Synthesis of Ladder-Like Polynorbornenes with n-Type Perylenendiimide Derivatives as Bridges

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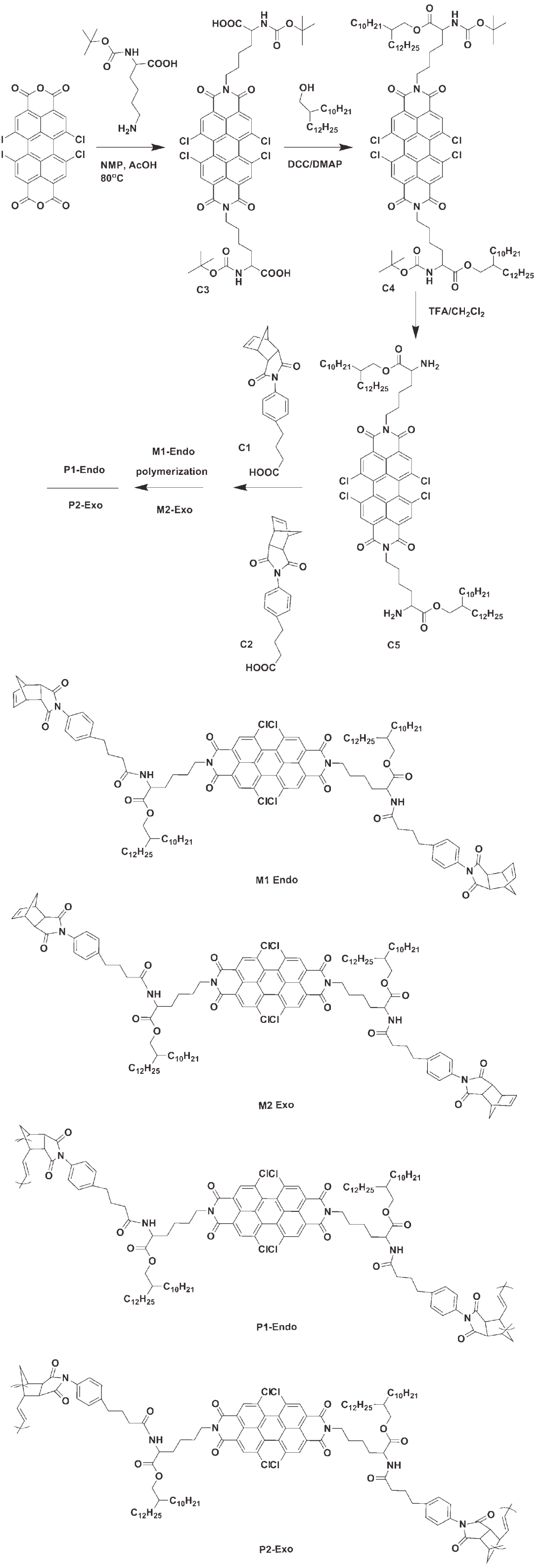
ABSTRACT: Polymerizable tetrachloro-perylenediimdes containing endo/exo-norbornene groups on both imide sides were designed and synthesized. Endo/Exo-type soluble ladder-like polynorbornenes with perylenediimide (PDI) as bridges were prepared by ring-opening metathesis polymerization (ROMP). XRD characterizations showed that the ladder-like polynorbornenes had ordered structures similar to the supramolecular precursors assembled from the corresponding monomers. TGA measurements demonstrated great thermal stabilities for the both target P1-Endo and P2-Exo with T_d of about 320 °C at 5 wt % loss, respectively, which is important for further application in devices. Both polymers have good solubility in common organic solvents and easy to form thin films. Photophysical studies and cyclic voltammetry investigations reveal that polynorbornene films have wide-range absorption from 400 nm to 600 nm and the HOMO/LUMO energy levels could be matched well with the donor-PCzTh-TVDCN. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 1333–1341, 2012

KEYWORDS: ladder-like polymer; perylenediimide; polyborbornene; ROMP; semiconductor; supramolecular structures; synthesis; self-assembly

INTRODUCTION As a promising alternative energy material, polymer solar cells (PSCs) have attracted extensive research interests because of their easy fabrication and processing feasibility. The devices can be prepared via spin-coating to realize the manufacture of large area, flexible, lightweight, inexpensive, and renewable devices.[1–3] Generally, the hole-transporting (p-type) and electron-transporting (n-type) materials are two basic components in the active layer to form a bulk heterojunction.[4–8] Currently, fullerene derivatives, for example, [6, 6]-Phenyl-C_{61}-butyric acid methyl ester (PCBM), are the widely used acceptor materials because these fullerene semiconductors have narrow band width in solid state, high electron mobility and high electron affinity with a lowest unoccupied molecular orbital (LUMO) level of −4.3 eV in vacuum.[9] Despite these advantages, there are still some limitations for PCBM, including the weak absorption in the visible region, high energy costs for production and easy generation of reactive singlet oxygen which jeopardizes device's long term stability.[10–12] Thus, it's greatly desirable to explore new n-type alternatives with good mobility and thermal stability for PSCs.[13] Perylenediimide (PDI) and its derivatives are well-studied n-type organic semiconductors with high electron mobility,[14–16] but their poor solubility makes them difficult to process. Some studies have reported to improve the solubility of perylene diimide via chemically incorporating substitutes into the N atoms of the imide groups or the bay positions in the PDI core.[17–19] Another strategy is to introduce PDI moiety to polymer side chain.[20] For the former, Schwartz and coworkers reported perylene-functionalized polyisocyanides, in which the perylene molecules could form overlapping pathways.[21] For the latter case, we recently reported a ladder polysiloxane based on perylenediimide derivatives to minimize the conglomeration of PDI core and improve materials' thermo-stability and solubility while retaining its optoelectronic properties.[22] However, the degree of polymerization was still low due to the limitation of the stepwise coupling polymerization (SCP) method.

To circumvent this problem, we reconsidered the motif of monomer design. We still chose tetrachloro-perylenediimide as the core molecule, while introducing norbonene as polymerizable unit and branched C10/C12 alkyl chain to improve sample solubility. Moreover, we employed ring-opening metathesis polymerization (ROMP), which has been demonstrated an efficient method to prepare polymers with high molecular weight and complicated architectures in spite of the steric bulk of monomers.[23–25] For example, Luh and coworkers reported the ROMPs of endo-fused norbornene derivatives catalyzed by Grubbs-I catalyst can give the corresponding polynorbornenes with ladder-like backbones.[26]

Additional Supporting Information may be found in the online version of this article.



