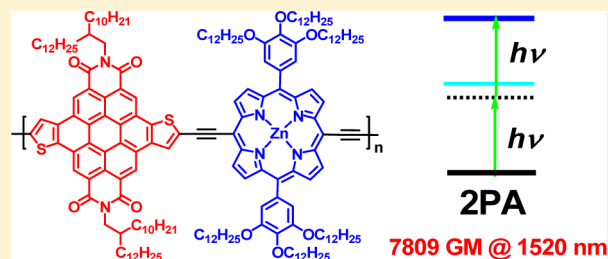


A Low-Bandgap Conjugated Copolymer Based on Porphyrin and Dithienocoronene Diimide with Strong Two-Photon Absorption

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S Supporting Information

ABSTRACT: A new low-bandgap donor–acceptor (D–A) conjugated copolymer poly(DTCDI–POR) of planar acceptor dithienocoronene diimide (DTCDI) and strong donor porphyrin (POR) has been synthesized by Sonogashira coupling polymerization. Poly(DTCDI–POR) exhibits good thermal stability (decomposition temperature of 323 °C), strong absorption (molar extinction coefficient per repeat unit is 1.05×10^5 L mol⁻¹ cm⁻¹ at 468 nm in CHCl₃ solution) in visible and near-infrared region (300–900 nm), low bandgap (1.44 eV), and strong two-photon absorption (2PA) at telecommunication wavelengths with 2PA cross sections per repeat unit as high as 7809 GM at 1520 nm.



■ INTRODUCTION

Thanks to a wide variety of potential applications in microscopy,^{1–3} microfabrication,^{4,5} three-dimensional data-storage,^{6,7} optical limiting,⁸ and photodynamic therapy,^{9,10} two-photon absorption (2PA) materials have been the subject of intensive academic and commercial interest over the past 2 decades, and a number of 2PA dyes have been synthesized^{11–13} and investigated.^{14–19} Small molecule based 2PA materials have been investigated extensively, and their 2PA cross sections (δ) are as high as 10^5 GM ($1 \text{ GM} = 1 \times 10^{-50} \text{ cm}^4 \text{ s}^{-1}$), while the literature on 2PA polymers is significantly sparser than that for their small molecule counterparts, most of 2PA polymers exhibited 2PA cross sections below 10^4 GM.^{20–27} Current trends in device fabrication favor solution-processing. In general, polymers are more suitable for solution processing than small molecules to obtain high-quality thin films.

Experimental and theoretical results on model compounds revealed that increasing the planarity and rigidity of the molecules is beneficial to 2PA enhancement.¹⁹ Owing to a planar and rigid conjugated framework with π -electrons extending in two dimensions, porphyrins (POR) represent an effective building block for 2PA materials. There have been several reports on 2PA small molecules based on porphyrin,^{28–40} while there are significantly sparser reports on porphyrin-based 2PA polymers. Actually, there are only three reports of porphyrin-based 2PA polymers at telecommunication wavelengths ($1.3\text{--}1.55 \mu\text{m}$).^{41–43} Rebane et al. reported that double-strand conjugated porphyrin ladder arrays exhibited

a δ per repeat unit of 8900 GM at 1325 nm.⁴¹ Perry et al. reported that a lead-containing bis(ethynyl)porphyrin polymer exhibited a δ per repeat unit of 5200 GM at 1300 nm and of 650 GM at 1550 nm.⁴² We reported that a D–A conjugated copolymer of porphyrin and perylene diimide (PDI) (poly(PDI–POR), Figure 1) exhibited a δ per repeat unit of 7041 GM at 1320 nm and of 7704 GM at 1520 nm; poly(PDI–POR) is the first D–A main-chain conjugated polymer based on porphyrin.⁴³

Recently, dithienocoronene diimide (DTCDI) was used for synthesis of organic semiconductors.^{44–46} Ko and co-workers reported D–A–D small molecule donors with DTCDI as acceptor, triphenylamine as donor, and bithiophene as bridge for organic solar cells, which exhibited the highest power conversion efficiency of 1.42%.⁴⁴ Facchetti and co-workers reported D–A polymers of DTCDI and thiophene or bithiophene for ambipolar field-effect transistors, which exhibited electron mobilities of up to $0.30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and hole mobilities of up to $0.04 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁴⁵ DTCDI has a larger size core than PDI, which could promote strong intermolecular interactions and highly ordered π -stacked structures. Moreover, DTCDI exhibits a linear monomer-linkage geometry with negligible dihedral angles and coplanar backbone in polymers,

