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Doublet Chirality Transfer and Reversible Helical Transition in Poly(3,5-disubstituted phenylacetylene)s with Pyrene as a Probe Unit

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Summary of main observation and conclusion A novel doublet chirality transfer (DCT) model was demonstrated in *cis* poly(3,5-disubstituted phenylacetylene)s, i.e., **S-I**, **R-I**, and **S-I-NMe**. The chiral message from the stereocenter of alkylamide substituent at 3-position induced the polyene backbone to take *cis-transoid* helical conformation with a predominant screw sense. And in turn the helical backbone acted as a scaffold to orient the pyrene probes, that was linked to phenyl rings through 5-position, to array in an asymmetric manner. A combinatory analyses of ¹H NMR, Raman, FTIR, UV-vis absorption, CD, and computer simulation suggested that the main-chain stereostructure, solvent nature, and intramolecular hydrogen bonds played important and complex roles on DCT. High *cis*-structure content and intramolecular hydrogen bonds were beneficial for the realization of DCT. Reversible helix-helix transition was observed in **S-I** by changing the nature of solvents. In DMF, **S-I** adopted a relatively contracted helix, where the main chain strews the weakest. This helix-helix formed in CHCl₃, in which the optical activity of pyrene was much larger, whereas that of the polyene backbone was the weakest. This helix-helix transition was attributed to the intramolecular hydrogen bonds, which was confirmed by solution-state FTIR spectra and computer calculations.

Background and Originality Content

Since the discovery of helical conformations in biopolymers,^[1] synthetic scientists have developed various artificial helical polymers and supramolecules,^[2] some of which have been utilized in chiral separation,^[3] asymmetric synthesis,^[4] and so on.^[5] When functionalized units are introduced, they are usually linked directly with or close to the chiral centers for the better chiral transition.^[6] Such a strategy not only makes molecular design less flexible, but could bring about some undesired effects. As an example, optical active helical poly(phenylacetylene)s (PPAs) containing cinchona alkaloid pendants were found to promote asymmetric synthesis.^[4a,7] However, the enantioselectivities of some polymers were lower than the corresponding monomers due to the antagonism effect exerted by the configuration chirality of stereo centers and the conformation chirality of polymer backbone. In a contrast, Feringa, Roelfes, and co-workers successfully built an interesting chiral catalyst system by linking achiral catalytic sites to DNA double helices and achieved excellent enantioselectivities (up to 99 ee%).^[8] Similarly, Suginome et al. prepared series of а poly(quinoxaline-2,3-diyl)-based chiral catalysts through the copolymerization of chiral quinoxaline-2,3-diyl monomers without sites and achiral metal-binding monomers bearing diarylphosphino pendant as the metal-binding sites.^[9] The 3D asymmetric environment provided by the single-handed helical structure of poly(quinoxaline-2,3-diyl) endowed the polymeric metal complex with an excellent enantioselectivity in a number of organic reactions. These results suggest a route to construct novel chiral materials avoiding antagonism by separating functional sites and chiral inducing groups.

Doublet chirality transfer (DCT), first mentioned by Gawroński *et al.* and applied to determine the absolute configuration of chiral amines,^[10] is seldom employed in the helical polymer system. Wu *et al.* built a three component system consisting of azobenzene-modified Anderson-type polyoxometalate (POM), α -CD, and methylene blue dye (MB) via multi-supramolecular interactions.^[11] Chirality was efficiently transferred from α -CD to

MB bridged by Azo-POM. Yashima and co-workers dexterously used the induced helical PPAs as a novel template for the formation of supramolecular helical aggregates of achiral porphyrin^[12] and cyanine^[13] dyes in water, also embodying the idea of DCT. Recently, Lee^[14] and Maeda^[15] actualized DCT in poly(phenylacetylene)-*g*-poly(isocyanate) by means of domino effect and a preferred-hand helicity was unerringly imparted to the PPA backbone. However, the examples on DCT were very limited and astaticism in supramolecular system hampered the development of DCT. Universal DCT system is to be empoldered to realize the functionalization of helical polymers.