SCHEME 1 Synthetic routes to target ladder-like polynorbornenes.

Cheng and coworkers applied ROMP and ROP to prepared molecular bottlebrush with polynorbornene as backbone and polypeptide as side chain via one-pot reaction.[27] Also, note that the configuration of norboenenes has significant influences on their reactivity. Sridhar Rajaram et al., found that the endo-type monomer can effectively shield the alkene from the catalyst so that the polymer's molecular weight was limited for monomers containing large side-chain groups. In contrast, exo-type monomers have higher reactivity and are much easier to obtain higher molecular weight polynorbornene.[23]

Herein, we adopted ROMP approach and integrated norbornene units and PDI core together to synthesize a ladder-like polynorbornene as polymeric electron acceptors. The corresponding synthetic scheme is illustrated in Scheme 1. Aiming to improve materials' stability, solubility and absorption in the visible region, we consider the following aspects in monomer design: (i) selecting n-type tetrachloro-perylenediimide as ladder bridge to provide the n-channel for electron transport and cofacial π–π interactions; (ii) incorporating 2-decyl-1-tetradecanol into the target product to enhance the polymer's solubility and minimize undesired cross-coupling between different units; (iii) using norbornene as polymerizable monomer to obtain high molecular weight polymers via ROMP.

RESULTS AND DISCUSSION

Synthesis and Characterization of Monomers and Polynorbornenes

First, the NαBoc-lysine functionalized perylenediimide **C3** as molecular core was synthesized according to literature procedure,[28,29] and purified by flash column chromatography with yield of about 60%. Subsequently, **C4** was synthesized by direct esterification reaction between **C3** and 2-decyl-1-tetradecanol in the presence of DCC/DMAP.[30] Note that excessive DCC was used in the reaction system as the DCU byproducts can be completely removed through successive filtration, methanol wash and flash column chromatography. After that, the protective Boc group was selectively removed using TFA to give product **C5**. Note that the reaction mixture needs to be purified by flash column chromatography for subsequent coupling with **C1** or **C2**. Otherwise, serious byproducts contamination will happen as revealed by TLC (methanol/CH_2Cl_2 = 1/10). After purification, **C5** was found to be stable in ambient condition. In the meantime, the functional groups of endo-NDA and exo-NDA were converted into carboxylic acid groups. **M1-Endo** and **M2-Exo** were obtained by standard procedure of amidation reaction with **C1** and **C2**, respectively, in the presence of EDC·HCl/DMAP. All the monomers described above were exclusively characterized using ^{1}H NMR, ^{13}C NMR and mass spectroscopy with corresponding data shown in Supporting Information.

After successfully prepared **M1-Endo** and **M2-Exo** monomers with high purity, we initially attempted their polymerizations in the presence of the first-generation Grubbs catalyst however without success as indicated from TLC characterizations, which showed only the monomers' spots in THF/CH_2Cl_2 = 1/20 with R_f = 0.5 and 0.7 for **M1-Endo** and **M2-Exo**, respectively. A possible reason we presume is

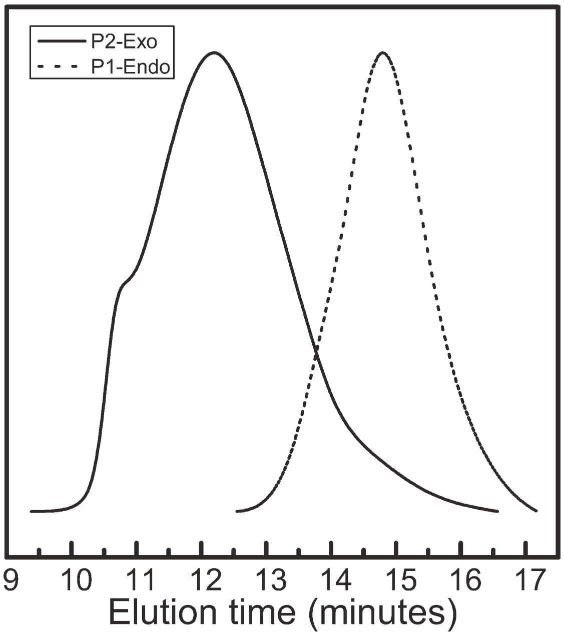


FIGURE 1 GPC traces of ladder-like **P1-Endo** and **P2-Exo**.

due to the steric hindrance of the long alkyl side chain (-$C_{10}H_{21}C_{12}H_{25}$), which practically prevents the ROMP.[23] We thus used the second generation of Grubbs catalyst and found that both **M1-Endo** and **M2-Exo** underwent polymerization in the presence of the second generation Grubbs catalyst. Presumably, ROMP of **M1-Endo** and **M2-Exo** will form ladder-like polymers. Figure 1 shows the GPC traces of **P1-Endo** and **P2-Exo**. Apparently, the ROMP of exo-type monomer gives higher molecular weight compared to endo-type monomers under identical conditions. The reason we believe is that exo-type monomer has higher reactivity than endo-type monomer arising from steric effects as proposed by Sridhar.[23] Note that **P2-Exo** shows a high molecular weight shoulder in its GPC trace (Fig. 1). A possible reason is due to side-reactions of ROMP as proposed by Percec et al.[31] They found that a nonliving chain polymerization accompanied by backbiting and other secondary metathesis reactions with exo-type monomers could occur, which could cause the broadening of the polymer peak and formation of a shoulder in GPC traces. Another possible reason is due to the cross ROMP between different ladder polymers arising from defects of supramolecular template. Whereas, we could determine which one is the main reason from available data. The corresponding molecular parameters of these polymers are summarized in Table 1.

