t, 3H, CH3, 3JH-H = 6.8 Hz) ppm. 13C{1H} NMR (150 MHz, CDCl3, δ): 140.0, 139.8, 130.8, 130.7, 128.8, 130.4, 32.0, 31.8, 31.7, 30.7, 30.5, 29.6, 29.4, 28.8, 28.1, 22.8, 14.3. UV–vis (toluene): λmax (ε) = 458 nm; SEC (THF, PS standards): Mn = 23800 g mol−1, D = 1.17.

Poly(3-Hexylthiophene-2,5-Diyl)-Ran-Poly[3-(6′-(1′-Imidazolyl)-Hexyl)Thiophene-2,5-Diyl] Random Copolymer (P3HT-r-P3HTIm): THF (10 mL) was placed into a two-neck round-bottomed flask (100 mL) containing sodium hydride (60% in oil; 0.24 g, 6.10 mmol). Imidazole (0.35 g, 5.10 mmol) in THF (10 mL) was added dropwise to this suspension at 0 °C and then, the mixture was stirred for 2 h at room temperature. P3HT-r-P3HTBr (2.25 mmol) dissolved in THF (20 mL) was added to the previous solution and the mixture was refluxed for two days. After cooling to room temperature, the mixture was hydrolyzed. The organic layer was extracted with chloroform (100 mL), washed with water (3 × 100 mL), and then, dried over anhydrous MgSO4. The solution was concentrated and the polymer was precipitated in cold MeOH. The polymer was isolated by filtration, washed with water and methanol. It was further purified with refluxing methanol and pentane by using a Soxhlet apparatus and finally, dried under vacuum to afford P3HT-r-P3HTIm (90/10). Yield:
76%. 1H NMR (300 MHz, CDCl3, δ): 7.42 (s, 1H, ImH), 7.02 (s, 1H, Th), 6.99 (s, 1H, Imd), 6.82 (s, 1H, Imd), 3.86 (m, 2H, CH2-Im), 1.41 (m, 8H, CH2-O), 0.95 (m, 3H, CH3). 13C{1H} NMR (75 MHz, CDCl3, δ): 140.1, 137.2, 133.9, 130.7, 129.6, 128.8, 118.9, 47.2, 31.9, 30.7, 29.6, 29.4, 26.6, 22.8, 14.3 ppm. UV–vis (toluene): λmax = 458 nm.

Complexation Procedure of the Zinc Porphyrins with the P3HT-r-P3HTIm Copolymer: To a solution of zinc porphyrin (0.5 mmol) in toluene was added P3HT-r-P3HTIm (0.4 mmol, calculated from the imidazole part). The reaction mixture was then stirred at 70 °C for 1 h. The complexation was followed by UV–vis absorption spectroscopy. A second portion of P3HT-r-P3HTIm (0.1 mmol, calculated from the imidazole part) was added to complete the complexation. The mixture was stirred for an additional hour at 70 °C and then, the solvent was removed by evaporation. The residue was redisolved in a minimum volume of chloroform and poured into n-pentane. The solid was filtered, washed with n-heptane, and dried under vacuum to afford a black solid.

PTim-1Zn: Yield: 92%. 1H NMR (600 MHz, CDCl3, δ): 8.85 (s, PyrH), 8.05 (d, JH-H = 7.4 Hz, ArH), 7.48 (d, JH-H = 7.4 Hz, ArH), 6.99–6.84 (br., ThH and ImH), 5.14 (br., NCH2), 2.81 (br., ThCH2), 2.66 (s, CH3), 1.71 (br., CH2), 1.37 (br., CH2), 0.92 (br., CH3) ppm. 13C{1H} NMR (150 MHz, CDCl3, δ): 150.2, 140.8, 140.1, 136.8, 134.6, 133.9, 131.6, 130.7, 128.8, 127.2, 120.6, 31.9, 30.7, 29.6, 29.4, 22.8, 21.6, 14.3 ppm. UV–vis (toluene): λmax = 436, 500, 566, 610 nm.

PTim-2Zn: Yield: 95%. 1H NMR (600 MHz, CDCl3, δ): 8.87 (s, PyrH), 8.05 (d, JH-H = 7.4 Hz, ArH), 7.48 (d, JH-H = 7.4 Hz, ArH), 6.99–6.84 (br., ThH and ImH), 5.14 (br., NCH2), 2.81 (br., ThCH2), 2.66 (s, CH3), 1.71 (br., CH2), 1.37 (br., CH2), 0.92 (br., CH3) ppm. 13C{1H} NMR (150 MHz, CDCl3, δ): 150.2, 140.8, 140.1, 136.8, 134.6, 133.9, 131.6, 130.7, 128.8, 127.2, 120.6, 31.9, 30.7, 29.6, 29.4, 22.8, 21.6, 14.3 ppm. UV–vis (toluene): λmax = 438, 516, 566 nm.

