Synthesis and Characterization of Near-Infrared Emissive Chiral π-Conjugated Polymers Incorporating Perylenyl Moieties with Visible-Light Absorption

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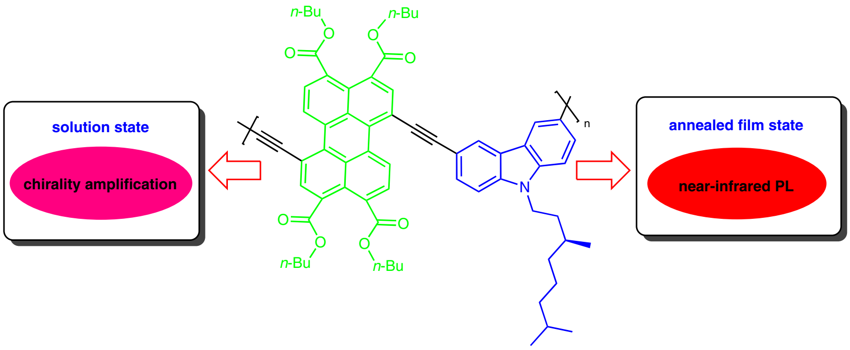

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Abstract A novel set of multifunctional optically active π-conjugated polymers incorporating perylenyl moieties, were designed and synthesized. Chirality transfer and amplification from chiral unit to the main-chain backbone in dilute solution was achieved, which was closely related to the stereocenter in the pendant of a π-conjugated polymer. In addition, annealed films of these polymers exhibited near-infrared emission by direct absorption of visible light, resulting from the introduction of a strong fluorophore perylenyl moiety. Such a design strategy opens up new perspectives for the future development of novel optically active materials with near-infrared emission for photonic applications.

Key words π-conjugated polymers, near-infrared emission, visible-light absorption, perylenyl moieties, circular dichroism

