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Circular dichroism and circularly polarized luminescence triggered by self-assembly of tris(phenylisoxazolyl)benzenes possessing a perylenebisimide moiety[†]

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Chiral tris(phenylisoxazolyl)benzenes possessing a perylenebisimide moiety assembled to form helical stacks. The self-assembling behavior of the helical stacks responded to changes in solvent properties, temperature, and concentration. Strong circular dichroism (CD) and circularly polarized luminescence (CPL) of their assemblies were displayed, and were controlled by external stimuli.

Circularly polarized luminescence (CPL) is the selective emission of right- and left-handed circularly polarized lights from chiral molecular systems. This field has been dominated by chiral lanthanide complexes so far.¹ In recent years, there has been a growing interest in developing organic molecules capable of emitting CPL towards their potential applications in optoelectronic devices.^{2,3} Strategies to create CPL emitting organic materials include attaching chiral side chains to conjugated polymers,^{2,4} embedding organic chromophores in a chiral matrix,⁵ and developing inherently chiral conjugated molecules.⁶ Some conjugated materials in condensed states exhibit an enhanced CPL dissymmetry factor, $g_{\text{lum}} = 2(I^{\text{L}} - I^{\text{R}})/(I^{\text{L}} + I^{\text{R}})$, where I^{L} and I^{R} , respectively, denote intensity of left and right circularly polarized light.^{2,4,6} Controlling CPL by a supramolecular method represents a prime scientific challenge,⁷ because CPL emission can be turned "on" and "off".6e However, there are very few reports describing that CPL emission is triggered by supramolecular assembly.

Recently, we have reported that tris(phenylisoxazolyl)benzenes form one-dimensionally stacked helical assemblies.⁸ The size and dimension of the helical self-assemblies are sensitive to a solvent system; thus, the assembling behavior can be controlled by using a certain solvent. Perylenebisimide (PBI) is



Fig. 1 Structure of molecules *S*- and *R*-1 and the schematic scheme of their chiral self-assembly and circularly polarized luminescence (CPL).

a well-known chromophore that creates very strong fluorescence with high quantum yield in the visible region.⁹ The introduction of PBI units onto the helical assemblies should arrange them in a helical fashion, capable of developing the CPL emission.^{6b,c} Herein, we report novel CPL emitting assemblies formed from chiral tris(phenylisoxazolyl)benzenes 1 possessing a perylenebisimide (PBI) moiety and its selfassembling behaviors, providing the distinctive CD and CPL properties (Fig. 1).

The self-assembling behavior of S-1 was studied using ¹H NMR and absorption spectroscopies. The signals that appeared in the aromatic region were assigned by 2D NMR techniques (see ESI[†]). The ¹H NMR signals of S-1 were concentration-dependent in chloroform- d_1 (Fig. 2). Most of the signals shifted upfield upon increasing the concentration from 0.2 to 20 mmol L⁻¹. This indicates that S-1 forms



Fig. 2 Concentration-dependent ¹H NMR spectra of *S*-1 at 298 K in chloroform- d_1 . The concentrations of *S*-1 are (a) 0.50, (b) 1.0, and (c) 5.0 mmol L⁻¹. * indicate solvent peaks.

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 † Electronic supplementary information (ESI) available: Synthetic

F Electronic supplementary information (ESI) available: synthetic procedure for S- and R-1, UV-vis absorption, fluorescence, and CD spectra of S- and R-1 in chloroform and MCH, the van't Hoff plot of S-1 in decalin, and NMR spectra of all new compounds. Correction for CPL is also provided. See DOI: 10.1039/c2cc31512b

stacked assemblies in which the aromatic protons are placed in the shielding regions produced by the neighboring aromatic rings. Plotting the chemical shift changes of the protons vs. the concentrations of S-1 produced hyperbolic curves. Non-linear curve-fitting analysis by applying the isodesmic model¹⁰ produced the estimated complexation-induced shifts $(\Delta \delta = -0.48, -0.56, -0.73, -1.07, -1.43, -0.45, -0.53,$ -0.14, and -0.86 ppm for H_a , H_b , H_c , H_d , H_e , H_f , H_g , H_h , and H_{PBI} , respectively) (see ESI[†]) and the association constant $(K_{\rm E} = 10.0 \pm 0.9 \text{ L mol}^{-1})$. The characteristic upfield shifts of the aromatic protons of H_c , H_d , H_e , and H_{PBI} imply that S-1 stacks around the pseudo C_3 -axis on the tris(phenylisoxazolyl)benzene, and the peripheral substituent PBI creates a close contact with the neighbors.

The absorption spectral changes because of the selfassembly of S-1 depend on solvent properties. A diluted solution $(1.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$ of S-1 in chloroform displayed well-defined absorption bands with the characteristic $\pi - \pi^*$ transitions of the tris(phenylisoxazolyl)benzene unit and the PBI unit, at 270 nm and at 450, 480, and 515 nm.9 The absorption spectra were not temperature- and concentrationdependent (Fig. S2a and S3, ESI⁺). S-1 mostly exists in a monomeric form in chloroform at the low concentrations. By contrast, the absorption spectra of S-1 were highly influenced by the temperatures and concentrations of its solution in decahydronaphthalene (decalin). A diluted solution

1 0 300 400 500 600 wavelength / nm

Fig. 3 Temperature-dependent (a) CD and (b) UV-vis absorption spectra of S-1 $(1.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$ in decalin. The temperatures of the solution of S-1 are 353, 343, 333, 323, 313, 303, and 293 K. Arrows indicate changes upon decreasing the temperature.