PPAs are a classical type of dynamic helical polymers. They have attracted wide attentions for their robust tunable conformations and multiple functions. $^{\rm [2a,16]}$ Most PPAs reported in literature are derived from *para*-substituted phenylacetylenes.^[2a,16a] Introducing two or more substituents on the phenyl ring of PPA could supply more structural variety and function capacity for material design, but is seldom approached.^[17] Recently, we have designed and synthesized a series of poly(3,5-disubstituted phenylacetylene)s, and carefully studied their helical structures and chirality amplification.^[18] Herein, we give a new model of DCT based on 3,5-disubstituted PPAs (Scheme 1), in which functional and chiral inducing substituents are separated. At first, chirality is transferred to PPA backbone from the chiral amide pendant and induces a preferred one-handed helical conformation of polyene main chain. Then the achiral functional group is further dictated to arrange in helical form for the transition of chirality from the main-chain helical conformation. This separation of functional group and chiral inducing group not only enhances flexibility of molecular design, but also provides a novel type of chiral transfer, which may be able to attenuate the antagonism.

Scheme 1 Synthesis of R-I, S-I, and S-I-NMe

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Results and Discussion

Three novel PPAs, i.e., **R-I**, **S-I**, and **S-I-NMe**, were designed and synthesized in the present work. Disubstitution at *meta*-positions could endow the polymer with great macromolecular design freedom and robust functional capacity. The amide hydrogen of **S-I** was substituted by methyl group as in **S-I-NMe** to understand how the intramolecular hydrogen bonds influence DCT.

Synthesis. As outlined in Scheme S1, the monomer preparation began with (R)/(S)-3-methoxycarbonyl-5-[(1-phenylethyl)carbamoyl]phenylac (R-III/S-III) etvlene and (S)-3-methoxycarbonyl-5-[N-methyl-(1-phenylethyl)carbamoyl]ph envlacetylene (S-III-NMe), the synthesis of which was reported previously.^[18b] The ester bonds in R-III, S-III and S-III-NMe were cleaved in a strong basic medium. The followed acidification gave the corresponding acid. The resultant acids underwent esterification with 1-pyrenemethanol, in the presence of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) and 4-(dimethylamino)pyridine (DMAP) to yield the target monomers, R-II, S-II, and S-II-NMe. R-II and S-II precipitated from CH₂Cl₂, the reaction solvent, for their poor solubility, and were obtained with enough purity just by filtration and washing with CH₂Cl₂ for three times to remove the residual impurities. The crude product of S-II-NMe was purified by column chromatography. All of the new compounds were identified by ¹H NMR and ¹³C NMR spectroscopy as well as high-resolution mass spectrometry (Figures S1-S9).

 Table 1
 Polymerization results and properties of polymers^a

| Monomer | Solvent ^b | Conv. (%) ^c | $M_{\rm n}/10^{4e}$ | PDI ^e | Cis (%) ^f | $T_{d} (^{\circ}C)^{h}$ |
|----------|----------------------|------------------------|---------------------|------------------|----------------------|-------------------------|
| S-II | DMF | 93 | 22.9 | 1.71 | 97 | 315 |
| R-II | DMF | 90 | 20.8 | 1.85 | 95 | 316 |
| S-II-NMe | THF | 87 ^d | 7.4 | 2.12 | _g | 315 |

^aCarried out at room temperature under nitrogen for 12 h; [M] = 0.06 M, [cat.] = 1.5 mM. ^bPolymerization solvent. ^cAcetone-insoluble part. ^dAcetone/CH₃OH (v/v, 1/1)-insoluble part. ^eEstimated by GPC in THF on the basis of a polystyrene calibration. ^fDetermined by ¹H NMR analysis. ^gUnable to be accurately determined by ¹H NMR analysis. ^h5% weight loss temperature under nitrogen atmosphere at a heating rate of 20 °C/min.