3. Results and Discussion

3.1. Synthesis and Characterization


Before coordinating the zinc porphyrins 1Zn and 2Zn with the P3HT copolymer bearing imidazole ligands (P3HT-r-P3HTIm), 3-[6′-1″-imidazolyl)-hexyl]thiophene-zinc porphyrin dyads TIm-1Zn and TIm-2Zn were synthesized as model compounds to gain information on the coordination mechanism (Scheme 1).

3-[6′-1″-imidazolyl]-hexyl]thiophene (TIm) corresponds to the thiophene monomer units bearing an imidazolate ligand in the P3HT copolymer. In a first step, TIm was synthesized in 87% yield by reacting the imidazolate anion formed in situ with 3-[6′-bromohexyl]thiophene in THF.
were grown from CHCl₃/n-hexane to gain insight into the packing and to determine the nature of the intermolecular interactions. The molecular structures of TIm-1Zn and TIm-2Zn established by single crystal X-ray diffraction analyses are shown in Figure 2 and Figure S16 in the Supporting Information, respectively. The crystallographic data of TIm-1Zn and TIm-2Zn support the formation of zinc porphyrin:TIm complexes in a 1:1 ratio. In the crystal structures, the zinc atom is penta-coordinated, i.e., with four pyrrolic nitrogen atoms and the nitrogen atom of the imidazole ring. As a result, the zinc ion is located ≈ 0.4 Å above the plane defined by the four pyrrolic nitrogen atoms. The Zn–N distances are found to be 2.11 and 2.09 Å for TIm-1Zn and TIm-2Zn, respectively, which are slightly larger than the Zn–N distances in the pristine macrocycles (2.08 Å on average).

In addition, the crystallographic data of TIm-1Zn revealed the presence of several intermolecular interactions (Figure 2, bottom), namely a C–H–π interaction between a pyrrolic C–H and the thiophene ring with a distance of 2.83 Å and a π–π interaction between imidazole rings, with a centroid–centroid distance of 3.77 Å. In the case of TIm-2Zn, a short centroid–centroid distance between thiophene and pentafluorophenyl rings (3.98 Å) is observed indicating the presence of thiophene-pentafluorophenyl interactions. In contrast to 2Zn, no short intermolecular contacts between zinc and fluorine atoms were detected which may be related to the presence of solvent molecules (CHCl₃) in the TIm-2Zn dyad.

However, the inclusion of these solvent molecules led to the formation of Cl–F halogen bonds as indicated by the lengths of the halogen bonds shorter than the sum of the van der Waals radii.

The interactions between TIm and zinc porphyrins 1Zn and 2Zn were then also studied in solution in toluene using UV–vis absorption spectroscopy. This solvent does not solvate the zinc ion and does not interfere with the ability of the zinc ion to coordinate an additional molecular ligand. The unbound zinc porphyrins exhibit a strong UV–vis absorption band at 419 nm for 1Zn and 424 nm for 2Zn (Soret band) and two Q bands at 551 and 590 nm for 1Zn and 546 and 580 nm for 2Zn, respectively. Upon addition of TIm, the Soret and Q bands are redshifted and isosbestic points are clearly visible (Figure 3 and Figures S17 and S18 in the Supporting Information, respectively). These spectral changes are typical of an axial coordination of the zinc ion and fit well with the formation of a 1:1 complex. By monitoring the decrease in the absorption of the unbound porphyrin and the increase in
the absorption of the bound porphyrin, the binding constant can be determined from UV–vis absorption titrations. The binding constants for 1:1 complex formation for \( \text{TIm-1Zn} \) and \( \text{TIm-2Zn} \) were then evaluated by constructing the Benesi–Hildebrand plots (Figure 3, insets).\(^{[32]}\) From the linear plot of \( A_0/(A - A_0) \) versus \([\text{TIm}]^{-1}\), binding constants of 4600 and 7200 M\(^{-1}\) were found for \( \text{TIm-1Zn} \) and \( \text{TIm-2Zn} \), respectively. As expected, porphyrin \( \text{2Zn} \) with electron-withdrawing fluorinated substituents binds the imidazole ligand more effectively than \( \text{1Zn} \).\(^{[19]}\) The binding constants for \( \text{TIm-1Zn} \) and \( \text{TIm-2Zn} \) are in the same range as those reported in the literature for zinc porphyrin–imidazole complexes (around \( 10^3–10^4 \) M\(^{-1}\)).\(^{[18,19,33]}\)

