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Observation of Chiral Aggregate Growth of Perylene Derivative in Opaque Solution by Circularly Polarized Luminescence

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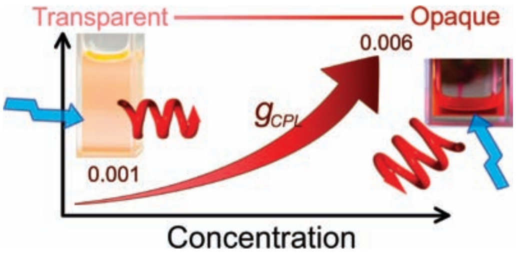
ABSTRACT



The concentration-dependent enhancement of the luminescence dissymmetry factor has suggested that π-conjugated chiral perylene derivatives in a high concentrated opaque solution grow to aggregated structures with higher optical chirality.

Molecular aggregates have specific physicochemical behaviors different from those of individual molecules in both their ground and excited states. Considerable recent interest has been focused on π-conjugated chiral molecules and polymers because specific intermolecular interaction could make their aggregates form specific self-organized helical and hierarchical structures,[1−10] showing characteristic chiroptical behaviors in their circular dichroism (CD)[11] and circularly polarized luminescence (CPL).[12,13] Such chiral molecular aggregates are expected to be potential candidates for chiroptical sensors[14,15] and sources for circularly polarized light.[6,16,17] Considerably enhanced chiroptical properties have been observed in some aggregated and/or condensed molecular structures such as self-assembled molecular architectures, films, and crystals.[18−20] Such enhanced optical chirality is also expected to provide structural insight into a wide variety of molecular aggregates whose structure cannot be evaluated by the usual X-ray diffraction study.

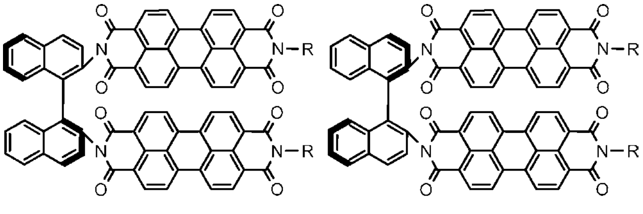


Figure 1. Structures of molecule **1** [R = C(C_6H_{13})$_2$].

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However, conventional measurements for optical chirality such as CD and CPL have been rather restricted to the transparent and homogeneous samples so far. Therefore, the reflection-mode or epi-illumination mode of CD and/or CPL is desired for evaluating the optical chirality of opaque samples. We here focus on CPL measurements with the epi-illumination optical system. CPL is usually given with the differential luminescence spectrum, $\Delta I = I_{\mathrm{left}} - I_{\mathrm{right}}$, between left- and right-handed circularly polarized light in the luminescence from chiral chromophores, and provides their optical chiralities in the excited state. The luminescent dissymmetry factor, g_{lum} ($= 2(I_{\mathrm{left}} - I_{\mathrm{right}})/(I_{\mathrm{left}} + I_{\mathrm{right}})$), is the characteristic parameter indicating optical chirality of a sample. To our best knowledge, no attempt has been performed to measure the CPL with the epi-illumination optical system, in which an illumination of excitation light and a detection of luminescence are performed on the same side of the samples. The authors are expecting significant advantages of the epi-illumination optics to measure CPL and determine g_{lum} of opaque samples such as molecularly aggregated colloidal solutions, microcrystalline samples, and living cells.

In the present study, we performed CPL measurements of concentrated opaque colloidal solution of chiral fluorescent molecules (*R*)- and (*S*)-**1** whose molecular structures are presented in Figure 1. Specific optical properties of **1**, including g_{lum} of approximately 3×10^{-3} at around 555 nm and fluorescence quantum yield of 88%, have already been reported previously.[21] All solutions were prepared by dissolving the powders of (*R*)-**1** and (*S*)-**1** in chloroform at various concentrations between 5×10^{-6} and 2×10^{-3} mol dm^{-3}.

