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COMMUNICATION

Red Color CPL Emission of Chiral 1,2-DACH-based Polymers *via* Chiral Transfer of the Conjugated Chain Backbone Structure

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Four chiral polymer enantiomers were designed and synthesized. Interestingly, only *R*-P-1 and *S*-P-1 can exhibit strong mirror image Cotton effects and emit red color circularly polarized luminescence, which can be attributed to the effective chiral transfer from 1,2-diaminocyclohexane Schiff base to chromophore BODIPY *via* the conjugated polymer chain backbone.

Circularly polarized luminescence (CPL), which can be regarded as the emission analogue of circular dichroism (CD), is the selective emission of left- and right-handed polarized light originated from chiral molecular system. Unlike traditional CD measurement for the chirality of ground state molecules, CPL signal has been primarily used to investigate structural information on the excited state of chiral molecule. In recent years, CPL has been receiving considerable interest not only due to the valuable information on the chirality of the electronic excited states, but also its potential applications in future optical technologies.^[1] So far, there have been some reports on various CPL emission materials, such as chiral lanthanide complexes, chiral conjugated polymers, chiral π -conjugated organic molecules, and so on. To the best of our knowledge, there has been few research work on red color CPL emission based on chiral conjugated polymers except chiral europium complexes.^[2] Therefore, development on red color CPL materials is of great significance.

The optical properties of organic fluorophores are very important for the development of new functional organic materials. In the past few decades, organic fluorophores have been extensively applied in optoelectronic devices, such as fluorescence sensors, solar cells, field effect transistors, biomedicines, electroluminescent devices.^[3] In particular, 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) and its derivatives have attracted much attention due to

their valuable characteristics, such as high absorption coefficients, a narrow absorption band and high emission quantum yields, etc.^[4] Recently, de la Moya's and Cheng's groups have reported red color CPL emission of several novel chiral BINOL-based *O*-BODIPY organic small molecules, respectively.^[5]

Optically active 1,2-diaminocyclohexane (DACH) is one of the most important C_2 symmetric compounds, which has been designed and used as chiral fluorescence chromophores for CPL emission materials.^[6] Kawai and co-workers have done some pioneer work on the CPL materials.^[7] Recently, they have designed and synthesized a novel chiral bichromophoric perylene bisimides which showed the enhanced CPL response behavior originated from the formation of chiral nanostructures through the effective integration of individual bichromophoric molecules.^[6b] But most investigations on CPL materials were mainly focused on chiral organic small molecules. So far, there have been few reports on chiral polymer-based CPL materials.^[8] Our group first developed aggregation-induced CPL of (*R*)-binaphthyl-based AIE-active conjugated polymer only at 3,3'-positions polymerization of 1,1'-binaphthene through the formation of self-assembly helical nanofibers from solution to aggregate state.^[9]

In this paper, we synthesized four chiral 1,2-DACH-based polymers incorporating chromophore BODIPY moiety in the polymer main chain backbone. Most interestingly, only the conjugated polymers ***R*-P-1** and ***S*-P-1** can exhibit mirror image CPL signals, which can be attributed to the effective chiral transfer from 1,2-DACH to chromophore BODIPY *via* the conjugated polymer chain backbone. Without the π -conjugated linkers between chiral 1,2-DACH moiety and chromophore BODIPY, no CD signals or CPL emission responses could be observed for ***R*-P-2** and ***S*-P-2**.

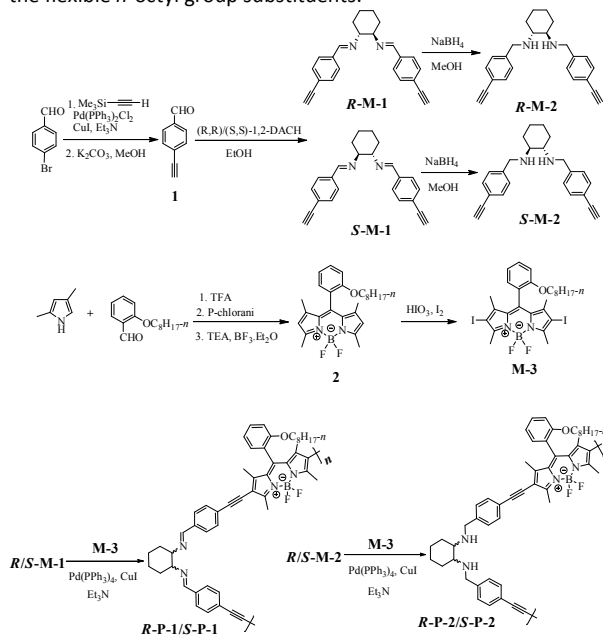
The detailed synthesis routes of the monomers and the chiral polymers are shown in Scheme 1. The intermediates **1** and BODIPY derivatives (**2**, **M-3**) were prepared according to reported literatures.^[10] ***R/S*-M-1** was synthesized by the reaction of **1** with (*R,R*)/(*S,S*)-1,2-DACH enantiomers *via* nucleophilic addition-elimination reaction. ***R/S*-M-2** could be obtained by the reduction reaction of ***R/S*-M-1** with NaBH₄ in 84% yield at ice-bath. ***R/S*-P-1** and ***R/S*-P-2** were synthesized by Pd-catalyzed Sonogashira coupling reaction of ***R/S*-M-1** and ***R/S*-M-2** with **M-3** in yields of 87% and