3.1.2. Complexation between the \( \text{P3HT-r-P3HTIm} \) and Porphyrins

Once the supramolecular approach was successfully proven for the model compounds, porphyrins \( \text{1Zn} \) and \( \text{2Zn} \)
were coordinated to a polythiophene random copolymer bearing imidazole ligands in a proper molar ratio (i.e., around 10%) on the side chains. As discussed above, an appropriate content of porphyrins may lead to enhanced photocurrent generation by simultaneous photoexcitation of the porphyrins. Thus, a polythiophene copolymer containing 10% of appended imidazole moieties was synthesized by a two-step procedure. In the first step, a regioregular head-to-tail bromide-bearing polythiophene random copolymer ($\text{P3HT-r-P3HTBr}$) was prepared via the Kumada catalyst transfer polycondensation from a mixture of 2-bromo-3-hexyl-5-iodothiophene and 2,5-dibromo-3-(6′-bromohexyl)thiophene, with a $\approx 7.3:1$ molar ratio (Scheme 2a).\[^{34}\]

After the transmetallation of the mixture of both monomers using isopropylmagnesium chloride, the polymerization was initiated by the addition of a catalytic amount of Ni(dppp)Cl$_2$. The reaction mixture was then quenched with $5 \times$ HCl, following the procedure described by Yokozawa and co-workers.\[^{35}\] This quenching procedure prevents the polymer chains from undergoing dimerization in order to maintain the narrow dispersity value while efficiently removing inorganic impurities from the product. SEC analysis of the $\text{P3HT-r-P3HTBr}$ precursor displayed a number-averaged molecular weight ($M_n$) of 23 800 g mol$^{-1}$ with a narrow dispersity ($D = 1.17$). The composition of the $\text{P3HT-r-P3HTBr}$ copolymer was determined from the 1H NMR spectrum by integrating the peaks observed at $\delta = 0.92$ (CH$_3$ groups in P3HT) and 3.42 ppm (CH$_2$Br groups in P3HTBr) (Figure S8 in the Supporting Information). From the integration of those two peaks, the molar ratio of the 3HT and 3HTBr segments was estimated to be 90:10 (feed ratio 88:12).\[^{36}\]

In a second step, the bromine atom at the end of the alkyl side chain was converted into an imidazole moiety by reaction of $\text{P3HT-r-P3HTBr}$ with the imidazolide anion formed in situ in THF. The conversion of the $\text{P3HT-r-P3HTBr}$ copolymer into the corresponding $\text{P3HT-r-P3HTIm}$ copolymer was followed by 1H NMR spectroscopy. The disappearance of the signal at 3.42 ppm (CH$_2$Br groups) and the appearance of additional signals at 6.82, 6.99, and 7.42 ppm from the imidazole ring were observed (Figure S9 in the Supporting Information). Attempts of SEC analysis in various solvents (THF, CHCl$_3$, chlorobenzene at room temperature and 145°C) were unsuccessful for this polymer.

With $\text{P3HT-r-P3HTIm}$ in hand, complexation of $1\text{Zn}$ and $2\text{Zn}$ was performed in a 1:1 ratio on the basis of the 3-[6′-(1″-imidazolyl)-hexyl]thiophene monomer unit, leading to the corresponding $\text{PTIm-1Zn}$ and $\text{PTIm-2Zn}$ materials in quantitative yields (Scheme 2b). The efficiency of the complexation was monitored by 1H NMR spectroscopy by following the shift of the terminal methylene group connected to the imidazole ring at $\approx 3.9$ ppm (in CDCl$_3$) for $\text{PTIm-1Zn}$ (Figure S11 and Figure S13 in the Supporting Information). As observed for model compounds $\text{TIm-1Zn}$ and $\text{TIm-2Zn}$, the imidazole protons are shifted upfield due to the influence of porphyrin ring current effects. From the integration of the peaks at $\approx 8.85$ ppm (pyrollic H of the porphyrins) and at $\approx 0.90$ ppm (CH$_3$ groups of P3HT), the molar ratio of P3HT and porphyrin was estimated to be $\approx 90:10$, indicating that all the imidazole groups in $\text{P3HT-r-P3HTIm}$ have complexed porphyrins $1\text{Zn}$ and $2\text{Zn}$. 