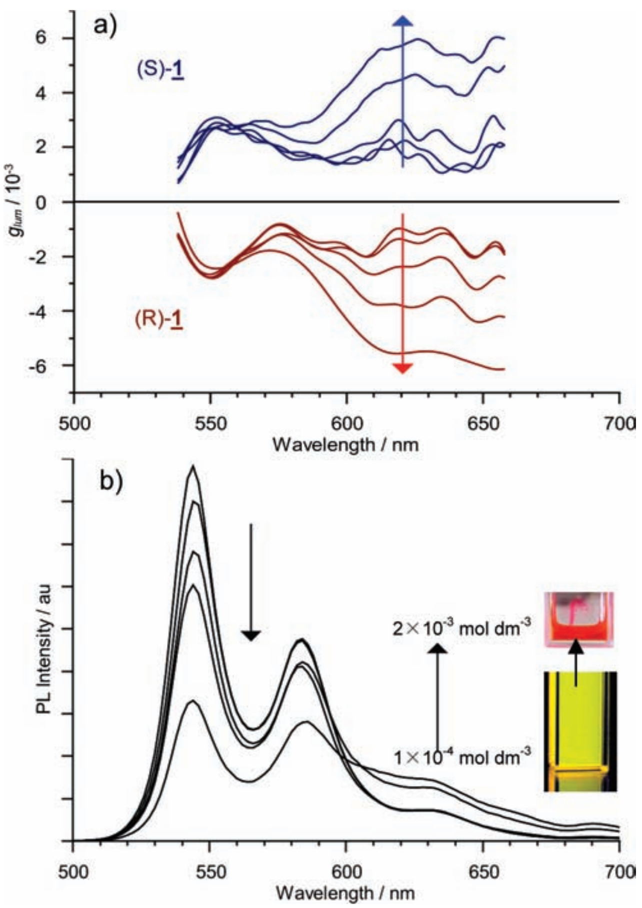

Figure 2. CPL and luminescent spectra of (*S*)-**1** and (*R*)-**1** with the concentration of 1×10^{-4}, 3×10^{-4}, 5×10^{-4}, 1×10^{-3}, and 2×10^{-3} mol dm^{-3}. (a) Mirror-image g_{lum} spectra and (b) photoluminescence spectra.

(*R*)- and (*S*)-**1** show good solubility in chloroform with a concentration lower than 2×10^{-4} mol dm^{-3}, in which well-defined absorption and emission spectra of individual molecules were observed. (*R*)- and (*S*)-**1** exhibited characteristic $\pi-\pi^*$ transition for the pair of perylene units with a substantial red shift from monoperylene derivatives and characteristic chiroptical dissymmetry in CPL and CD spectra, which originates from the intramolecular exciton coupling between the chromophores. They tend to form an opaque colloidal solution with a concentration higher than 2×10^{-4} mol dm^{-3}. Figure 2 shows photoluminescence and g_{lum} spectra of the chloroform solutions of (*R*)- and (*S*)-**1** of different concentrations ranging from 1×10^{-4} to 2×10^{-3} mol dm^{-3}. The spectra below 2×10^{-5} mol dm^{-3} showed no marked concentration dependence, and emission peaks were observed at 545 and 585 nm, which are typical for the emission profile of monomeric molecules with the characteristic vibrational structure.

In the g_{lum} spectra of the diluted solution (below 2×10^{-4} mol dm^{-3}), a broad peak was observed at 555 nm, and their characteristic wavelength dependence of the g_{lum} spectrum can be explained in terms of vibrational structure in the excited state.[11] The sample solution of concentration higher than 2×10^{-4} mol dm^{-3} becomes opaque, indicating the formation of aggregated particles.