As illustrated in Scheme 1, both **M1-Endo** and **M2-Exo** monomers contain two polymerizable norbornene units, so random ROMP of each unit has great chance of forming branched or crosslinked polymer network. Therefore, preformation of one-dimensional assembly, which can confine the ROMP to certain extent, is critical to form well-defined ladder-like polymers. To obtain well-defined one-dimensional ladder-like polymers, we carefully modified the monomer design and optimized polymerization conditions to obtain high molecular weight polymer while negligible cross-coupling between different strands. For the monomer design, we introduced supramolecular forces to confine monomers within an oriented space prior to ROMP. Several factors were considered. We introduce L-lysine as linkage between norbornene and PDI core. The resulting acylamide bonds are dedicated to offer hydrogen bonding interactions while the PDI bridges serve to provide π–π stacking forces between monomers. In this particular case, **M1-Endo** and **M2-Exo** were not only the precursors but also the supramolecular templates for ROMP. In principle, the noncovalnent linked supramolecular ladder polymer will be preserved after ROMP of norbonene.

Before ROMP, the determination of the supramolecular ladder polymer was important to form well-defined ladder-like polymer via covalent bond. We used XRD to characterize the ordering of supramolecular ladder polymer. To prepare the dried sample for XRD characterization, we adopted freeze-drying strategy, in which the super fast cooling could presumably preserve the nanostructure of supramolecular assemblies in solvent to a great extent. Figure 2 shows XRD spectra of supramolecular assemblies of **M1-Endo** and **M2-Exo** freeze-dried from THF solution (10 mg/mL), respectively. Apparently, both samples display two strong albeit diffusive peaks with spacing of about 1.8 and 1.1 nm. Using computer simulation, we can estimate dimension of individual monomers. Scheme 2 presents the computer simulation results, which give theoretical width and thickness of **P2-Exo** being about 2 and 1 nm, respectively. Meanwhile, both sample only show ill-defined diffusive diffraction around $2\theta = 18–25^\circ$ with *d*-spacing of about 0.4 nm, which corresponds to the π-π stacking distances presumably arising from cofacial interaction of PDI bridge core. The broad and diffusive peaks indicate lacking long range ordering of PDI cores.

TABLE 1 Molecular Parameters, Thermal and Photophysical Properties of **P1-Endo** and **P2-Exo**

Polymers	M_n (g/mol)	DP[a]	PDI (M_w/M_n)	T_d[b] (°C)	λ_{abs}[c] (nm)	E_g[d] (eV)	LUMO[e](eV)	HOMO[f](eV)
P1-Endo	20,000	10	1.2	320	568	2.18	−4.11	−6.29
P2-Exo	83,000	40	2.8	320	560	2.21	−4.15	−6.36

[a] Calculated from GPC results.
[b] 5% weight loss temperature measured by TGA under N_2.
[c] For the optical absorption band edge of polymer films.
[d] Band gap, estimated from the optical absorption band edge of the films.
[e] Calculated from the onset reduction potentials of the polymers.
[f] Estimated using empirical equations $E_{HOMO} = E_{LUMO} - E_g$.

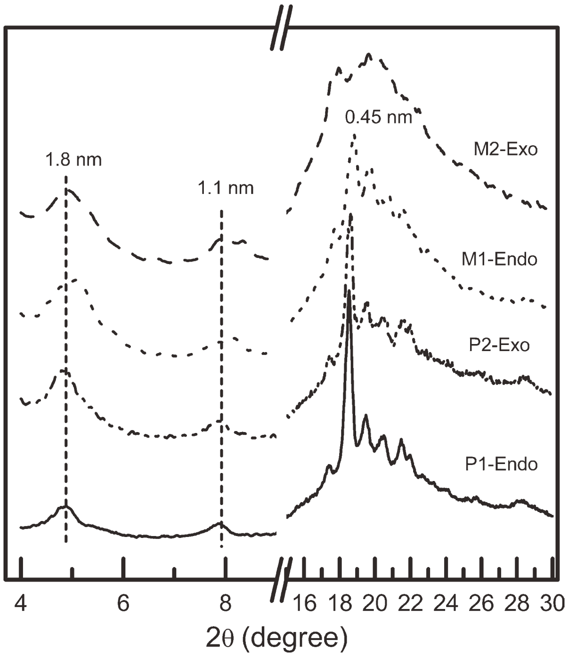
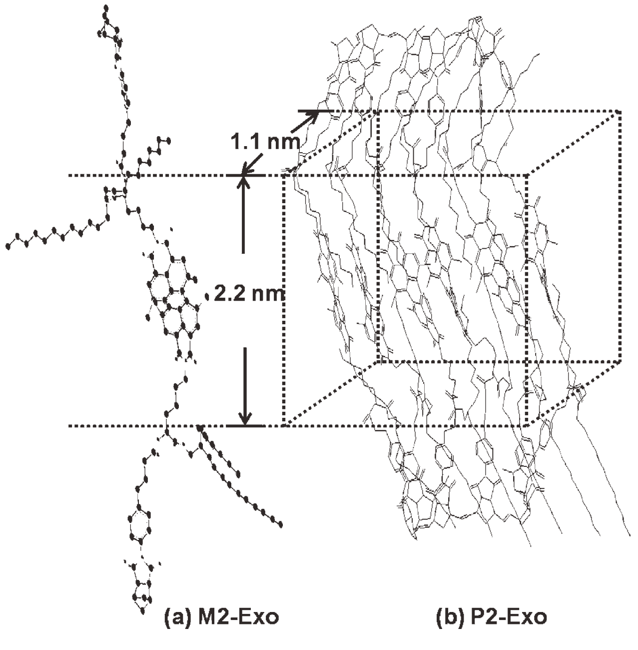


FIGURE 2 XRD spectra of M1-Endo, M2-Exo, P1-Endo, and P2-Exo.

Then, the supramolecular assemblies were directly used for ROMP in THF at RT. After polymerization, both **P1-Endo** and **P2-Exo** samples showed two peaks around 1.8 and 1 nm (Fig. 2), consistent with XRD spectra of **M1-Endo** and **M2-Exo**, responsively. These results indicate that the ordered assembly structures of monomers were retained after ROMP.



SCHEME 2 (a) Molecular model of **M2-Exo** and (b) 3D mode of molecular simulated **P2-Exo** with six repeat units (Hyper Chem7.0 geometry optimization with RMS gradient of 0.1 kcal/mol).

In addition, the diffusing peak in the region of $2\theta \approx 18$–$25°$, corresponding $d \approx 0.45$–0.35 nm, is assigned to the π–π interaction distance between adjacent PDI cores. The intensity of this peak is increased for **P1-Endo** and **P2-Exo** and the peaks become much sharper compared with **M1-Endo** and **M2-Exo** monomers, which can be attributed to the stronger π–π interactions within covalent-linked ladder polynorbornenes than those supramolecular counterparts.