 $(1.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$ of S-1 displayed sharp absorption bands at 353 K, consistent with those observed in chloroform (Fig. 3b). Upon cooling the solution, the absorption bands red-shifted, and new bands appeared at 310, 498, and 535 nm, characteristic of the J-aggregates of PBIs.9 Plots of the molar extinction coefficient at 540 nm vs. temperatures display a clear sigmoidal shape, indicating that the self-association of S-1 obeys an isodesmic model (Fig. S4, ESI[†]).^{11,12}

To obtain an insight into the self-association of S-1, the thermodynamic parameters ΔH , ΔS , and the association constant (K_E) at 338 K were determined by a van't Hoff plot to be -39 ± 1 kcal mol⁻¹, -90 ± 3 cal mol⁻¹ K⁻¹, and $(2.6 \pm 0.8) \times 10^5$ L mol⁻¹, respectively (Fig. S5 and S6, ESI[†]). These values are quite large as compared to those of a simple tris(phenylisoxazolyl)benzene reported previously.⁸ This rationalizes that the assembly of S-1 receives the additional gain of the enthalpic contribution which probably resulted from the attractive intermolecular stacking interactions of the PBI units; but, the large enthalpic contribution reduces the freedom of molecular movement, leading to the large negative entropic component, which cannot be compensated by desolvation.

During the self-assembly of S- and R-1, the chiral side chains get closer to ensure the steric communications with their neighbors, and reduce the symmetry of the assembly, leading to the chiral induction. This prompted us to study the chiroptical response of S- and R-1. The CD spectra of S- and R-1 exhibited a mirror image relationship with respect to the line of $[\theta] = 0$ in decalin at 293 K (Fig. 4a and S10, ESI[†]). The assembly of S-1 gave rise to strong Cotton effects in the visible region, characteristic of the stacked structure of the PBI moiety with fairly large g_{abs} value of 0.0014 at 545 nm. The strong CD bands were temperature-dependent. Upon warming the solution of S-1 to 353 K, the CD turned silent (Fig. 3a). Accordingly, the induced CD bands originated from the assembly of S-1. A right-handed helicity of the assembly of S-1 was confirmed by the plus-to-minus patterns observed in ascending energy terms in the CD spectrum of S-1 at around 545 nm and 300 nm.^{8a,d,9b,13}

Non-aggregated S-1 displayed a well-defined fluorescence band at 539 nm with high quantum yield ($\phi = 0.56$) in chloroform. By contrast, S-1 exhibited two characteristic bands in decalin; the sharp emission band at 525 nm is assigned to its monomeric form, and the broad emission band at 650 nm with moderate quantum yield ($\phi = 0.07$) originated from the chiral assembly of S-1 (Fig. 4b and S7, ESI⁺).⁹ This created clear CPL at the band, assigned to its assembly, with a dissymmetry factor g_{lum} of 0.007 in decalin, whereas no CPL signal was observed in chloroform (Fig. 4a).14 The CPL spectrum of R-1 displayed the mirror image of S-1. These results clearly conclude that the CPL signals observed in decalin are induced by the chiral assemblies of S- and R-1. The CPL of S- and R-1 can be regulated via assembling and disassembling of the chiral monomers in response to the solvent properties. The present g_{lum} is rather larger than the typical g_{lum} values of π -conjugated chiral molecules. Generally, the g_{lum} is inversely proportional to the transition dipole moment.1 Although the emission rate constant of





Fig. 4 (a) CD (solid line) and CPL (dotted line) spectra of *S*-**1** in chloroform (black), *S*-**1** in decalin (red), and *R*-**1** in decalin (blue) at 298 K. (b) UV–vis absorption (solid line) and fluorescence (dotted line) spectra of *S*-**1** in chloroform (black), and in decalin (red) at 298 K. The concentration is 1.0×10^{-4} mol L⁻¹. $\lambda_{ex} = 488$ nm.

the present chiral assembly was not determined because of non-linear transient emission decay, the transition dipole moment seems to be suppressed in the π -stacked state, which could be the origin of the suppressed emission quantum yield and enhanced g_{lum} values.

In summary, we have demonstrated the unique chiroptical properties induced by the chiral self-assembly of the tris(phenylisoxazolyl)benzenes possessing a PBI moiety. The self-assembling behaviors of *S*- and *R*-1 were discussed using ¹H NMR, UV–vis absorption, and fluorescence spectroscopies. Most of the *S*- and *R*-1 did not form aggregates in chloroform, whereas they assembled to form the helical stacks in decalin. The CD signals of *S*-1 were enhanced with decreasing temperature in decalin, and g_{abs} reached 0.0014 at 293 K. *S*- and *R*-1 exhibited CPL with $g_{lum} = 0.007$ in decalin. The photophysical properties including UV–vis absorption, fluorescence, CD, and CPL are now controllable by changing the solvent, temperature, and concentration.

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