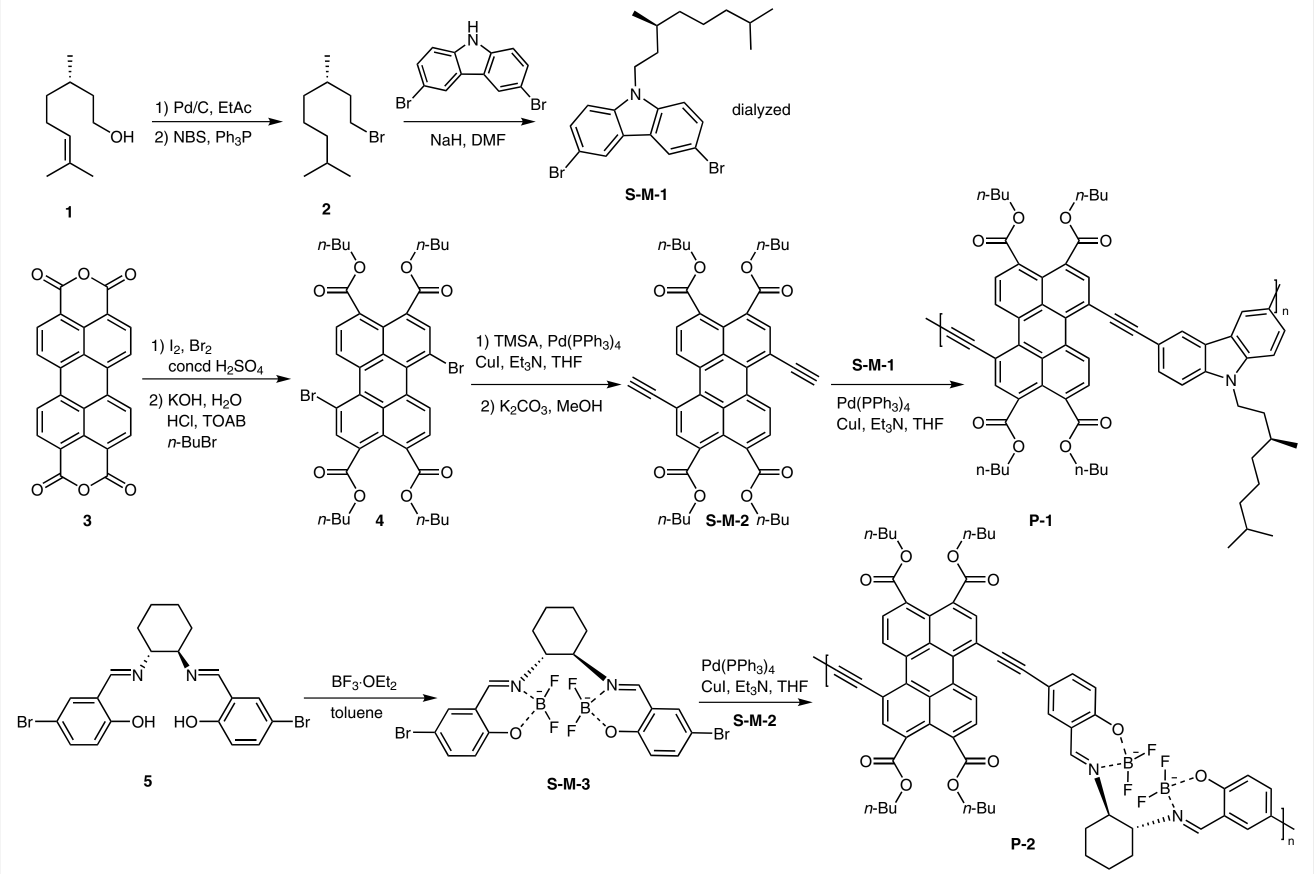
π-Conjugated polymers that can be deposited in large areas via solution processing have attracted much interest in organic electronics, such as organic light-emitting diodes (OLED),[1,2] organic field-effect transistors (OFET),[3] photovoltaic cells,[4] and biosensors,[5] due to their excellent conductivity, photo- and/or electroluminescence with high quantum yields, and mechanical flexibility. Among these, helical conjugated polymers are attracting increasing attention because of their potential application in 3D optical displays, circularly polarized luminescence (CPL), and nonlinear second harmonic optics, which might be applied to next-generation plastic electronics.[6] From a structural perspective, the optical activity was elucidated as a consequence of a helical conformation of the π-conjugated main chain that was induced by the introduction of regio- and stereoregularity of the substituents on the main chain. However, the described circular dichroism (CD) effects were nearly observed in the solid state or in 'poor solvents', and, therefore, it was obvious a cooperative aggregation phenomenon. This well-established interpretation of the CD effects emphasized that these π-conjugated polymers aggregated stable colloidal solutions in 'poor solvents' or in 'poor solvent and good solvent' mixtures, specifically for polyfluorene derivatives.[7]

π-System, owing to their delocalized π-electrons, has intrinsic electronic properties, which has been broadly utilized as key building blocks to construct chemical sensors, chiral catalysts, chiro-optical switches, nanotubes, etc.[8] For π-conjugated polymers, a long-term challenge in the supramolecular chemistry is to control the local stacking arrangements, which, in turn, greatly affects the optoelectronic properties of chromophores. In this regard, perylenyl dyes have gained much attention owing to the wide range of possibilities available for fine-tuning their properties by the introduction of suitable functional groups at the core as well as the periphery. Recently, the Kawai group reported that perylene bis(imide) (PBI) derivatives, with the axial binaphthyl moiety, formed helically associated species through supramolecular assemblies and exhibited chiroptical properties.[9] So far, work on CD active π-conjugated polymers incorporating perylenyl moieties in dilute solutions has rarely been investigated.[10]

The stereocenter in the pendant/main chain of a π-conjugated polymer has played an important role in determining their conformation and optoelectronic properties. Our previous study has demonstrated that π-conjugated polymers with perylenyl moieties in an alternating system can act as a mercury ion detector without interference from other metal ions.[8a] Further research has reported that the chromaticity of europium(III)-grafting polymer possessing perylenyl moieties can be tuned by the selected excitation wavelengths.[11] Despite this progress, there is still little literature in terms of chirality amplification in dilute solution and near-infrared emission in annealed films by absorbing visible light. Alternating copolymers were thus designed and synthesized to investigate their chiroptical properties to further elucidate structure–property relationships. In this paper, perylene is chosen as a fluorophore, and carbazole or (*R*,*R*)-salen acts as an enantiomeric center. It is indicated that, introduction of chiral moieties into main-chain π-conjugated polymers (denoted as **P-1** and **P-2**), can lead to a chiral conformation in dilute solution. More importantly, annealed films of **P-1** and **P-2** emitted near-infrared emission upon direct absorption of visible light.