As the PDI core was invariable between monomers and polymers, we took **P2-Exo** as an example. The XRD data of **P2-Exo** regarding the spacing ordering were also consistent with molecular simulation shown in Scheme 2. The theoretical width of **P2-Exo** is about 2 nm and the thickness is around 1 nm. We suppose that **P1-Endo** and **P2-Exo** would have much better stabilities as the double covalent linkages between PDI cores would certainly enhance their thermal stability and intramolecular ordering.

We demonstrated that it is applicable to converted supramolecular assembly of bifunctional PDI monomers into covalent linked ladder polymer with PDI as central bridge while having minimal crosslinking between different ladder-like polymers. Since the PDI core was chemically linked together, a good thermal stability is thus expected for such polymeric semiconductor. We investigated the thermal properties of two polymers, and found that the 5% weight-loss temperatures for **P1-Endo** and **P2-Exo** were about 320 °C. Meanwhile, the TGA data showed that there was about 3% weight loss at about 200 °C for both polymers, which was just consistent with the thermal decomposition temperature of ester bond. The results are shown in Figure 3 and Table 1. These results demonstrate that their thermal stability is adequate for application of the polymers as active materials in the optoelectronic devices.[32]

Photophysical Properties

A key question is the photophysical properties of **P1-Endo** and **P2-Exo** since the active PDI domains were chemically

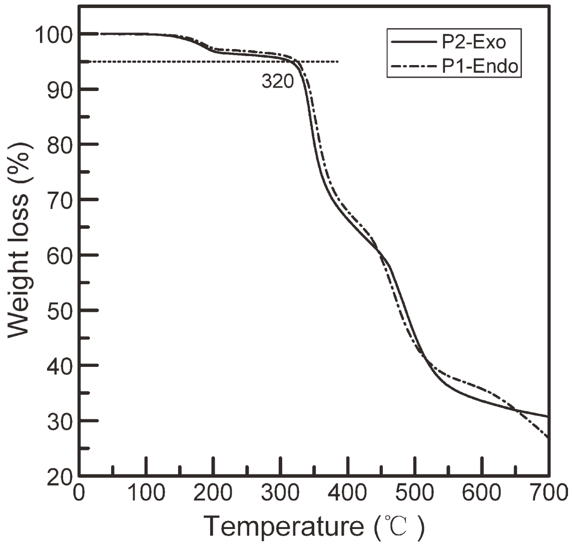


FIGURE 3 TGA traces of **P1-Endo** and **P2-Exo**.

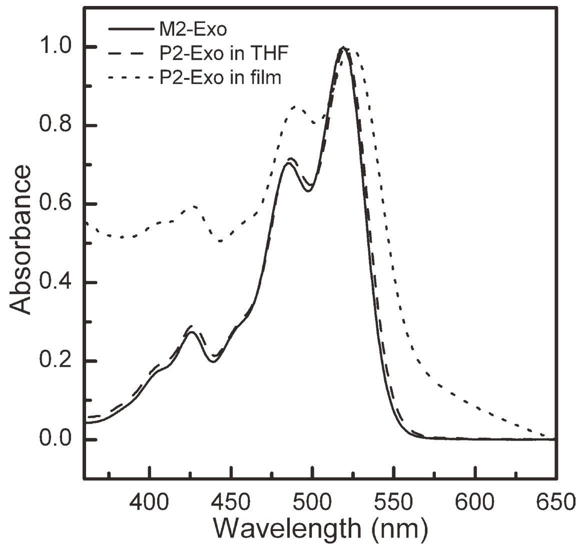


FIGURE 4 UV–visible absorption spectra of **M2-Exo**, **P2-Exo** in THF and **P2-Exo** in film.

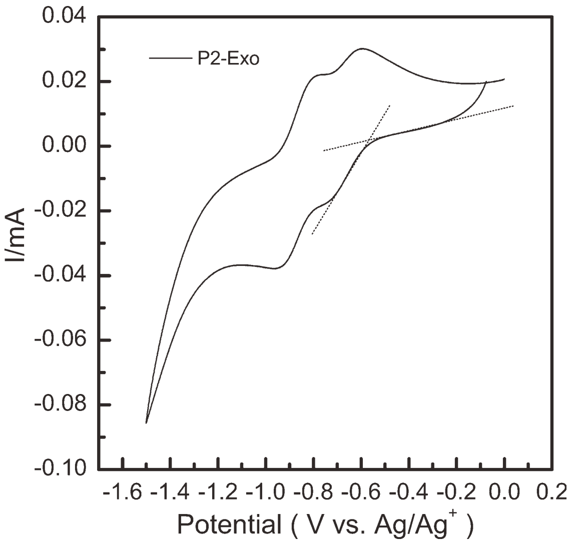


FIGURE 5 Cyclic voltammetry trace of **P2-Exo**.

confined within one-dimensional space. Figure 4 compares the UV–Vis spectra of **M2-Exo** and **P2-Exo**, whereas the corresponding spectra of **M1-Endo** and **P1-Endo** are shown in Supporting Information (Supporting Information Fig. S1). Apparently, both monomers and polymers have the characteristic absorption of PDI core. The absorption maximum at 519 nm belongs to the electronic S_0–S_1 transition, with a transition dipole moment along the long molecular axis[33] and the absorption band in the region of 400–460 nm is attributed to the electronic S_0–S_2 transition, with a transition dipole moment perpendicular to the long molecular axis.[34] Meanwhile, compared with **M2-Exo** in THF, **P2-Exo** doesn't show significant red-shift indicating negligible crosslinking in great agreement with GPC results. In film state, the absorption spectrum of **P2-Exo** becomes broad, and the overall intensity was enhanced, which are also beneficial to PSCs. From the film UV–Vis spectrum, we could estimate the corresponding energy band gap, that is, $\lambda_{abs} = 560$ nm, $E_g = 2.21$ eV. Similar results can also be obtained for **P1-Endo**.

