

Near-Infrared, Circularly Polarized Luminescence from Rotaxane-Type Fluorophores Encapsulating Thiophene-Conjugated Fluorescence Dyes

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Circularly polarized luminescence (CPL) is the anisotropic emission from chiral fluorescence molecules. CPL materials emitting near-infrared (NIR) light have gained attention in terms of bio-permeability, being advantages for in vivo imaging. However, NIR-emitting dyes often have poor water solubility due to their π -extended structure. This drawback makes these dyes difficult to use in biological applications.

We had developed rotaxane-type CPL fluorophores in which two achiral polycyclic aromatic hydrocarbons are encapsulated by cyclodextrins (CDs).^[1] These rotaxanes have good water solubility because water-soluble CDs wrap hydrophobic fluorophores entirely. In addition, the rotaxanes showed CPL with a large luminescence dissymmetry factor (g_{lum}).

In this research, we developed a novel rotaxane-type CPL fluorophore with NIR emission. A fluorescence dye **1** having acceptor- π -acceptor structure showed absorption in long wavelength region. Applying **1** for “cooperative capture strategy” previously we established,^[2] doubly 1-threaded [8]rotaxane **2** was efficiently synthesized (Figure 1). The [8]rotaxane **2** exhibited stronger emission than axis **1** and CPL emission around the NIR region in water ($\Phi_{FL} = 0.05$, $g_{lum} = -4.0 \times 10^{-3}$) (Figure 2). Furthermore, [8]rotaxane **2** demonstrated good stability against photo-irradiation because the fluorescence axes were protected from outer reactive species by the macrocyclic components. These results showed that rotaxane strategy is suitable for preparing various CPL fluorescence materials having wide range of emission wavelengths.

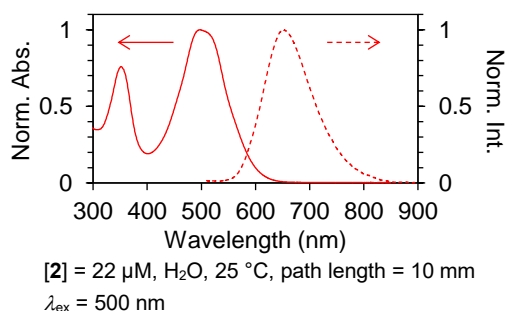
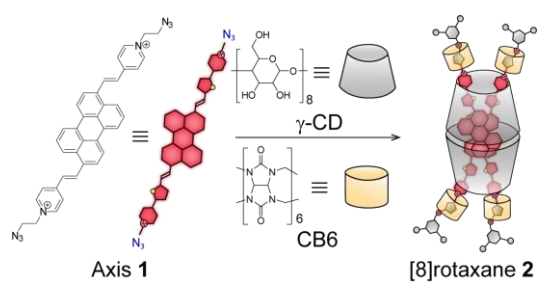


Figure 1. Synthesis of [8]rotaxane **2**

Figure 2. Absorption and emission spectra of **2**

[1] M. Inouye et al. *Angew. Chem. Int. Ed.* **2014**, *53*, 14392; *Chem. Eur. J.* **2018**, *24*, 14613.

[2] K. Nishioki et al. *Adv. Opt. Mater.* **2024**, *12*, 2301457.