Circularly Polarized Luminescence from Supramolecular Chiral Complexes of Achiral Conjugated Polymers and a Neutral Polysaccharide

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We have developed a novel approach to the preparation of a circularly polarized luminescence material from a natural polysaccharide host and an achrial polythiophene guest.

Conjugated polymers (CPs) are nowadays used in several devices, such as light-emitting diodes (LEDs), field-effect transistors, sensors, and solar cells.[1] One of the most interesting features arising from CPs is that the properties can be finely tuned by conformational changes. Circularly polarized luminescence (CPL) is one of the most fascinating applications taking such advantages of CPs. In principle, it is possible to design a LED that directly emits circularly polarized light by introducing molecular chirality into the conjugated polymer by covalent-bond formation. In many cases however, circular dichroism (CD) and CPL in the π–π^* transition region are generally observed only when the polymer chains are aggregated, such as in a solid film or microcrystalline phase which is formed during the onset of precipitation in a poor solvent or cooling in a good solvent.[2] There are therefore, a few reports which show CPL phenomena from CPs in a molecularly dispersed state.[3] Recently, we found a novel preparation method for a chiral insulated molecular wire by supramolecularly self-assembling an achiral water-soluble polythiophene (PT-1) and a neutral helix-forming polysaccharide, schizophyllan (SPG) (Chart 1).[4] In this paper, we report the CPL properties of this chiral insulated molecular wire (SPG/PT-1 complex) and demonstrate that the SPG/PT-1 complex shows CPL high quantum yields not only in the solution state but also in the precipitated powder, which would reflect the (chiro)optical properties of the solid state.

SPG is a β-1,3-glucan polysaccharide that exists as a right-handed triple helix (t-SPG) in water but as a single random coil (s-SPG) in dimethyl sulfoxide (DMSO).[5] When water is added to its DMSO solution, s-SPG collapses owing to hydrophobic interaction and retrieves its original triple helical structure (renaturation). These specific structural characteristics make s-SPG form stable water-soluble complexes with several hydrophobic guests during renaturing.[6] Typically, the SPG/PT-1 complex was prepared by adding a DMSO solution of SPG to an aqueous solution of PT-1, and then the mixed solution was incubated for 12 h at 60 °C. After incubation, the SPG/PT-1 complex was purified by dialysis with distilled water before lyophilizing. The orange powder thus obtained by lyophilization was dissolved in water and the (chir)optical observations were carried out. Figure 1a shows the degree of circular polarization in absorption and luminescence of the SPG/PT-1 complex. Figure 1b displays the corresponding UV–vis absorption and fluorescence spectra. The absorption maximum of the SPG/PT-1 complex was observed at 454 nm, whereas the absorption maximum of PT-1 in the absence of SPG was observed at 403 nm. The 51 nm red-shift means that the interaction between PT-1 and SPG forces the PT-1 backbone to adopt a more conjugated conformation.[4] A characteristic CD signal was confirmed in the π–π^* transition region of PT-1. The CD intensity showed a linear relationship with the concentration, which indicates that the CD spectra originated from the right-handed backbone helical structure of PT-1, but not from the intermolecular stacking (Figure S3).[7,8] Together with our previous findings based on AFM measurements and thermal analyses one may assume that the present SPG complex mostly contains one PT-1 chain.[4] Furthermore, the strong positive CPL signal was observed in the π–π^* transition region of PT-1. The CPL maximum was observed at 560 nm, which is well in accord with the maximum of the fluorescence. The g values of absorption (g_{abs}) and luminescence (g_{lum}), which are defined as $g_{abs} = 2(\varepsilon_L - \varepsilon_R)/(\varepsilon_L + \varepsilon_R)$ and $g_{lum} = (I_L - I_R)/(I_L + I_R)$, were estimated to be $+7.7 \times 10^{-3}$ (525 nm) and $+4.5 \times 10^{-3}$ (561 nm), respectively. These values are very close to each other, which means that both of the CD

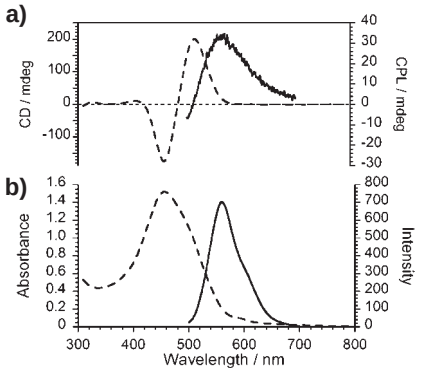

Figure 1. (a) (Dash line) CD and (solid line) circularly polarized luminescence CPL and (b) (dash line) UV–vis and (solid line) fluorescence spectra of the SPG/PT-1 complex in water–DMSO mixed solvent; $\lambda_{ex} = 400$ nm, rt.