Polymerization. The monomers were polymerized in solution at 25 °C by using $[Rh(nbd)Cl]_2$ as the catalyst with a constant monomer/catalyst molar ratio of 40/1 (Scheme 1). DMF was chosen as the polymerization solvent of S-II and R-II while THF was chosen as the solvent for S-II-NMe, depending on their solution power toward both monomers and polymers. The reaction mixtures became very viscous within 30 min in all cases. After 12 h, the obtained polymers R-I/S-I and S-I-NMe were collected by precipitation in acetone and the mixture of acetone and methanol (v/v, 1/1), respectively. All the monomers were converted to the corresponding polymers with high yields and molar masses (Table 1). The resultant polymers displayed good thermal resistance and possessed the temperatures of 5% weight loss ($T_{\rm d}s$) under inert atmosphere above 310 °C.





Figure 1a depicts the ¹H NMR spectrum of monomer **S-II** in DMSO-d⁶. The resonance absorption at δ = 4.41 ppm was assigned to ethynylic proton. The protons of phenyl ring bearing acetylene triple bond and those of pyrene group resonated from 8.57 to 8.03 ppm. The signal of amide proton was observed at δ = 9.10 ppm. Although well-resolved proton NMR spectrum was recorded for S-II, S-I was unable to be characterized clearly in either $CDCl_3$ or DMF-d' (Figure S10) for its large and crowded side-groups, which restricted proton mobility and shielded backbone signal. To characterize the stereostructure of S-I, this polymer was transformed to S-I-HE through hydrolysis by TFA and subsequent esterification with trimethylsilyldiazomethane (Scheme 2). As shown in Figure 1b, the resonances of protons of the ester (CO_2CH_3) , chiral carbon atom (HC), and amide (HNCO)groups were observed at 3.55, 5.04, and 8.82 ppm, respectively. Moreover, the resonance absorption of ethynylic proton at 4.41 ppm disappeared after polymerization, and a new olefinic proton peak at δ = 5.67 ppm appeared from the conjugated main chain. The *cis*-structure content of **S-I** was estimated as 97%, according to the calculation method developed by Percec and co-workers.^[19] The stereostructure of R-I was characterized with a similar method. The detailed results are summarized in Table 1.

Scheme 2 Hydrolysis and esterification reaction



As for **S-I-NMe**, the signal of methine proton overlapped with that of polyene backbone (Figure S12).^[18b] As a result, its *cis*-structure content was unable to be calculated accurately by NMR method and Raman spectroscopy was employed instead.^[20] As shown in Figure 2, **S-I** exhibited intense peaks at 1590, 1236, and 1000 cm⁻¹, which could be ascribed to the C=C, C–C, and C–H vibrations of *cis* PPAs, respectively.^[20] **S-I-NMe** showed the Raman spectra similar to **S-I**, evincing its *cis-transoid* main-chain structure.



Figure 2 Raman spectra of S-I, S-I-NMe, and *trans*-S-I obtained via grinding.

 Table 2
 Specific optical rotations in different solvents

| Sample | $\left[\alpha\right]_{D}^{20} \left(^{\circ}\right)^{a}$ | | | - Comula - | $\left[\alpha\right]_{D}^{20}\left(\circ\right)^{b}$ | | |
|----------|--|-----|-------|------------|--|------|-------|
| | DMF | THF | CHCl₃ | - Sample - | DMF | THF | CHCl₃ |
| S-II | +32 | +9 | +26 | S-I | +378 | +303 | +106 |
| R-II | -36 | -12 | -20 | R-I | -409 | -381 | -149 |
| S-II-NMe | -64 | -68 | -86 | S-I-NMe | × | +486 | +610 |

 ${}^{a}c = 0.2 \text{ g/dL}$. ${}^{b}c = 0.02 \text{ g/dL}$. ×: insoluble.