The targets **P-1** and **P-2** were synthesized according to the routes depicted in Scheme 1. The monomer **S-M-1**, bearing a highly enantiopure alkyl side chain at the carbazole moiety, was synthesized in 90% yield by reaction of 3,6-dibromo-9*H*-carbazole with (*S*)-3,7-dimethyloctylbromide (**2**) in DMF solution using NaH as the catalyst stirring overnight at room temperature.[12] The corresponding monomer 1,7-diethynylperylene-3,4:9,10-tetracarboxylic tetrabutylate (**S-M-2**) was synthesized by a four-step reaction from the starting materials 3,4:9,10-perylene-tetracarboxylic acid dianhyride (**3**).[13] The starting material **5** was reacted with two equivalents of $BF_3 \cdot OEt_2$ in a mixed solution of *N*-ethyldiisopropylamine and toluene to afford **S-M-3** in 52% yield. The polymerization was carried out in anhydrous THF via Sonogashira coupling by reaction of **S-M-1** or **S-M-3** with **S-M-2** at 70 °C for 48 hours to afford the deep-red solids of **P-1** and **P-2** in yields of over 50%. According to gel permeation chromatography (GPC) using THF as eluent and polystyrene as standard, the number-average molecular weights (M_n) of **P-1** and **P-2** are 9850 and 9120, respectively, and the polydispersity indexes (PDI) are 1.8 and 1.6, respectively. GPC results show a moderate molecular weight. The specific optical rotations ($[\alpha]_D^{25}$) of **S-M-1** and **S-M-3** were +45 and –26 (*c* 0.01, THF), respectively, and the corresponding $[\alpha]_D^{25}$ of **P-1** and **P-2** were +460 and –300 (*c* 0.01, THF), respectively. The chemical structures of **P-1** and **P-2** were further confirmed by ^1H NMR and IR spectroscopy. **P-1** and **P-2** are readily soluble in common organic solvents, such as $CHCl_3$, CH_2Cl_2, THF, and toluene, due to the flexible *n*-butoxy substituents in the polymers. The perylenyl moiety acts as a chromophore, and the carbazole and (*R*,*R*)-salen, as the well-known building blocks, are chosen as the chiral induction center. Moreover, the ethynyl linker can reduce the steric hindrance between perylenyl and chiral units, improving the stability of the resulting polymers.

Thermogravimetric analysis (TGA) of **P-1** and **P-2** was carried out under N_2 atmosphere at a heating rate of 10 °C min^{-1} (Figure S10, Supporting Information). **P-1** has a high-



Scheme 1 Synthetic routes towards **P-1** and **P-2**

er thermal stability than **P-2** and does not show weight loss till 344 °C. Therefore, the resulting polymers can provide desirable thermal properties for practical applications in organic optoelectronic devices.

The optical properties of **P-1** and **P-2** were investigated in THF solution ($1.0\cdot10^{-5}$ mol·L^{-1}) and in annealed films. As shown in Figure S11 (Supporting Information), UV-vis absorption spectrum of **S-M-2** showed prominent peaks at 483, 454, and 428 nm along with a weak shoulder around 405 nm, which were attributed to the 0–0, 0–1, 0–2, and 0–3 transitions of the perylenyl moiety, respectively.[14] The fluorescence spectrum of **S-M-2** exhibited a mirror image of the absorption spectrum with a maximum at 506 nm. In Figure 1 (a), **P-1** and **P-2** displayed well-defined absorption bands with the characteristic π–π^* transitions of PBI units in the region from 450–550 nm, whereas the absorption bands ranging from 550–600 nm corresponded to π–π^* transition of π-conjugated backbones. Figure 1 (b) shows that annealed films of **P-1** and **P-2**, fabricated by spin-coating from 1.0 mg/mL solution on quartz substrates, exhibited a strong and broad absorption in the region of 550–700 nm, originating from strong π–π stacking interaction of the rigid conjugated polymers.