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85%, respectively. The detailed procedures and characterizations are described in ESI. The chemical structures of the polymers could be confirmed by ^1H NMR. (*R,R*)/(*S,S*)-1,2-DACH moiety of **P-1** and **P-2** as a chiral group can orient a well-defined spatial arrangement in the regular polymer main chain backbone. All these four polymers are air stable solids and have good solubility in common organic solvents, such as toluene, THF, CHCl_3 and CH_2Cl_2 , which can be attributed to the nonplanarity of the twisted polymer backbone and the flexible *n*-octyl group substituents.



The UV-vis absorption and fluorescence spectra of **2**, **P-1** and **P-2** were conducted in THF (1.0×10^{-5} mol/L) at room temperature. As shown in Fig. 1, chromophore BODIPY **2** appears a strong $S_0 \rightarrow S_1$ ($\pi-\pi^*$) transition centered at 503 nm, and a much weaker broad band at a shorter wavelength 353 nm, which can be attributed to $S_0 \rightarrow S_2$ ($\pi-\pi^*$) transition. **P-1** and **P-2** appear two distinct bands in the absorption spectra. One band at shorter wavelengths is assigned to their localized $\pi-\pi^*$ transition, and the other band at longer wavelengths can be regarded as intramolecular charge transfer (ICT) between 1,2-DACH Schiff base moiety as electron-rich donors and BODIPY as electron-deficient acceptors. Compared with chromophore BODIPY **2**, the absorption wavelength λ_{max} is red-shifted as high as by 60 nm for **P-1** and **P-2**, probably ascribing to the extended π -conjugation structure. Moreover, the absorption peaks of the conjugated polymers appear broader than that of compound **2** due to a result of the extended π -conjugation.

As is evident from Fig. 2, chromophore BODIPY **2** has an emission peak at 514 nm. When the **M-1** or **M-2** moiety is introduced into the main chain backbone of the polymer, the maximum emission peaks of **P-1** (607 nm) and **P-2** (608 nm) are red-shifted by 93 nm and 94 nm, respectively. All these four polymers can emit bright red light due to the extended π -electronic structure in the main chain backbone. The weight average lifetimes of **P-1** and **P-2** were 3.28 ns and 3.24 ns, respectively (Fig. S13 and Fig. S14).

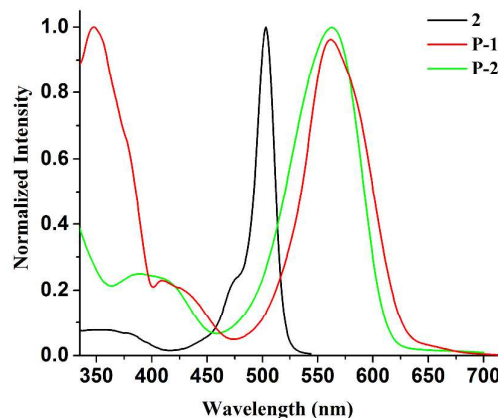


Figure 1. Normalized UV-vis absorption spectra of **2**, **P-1** and **P-2** in THF (1.0×10^{-5} mol/L corresponding to BODIPY unit in the chiral polymer).

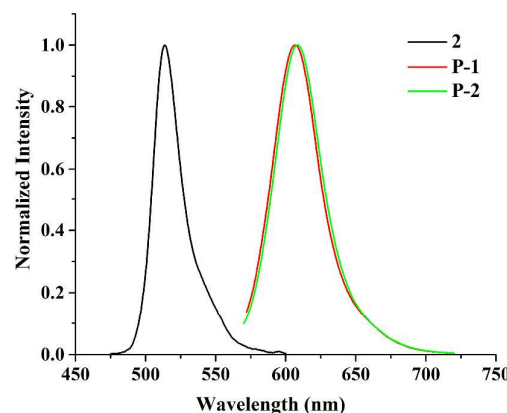


Figure 2. Normalized emission spectra of **2**, **P-1** ($\lambda_{\text{ex}} = 349$ nm) and **P-2** ($\lambda_{\text{ex}} = 387$ nm) in THF (1.0×10^{-5} mol/L corresponding to BODIPY unit in the chiral polymer).