The optical rotations of polymers and monomers measured in CHCl₃, THF, and DMF, respectively, were summarized in Table 2. The monomers displayed specific optical rotations ($[\alpha]^{20}_{D}$) ranging from -86° to +32°. Their corresponding polymers presented rather larger optical rotations, implying the formation of chiral secondary structures. Moreover, the sign and magnitude of optical rotations depended on the solvent nature and polymer structure. In DMF, **S-I** and **R-I** also exhibited very large optical rotations. However, their optical rotations in CHCl₃ were apparently poorer than those in THF and DMF, indicating an interesting solvent effects, which would be discussed later.

Figure 3 depicts the UV-vis absorption and CD spectra of **R-II**, **S-II**, and their polymers in DMF at a concentration of 5.0×10^{-5} mol/L.^[21] **S-II/R-II** exhibited strong absorptions at 312 nm, 327 nm, and 343 nm, which were attributed to pyrene units. No obvious absorption above 380 nm was observed in the absorption spectra. However, their polymers S-I/R-I not only showed the similar characteristic absorptions of pyrene units at 315 nm, 329 nm, and 346 nm, but also a broad absorption from 380 nm to 520 nm, which was assigned to the conjugated polyene backbone. As shown in CD spectra, S-II and R-II were optical inactive and no obvious Cotton effects were observed in the range 280~600 nm, while S-I and R-I presented strong CD signal at around 450 nm associated with the absorption of its conjugated main chain, proving that the polyene backbone adopted a stretched cis-transoid helix with an excess one-handedness. Moreover, the characteristic Cotton effects of pyrene units appeared in the range 300-350 nm, which strongly evinced that chirality was successfully transferred from the chiral amide to PPA backbone then to the achiral pyrene. Namely, doublet chirality transfer (DCT) was realized in S-I/R-I and the achiral pyrene moieties took a preferred one-handed helical arrangement around the main chain.^[22] R-I presented a mirror CD image to that of S-I, illustrating the enantiomeric conformations with opposite helicities adopted by them.



Figure 3 UV-vis absorption and CD spectra of **R-II**, **S-II**, **R-I**, **S-I**, and *trans*-**S-I** in DMF. The spectra were measured in a 10 mm quartz cell at a concentration of 5.0×10^{-5} mol/L (monomer unit).

One prerequisite for a poly(phenylacetylene) molecule to take a predominant helical conformation is the high cis-structure content. And helical polyene backbone serves as a scaffold to induce chiral array of pyrene groups. In this context, the stereoregularity of polymer backbone should exert remarkable effect on DCT. To make this point clear, a trans-enriched polymer, i.e. trans-S-I, was obtained from S-I through grinding.^[23] As depicted in Figure 3, trans-S-I exhibited much broader and obviously red-shifted absorption of polyene backbone than S-I, suggesting a cis-to-trans isomerization. Such a stereostructure change increased the stereoirregularity and conjugation length of polymer backbone. Whereas, the spectrum in pyrene absorption region showed no discernible variation, implying inert chemical structure of S-I toward grinding. The lack of Cotton effects in polyene backbone absorption region of trans-S-I suggested the vanishment of helical structure, while the reduced Cotton effects belong to pyrene moiety corroborated the significant role of main-chain secondary structure on DCT.

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Figure 4 CD (a) and UV-vis absorption (b) spectra of **R-I** and **S-I** in THF, DMF, and CHCl₃. The spectra were measured at a concentration of 5.0×10^{-5} mol/L (monomer unit).