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**Scheme 2.** Syntheses of a) $\text{P3HT-r-P3HTIm}$ and b) supramolecular polymers $\text{PTIm-1Zn}$ and $\text{PTIm-2Zn}$. 

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3.2. Optical Properties

The complexation of 1Zn and 2Zn by P3HT-P3HT(pm) was studied by UV–vis absorption spectroscopy (Figure 4 and Figure S19 in the Supporting Information, respectively). As for model compounds TIm-1Zn and TIm-2Zn, a gradual redshift of the Q bands was observed with isosbestic points unambiguously indicating the formation of the supramolecular polymers PTIm-1Zn and PTIm-2Zn. Copolymers PTIm-1Zn and PTIm-2Zn exhibit broadened UV–vis absorption spectra between 550 and 650 nm with respect to pristine P3HT due to the Q band absorption of the porphyrins complexed to the side chains of the copolymer.

The concentration dependence of the optical properties of PTIm-1Zn and PTIm-2Zn in solution was then studied. Since similar characteristics were obtained for both compounds, we focus the discussion on PTIm-2Zn. The normalized UV–vis absorption and emission spectra of the individual components 2Zn and P3HT-P3HT(pm) in dilute solution are shown in Figure 5. The absorption spectrum of 2Zn is dominated by the intense Soret (B) band at 420 nm with two weaker bands at 545 nm (vibrational hot state Q(0,0)) and 580 nm (vibrational ground state Q(0,0)). Excitation at 420 nm leads to a broad emission band with maxima at 585 and 645 nm, which is again reminiscent of the porphyrin emission except for the lowest vibrational progression of the C=C stretching mode.

As depicted in Figure 5, there is significant spectral overlap of the Q absorption bands of 2Zn with the emission band of P3HT-P3HT(pm), suggesting that polythiophene to porphyrin energy transfer may occur in this system. Excitation at 420 nm will sensitize both 2Zn and P3HT-P3HT(pm). However, the huge oscillator strength of the Soret band for metalloporphyrins (f ≈ 1) suggests that the porphyrin will be the primary absorber at this wavelength for PTIm-2Zn. In contrast, excitation at 460 nm enables selective excitation of P3HT-P3HT(pm).

The photoluminescence emission and excitation spectra obtained for PTIm-2Zn as a function of concentration (C = 0.05–1.36 × 10^-6 M in toluene) are shown in Figure 6. Upon excitation at 420 nm, a broad emission band, with maxima at 585 and 645 nm, is observed, characteristic of the porphyrin emission. However, the emission profile is significantly broadened compared to the pure 2Zn, indicating that P3HT-P3HT(pm) also provides a contribution. As the concentration is increased to 10^-6 mol L^-1, strong quenching (99%) of the fluorescence emission is observed. Porphyrins are well known to show the tendency to aggregate, even at rather low concentrations in solution, which often leads to fluorescence quenching.

Excitation at 450 nm leads to a broad emission band with peak maxima at 582 and 657 nm, which is again reminiscent of the porphyrin emission except for the lowest concentration, where the emission spectrum is very similar to the polymer. Since only P3HT-P3HT(pm) absorbs light at 450 nm, this suggests that energy transfer from P3HT to 2Zn must occur at concentrations above 0.1 × 10^-6 M. As the concentration is increased from 10^-8 to 10^-7 mol L^-1, the intensity of the Q(0,0) band initially increases, before subsequently decreasing with increasing sample concentration. The energy transfer efficiency depends not only on the spectral overlap of the donor and acceptor moieties but also on their proximity. The similarity of the photoluminescence spectrum to that of the parent P3HT-P3HT(pm) at the lowest concentration studied (Figure 6b, solid black line) suggests that intramolecular energy transfer between the polymer and the porphyrin is absent.
As the concentration is increased, the initial increase in the porphyrin emission (≈657 nm) intensity is thus attributed to enhanced intermolecular energy transfer due to a decrease in the average donor–acceptor distance, which effectively quenches the P3HT contribution. At higher concentrations, fluorescence quenching due to aggregation of the porphyrin moieties also becomes more important.