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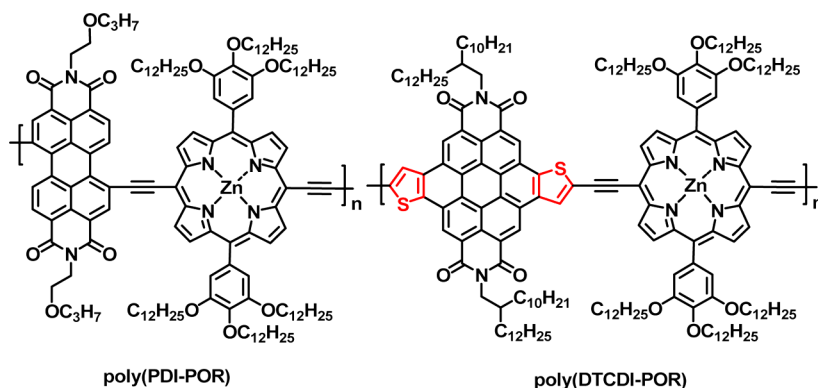
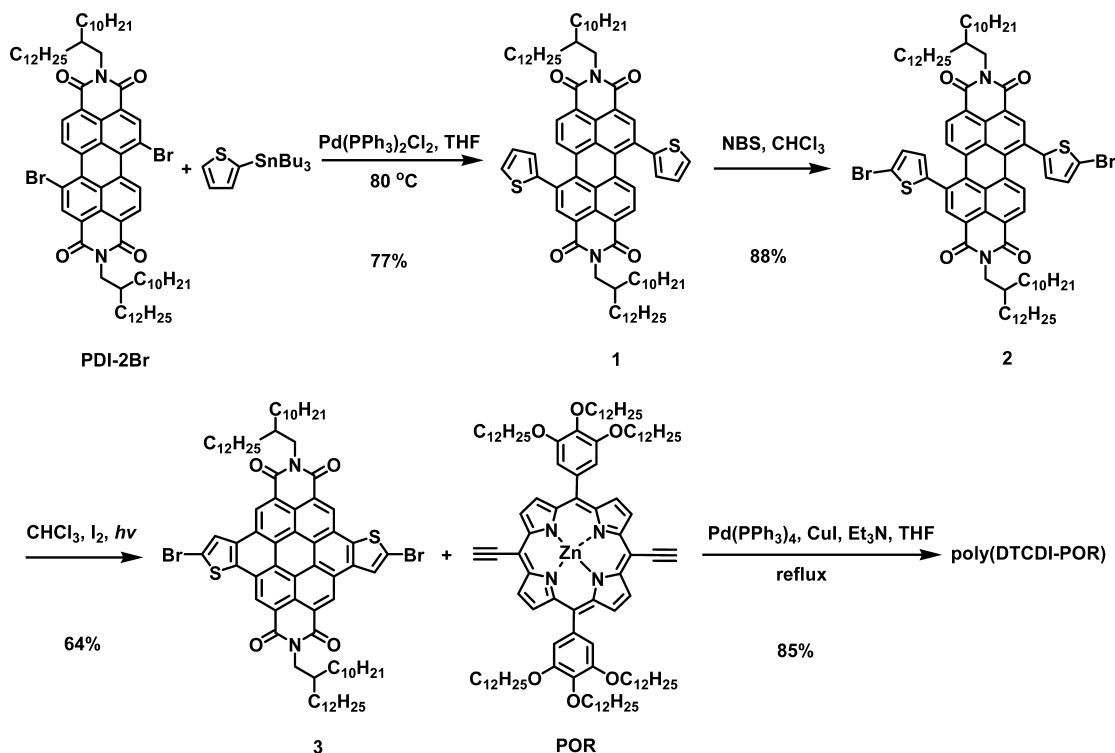


Figure 1. Chemical structure of poly(PDI-POR) and poly(DTCDI-POR).