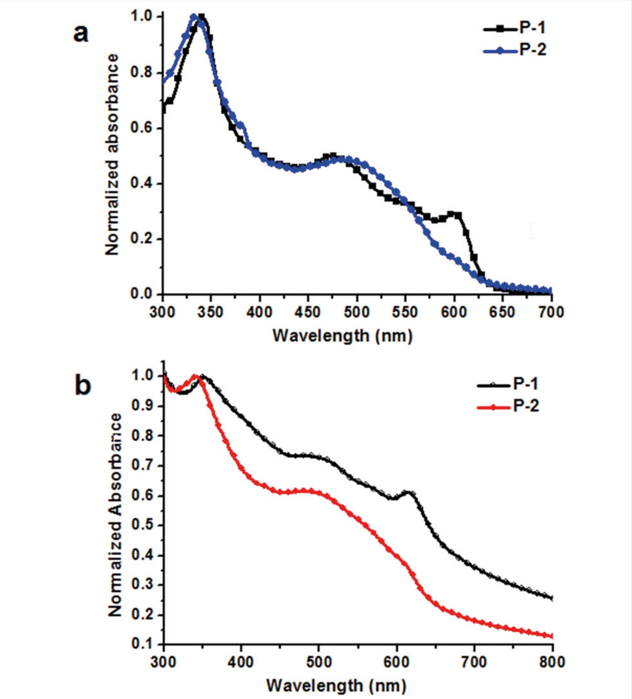


Figure 1 a) Normalized UV-vis spectra of **P-1** and **P-2** in THF solution ($1.0\cdot10^{-5}$ mol·L^{-1}); b) Normalized UV-vis spectra of **P-1** and **P-2** in annealed films.

Generally, π-conjugated polymers possess a high tendency for molecular random conformation via aromatic π-stack interactions. To get a deeper insight into the nature of structure information in ground states, preferably in dilute solution, we have measured their optical activity of **P-1** and **P-2** by CD spectra (Figure 2). As depicted in Figure S12 (Supporting Information), **S-M-1** displays a bisignate Cotton effect with a negative wave at around 267 nm accompanied by a pronounced wavelength at around 245 nm, and a positive wave at around 277 nm. Meanwhile, a well-resolved bisignate CD signal of model **S-M-3** was observed with a positive maximum at around 380 nm and a negative maximum at around 352 nm in THF solution (Figure S13, Supporting Information). An additional moderate CD band with a negative band situated at around 323 nm, with the sign same to that of the band at around 278 nm, was observed for **S-M-3**. Interestingly, **P-1** and **P-2** exhibited prominent Cotton effects in the range of 450–600 nm at the position of the π–π^* band of π-conjugated backbones. Such results suggested that the Cotton effects which were observed in the polymers were induced by the chirality of the main chain. Moreover, the existence of the main-chain chirality was also supported by the CD data of the other optically active polyfluorenes and BODIPY molecules. For example, Konishi's optically active polyfluorene exhibited the Cotton effect in the π–π^* transition region duo to polymer backbone.[15] According to Moya's report,[10a] the strong Cotton effect observed for the BODIPY in visible region of CD spectra demonstrated that BODIPY were present of the molecular scaffold chirality conformation. The Cotton effect observed for **P-1** and **P-2** was indicative of exciton coupling between obliquely oriented neighboring polymer backbones, suggesting the existence of a certain chiral conformation such as helical conformation in the π–π^* transition region for π-conjugated polymers.[16] Thus, analysis of CD data demonstrates that the chirality amplification can be achieved through chirality transfer from the chiral moiety to the main chain of π-conjugated polymers.

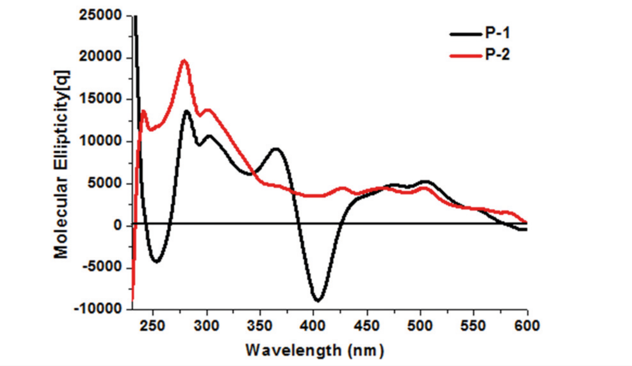


Figure 2 CD spectra of **P-1** and **P-2** in THF solution ($1.0\cdot10^{-5}$ mol L^{-1})

