Development of CPL-emitting molecules based on the understanding of efficient CPL emission from photoexcited dimers

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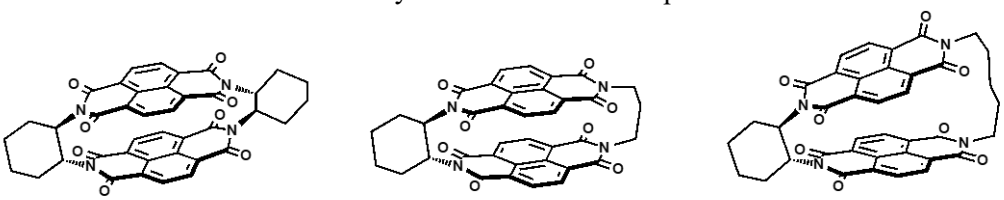
Keywords: Circularly polarized light; Chirality; Photo-excited state

In recent years, research on molecules that can emit circularly polarized light (CPL) has attracted much attention from the viewpoint of direct 3D display and security printing applications. While the CPL properties of a wide variety of molecules have been reported, CPL from excited dimers (so-called excimer) is more interesting because of the high anisotropy factor (g_{em}) [1,2]. The high g_{em} may facilitate good CPL luminescence in the excimer state; however, excimer formation in solution is a collisional process between two freely rotating molecules, and it is often difficult to form chiral excimer molecules with retention of chirality, i.e., the relative arrangement between the two molecules. Therefore, to investigate the properties of a chiral excimer in solution, the conformations of two identical molecules as an excimer must be fixed[3] so that chirality is maintained before photoexcitation.

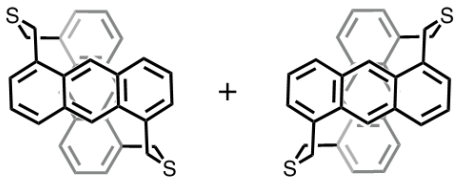


	(*M*)-D2	n3	n5
Φ_{fl}	0.047	0.039	0.031
g_{em}	6×10^{-2}	5×10^{-2}	1×10^{-2}

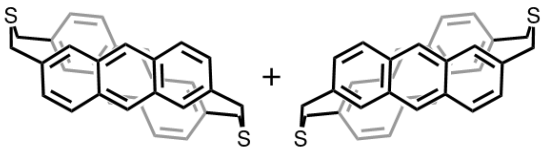
Wasielewski *et al.* reported that the chiral dimer of the nonfluorescent naphthalene diimide (**D2**) emits excimer-like luminescence with a fluorescence quantum yield (Φ_{fl}) of a few percent[4]. Based on CPL measurements, we demonstrated that **D2** is a good CPL emitter. Therefore, we synthesized **D2** analogs (**n3** and **n5**) and measured their CPL, as well as the fluorescence and CPL. Interestingly, g_{em} for the CPL of these compounds was on the order of 10^{-2} in non-polar solvents.

Although it is possible to maintain the chiral excimer, we believe that a fundamental question remains unanswered: “Why and how does the excimer state emit CPL efficiently?”

To answer this question, we recently prepared chiral anthracene dimers based on the cyclophane structure and investigated their photophysical properties, including their CPL performance. We believe that we can find a new approach to utilize excimers for the development of CPL-emitting molecules by elucidating the theoretical background of the excimer system and proposing a new compound to verify the theory.



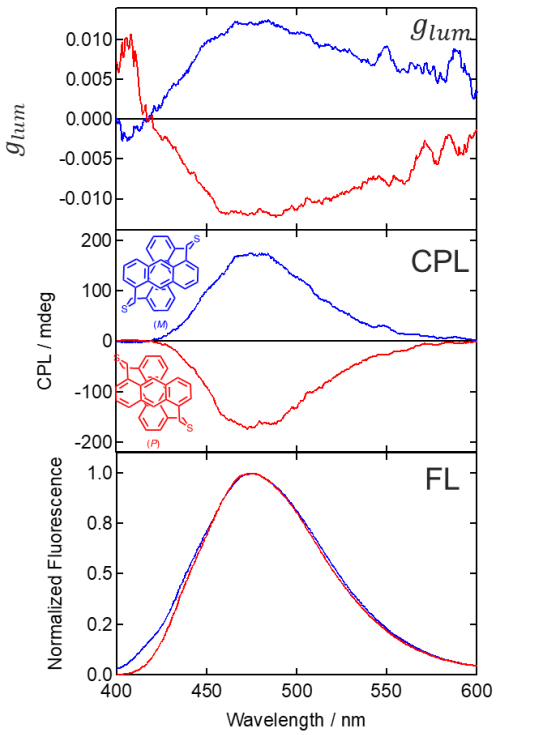
(1,5)[3.3]DTA : Dithia(1,5)[3.3]anthracenophane



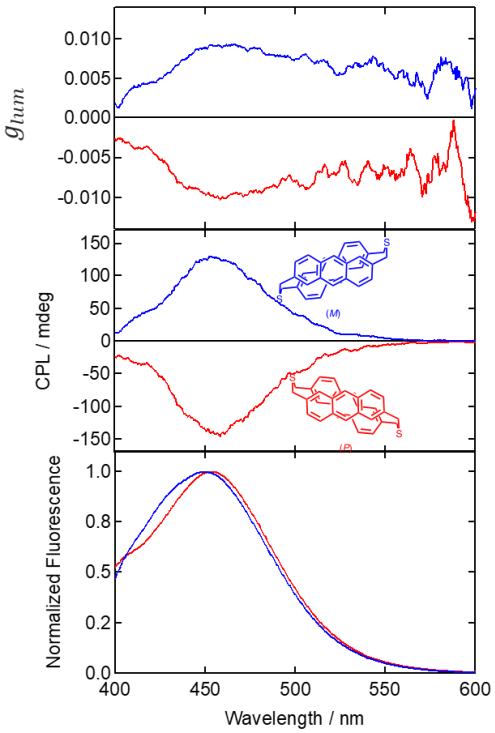
(2,6)[3.3]DTA : Dithia(2,6)[3.3]anthracenophane

The fluorescence and CPL spectra of (1,5)[3,3]DTA are shown below. It has been reported that the lowest excited singlet state of (1,5)[3,3]DTA has excimer character[5], and our measurements revealed that (1,5)[3,3]DTA emits CPL with a g_{em} of ~ 10^{-2} only in the excimer emission wavelength range. Interestingly, (2,6)[3,3]DTA also showed CPL with a g_{em} of ~ 10^{-2}, suggesting that the angle between the anthracenes was hardly affected the g_{em} value. TD-DFT calculations suggested that the CPL sign and transition energy were reproducible if structural relaxation in the lowest excited singlet state was considered.

In this work, we discuss the details of the experimental results and the theoretical background.



$|g_{lum}| = 1.2 \times 10^{-2}$ (λ= 473, 489 nm)



$|g_{lum}| = 1.0 \times 10^{-2}$ (λ= 460 nm)

1) K. Kano, et al., *J. Am. Chem. Soc.* **1985**, *107*, 6117. 2) Y. Chujo et al., *J. Mater. Chem. C* **2015**, *3*, 521. 3) K. Takaishi et al., *Chem. Commun.* **2018**, *54*, 1449. 4) Y. Wu, M. R. Wasielewski et al., *Angew. Chemie Int. Ed.* **2014**, *53*, 9476. 5) S. Sato et al., *J. Phys. Chem. A* **2003**, *107*, 10019.