Scheme 1. Synthesis of Polymer Poly(DTCDI-POR)



while sterically hindered bay region in PDI causes significant polymer backbone torsion.⁴⁵

In this paper, we report a low-bandgap D–A conjugated copolymer based on porphyrin and DTCDI (poly(DTCDI-POR), Figure 1). DTCDI and porphyrin units have conformational rigidity and large π -conjugation, which is common features of efficient 2PA materials. Acceptor, donor, and a polarizable π -bridge are three essential components required for strong 2PA dyes. In poly(DTCDI-POR), porphyrin is a strong π -electron donor (D), DTCDI is a strong π -electron acceptor (A), and acetylene is a π -bridge between D and A units. Polymer poly(DTCDI-POR) exhibits strong NIR absorption and large 2PA cross sections at telecommunication wavelengths (up to 7809 GM/repeat unit).

RESULTS AND DISCUSSION

Synthesis and Characterization. The synthetic route to the polymer is outlined in Scheme 1. 1,7-Dibromoperylene diimide (PDI-2Br)⁴⁷ and diethynylporphyrin zinc (POR)⁴⁸

were synthesized according to our reported procedures. Stille coupling reaction between PDI-2Br and 2-(tributylstannyl)-thiophene afforded *N,N'*-bis(2-decyltetradecyl)-1,7-bis(thien-2-yl)-perylene-3,4,9,10-tetracarboxylic diimide (**1**) in 77% yield, which was brominated by NBS to give *N,N'*-bis(2-decyltetradecyl)-1,7-bis(2-bromothiophen-5-yl)-perylene-3,4,9,10-tetracarboxylic diimide (**2**) in 88% yield. Then photocyclization of compound **2** in the presence of I₂ yielded the monomer **3** in 64% yield. The final copolymer was synthesized through Sonogashira coupling reaction of diethynylporphyrin Zinc with the monomer **3** in a yield of 85%.

The polymer has good solubility in common organic solvents such as chloroform, toluene, and THF. Molecular weight of the polymer was determined by gel permeation chromatography (GPC), using polystyrene standards as calibrants with THF as eluent. The polymer exhibits a number-average molecular weight (M_n) of 2.1×10^4 , a weight-average molecular weight (M_w) of 7.8×10^4 , and a polydispersity index (M_w/M_n) of 3.69. The thermal property of the polymer was determined by

thermogravimetric analysis (TGA) under nitrogen and air. The polymer has good thermal stability with decomposition temperature (T_d) at 5% weight loss of 323 °C under nitrogen and 321 °C under air (Figure 2). The T_d of poly(DTCDI–POR) is lower than that (362 °C) of poly(PDI–POR) under nitrogen.⁴³

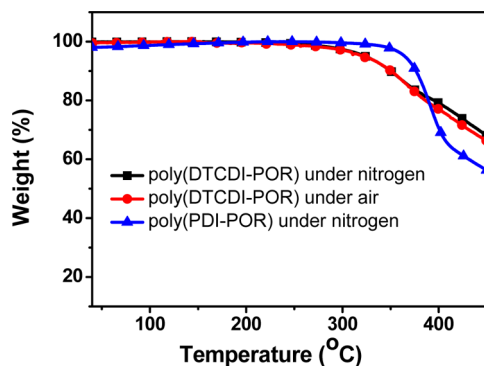


Figure 2. TGA curves of polymer poly(DTCDI–POR) under nitrogen and air and of polymer poly(PDI–POR) under nitrogen.

One-Photon Absorption. Figure 3 shows UV–vis spectra of polymer poly(DTCDI–POR) as well as its monomers in

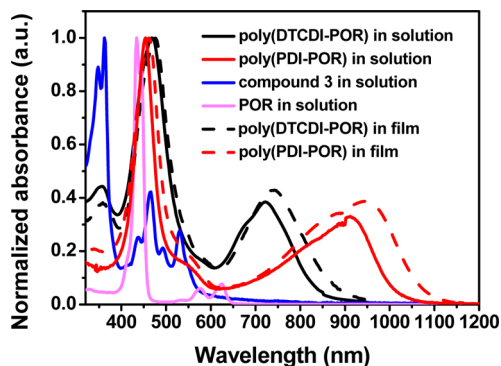


Figure 3. UV–vis spectra of poly(DTCDI–POR) and poly(PDI–POR) in chloroform and in film as well as of the monomers POR and 3 in chloroform.