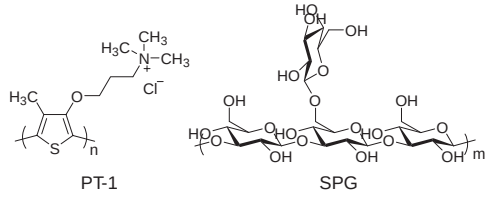

Chart 1. Chemical structures of PT-1 and SPG.

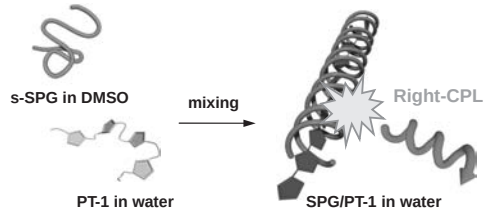

Figure 2. Schematic illustrations of the supramolecular chiral insulated molecular wire formation and their circularly polarized luminescence (CPL).

and the CPL originate from the same chiral structural origin that is, the right-handed helical structure of the PT-1 backbone (Figure 2). PT-1 is a priori optically inactive, so that no characteristic CD and CPL signals are detected. Also, the luminescence of PT-1 is enhanced because of the restriction of the molecular motion upon complexation with SPG (Figure S2).[4] These trends consistently indicate that SPG can form a supramolecular chirally-twisted polymer complex with PT-1, which serves as a unique candidate for superior CPL materials.

We have confirmed that in addition to optical activity in solution, (chir)optical properties of the SPG/PT-1 complex are also presented in the precipitated powder. To prepare precipitates of the SPG/PT-1 complex, acetone was added to the aqueous SPG/PT-1 complex solution. As acetone acts as a poor solvent for both SPG and PT-1, the SPG/PT-1 complex can be easily precipitated. These dispersed precipitates are suitable for the present purpose because one can eliminate the signal arising from macroscopic chirality. Figure S4 shows the UV–vis and CD spectra of the SPG/PT-1 complex dispersed in acetone/water mixed solvent. The SPG/PT-1 complex did not show any significant spectral change whereas PT-1 in the absence of SPG showed a dramatic color change from yellow to purple under the same conditions (Figure S6). This dramatic color change is attributed to the π–π stacking aggregate formation of PT-1. It is clear therefore, that SPG suppresses stacking of PT-1 by the insulating effect arising from the wrapping ability of its inherent helical structure. It is particularly worthy mentioning that the fluorescence intensity of the SPG/PT-1 complex is maintained in contrast to dramatic concentration quenching of PT-1 in the absence of SPG (Figure S5). Figure 3 shows the degrees of circular polarization in the luminescence and the corresponding fluorescence spectra of the SPG/PT-1 complex in the precipitated powder. The positive CPL signals were observed and the

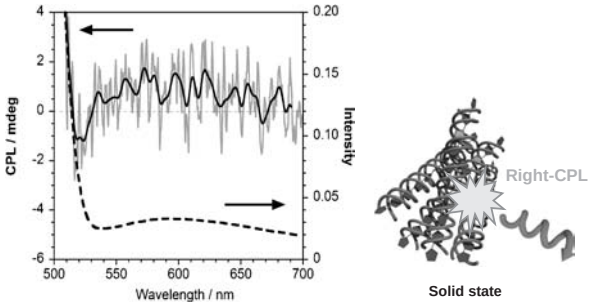

Figure 3. (Solid line) CPL and (dash line) fluorescence spectrum of the SPG/PT-1 complex participate dispersed in acetone/water mixed solvent; acetone:water = 70:30 (v/v), $\lambda_{ex} = 410$ nm, rt.

g_{lum} also maintained the order of 10^{-3}, indicating that the SPG/PT-1 complex keeps the supramolecular chiral insulated molecular structure in the precipitated powder. It is known that chiral conjugated polymers induce a dramatic conformational change during aggregation and the behavior can be controlled with solvents, dopants, and temperature.[2e] In our case however, SPG suppresses the conformational change of guest polymers and the complex can attain high quantum yields of CPL.

In summary, we have developed a novel efficient approach to the preparation of a CPL material from a natural SPG host and an achiral polythiophene guest, PT-1. The SPG/PT-1 complex showed high quantum yield of CPL not only in the solution state but also in the precipitated powder owing to the insulating effect of SPG which cannot be achieved in the conventional chiral supramacromolecular aggregates. To the best of our knowledge, this is the first observation of CPL from the supramolecular host–guest complex of conjugated polymers. We expect that supramolecular chiral insulated molecular wires can be designed from these strategies, which can be applied to the creation of novel optical devices.

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References and Notes

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