Cyclic Voltammetry Study

For semiconducting materials, the highest occupied molecular orbital (HOMO) and LUMO energy levels are important parameters, and they can be estimated from the onset oxidation and reduction potentials.[35] Electrochemical behaviors of **P1-Endo** and **P2-Exo** were thus investigated using cyclic voltammetry. The corresponding results are shown in Figure 5 (**P2-Exo**) and Figure S2 (**P1-Endo**), from which the LUMO energy levels of polymers are determined using the onset reduction potentials using following equation: $E_{\mathrm{LUMO}} = -(4.4 + E^{\mathrm{red}}_{\mathrm{onset}})$.[35] The LUMO and HOMO values are −3.84 eV and −6.05 eV for **P2-Exo**, and −3.8 eV and −5.98 eV for **P1-Endo**, respectively. Compared with the low molar mass PDI derivatives (e.g., PDI-FCN$_2$ and PDI-8CN$_2$[36]), **P1-Endo** and **P2-Exo** have higher LUMO levels, which could offer the solar cell devices with high open-circuit voltage. Because these values turn out to be good match for PCzTh–TVDCN[32] in terms of energy level, we chose PCzTh–TVDCN as the donor for device fabrications.

Device Fabrication

When the weight ratio of PCzTh–TVDCN and polymers was 1:2, we tested the short circuit current density (J_{sc}) and power conversion efficiency (PCE) with the device configuration of ITO/PEDOT: PSS/PCzTh-TVDCN: polymers/Al. The device energy diagram is shown in Figure 6 and Table 2, which indicates the performances of two devices. It was not surprising that the PCE turned out to be as low as 0.012% since we did not choose optimized materials. Our aim here is to demonstrate that we can use chemical bond to confine the organic semiconductors within a limited but highly oriented space. The corresponding solubility and thermal stability are

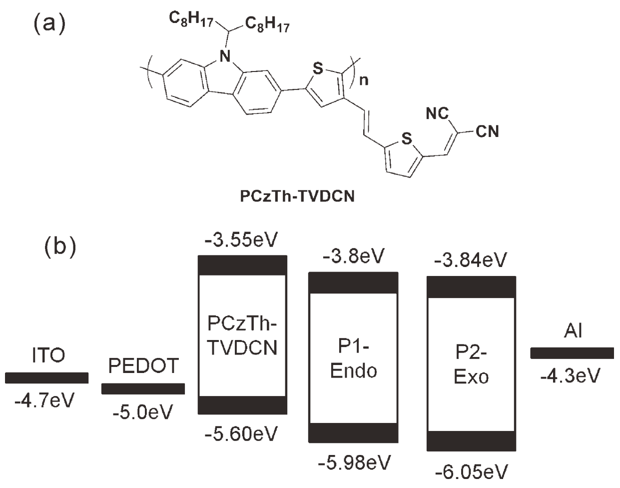


FIGURE 6 (a) Chemical structure of PCzTh-TVDCN and (b) energy diagram of ITO/PEDOT: PSS/PCzTh-TVDCN/**P1-Endo**/**P2-Exo**/Al.

TABLE 2 Photovoltaic Parameters of the **PSC**s Based on PCzTh-TVDCN/Polymers (1:2, w/w)

Active Layer	V_{oc} (V)	J_{sc} (μA/cm^2)	FF (%)	PCE (%)
PCzTh-TVDCN / P1-Endo	0.74	64	25	0.012
PCzTh-TVDCN / P2-Exo	0.73	38	28	0.008

improved substantially however without losing PDI's photophysical properties.

EXPERIMENTAL

Materials

NαBoc-*L*-lysine-OH (Boc-lys-OH) was purchased from GL Biochem (Shanghai). 1,6,7,12-Tetrachloroperylene tetracarboxylic acid dianhydride (TCP) was purchased from commercial sources at analytical grade and used without further purification. *cis*-5-Norbornene-endo-2,3-dicarboxylic anhydride (Endo-NDA), *cis*-5-Norbornene-exo-2,3-dicarboxylic anhydride (Exo-NDA), 4-(4-aminophenyl)butanoic acid, 2-decyl-1-tetradecanol, dicyclohexyl-carbodiimide (DCC), 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl), 2nd Generation Grubbs' Catalyst and 4-dimethylaminopyridine (DMAP) were purchased from Sigma-Aldrich. *N*-methyl pyrrolidone (NMP), trifluoroacetic acid (TFA), acetic acid (AcOH), tetrahydrofuran (THF), and dichloromethane were purchased from Sinopharm Chemical Reagent Beijing. THF was distilled over sodium benzophenone complex.

Characterizations

FTIR measurements were performed on a Perkin–Elmer 80 spectrometer and the samples were prepared by casting solution sample on KBr flake. UV–Vis spectra were obtained on a Shimadzu UV–Vis spectrometer (UV-1601PC). Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrometer and corrected against photomultiplier and lamp intensity. The slit width of both monochromators was 5.0 nm. ^{1}H,^{13}C spectra were obtained on a Bruker Advance DPS-400 (400 MHz) spectrometer. Gel permeation chromatography (GPC) was performed on a Waters PL-GPC 50 machine using THF as the eluent (flow rate =1.0 mL/min), Waters Styragel HT 3 and HT 4 columns with effective molecular weight range from 500 Da to 600, 000 Da. X-ray diffraction (XRD) analysis was performed on a Rigaku D/MAX 2400 diffractometer. Thermogravimetry analysis (TGA) was performed on Pyris 1 TGA machine under N_2 protection with heating rate = 10 °C/min. Cyclic voltammetry was performed on CHI660D voltammetric analyzer (CH Instruments) with a standard three-electrode electrochemical cell in a 0.1 M tetrabutylammonium tetrafluoroborate solution in acetonitrile at RT under nitrogen purge. The scanning rate is 50 mV/s. A glassy carbon working electrode, a Pt wire counter electrode, and a silver wire as a quasi-reference electrode were used.

Preparation of 4-(4-phenyl butyric acid)-4-aza-tricycle[5.2.1.0$^{2,6\text{-}endo}$]dec-8-ene-3,5-dione (C1)

Endo-NDA (8.2 g, 50 mmol) and 10 g 4-(4-aminophenyl)butanoic acid (56 mmol) were added into a two-necked round bottle flask with magnetic stirring bar. The flask was then evacuated and purged with argon three times. NMP (250 mL) was added under argon purge followed by 2 mL AcOH. The mixture was stirred at 100 °C for 12 h under argon purge. After that, the reaction mixture was cooled to RT and precipitated with 2 L water. The precipitates was subsequently washed with 500 mL DI water twice; 12.5 g product **C1** was obtained using flash chromatography on a silica gel column (methanol/CH_2Cl_2 = 1/80) with about 76 % yield; $R_f = 0.4$ (CH_2Cl_2/petroleum ether = 1/60).