CHCl_3 solution (ca. 10^{-6} M). The DTCDI monomer 3 exhibits two main absorption bands with low energy λ_{max} located at 530 nm. The DTCDI monomer exhibits well-defined vibronic features, similar to nonsubstituted PDIs, indicating enhanced π -conjugation along the short molecular axis and improved planarity and rigidity of the molecular backbone.⁴⁵ The porphyrin monomer POR shows typical strong Soret band at 434 nm and weak Q-band at 624 nm. In comparison with the monomers, the polymer poly(DTCDI–POR) shows a significant red shift (100 nm) of the low-energy band. Poly(DTCDI–POR) shows three absorption bands at 358 nm, 468 and 722 nm with high molar extinction coefficient (per repeat unit) of $1.05 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 468 nm in chloroform. The band at ca. 358 nm can be assigned to a DTCDI-centered transition, the 468 nm intense band to overlap of DTCDI-based and porphyrin-based transition, and the broad low-energy band located at 722 nm to a transition with significant donor-to-acceptor (porphyrin to DTCDI) charge-transfer character.

Previously reported copolymer poly(PDI–POR) shows two absorption bands at 454 and 912 nm in CHCl_3 solution (Figure 3).⁴³ The high-energy band of the copolymer poly(DTCDI–POR) red-shifts 14 nm relative to that of poly(PDI–POR) as a result of relatively more intense electron delocalization caused by large and planar DTCDI unit. On the other hand, the low-energy charge-transfer band of poly(DTCDI–POR) blue-shifts 190 nm compared to that of poly(PDI–POR), due to the weaker electron-withdrawing ability of DTCDI.

The low-energy band of the polymer poly(DTCDI–POR) in film red shifts 20 nm compared to that in solution due to strong electronic coupling between neighboring molecules caused by large and coplanar structure of DTPDI and porphyrin (Figure 3). The optical band gap estimated from the absorption edge in film is 1.44 eV.

Electrochemistry. To estimate the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy level of the conjugated copolymer, we studied electrochemical properties using cyclic voltammetry (CV) of films drop cast onto glassy carbon working electrodes. The cyclic voltammogram of the polymer is shown in Figure 4. Copolymer poly(DTCDI–POR) exhibits a

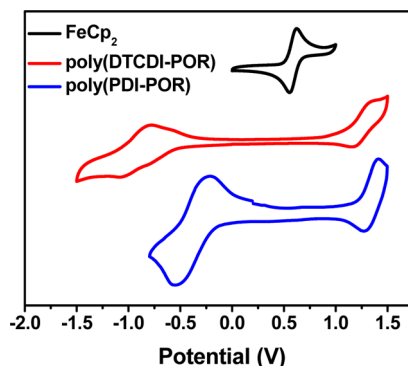


Figure 4. Cyclic voltammogram of poly(DTCDI–POR) and poly(PDI–POR) films in $\text{CH}_3\text{CN}/0.1 \text{ M } [\text{nBu}_4\text{N}]^+[\text{PF}_6]^-$ at 50 mV s^{-1} . The horizontal scale refers to an anodized Ag wire pseudoreference electrode.

quasi reversible oxidation peak and a quasi reversible reduction wave. The HOMO and LUMO values of the polymer (Table 1) are estimated from the onset oxidation and reduction potentials, assuming the absolute energy level of $\text{FeCp}_2^{+/0}$ to be 4.8 eV below vacuum. The LUMO level is -3.69 eV and HOMO level is -5.29 eV . The band gap estimated from electrochemistry is 1.60 eV. The LUMO level of poly(DTCDI–POR) is similar to those (-3.7 eV) of DTCDI-thiophene copolymers.⁴⁵ Compared with poly(PDI–POR) which possesses LUMO level of -4.00 eV and HOMO level of -5.41 eV ,⁴³ poly(DTCDI–POR) exhibits up-shifted LUMO and HOMO levels since DTCDI is a weaker electron acceptor relative to PDI.