Further evidence for energy transfer can be obtained from the corresponding excitation spectrum (Figure 6c). In dilute solution, the excitation spectrum measured at 650 nm (predominantly porphyrin Q(0,1) emission band) is comparable to the UV–vis absorption spectrum (see Figure S20 in the Supporting Information), clearly exhibiting the Soret and Q bands at 420 and 540 nm, respectively, along with a broader band contribution from P3HT→P3HTIm (Figure 6c(i)). However, as the concentration is increased to 0.45 × 10⁻⁶ M, bleaching of the Soret band is accompanied by the emergence of two distinct peaks at 402 and 450 nm. The wavelength maximum and shape of the latter peak are characteristic of the polythiophene absorption band, suggesting that P3HT to 2Zn energy transfer also occurs. The inversion of the Soret band and emergence of a new bands at higher energy in the excitation spectrum has previously been attributed to the formation of H- or J-type aggregates through π–π stacking interaction. [40] Since H-aggregates typically exhibit blueshifted excitation (or absorption bands) and are typically non- or weakly fluorescent, we suggest that the concentration-dependence of the photoluminescence properties observed for PTIm-2Zn is consistent with the formation of this class of aggregate. At higher concentrations, the Q(1,0) band at 546 nm becomes more prominent in the excitation spectrum, supporting the observation that self-absorption also contributes to the decrease in the fluorescence intensity. The corresponding excitation spectrum measured at 580 nm exhibits a comparable trend (see Figure S21 in the Supporting Information), providing further evidence for energy transfer between the two components.

To investigate the self-assembly of the polymer chains in the solid-state, the UV–vis absorption spectra of P3HT→P3HTIm, PTIm-1Zn, and PTIm-2Zn in films were recorded (Figure 7). The solid-state spectrum of P3HT→P3HTIm exhibits a bathochromic shift of the absorption maximum attributed to the π–π* transition in the polymer main chain at 550 nm as well as a vibrational structure, which is quite similar to pure P3HT. [41] The presence of a shoulder at about 620 nm is assigned to the vibronic progression of the C=C stretching mode (ΔE ≈ 0.15 eV). [42] In the case of PTIm-1Zn and PTIm-2Zn, a strong contribution of the absorption of the porphyrins was observed at around 420 nm (Soret Band) and between 550 and 650 nm (Q bands). Compared to P3HT→P3HTIm, the P3HT absorption is blueshifted (~520 vs 550 nm for P3HT→P3HTIm) indicating that the presence of porphyrins in the side chains disturbs the polymer organization and thus decreases the effective conjugation length.
3.3. Thermal, Morphological, and Photovoltaic Properties

The thermal properties of supramolecular copolymers PTIm-1Zn and PTIm-2Zn were examined by TGA and DSC measurements. The TGA curves of PTIm-1Zn and PTIm-2Zn (shown in Figure S22 in the Supporting Information) show that the polymers exhibit high thermal stability, with 5% weight loss temperature ($T_d$) around 420 and 330 °C, respectively. The DSC analyses show different thermal behavior depending on the nature of the porphyrin complexed with P3HT-$r$-P3HTIm (Figure S21 in the Supporting Information). PTIm-1Zn (Figure S22, top, in the Supporting Information) shows a clear first-order transition with a melting temperature ($T_m$) at 194 °C and crystallization temperature ($T_c$) at 140 °C, which are lower than the melting and crystallization temperatures of neat P3HT ($T_c = 200 °C$ and $T_m = 210 °C$).[43] On the contrary, no melting and crystallization peaks were detected for polymer PTIm-2Zn, suggesting that this polymer is amorphous (Figure S22, bottom, in the Supporting Information). These results are consistent with the conclusion drawn from UV–vis absorption spectra described above (Figure 7).

The microscopic morphology of PTIm-1Zn and PTIm-2Zn in thin films was analyzed by tapping-mode atomic force microscopy (TM-AFM). We initially focused on the film deposition conditions for which pure P3HT is known to form fibrillar nanostructures, based on earlier works.[44] This fibrillar (nanowire-like) morphology is the signature of the crystallization of P3HT, as a result of the π-stacking of the polythiophene backbones and the lateral interdigitation of the alkyl groups.[45] Thin deposits of PTIm-1Zn from xylene solutions show fibrillar nanostructures having a width around 20 nm, in the range of what is observed for fibrils of pure P3HT, but with a shorter length and higher roughness (Figure 8, left). In contrast, thin films of PTIm-2Zn are relatively flat and exhibit no fibrillar morphology (Figure 8, right). These results are in agreement with the thermal characterization of the polymers, showing crystallization only in the case of PTIm-1Zn. The reduced or lack of crystalline order (fibrillar morphology) in these polymers could be a drawback for their use as electron donor materials in BHJ organic solar cells, since the formation of ordered nanostructures is crucial for efficient hole transport.[46]