^{1}H NMR (400 MHz, THF) δ 7.23–7.15 (d, *J* = 8.1 Hz, 2H, Ph-H), 7.10–7.01 (d, *J* = 8.1 Hz, 2H, Ph-H), 6.23–6.14 (s, 2H, norbornene-CH=CH), 3.41–3.31 (s, 4H, norbornene-$(CH)_4$), 2.70–2.59 (t, *J* = 7.7 Hz, 2H, Ph-CH_2), 2.54–2.36 (s, 1H, —COOH), 2.30–2.19 (t, *J* = 7.3 Hz, 2H, CO—CH_2), 1.94–1.81 (p, *J* = 7.4 Hz, 2H, COOH—CH_2—CH_2), 1.69–1.65 (d, *J* = 8.5 Hz, 1H, norbornen-tricycle-CH), 1.62–1.57 (d, *J* = 8.5 Hz, 1H, norbornen-tricycle-CH).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.17, 177.14, 141.91, 134.62, 129.77, 129.17, 126.62, 77.48, 77.16, 76.84, 52.25, 45.78, 45.50, 34.64, 33.26, 26.00; EI MS (*m*/*z*) Calcd for $C_{19}H_{19}NO_4$ 325.13; found: 325.

Preparation of 4-(4-phenyl butyric acid)-4-aza-tricycle[5.2.1.0$^{2,6\text{-}exo}$]dec-8-ene-3,5-dione (C2)

The synthesis of product **C2** was similar to product **C1**. **C2** was also purified by flash chromatography on a silica gel column (methanol/CH_2Cl_2 = 1/80) with about 83 % yield; R_f = 0.4 (methanol/CH_2Cl_2 = 1/60).

^{1}H NMR (400 MHz, THF) δ 7.28–7.22 (d, *J* = 8.1 Hz, 2H, Ph-H), 7.22–7.16 (d, *J* = 8.1 Hz, 2H, Ph-H), 6.36–6.30 (s, 2H, norbornene-CH=CH), 3.29–3.22 (s, 2H, norbornene-$(CH)_2$), 2.79–2.72 (s, 2H, norbornene-$(CH)_2$), 2.71–2.62 (t, *J* = 7.7 Hz, 2H, Ph-CH_2), 2.54–2.37 (s, 1H, —COOH), 2.30–2.21 (t, *J* = 7.3 Hz, 2H, CO—CH_2), 1.96–1.83 (p, *J* = 7.5 Hz, 2H, COOH—CH_2—CH_2), 1.54–1.43 (q, *J* = 9.8 Hz, 2H, norbornen-tricycle-$(CH)_2$).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.34, 177.34, 142.05, 138.07, 129.85, 129.33, 126.40, 77.48, 77.16, 76.84, 47.93, 45.89, 43.03, 34.72, 33.30, 26.07; EI MS (*m*/*z*) Calcd for $C_{19}H_{19}NO_4$ 325.13; found: 325.

Preparation of 1,6,7,12-tetrachloro-*N*-*N*′-bis(2-(tert-butoxycarbonylamino)hexanoic acid)-perylene-3,4,9,10-tetracarboxylic acid diimide (C3)

TCP (10.6 g, 20 mmol) and 14.8 g NαBoc-lys-OH (60 mmol) were added into a two-necked flask with magnetic stirring bar. The flask was then evacuated and purged with argon three times. 250 mL NMP was added under argon atmosphere followed by 2 mL AcOH. The mixture was stirred at 80 °C for 10 h under argon purge. After that, the reaction mixture was cooled to RT and precipitated with 2 L water. The product as a dark red fluffy cake was collected by filtration and washed with water twice; 11.5 g of C3 was obtained using flash chromatography on a silica gel column (methanol/$CH_2Cl_2 = 1/10$) with 60 % yield; $R_f = 0.3$ (methanol/$CH_2Cl_2 = 1/10$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.52 (s, 2H, lys-COOH), 8.61 (s, 4H, perylene-H), 5.23 (d, $J = 6.7$ Hz, 2H, α-lys-H), 4.24 (d, $J = 43.1$ Hz, 4H, perylene-N—CH_2), 3.39 (t, $J = 7.1$ Hz, 4H, perylene-N—CH_2—CH_2), 2.40 (t, $J = 8.1$ Hz, 4H, lys-CH_2—CH_2), 2.08–1.97 (m, 4H, lys-CH_2), 1.40 (s, 18H, COO—C— $(CH_3)_3$).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.79, 175.20, 162.23, 155.64, 135.35, 132.95, 131.39, 128.59, 123.24, 79.75, 53.25, 49.66, 40.47, 32.32, 30.63, 29.75, 28.34, 27.70, 22.74, 17.64; MALDI–TOF MS (*m*/*z*) Calcd for $C_{46}H_{44}Cl_4N_4O_{12}$ 986.17; found: 986.5.

Preparation of 1,6,7,12-tetrachloro-*N*-*N'*-bis (2-decyltetradecyl-2-(tert-butoxycarbonyl amino) hexanoate)-perylene-3,4,9,10-tetracarboxylic acid diimide (C4)