Two-Photon Absorption. The 2PA cross sections (δ) of copolymer poly(DTCDI–POR) were measured at 1320, 1380, 1440, 1480, and 1520 nm in CHCl_3 solution by using the open-aperture Z-scan method. Figure 5 shows typical Z-scan traces and 2PA cross sections per repeat unit of the polymer at all these wavelengths. The polymer exhibits large 2PA cross sections up to 7809 GM/repeat unit at 1520 nm, which is a little higher than that (7704 GM at 1520 nm) of poly(PDI–POR). Although DTCDI has weaker electron withdrawing

Table 1. Absorption Maxima and Energy Levels of Poly(DTCDI–POR) and Poly(PDI–POR)

polymer	λ_{\max}^a (nm)	λ_{\max}^b (nm)	E_g^c (eV)	E_{ox}^d (V)	E_{red}^d (V)	HOMO ^e (eV)	LUMO ^e (eV)	$E_g^{\text{CV}}^f$ (eV)
poly(DTCDI–POR)	468, 722	476, 742	1.44	0.49	−1.11	−5.29	−3.69	1.60
poly(PDI–POR)	454, 912	462, 948	1.15	0.61	−0.80	−5.41	−4.00	1.41

^aAbsorption maxima in solution. ^bAbsorption maxima in film. ^cOptical band gap estimated from the absorption edge in film. ^d E_{ox} is the onset potentials vs $\text{FcP}_2^{+/0}$ corresponding to oxidations, while E_{red} is the onset potentials vs $\text{FcP}_2^{+/0}$ corresponding to reductions. ^eHOMO and LUMO estimated from the onset oxidation and reduction potentials, respectively, assuming the absolute energy level of $\text{FcP}_2^{+/0}$ to be 4.8 eV below vacuum. ^fHOMO–LUMO gap estimated by electrochemistry.

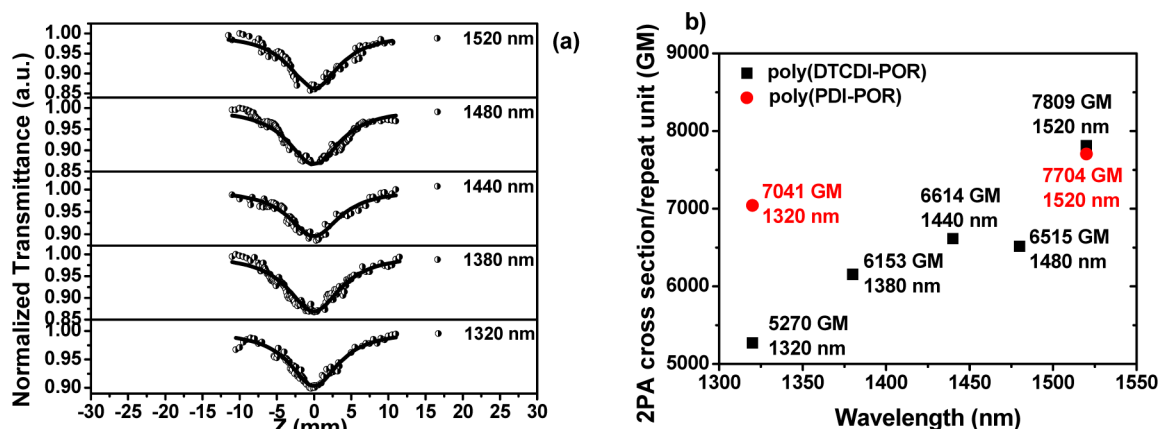


Figure 5. (a) Z-scan traces of poly(DTCDI–POR) (1.21×10^{-4} M per repeat unit) in CHCl_3 in a 1 mm cell at 1520 nm ($I_0 = 39.3 \text{ GW/cm}^2$), 1480 nm ($I_0 = 47.0 \text{ GW/cm}^2$), 1440 nm ($I_0 = 51.6 \text{ GW/cm}^2$), 1380 nm ($I_0 = 52.4 \text{ GW/cm}^2$), and 1320 nm ($I_0 = 64.1 \text{ GW/cm}^2$) with a theoretical fit assuming a 2PA process. (b) 2PA cross sections per repeat unit of poly(DTCDI–POR) and poly(PDI–POR). Errors associated with values were determined to be $\pm 15\%$.

ability than PDI, it has better planarity, rigidity and conjugation than PDI, which is beneficial to 2PA enhancement.