As shown in Figure 3 (a), the maximum emission wavelength of **P-1** appeared at 617 nm with the excitation of 460 nm, which was red-shifted about 10 nm with respect to that of **P-2** in THF solution. Such a red-shift emission was ascribed to excitation extending over π-conjugated chromophores. Moreover, the internal fluorescent quantum yields

(Φ_{EM}) of **P-1** and **P-2** estimated using an integrating sphere were 14% and 10%, respectively. Furthermore, when **P-1** and **P-2** in THF were irradiated by 365 nm, the color fluorescence of **P-1** and **P-2** was red and orange, respectively. The nature of different emitting species was investigated by means of time-resolved single-photon counting (TCSPC) measurements. The luminescent decay profiles curves of **P-1** and **P-2** were fitted with two-ordered exponential decay as shown in Figures S14 and S15 (Supporting Information). A short-lived species with a lifetime of 1.3 ns (31.2%) and a relatively long-lived species with a lifetime of 5.0 ns (68.8%) were observed for **P-1** in dilute solution, whereas **P-2** exhibited the corresponding species with lifetimes of 1.7 ns (51.1%) and 4.7 ns (48.9%) for emission monitored at 607 nm. Based on the luminescent decay, **P-1** and **P-2** demonstrated rather high chiroptical anisotropies within the delocalized π–π* transition band. In addition, **P-1** and **P-2**, in annealed films, exhibited a relatively weak near-infrared emission centered at 734 nm when excited at 637 nm with a low quantum yield of 6%, suggesting direct formation of molecular aggregates driven by interchain interactions.[17]

In order to investigate the electrochemical properties of **P-1** and **P-2** and estimate the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels, cyclic voltammetry (CV) were carried out. The results are shown in Figure 4, and their electrochemical data are summarized in Table 1. Their HOMO/LUMO energy levels of **P-1** and **P-2** were estimated from the corresponding onsets of the oxidation/reduction waves by the empirical formula.[18] The HOMO energy levels of **P-1** and **P-2** are –5.27 and –5.15 eV, and the corresponding LUMO energy levels are –4.27 and –4.01 eV, respectively. Calculated band gaps (E_g) of **P-1** and **P-2** are 1.00 and 1.14 eV, respectively. Especially, **P-1** exhibited a lower-lying HOMO level with respect to **P-2**, suggesting that the chiral moiety played an important role in π-conjugated polymer's configuration and even the electrical distribution over polymer's backbone.

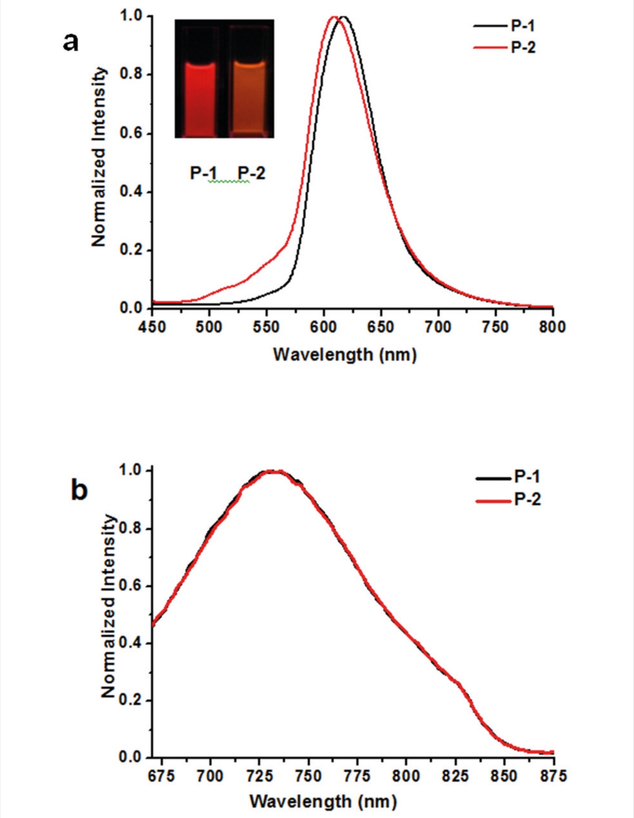


Figure 3 (a) Normalized emission spectra of **P-1**and **P-2** in THF solution ($1.0 \cdot 10^{-5}$ mol L^{-1}); (b) normalized emission spectra of **P-1** and **P-2** in annealed films. Inset: The photographs show **P-1** and **P-2** emission in THF solution ($1.0 \cdot 10^{-5}$ mol L^{-1}) with UV lamp (λ_{ex} = 365 nm).