C3 (9.9 g, 10 mmol) was firstly dissolved in 300 mL anhydrous THF. To this solution, 10.7 g 2-decyl-1-tetradecanol (30 mmol), 12.4 g DCC (60 mmol) and four granules of DMAP were added under stirring at RT. The reaction progress was monitored by TLC (THF/$CH_2Cl_2 = 1/80$). After 24 h, 200 mL diethylether and 80 mL water were added. The ether layer was separated and washed with 80 mL water three times. The organic layer was then dried over sodium sulfate and filtered. The solvent was removed by rotary evaporator, and 11.6 g product **C4** was obtained using flash chromatography on a silica gel column (THF/$CH_2Cl_2 = 1/160$) with 70 % yield; $R_f = 0.6$ (THF/$CH_2Cl_2 = 1/60$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 4H, perylene-H), 5.10 (d, $J = 8.0$ Hz, 2H, α-lys-H), 4.30 (s, 2H, lys-COO—CH_2—CH), 4.21 (t, $J = 7.0$ Hz, 4H, lys-COO—CH_2), 4.11–3.96 (m, 4H, perylene-N—CH_2), 3.75 (d, $J = 5.9$ Hz, 4H, perylene-N—CH_2—CH_2), 1.89 (d, $J = 9.6$ Hz, 2H, $(C_{10}H_{21}C_{12}H_{25})$CH), 1.85 (s, 4H, lys-$CH_2$—$CH_2$), 1.82–1.69 (m, 6H, lys-CH_2), 1.42 (d, $J = 2.9$ Hz, 18H, COO—C—$(CH_3)_3$), 1.23 (s, 80H, —$C_9H_{18}C_{11}H_{22}$), 0.85 (t, $J = 6.4$ Hz, 13H, C_9H_{18}—CH_3,$C_{11}H_{22}$—CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.86, 162.10, 155.37, 135.36, 132.90, 131.39, 128.55, 123.22, 79.57, 67.92, 53.36, 40.31, 37.29, 32.49, 31.89, 31.16, 29.95, 29.64, 29.33, 28.30, 27.64, 26.69, 25.60, 22.72, 14.09; MALDI–TOF MS (*m*/*z*) Calcd for $C_{94}H_{140}Cl_4N_4O_{12}$ 1656.92; found: 1656.9.

Preparation of 1,6,7,12-tetrachloro-*N*-*N'*-bis(2-decyltetradecyl-2-aminohexanoate)-perylene-3,4,9,10-tetracarboxylic acid diimide (C5)

C4 (1.66 g, 1 mmol) was dissolved in 50 mL CH_2Cl_2, and then 50 mL TFA was added to the mixture. The reaction progress was monitored by TLC (methanol/$CH_2Cl_2 = 1/10$). After 18 h, **C4** was completely consumed and then 200 mL CH_2Cl_2 and 80 mL water were added. The organic layer was separated and washed with 80 mL water three times and 80 mL saturated $NaHCO_3$ solution twice. Then it was quickly dried over sodium sulfate and filtered. Finally, 1.3 g **C5** was obtained by flash chromatography on a silica gel column (methanol/$CH_2Cl_2 = 1/30$) with 89 % yield; $R_f = 0.6$ (methanol/$CH_2Cl_2 = 1/10$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 4H, perylene-H), 4.23 (t, $J = 7.3$ Hz, 4H, lys-COO—CH_2), 4.09–3.96 (m, 4H, perylene-*N*-CH_2), 3.48 (t, $J = 6.1$ Hz, 2H, α-lys-H), 1.91–1.73 (m, 8H, $(C_{10}H_{21}C_{12}H_{25})$CH, lys-$CH_2$), 1.64 (s, 8H, perylene-N—CH_2—CH_2, lys-CH_2—CH_2), 1.25 (d, $J = 19.5$ Hz, 80H, —$C_9H_{18}C_{11}H_{22}$), 0.85 (t, $J = 6.4$ Hz, 12H, C_9H_{18}—CH_3,$C_{11}H_{22}$—CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.16, 162.11, 135.38, 132.92, 131.41, 128.58, 123.23, 67.67, 54.40, 40.57, 37.33, 34.52, 31.90, 31.25, 29.97, 29.65, 29.34, 27.84, 26.71, 23.22, 22.67, 14.10; MALDI–TOF MS (*m*/*z*) Calcd for $C_{84}H_{124}Cl_4N_4O_8$ 1459.72; found: 1459.2.

Preparation of M1-Endo

C5 (1.4 g, 1 mmol) was first dissolved in 50 mL anhydrous CH_2Cl_2. To this solution, 1 g **C1** (3 mmol), 1.15 g EDC·HCl (6 mmol), and two granules of DMAP were added under stirring at RT. The reaction progress was monitored by TLC (THF/$CH_2Cl_2 = 1/20$). After 24 h, 100 mL CH_2Cl_2 and 50 mL water were added. The organic layer was separated and washed with 50 mL water three times. Then it was dried over sodium sulfate and filtered. The solvent was removed by rotary evaporator and 1.5 g product **M1-Endo** was obtained using flash chromatography on a silica gel column (THF/$CH_2Cl_2 = 1/40$) in 72 % yield; $R_f = 0.5$ (THF/$CH_2Cl_2 = 1/20$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, $J = 0.5$ Hz, 4H, perylene-H), 7.22 (dd, $J = 8.3$, 1.7 Hz, 4H, (—CH_2—Ph)-H), 7.03 (d, $J = 8.3$ Hz, 4H, norbornene-Ph-H), 6.24 (s, 4H, norbornene-CH═CH—), 4.64 (dd, $J = 12.8$, 6.2 Hz, 2H, α-lys-H), 4.20 (t, $J = 7.1$ Hz, 4H, lys-COO—CH_2), 4.12–3.97 (m, 4H, perylene-N—CH_2), 3.49 (s, 4H, norbornene-CH—C═O—CH—C═O), 3.41 (dd, $J = 5.2$, 3.7 Hz, 4H, (norbornene-CH═CH)—CH), 2.64 (t, $J = 7.5$ Hz, 4H, Ph-CH_2), 2.27 (s, 2H, $C_{10}H_{21}C_{12}H_{25}$)CH), 2.23 (t, $J = 7.4$ Hz, 4H, lys-NH_2—CO—CH_2), 2.02–1.88 (m, 4H, lys-CH_2), 1.76 (t, $J = 12.0$ Hz, 4H, Ph-CH_2—CH_2), 1.65 (s, 2H, norbornen-tricycle-CH), 1.60 (d, $J = 5.8$ Hz, 2H, norbornen-tricycle-CH), 1.23 (s, 80H, —$C_9H_{18}C_{11}H_{22}$), 0.85 (t, $J = 6.7$ Hz, 12H, C_9H_{18}—CH_3,$C_{11}H_{22}$—CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.87, 172.72, 172.27, 162.20, 142.05, 135.38, 134.59, 132.91, 131.41, 129.74, 129.13, 128.59, 126.53, 123.26, 68.24, 52.07, 45.76, 45.49, 40.33, 37.29, 35.50, 34.77, 32.08, 31.17, 29.97, 29.67, 29.35, 27.59, 26.70, 22.75, 14.13; MALDI–TOF MS (*m*/*z*) Calcd for $C_{122}H_{158}Cl_4N_6O_{14}$ 2074.4; found: 2073.1.