The previously reported analogous polymer with lead-containing alkyne-linked porphyrins and no DTCDI units exhibited a considerably large 2PA cross section about 5200 GM/repeat unit at 1300 nm and a much smaller 2PA cross section of 650 GM/repeat unit at 1550 nm.⁴² The previously reported analogous polymer with zinc-containing alkyne-linked porphyrins and no DTCDI units exhibited an even smaller 2PA cross sections <450 GM/repeat unit at telecommunication wavelengths.^{41,42} Clearly, introduction of planar and rigid acceptor unit DTCDI into alkyne-linked porphyrin polymer backbones is beneficial to enhancement in 2PA at telecommunication wavelengths.

CONCLUSION

We have synthesized a new low-bandgap conjugated D–A copolymer poly(DTCDI–POR) of porphyrin donor and planar acceptor dithienocoronene diimide (DTCDI) by Sonogashira coupling polymerization. Poly(DTCDI–POR) exhibits good thermal stability, strong NIR absorption and low bandgap. Relative to its PDI counterpart poly(PDI–POR), poly(DTCDI–POR) exhibits up-shifted HOMO and LUMO levels and blue-shifted absorption due to weaker electron withdrawing ability of DTCDI. Poly(DTCDI–POR) exhibits high 2PA cross section per repeat unit at considerably broad telecommunication wavelengths with a maximum of 7809 GM per repeat unit at 1520 nm. The δ value of 7809 GM per repeat unit at 1520 nm is higher than those of poly(PDI–POR) and alkyne-linked porphyrin polymers without DTCDI units and is among the highest reported for conjugated polymers.

EXPERIMENTAL SECTION

Materials. Unless stated otherwise, starting materials were obtained from Aldrich or Acros and were used without further purification. PDI-2Br⁴⁷ and (5,15-diethynyl-10,20-bis(3,4,5-tridodecyloxyphenyl)porphyrinato)zinc(II)⁴⁸ were synthesized according to our published methods. THF was distilled from sodium benzophenone under nitrogen prior to use. Triethylamine was distilled from CaH_2 under nitrogen prior to use. All other reagents were used as received.

Characterization. The ^1H and ^{13}C NMR spectra were measured on a Bruker AVANCE 400 MHz spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as an internal standard. Mass spectra were measured on a Bruker Daltonics BIFLEX III MALDI–TOF analyzer using MALDI mode. Elemental analyses were carried out using a FLASH EA1112 elemental analyzer. Solution (chloroform) and thin-film (on quartz substrate) UV–vis absorption spectra were recorded on a JASCO V-570 spectrophotometer. Electrochemical measurements were carried out under nitrogen on a deoxygenated solution of tetra-*n*-butylammonium hexafluorophosphate (0.1 M) in acetonitrile using a computer-controlled Zahner IM6e electrochemical workstation, a glassy-carbon working electrode coated with polymer films, a platinum-wire auxiliary electrode, and an Ag wire anodized with AgCl as a pseudoreference electrode. Thermogravimetric analysis (TGA) measurements were performed on Shimadzu thermogravimetric analyzer (Model DTG-60) under a nitrogen flow or in air at a heating rate of $10^\circ\text{C min}^{-1}$. The gel permeation chromatography (GPC) measurements were performed on a Waters 515 chromatograph connected to a Waters 2410 refractive index detector, using THF as eluent and polystyrene standards as calibrants, three Waters Styragel columns (HT3, 5, 6E) connected in series were used.

2PA Measurement. The 2PA cross sections (δ) of copolymer poly(DTCDI–POR) were measured at 1320, 1380, 1440, 1480, and 1520 nm in CHCl_3 by using the open aperture Z-scan method,^{49,50} with ~ 120 fs pulses from an optical parametric amplifier (OPA) operating at a 1 kHz repetition rate generated from a mode-locked Ti:sapphire femtosecond laser (Tsunami, Spectra-Physics). The laser

beam was divided into two parts. One was used as the intensity reference and monitored by EPM2000 power meter (Coherent Inc.). The other was used for transmittance measurement; the laser beam was focused by passing through a lens ($f = 15$ cm) and was then passed through a quartz cell with a sample thickness of 1 mm. The position of the sample cell could be varied along the laser-beam direction (z -axis), so the local power density within the sample cell could be changed under a constant laser power level. The transmitted laser beam from the sample cell was then detected by the same power meter as used for reference monitoring. The on-axis peak intensity of the incident pulses at the focal point, I_0 , ranged from 40 to 65 GW/cm². Assuming a Gaussian beam profile, the nonlinear absorption coefficient β can be obtained by curve fitting to the observed open-aperture traces with eq 1

