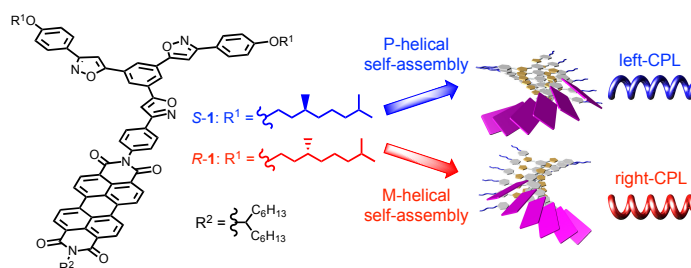


Self-assembly and chiroptical properties of chiral tris(phenylisoxazolyl)benzene possessing perylenebisimide

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Helical columnar stacks of photo-functional π -conjugated molecules show characteristic chiroptical behaviors in their circular dichroism (CD) and circularly polarized luminescence (CPL). Their photophysical properties can be controlled by the association and dissociation of the assemblies. Recently, we have reported that a chiral tris(phenylisoxazolyl)benzene forms the helical columnar structure via π - π stacking and dipole-dipole interactions.^{1,2} A perylenebisimide (PBI) moiety can be attached to the periphery of a tris(phenylisoxazolyl)benzene to construct a helical stacks, displaying chiroptical properties. Tris(phenylisoxazolyl)-benzenes possessing PBI unit and chiral side-chain (*S*- and *R*-**1**) were synthesized and their self-assembling behaviors and photophysical properties were studied.



Upon increasing the concentration, the aromatic protons of *S*-**1** showed large up-field shifts that indicate the formation of the columnar structure. The UV/vis absorption spectra of *S*-**1** in chloroform displayed the well-defined absorption bands of the monomer. New bands, assigned to J-aggregates, appeared at approximately 498 and 535 nm upon decreasing the temperature in decaline. This result suggested that *S*-**1** formed J-aggregates in decaline at low temperature. *S*-**1** exhibited strong Cotton effect upon the absorption band of PBI unit in decaline at 293 K and *R*-**1** displayed its mirror image. The CD signals decreased as increasing temperature. Accordingly, the Cotton effect was induced by the chiral assembly of *S*- and *R*-**1**. *S*- and *R*-**1** displayed CPL at approximately 650 nm in decaline, whereas CPL was not observed in chloroform. We demonstrated that the chiroptical properties of *S*- and *R*-**1** were responded to the solvent properties, temperatures, and concentrations.

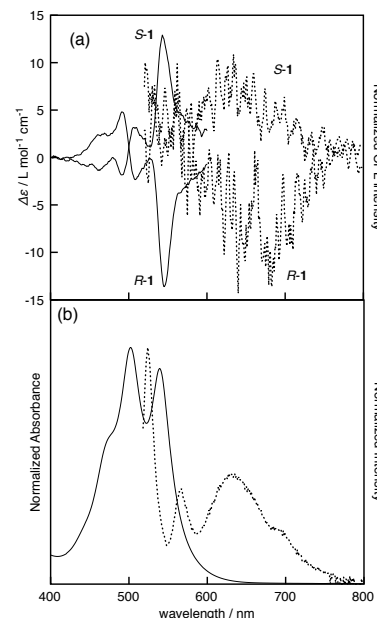


Figure 1. (a) CD and CPL spectra of (*S*- and (*R*)-**1** in decaline at 298 K. (b) UV/vis absorption and fluorescence spectra of (*S*)-**1** in decaline at 298 K.

1) T. Haino, M. Tanaka, Y. Fukazawa, *Chem. Commun.* **2008**, 468-470.

2) M. Tanaka, T. Ikeda, J. Mack, N. Kobayashi, T. Haino, *J. Org. Chem.* **2011**, 76, 5082-5091.