The CD spectra of *R/S*-**M-1**, *R/S*-**M-2** and *R/S*-**P-2** are shown in Fig. S1. *R/S*-**M-1** exhibited obvious mirror-image CD bands in THF solution which is due to the extension of conjugated structure. On the opposite, *R/S*-**M-2** did not have any CD signals, which is caused by no conjugated structure between chiral 1,2-DACH center and aromatic group. In Fig. 3, it could be clearly observed that *R/S*-**P-1** had strong Cotton effect at wavelengths of 342 nm, which can be regarded as the extended conjugated structure in the repeating unit and a high rigidity of polymer backbone.^[10a] *R-P-1* and *S-P-1* also appeared strong Cotton effects in the long wavelength centered at about 586 nm, which could be attributed to effective chiral transfer from 1,2-DACH moiety to chromophore BODIPY through the conjugated chain backbone structure. The absorption dissymmetry factors $|g_{\text{abs}}|$ of *R/S*-**P-1** obtained from the CD spectra were about 0.0024 at 586 nm. Almost no Cotton effect in CD spectra of *R-P-2* and *S-P-2* can be observed (Fig. S1), which is the result of no π -conjugated linkers between chiral 1,2-DACH moiety and chromophore BODIPY. In this paper the resulting chiral conjugated polymers *R/S*-**P-1** can adopt a stable chiral conformation since the (*R,R*)/(*S,S*)-Schiff base moiety can orient a well-defined spatial arrangement in the regular and rigid polymer backbone, that is, each unit in the chiral polymer *R/S*-**P-1** independently acts as an organized conjugated chain backbone structure.

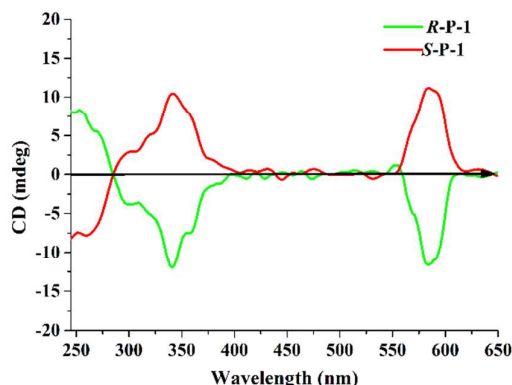


Figure 3. CD spectra of *R/S-P-1* in THF (1.0×10^{-5} mol/L corresponding to BODIPY unit in the chiral polymer).

Herein, the resulting chiral polymer enantiomers *R/S-P-1* could exhibit strong fluorescence emission and CD absorption response behaviors in THF, which inspired us to further investigate their CPL behaviors. As is evident from Fig. 4, it is clearly found that *R-P-1* and *S-P-1* showed mirror-image CPL signals centered at 607 nm which is due to effective chiral transfer from chiral 1,2-DACH Schiff base moiety to chromophore BODIPY *via* the conjugated chain backbone structure. As for *R-P-2* and *S-P-2*, no CPL signals could be detected, which can be attributed to no conjugated linkers between chiral 1,2-DACH moiety and the conjugated backbone structure (Fig. S2). It is also corresponding to their CD responses.

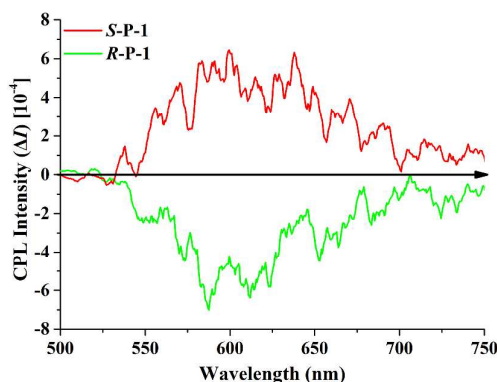


Figure 4. CPL spectra of *R/S-P-1* in THF (1.0×10^{-5} mol/L corresponding to BODIPY unit in the chiral polymer).

As the essential parameter of CPL, the optical anisotropy factor (g_{lum}) can be obtained from $g_{lum} = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R are the emission intensities of left and right circularly polarized luminescence, respectively.^[11] The $|g_{lum}|$ of *R/S-P-1* at 608 nm is about 0.0015, which is in the range of most CPL materials from 10^{-5} to 10^{-2} .^[12]

In summary, the resulting chiral conjugated polymers can exhibit strong Cotton effect and CPL signals due to the effective chiral transfer from chiral 1,2-DACH Schiff base moiety to chromophore BODIPY *via* conjugated chain backbone structure. This work can provide critical information

on a better understanding of chiral transfer mechanism for the design of novel CPL materials.

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Red Color CPL Emission of Chiral 1,2-DACH-based Polymers *via*

Chiral Transfer of the Conjugated Chain Backbone Structure

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Chiral polymers incorporating chiral 1,2-DACH moiety and BODIPY can exhibit strong mirror image Cotton effects and emit red color CPL signals *via* effective chiral transfer of the conjugated polymer chain backbone.