$$T(z) = 1 - \frac{\beta I_0 (1 - e^{-\alpha_0 l})}{2\alpha_0 (1 + (z/z_0)^2)} \quad (1)$$

where α_0 is the linear absorption coefficient, l the sample length, and z_0 the diffraction length of the incident beam. We obtained the nonlinear absorption coefficient β at the corresponding wavelength, where linear absorption is negligible, to satisfy the condition of $\alpha_0 l \ll 1$. When $\alpha_0 l \ll 1$, eq 1 can be simplified as eq 2.

$$T(z) = 1 - \frac{\beta I_0 l}{2(1 + (z/z_0)^2)} \quad (2)$$

The 2PA cross section δ /repeat unit of copolymer poly(DTCDI-POR) (in units of 1 GM = 1×10^{-50} cm⁴ s⁻¹) can be determined by eq 3.

$$\beta = \frac{\delta N_A d \times 10^{-3}}{h\nu} \quad (3)$$

where N_A is the Avogadro constant, d is the concentration of the repeated unit of copolymer poly(DTCDI-POR) in CHCl₃ (the corresponding concentration for copolymer poly(DTCDI-POR) is 1.21×10^{-4} M), h is the Planck constant, and ν is the frequency of the incident laser beam.

Synthesis. *N,N'*-Bis(2-decyltetradecyl)-1,7-bis(thien-2-yl)-perylene-3,4,9,10-tetracarboxylic Diimide (1). PDI-2Br (248.2 mg, 0.2 mmol), 2-(tributylstannyl)thiophene (199.6 mg, 0.5 mmol), and THF (20 mL) were added to a 50 mL three-neck round-bottom flask. The reaction container was purged with N₂ for 10 min to remove O₂. Pd(PPh₃)₂Cl₂ (71.6 mg, 0.1 mmol) was added, and the reaction mixture was heated to 80 °C and stirred overnight. The mixture was poured into water and extracted with CH₂Cl₂. The combined organic layers were dried over MgSO₄, and the solvents were removed by rotary evaporation. The residue was purified by column chromatography on silica gel with a mixture of CH₂Cl₂:petroleum ether (1:1, v/v) as eluent, affording a dark purple solid (191.4 mg, 76.7%). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 8.67 (s, 2H), 8.25 (d, $J = 8.0$ Hz, 2H), 8.08 (d, $J = 8.0$ Hz, 2H), 7.50 (dd, $J_1 = 5.2$ Hz, $J_2 = 0.8$ Hz, 2H), 7.32 (dd, $J_1 = 3.6$ Hz, $J_2 = 1.2$ Hz, 2H), 7.19 (dd, $J_1 = 5.0$ Hz, $J_2 = 3.6$ Hz, 2H), 4.11 (d, $J = 7.2$ Hz, 4H), 1.99 (br, 2H), 1.5–1.1 (m, 80H), 0.95–0.75 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 163.64, 163.46, 143.72, 135.64, 134.16, 133.20, 132.90, 129.68, 129.63, 129.12, 128.89, 128.47, 127.65, 127.62, 122.23, 122.12, 44.96, 36.84, 32.11, 31.91, 30.26, 29.89, 29.86, 29.55, 26.72, 22.87, 14.29. MS (MALDI-TOF): m/z 1227 (M⁺). Anal. Calcd for C₈₀H₁₁₀N₂O₄S₂: C, 78.25; H, 9.03; N, 2.28. Found: C, 78.18; H, 8.87; N, 2.19.