Preliminary photovoltaic studies were then performed to investigate the behavior of PTIm-1Zn and PTIm-2Zn as electron donor materials. BHJ polymer solar cells with a classical architecture (glass/ITO/PEDOT:PSS/active layer/Ca/Al) were fabricated. The photoactive layers, consisting of either one of the two supramolecular polymers blended with PC_{61}BM in a 1:0.8 (wt/wt) ratio, were spin-coated from xylene (cf. AFM studies). PC_{61}BM was preferred over other (methano)fullerenes (e.g., PC_{71}BM) for this initial
the porphyrins in the visible region. Photoluminescence supramolecular polymers showed a strong contribution of for the complex formed with the fluorinated porphyrin. Evaluated from the optical data were revealed to be higher hexyl-thiophene monomer unit. The binding constants \( \text{PTIm-1Zn} \) have been successfully prepared through the coordination of the central zinc ion ized polythiophene copolymer. The supramolecular inter-
actions (solvent, annealing, additives, etc.) is mandatory to enhance the electron donor aggregation/crystallization and to optimize the photovoltaic performance. Further experiments and analyses are also required to elucidate if the projected benefits of the fluorinated porphyrin (e.g., reduced charge recombination) can be realized in the final devices.

4. Conclusions

Conjugated poly(3-hexyli thiophene) copolymers decorated with 10% of fluorinated or nonfluorinated porphyrin sensitizers (PTIm-12Zn and PTIm-22Zn) have been successfully prepared through the coordination of the central zinc ion of the porphyrin moieties with an imidazole-functionalized polythiophene copolymer. The supramolecular interaction was evidenced by \(^1\text{H} \) NMR spectroscopy, single crystal X-ray diffraction, and optical absorption studies on model compounds based on the 3-[6-(1″-imidazolyl)-hexyl]thiophene monomer unit. The binding constants evaluated from the optical data were revealed to be higher for the complex formed with the fluorinated porphyrin. The absorption spectra of these polythiophene–porphyrin supramolecular polymers showed a strong contribution of the porphyrins in the visible region. Photoluminescence screening because of its lower cost and similar efficiencies with P3HT-like donor materials.\(^{47}\) As summarized in Table 1 and Figure S24 in the Supporting Information, the resulting devices exhibit modest short-circuit current densities and fill factors in comparison with standard P3HT:PC$_{61}$BM cells. To investigate whether the reduced performances were originating from limited absorption by the photoactive layer, EQE spectra were measured (Figure S25 in the Supporting Information). As can be observed, the EQE spectra from both PTIm-12Zn and PTIm-22Zn closely resemble the UV–vis absorption spectra, with some PC$_{61}$BM contribution in the low-wavelength area, but the absolute quantum efficiencies remain below 15% over the entire absorption range. Consequently, the lower \( J_{sc} \) values might be related to the reduced or lack of crystalline order as previously noticed from DSC and AFM analyses. Further optimization of the processing conditions (solvent, annealing, additives, etc.) is mandatory to enhance the electron donor aggregation/crystallization and to optimize the photovoltaic performance. Further experiments and analyses are also required to elucidate if the projected benefits of the fluorinated porphyrin (e.g., reduced charge recombination) can be realized in the final devices.

Table 1. Photovoltaic performances of the polymer solar cells based on PTIm-12Zn:PC$_{61}$BM and PTIm-22Zn:PC$_{61}$BM.

<table>
<thead>
<tr>
<th>Donor material</th>
<th>( V_{oc} ) ([\text{V}])</th>
<th>( J_{sc} ) ([\text{mA cm}^{-2}])</th>
<th>FF</th>
<th>Average PCE ( [%]^{b} )</th>
<th>Best PCE ( [%] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTIm-12Zn</td>
<td>0.79</td>
<td>0.60</td>
<td>0.29</td>
<td>0.14</td>
<td>0.15</td>
</tr>
<tr>
<td>PTIm-22Zn</td>
<td>0.84</td>
<td>0.75</td>
<td>0.29</td>
<td>0.23</td>
<td>0.24</td>
</tr>
</tbody>
</table>

\( a \)Device structure: glass/ITO/PEDOT:PSS/polymer:PC$_{61}$BM/Ca/Al. Active area: 3 mm$^2$. Spin-coated from a xylene solution with a (total) concentration of 36 mg mL$^{-1}$;

\( b \)Averages over at least four devices.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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