R-I and **S-I** showed good solubility in THF, DMF, and CHCl₃. Their CD and UV-vis spectra in these three solvents are displayed in Figure 4. The absorption wavelengths of pyrene in different solvents showed no obvious shifts. The absorption intensities of pyrene in DMF were the strongest, but those in CHCl₃ were the weakest, suggested that strong π - π interactions between pyrene

units probably existed in CHCl₃. In DMF, the main chain of **S-I** absorbed strongly at 440 nm, which shifted to longer wavelengths, 444 nm and 450 nm, respectively, when the solvent was changed to THF and CHCl₃. It implied that the polyene backbone took a more extended planar conformation in CHCl₃ with a longer conjugated length. Moreover, the optical activity of **S-I** also presented strong solvent dependence. The pyrene units exhibited the strongest CD intensity in CHCl₃, whereas the CD intensity of polyene backbone was the weakest which probably stemmed from the formation of intramolecular hydrogen bonding.

Furthermore, reversible helix-helix transition in S-I can be achieved by altering the ratios of DMF and CHCl₃. As shown in Figure 5, with the addition of DMF in CHCl₃ solution, the CD intensity of polyene backbone gradually increased and that of pyrene decreased slowly. Meanwhile, in UV-vis absorption spectra, the absorption of main chain shifted to the shorter wavelength and the absorption intensity of pyrene gradually increased. With the content of CHCl₃ increasing in DMF solution, opposite phenomenon occurred in CD and UV-vis spectra, indicating a good reversibility of conformation modulation.

To further investigate the effect of hydrogen bonds on DCT, the hydrogen atoms of amide groups in S-I were substituted by methyl pendants. As shown in Figure 6, the absorption intensities of pyrene in S-I-NMe were apparently stronger than those in S-I, and nearly equal to the intensities of pyrene of the monomer **S-II-NMe** (Figure S14), implied the lack of π - π interactions between pyrene pendants. Although the main-chain CD intensity of S-I-NMe in CHCl₃ was obviously stronger than that of S-I due to the increased steric hindrance, the CD signal of pyrene was much weaker demonstrating the important role of hydrogen bonds in DCT. The helical arrangement of pyrene units was destroyed for the existence of methyl groups in amide groups and the lack of intramolecular hydrogen bonds. The strong Cotton effect of polyene backbone in S-I-NMe further authenticated that the decrease of the main-chain CD signal of S-I in CHCl₃ originated from the strong intramolecular hydrogen bonding. Without hydrogen bond interaction, the CD spectra of S-I-NMe in CHCl₃ didn't change with the addition of DMF (Figure S15).



Figure 5 CD (a) and UV-vis absorption (b) spectra of DMF solution of **S-I** added different CHCl₃ fractions; CD (c) and UV-vis absorption (d) spectra of CHCl₃ solution of **S-I** added different DMF fractions.



Figure 6 UV-vis absorption and CD spectra of **S-I** and **S-I-NMe** in CHCl₃. The spectra were measured at a concentration of 5.0×10⁻⁵ mol/L (monomer unit).

Then the solution-state IR spectra of **S-II**, **S-II-NMe**, and their corresponding polymers in $CHCl_3$ at c = 5-10 mg/mL were performed to check the presence of hydrogen bonds. The solution-state IR spectra are shown in Figure S18, and the eventual results are listed in Table 3. The amide I absorption (C=O stretching) peak of **S-II** was observed at about 1638 cm⁻¹, whereas that of corresponding polymer appeared at 28 cm⁻¹ lower position. The amide II (N–H bending) peak of **S-II** was observed at 1510 cm⁻¹, while that of its polymer appeared at 29 cm⁻¹ higher position. Furthermore, the N–H stretching peak of **S-I** was observed at 3272 cm⁻¹, 167 cm⁻¹ lower than that of its monomer, which further verified the formation of strong intramolecular hydrogen bonding in **S-I**.^[18a,24] Different from **S-I**, the solution-state IR spectrum of **S-INMe** was nearly the same with its monomer. These results clearly convinced the existence of strong intramolecular hydrogen

bonds between amide groups in the ${\rm CHCl}_3$ solution of ${\rm S-I},$ which led to the above spectral differences of main chain and pyrene unit.