N,N'-Bis(2-decyltetradecyl)-1,7-bis(2-bromothien-5-yl)-perylene-3,4,9,10-tetracarboxylic Diimide (2). In a 25 mL double-neck round-bottom flask covered with aluminum foil, compound 1 (120.9 mg, 0.1 mmol) was dissolved in 10 mL of CHCl₃. *N*-Bromosuccinimide (59.4 mg, 0.3 mmol) was added portionwise, and the reaction mixture was stirred overnight at room temperature. The reaction mixture was poured into water, and the organic phase was extracted with CH₂Cl₂ and washed with water. The organic layers were dried over MgSO₄ and concentrated by rotary evaporation. The residue was purified by column chromatography on silica gel with a mixture of

CH₂Cl₂:petroleum ether (1:1, v/v) as eluent, affording a dark purple solid (120.7 mg, 88.4%). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 8.63 (s, 2H), 8.34 (d, $J = 8.4$ Hz, 2H), 8.22 (d, $J = 8.0$ Hz, 2H), 7.16 (d, $J = 4.0$ Hz, 2H), 7.11 (d, $J = 3.6$ Hz, 2H), 4.12 (d, $J = 7.2$ Hz, 4H), 1.99 (br, 2H), 1.5–1.1 (m, 80H), 0.95–0.75 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 163.58, 163.47, 145.25, 135.51, 134.18, 133.09, 132.21, 131.76, 130.09, 129.88, 129.08, 128.12, 128.04, 122.60, 122.48, 115.22, 44.94, 36.79, 32.06, 31.84, 30.19, 29.84, 29.80, 29.50, 26.65, 22.83, 14.25. MS (MALDI-TOF): m/z 1385 (M⁺). Anal. Calcd for C₈₀H₁₀₈Br₂N₂O₄S₂: C, 69.34; H, 7.86; N, 2.02. Found: C, 69.11; H, 7.82; N, 1.98.

N,N'-Bis(2-decyltetradecyl)-5',5''-dibromo-dithieno-[2',3':5,6;2'',3'':11,12]coronene-2,3,8,9-tetracarboxylic Diimide (3). A mixture of compound 2 (0.92 g, 0.66 mmol) and iodine (0.06 g, 0.24 mmol) in chloroform (200 mL) was exposed to sunlight for 12 h. The solvent was removed in vacuo. The crude compound was washed twice by hot toluene, affording a red solid (590.1 mg, 64.3%). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 8.89 (br, 2H), 8.66 (br, 2H), 8.05 (br, 2H), 4.12 (br, 4H), 1.82 (br, 2H), 1.6–0.9 (m, 80H), 0.9–0.6 (m, 12H). MS (MALDI-TOF): m/z 1381 (M⁺). Anal. Calcd for C₈₀H₁₀₄Br₂N₂O₄S₂: C, 69.55; H, 7.59; N, 2.03. Found: C, 68.98; H, 7.21; N, 1.90. The solubility of compound 3 was not good enough (2.1 mg in 100 mL chloroform at room temperature) to measure ¹³C NMR.

Poly(DTCDI-POR). To a 25 mL three-neck round-bottom flask were added [5,15-diethynyl-10,20-bis(3,4,5-tridodecyloxyphenyl)-porphyrinato]zinc(II) (172.2 mg, 0.1 mmol), compound 3 (142.7 mg, 0.1 mmol), anhydrous THF (10 mL), and triethylamine (5 mL). The mixture was deoxygenated with N₂ for 30 min. Pd(PPh₃)₄ (12.5 mg, 0.015 mmol) and CuI (9.7 mg, 0.05 mmol) were added under nitrogen. The mixture was stirred with reflux for 3 days. After being cooled to room temperature, the reaction mixture was added chloroform (10 mL) and filtered. The solution was dropped into methanol (100 mL). After filtration, the polymer was purified by size exclusion column chromatography over Bio-Rad Bio-Beads S-X1 eluting with chloroform to afford a brown solid (255.2 mg, 85%). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 10.2 (br, 4H), 9.3 (br, 4H), 8.4 (br, 4H), 7.1 (br, 4H), 6.6 (br, 2H), 4.8–3.5 (br, 16H), 2.4–0.7 (br, 232H). Anal. Calcd for C₁₈₈H₂₆₆N₆O₁₀S₂Zn: C, 77.87; H, 9.25; N, 2.90. Found: C, 75.97; H, 9.04; N, 2.78. M_n , 2.1×10^4 ; M_w , 7.8×10^4 ; M_w/M_n , 3.69.

■ ASSOCIATED CONTENT

● Supporting Information

¹H NMR spectra of compounds 1, 2, and 3, ¹³C NMR spectra of compounds 1 and 2 and a GPC trace of polymer poly(DTCDI-POR). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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