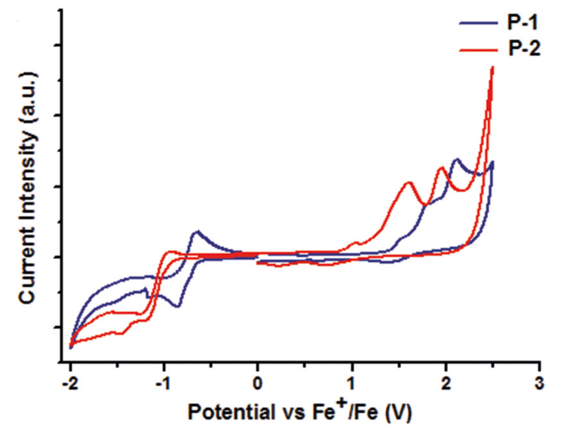


Figure 4 CV curves of **P-1** and **P-2**

To theoretically support the optical and electrochemical behaviors of π-conjugated polymers, density functional theory (DFT) calculations were carried out. Herein, the alkyl chains of the repeating units were replaced by methyl or ethyl groups to simplify the calculation. As depicted in Figure 5, the LUMO of repeating units of **P-1** is primarily distributed over π-conjugated moieties. The HOMO of the repeating units of **P-2** mainly centers on the perylenyl moieties and alkynes. As shown in Table 1,DFT calculations showed that the HOMO energy level of **P-1** was higher than that of **P-2**, although the CV data gave the opposite trend. In fact, DFT calculations simulate the single-molecule energy levels and band gaps of the repeating unit rather than the polymer, while CV measurements reflects the electrical energy levels and band gaps of the polymer in condensed states. Moreover, the existence of chiral units in the polymer can lead to the different main-chain configuration, which exerted influence on the electrical distribution over the polymer's backbone. Thus, it is suggested that the energy levels of HOMO should be strongly affected by the π-conjugated polymers' configuration. It is therefore believed that such a difference is the origin for the difference of energy levels between DFT calculations and CV measurements.

Table 1 Electrochemical Data of **P-1** and **P-2** and the Calculated HOMO, LUMO Energy Values

	From CV[a]					From calculation		
	E_{ox}^{onset} (V)[b]	HOMO[c] (eV)	E_{red}^{onset} (eV)[b]	LUMO[c] (eV)	E_g[d] (eV)	HOMO[e] (eV)	LUMO[e] (eV)	E_g[e] (eV)
P-1	0.47	–5.27	–0.53	–4.27	1.00	–5.14	–2.58	2.56
P-2	0.35	–5.15	–0.79	–4.01	1.14	–5.49	–2.86	2.63

[a] Ferrocence couple (Fc^+/Fc) was used as the internal reference and under our experimental conditions, $E(Fc^+/Fc) = 0.42$ V vs. Ag/AgCl.
[b] E_{ox} and E_{red} were determined from the onset potentials of the oxidation and reduction waves.
[c] HOMO = $-(E_{ox}^{onset} + 4.8)$ eV and LUMO = $-(E_{red}^{onset} + 4.8)$ eV.
[d] E_g = LUMO – HOMO.
[e] DFT quantum mechanical calculations (B3LYP/6-31G*).

Furthermore, the HOMO–LUMO band gaps and each energy level estimated from the DFT calculations show similar trends to the experimental data estimated from CV measurements.