 Table 3
 Solution-state IR absorption data.^a

| Sample | Amide I | [cm ⁻¹] Amide II [c | | I [cm ⁻¹] | NH Stretching [cm | |
|----------|---------|---------------------------------|----------|-----------------------|-------------------|--------|
| S-II | 1666 | | 1510 | | 3438 | |
| S-I | 1638 | (-28) | 1539 | (+29) | 3271 | (-167) |
| S-II-NMe | 1624 | | | | | |
| S-I-NMe | 1627 | (+3) | | | | |
| | | 10 |) ma/mal | The | | d:46 |

⁶ Measured in CHCl₃, c = 5-10 mg/mL. The wavenumber difference between the monomer and the corresponding polymer is given in parentheses.

To further characterize the helical conformations of the resultant polymers, computer calculations were carried out. The most energetically favored helical conformations of S-I were simulated using the S-II 50mer as the model compound. Set the initial dihedral angle (θ) of C–C=C–C as 0° and rotate the dihedral angle (ϕ) 5° around C–C bond in the C=C–C=C moiety of the main chain. Figure 7 displays the optimized contracted and stretched helices, which are in accordance with the spectral results in DMF and CHCl₃, respectively. The detailed helical parameters are listed in Table 4. As shown in Figure 7, they both presented a 2/1 helix in either solvents. In DMF, the helical structure was relatively more contracted than that in CHCl₃. The overlapped extent of adjacent pyrene pendants in n th and (n+2) th monomer units was lower with a longer parallel distance, resulting in the weaker π - π interactions (Figure 7c,d). However, in CHCl₃, the adjacent pyrene pendants exhibited the larger overlapping with a shorter distance (Figure 7g,h). Therefore, the pyrene pendants are prone to interact with each other strongly, giving rise to the stronger Cotton effects and lower absorption intensities in CHCl₃.



Figure 7 Possible 3D helical models of **S-I** in DMF (a-d) and CHCl₃ (e-h). (c), (d), (g), and (h) are the partial amplifications. The blue dot lines in (e) are the possible intramolecular hydrogen bonds.

| Bond | $\theta_0 = 0^\circ, \ \phi_0 = -155^\circ$ | | | $\theta_0 = 0^\circ$, $\phi_0 = -170^\circ$ | | |
|--------|---|--------|-------|--|------------|-------|
| number | ф | θ | N-H…O | φ | θ | N−H…O |
| 1 | -166.23 | 6.21 | 4.06 | -169.67 | -5.80 | 1.96 |
| 2 | -169.64 | 4.90 | 4.46 | -162.30 | -8.59 | 1.72 |
| 3 | -172.46 | 6.20 | 4.99 | -167.80 | 1.69 | 1.74 |
| 4 | -164.83 | 15.22 | 4.48 | -172.42 | 6.08 | 1.86 |
| 5 | -165.11 | -0.17 | 4.55 | -165.17 | -6.64 | 1.79 |
| 6 | -168.60 | 6.77 | 4.41 | -155.81 | -0.54 | 1.75 |
| 7 | -160.17 | 7.35 | 3.47 | -159.57 | -9.83 | 1.82 |
| 8 | -152.30 | -11.28 | 3.96 | -173.53 | 6.71 | 1.81 |
| 9 | -153.18 | 2.98 | 5.04 | -175.36 | 1.95 | 1.73 |
| 10 | -172.05 | 10.15 | 3.49 | -175.93 | -4.46 | 1.79 |
| 11 | -159.04 | -4.82 | 3.11 | -172.98 | 7.71 | 1.95 |
| 12 | -153.21 | 12.04 | 2.22 | -166.63 | -0.66 | 1.93 |
| 13 | -152.92 | 7.34 | 2.74 | -173.32 | 5.36 | 1.74 |
| 14 | -159.23 | 7.07 | 3.74 | -174.86 | -4.07 | 1.92 |
| 15 | -168.60 | 1.74 | 3.51 | -168.07 | 11.50 | 1.86 |
| av. | -162.50 | 4.78 | 3.88 | -168.90 | 0.08 | 1.82 |
| Energy | 1484 kJ/(unit mol) | | | 1453 | 3 kJ/(unit | mol) |

Table 4Dihedral angles and length of N-H···O in $S-I^a$

^{*a*} ϕ : dihedral angle of C=C–C=C in the main chain; θ : dihedral angle of C–C=C–C in the main chain.