Preparation of M2-Exo

The synthesis of **M2-Exo** was similar to **M1-Endo**. **M2-Exo** was also purified by flash chromatography on a silica gel column (THF/$CH_2Cl_2 = 1/50$) in 75 % yield; $R_f = 0.7$ (THF/$CH_2Cl_2 = 1/20$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 4H, perylene-H), 7.28 (s, 4H, (—CH_2—Ph)—H), 7.16 (d, $J = 8.2$ Hz, 4H, norbornene-Ph-H), 6.33 (s, 4H norbornene-CH═CH—), 4.64 (dd, $J = 12.9$, 6.3 Hz, 2H, α-lys-H), 4.20 (t, $J = 7.1$ Hz, 4H, lys-COO—CH_2), 4.11–3.98 (m, 4H, perylene-N—CH_2), 3.38 (s, 4H, norbornene-CH—C=O—CH—C=O), 2.84 (d, $J = 6.3$ Hz, 4H, (norbornene-CH=CH)—CH), 2.66 (t, $J = 7.5$ Hz, 4H, Ph-CH_2), 2.28–2.20 (m, 5H, $C_{10}H_{21}C_{12}H_{25}$)CH, lys-NH_2—CO—CH_2), 2.05–1.89 (m, 4H, lys-CH_2), 1.86–1.71 (m, 4H, Ph-CH_2—CH_2), 1.69–1.56 (m, 4H, norbornen-tricycle-CH), 1.24 (d, $J = 8.4$ Hz, 88H, —$C_9H_{18}C_{11}H_{22}$), 0.85 (t, $J = 6.6$ Hz, 17H, C_9H_{18}—CH_3, $C_{11}H_{22}$—CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.07, 172.72, 172.28, 162.18, 142.15, 137.97, 135.35, 132.89, 131.39, 129.73, 129.20, 128.57, 126.23, 123.25, 68.21, 51.97, 47.83, 45.81, 42.95, 40.31, 37.28, 35.44, 34.75, 32.21, 31.90, 31.16, 29.86, 29.66, 29.35, 27.58, 26.69, 22.75, 14.13; MALDI–TOF MS (m/z) Calcd for $C_{122}H_{158}Cl_4N_6O_{14}$ 2074.4; found: 2073.1.

General Procedure of ROMP for P1-Endo and P2-Exo

In glovebox, 100 mg **M1-Endo** or **M2-Exo** (0.05 mmol) was dissolved in 8 mL anhydrous THF. 1.36 mg 2nd Generation Grubbs' Catalyst (0.0016 mmol) in 0.1 mL THF was added to the monomers. The reaction mixture was stirred at RT for 2 h. After the polymerization was complete (monitored by TLC), the reaction was quenched by adding 2 mL ethyl vinyl ether into the reaction mixture. Then the mixture was poured into 40 mL methanol and the precipitated solid was collected via centrifugation. The products was subsequently washed with diethyl ether (3 × 5 mL), methanol (3 × 10 mL), and dried under vacuum (80–90% isolated yield).

For **P1-Endo**, ^{1}H NMR (400 MHz, THF) δ 10.84 (br s, 1H, CO—NH), 8.57 (br s, 4H, perylene-H), 7.10 (br s, 13H, Ph-H), 5.76 (br s, 4H, norbornene—CH=CH—), 4.51 (br s, 2H, α-lys-H), 4.19 (br s, 3H, lys-COO—CH_2), 4.00 (br d, $J = 25.5$ Hz, 5H, perylene-N—CH_2), 3.35 (br d, $J = 41.0$ Hz, 5H, norbornene-CH—C=O—CH—C=O), 2.97 (br s, 3H, (norbornene-CH=CH)—CH), 2.51 (br s, 16H, Ph-CH_2), 1.85 (br s, 7H, $C_{10}H_{21}C_{12}H_{25}$)CH), 1.65 (br s, 7H, lys-NH_2—CO—CH_2), 1.56 (br s, 2H, norbornen-tricycle-CH), 1.36 (br d, $J = 63.4$ Hz, 98H, —$C_9H_{18}C_{11}H_{22}$), 0.87 (br s, 15H, C_9H_{18}—CH_3, $C_{11}H_{22}$—CH_3). IR (KBr): ν 2924, 2847, 1706, 1665, 1588, 1513, 1460, 1437, 1390, 1373, 1286, 1236, 1183, 1169, 1077, 803, 748, 686, 543 cm^{-1}. GPC (THF): $Mn = 2.0\times10^4$, PDI = 1.2.

For **P2-Exo**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (br s, 4H, perylene-H), 7.19 (br d, $J = 16.2$ Hz, 12H, , Ph-H), 5.81 (br s, 4H, norbornene-CH=CH—), 4.51 (br s, 2H, α-lys-H), 4.19 (br s, 3H, lys-COO—CH_2), 4.02 (br s, 5H, perylene-N—CH_2), 3.12 (br s, 13H, norbornene-CH—C=O—CH—C=O), 2.83 (br s, 3H, (norbornene-CH=CH)—CH), 2.65 (br s, 11H, Ph-CH_2), 1.89 (br s, 14H, $C_{10}H_{21}C_{12}H_{25}$)CH), 1.67–1.59 (br m, 9H, lys-NH_2—CO—CH_2), 1.58–1.53 (br m, 2H, norbornen-tricycle-CH), 1.29 (br s, 98H, —$C_9H_{18}C_{11}H_{22}$), 0.87 (br s, 15H, C_9H_{18}—CH_3, $C_{11}H_{22}$—CH_3). IR (KBr): ν 3359, 2925, 2853, 1706, 1665, 1590, 1515, 1392, 1174, 1066, 1032, 965, 927, 774, 541 cm^{-1}. GPC (THF): $Mn = 8.3\times10^4$, PDI = 2.8.

CONCLUSIONS

In summary, we successfully synthesized two novel ladder-like polynorbornenes based on PDI derivatives via ROMP method. XRD results supported that these polynorbornenes had similar ladder-like structures to their supramolecular precursors. As the polymeric electron acceptors, **P1-Endo** and **P2-Exo** exhibited outstanding physical properties such as good film-forming ability, thermal stability and a wide absorption region. The devices based on PCzTh-TVDCN/polynorbornenes had direct photovoltaic responses. Our results showed here presented a promising route to synthesize more confined polymeric organic semiconductor materials, which have improved stability and solution processing feasibility.

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