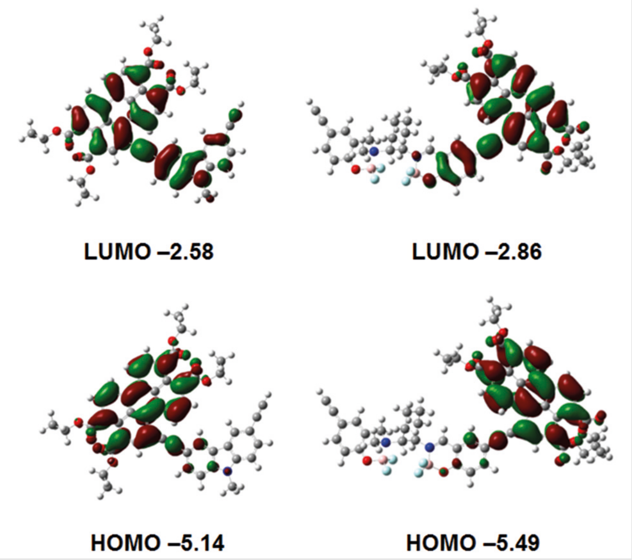


Figure 5 Molecular orbital diagrams for the HOMO and LUMO of the repeated units in **P-1** (left) and **P-2** (right) by DFT calculation

In summary, we have successfully designed and synthesized a novel series of multifunctional optically active π-conjugated polymers incorporating perylenyl moieties by Sonogashira coupling.[19] In dilute solution, the prominent Cotton effect can be detected for **P-1** and **P-2**, which corresponds to the exciton coupling between neighboring π-conjugated polymer backbones, indicating the presence of the main-chain chirality conformation. Moreover, the annealed films of **P-1** and **P-2** are able to emit near-infrared fluorescence by direct absorption of visible light. Further studies are now in progress to exploit the correlation between amplified chiral transformation and polymer's conformation.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1560206.

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(19) **Synthesis Procedures for the Perylenyl-Based Chiral Conjugated Polymers**

Synthesis of P-1

The monomer **S-M-1** (46.52 mg, 0.10 mmol), **S-M-2** (70.08 mg, 0.10 mmol), $Pd(PPh_3)_4$ (5.78 mg, 5 mol%), and CuI (1.90 mg, 10 mol%) were added to a mixture of THF (6 mL) and Et_3N (2 mL) in a 20 mL Schlenk tube. The reaction mixture was stirred at 70 °C for 3 d under N_2 atmosphere. After being cooled to r.t., the mixture was filtered through a short silica gel column in MeOH (50 mL) to precipitate the polymer. The solid was filtered and washed with MeOH several times and dried under vacuum to afford 62.06 mg of a dark-red solid in 60% yield. GPC: $M_w = 17730$; $M_n = 9850$; PDI = 1.8. $[\alpha]_D^{25}$ +460 (*c* 0.01, THF). ^1H NMR (300 MHz, $CDCl_3$): δ = 9.44 (d, *J* = 8.1 Hz), 8.41–8.16 (m), 7.62–7.55 (m), 7.29 (m), 7.26 (m), 4.39 (m), 2.06 (m), 1.81 (m), 1.51 (m), 1.27 (m), 1.02 (m), 0.87 (m) ppm. FT-IR (KBr): 2956, 2929, 2869, 1718, 1276, 1258, 1165, 1063, 1016, 801 cm^{-1}.

Synthesis of P-2

A mixture of THF (6 mL) and Et_3N (2 mL) was repeatedly degassed by purging with nitrogen gas, and then the compound **S-M-2** (70.08 mg, 0.10 mmol), **S-M-3** (57.58 mg, 0.10 mmol), and CuI (1.90 mg, 10 mol%) along with $Pd(PPh_3)_4$ (5.78 mg, 5 mol%) were added and refluxed over 3 d under a N_2 atmosphere. After being cooled to r.t., the reaction mixture was filtered through a short silica gel column in MeOH (50 mL) to precipitate out the polymer. The resulting polymer was filtered and washed with MeOH several times and dried under vacuum to afford 62.97 mg of a dark-red solid in 55% yield. GPC: $M_w = 14470$; $M_n = 9120$; PDI = 1.6. $[\alpha]_D^{25}$ –300 (*c* 0.01, THF). ^1H NMR (300 MHz, $CDCl_3$): δ = 9.47 (m), 8.87 (m), 8.62 (m), 8.37–8.28 (m), 7.74–7.41 (m), 6.83 (m), 6.80 (m), 4.38 (s), 2.05 (m), 1.81 (m), 1.53 (m), 1.27 (m), 1.02 (m) ppm. FT-IR (KBr): 2956, 2931, 2870, 1721, 1629, 1455, 1278, 1164, 1063, 1022, 804 cm^{-1}.