As shown in Table 4, in contracted helix, the average values of dihedral angle θ and φ were 4.78° and -162.50°, respectively. Along the main chain, most ϕ values were positive, suggesting the polyene backbone mainly twisted in one-handed direction. So less defects would exist leading to the stronger CD signal of main chain in DMF. Moreover, the average length of N-H…O was 3.88 Å, which was too large to form intramolecular hydrogen bonds. In stretched helix, the average values of dihedral angle θ and ϕ were 0.08° and -168.90°, respectively. The numbers of positive and negative ϕ values were almost the same, suggesting that many helical reversals probably existed along the main chain. On the other hand, the average length of N-H…O was 1.82 Å, which was beneficial to form strong intramolecular hydrogen bonding. For this reason, though the helicity of the main chain was decreased in stretched helix, the pyrene pendants still could keep in a good helical arrangement.

Conclusions

Three novel poly(3,5-disubstituted phenylacetylene)s with pyrene pendant were designed and synthesized. Based on this disubstitution structure, a new model of doublet chirality transfer was put forward. Achiral pyrenes were chosen as probe unit, which were induced to helically arrange around the polyene backbone through DCT, demonstrated by CD spectra and computer calculations. The main-chain stereostructure and intramolecular hydrogen bonds were confirmed to play important roles in realizing DCT. To achieve a good DCT, high *cis* structure of main chain, and strong intramolecular hydrogen bonds were indispensible. Reversible helix-helix transition was achieved in **S-I** by altering the nature of solvents. According to CD, UV-vis spectra, and computer simulations, the main chain of **S-I** in DMF adopted a relatively contracted helix which twisted along a predominant one direction. Nevertheless, the main chain of **S-I** in $CHCl_3$ was a relatively stretched helix with many helical reversals, and achiral pyrene units arranged in a better helical form for the formation of intramolecular hydrogen bonds supported by solution-state IR spectra. This work provided a new promising model for designing functionalized PPA materials. Taking advantage of doublet chirality transfer, the novel asymmetric catalyst and stimulus-responsive chiral electroptical materials based on poly(3,5-disubstituted phenylacetylene) could be anticipated. The related work is under way.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2018xxxxx.

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- [21] The molar concentration is based on monomer unit. It is calculated by the equation $c = m/(M \bullet V)$, in which m, M, and V represent the weight of sample, molar weight of repeated monomer unit, and the

solvent volume, respectively.

- [22] The induced chirality of pyrene may also come from the chiral microenvironment created by polyene backbones similar to the cyclodextrin recognition-induced chirality. It is difficult to exclude this possibility and estimate to what extent the chiral microenvironment play a role.
- [23] Cis-structure polyene backbone can be obtained with rhodium complex as polymerization catalyst, while trans-enriched PPAs are prepared by using the Mo- or W-based metathesis catalyst system. But the polar functional groups like amide commonly tend to poison this metathesis catalyst system. At this moment grinding is often chosen to get the trans-structure PPAs instead.
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Entry for the Table of Contents

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Doublet Chirality Transfer and Reversible Helical Transition in Poly(3,5-disubstituted phenylacetylene)s with Pyrene as a Probe Unit



Sheng Wang, Xuanyu Feng, Jie Zhang, Xinhua Wan* A new model of doublet chirality transfer (DCT) was put forward based on the disubstitution structure of poly(3,5-disubstituted phenylacetylene)s. High *cis* structure content and intramolecular hydrogen bonds were beneficial for the realization of DCT. And reversible helix-helix transition was observed by altering the nature of solvents