Unfortunately, dynamic light scattering (DLS) measurements failed because of their large optical absorbance around detection length. In the concentrated solutions, both emission and CPL intensity considerably decreased in the wavelength shorter than 600 nm, while both increased in the wavelength range between 600 and 700 nm. With increase in the concentration above 3×10^{-4} mol dm^{-3}, the g_{lum} value also

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showed remarkable increase in the wavelength range from 580 to 660 nm and reached a twice-larger value than those of the homogeneous solution at around 550 nm. The precise CPL spectrum of the concentrated opaque solution can be evaluated with the specific epi-illumination optics first presented here. It should be noted that the g_{lum} value at 555 nm was maintained to be approximately 3×10^{-3} even at the higher concentration. This unchanged g_{lum} value suggests that the conformation and the degree of optical chirality of individual molecules are maintained in the highly concentration solution. The enhanced g_{lum} value in the highly concentrated solutions at the longer wavelength range suggests the growth of the organized structures with higher optical chirality and the increase of the number of those structures. The red-shifted emission band at around 630 nm is attributed to the intermolecular exciton coupling between the adjacent molecules in each aggregated particle. It has already been reported that the π-stacked structures of perylene tetracarboxy diimide derivatives show a significant red shift in the emission wavelength,[22] which cannot be expected for the intramolecular interaction of compound **1**. Since the excited state energy is possible to migrate within an aggregated particle to some extent, the emission from the monomeric **1** molecules should be suppressed, and that from the aggregated states of lower emission energy should be enhanced in the concentrated solutions. In that sense, the emission at 555 nm in the concentrated solution might be mainly attributed to the remaining monomeric molecules **1** whose emission intensity was decreased, but the g_{lum} value is maintained even in the highly concentrated solutions. It should be noted that there is a notable possibility of the artifact in the CPL measurements associated with the linearly polarized emission as has been suggested.[13] We measured the CPL of the colloidal solution of an achiral perylene derivative to verify the effect of linearly polarized emission on the CPL, and no CPL signal was observed (see Supporting Information). The trend of enhanced g_{lum} values, the mirror image of g_{lum} profiles of (*R*)- and (*S*)-**1** solution, and the stable g_{lum} value at 555 nm suggest that such an artifact does not cause serious problems in the present study.

Figure 3 summarizes the concentration dependence of the g_{lum} value at different wavelengths. The dissymmetry factor at 630 ± 10 nm increases nonlinearly with a log-concentration above 3×10^{-4} mol dm^{-3}. Since the g_{lum} is the characteristic value for the structure of the emissive excited states, the marked increase in the g_{lum} value should not be caused by a simple increase in population of the aggregated particles, but by the growth and the increase of the aggregated structure with the higher optical dissymmetry. To examine the enhancement, we would roughly assume that the red-shifted emission originates from the quasi-dimer of **1** molecules in the aggregated structures; that is, the obtained g_{lum} is the average value between g_{lum} of individual molecule **1** and the quasi-dimer. The concentration-dependent g_{lum} values are analyzed by the fitting function based on this rough assumption (see Supporting Information). The absolute g_{lum} value is of the dimer state and was evaluated to be 0.018 ± 0.004. Judging from these results, enhanced luminescent dissymmetry is expected in the bulk powder of **1**. Unfortunately, however, its emission intensity in the solid state was too weak to determine the g_{lum} value precisely. Futher enhancement of the g_{lum} value in polymer-dispersed samples is now under study and will be described elsewhere.

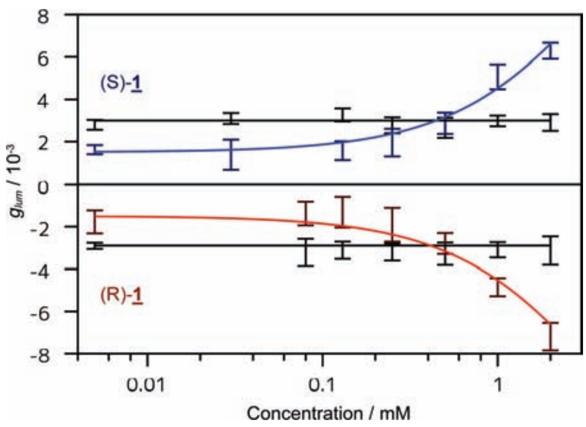

Figure 3. Concentration dependence of the g_{lum} value at 555 ± 5 nm (black) and 630 ± 10 nm (blue, (*S*)-**1**; red, (*R*)-**1**). The *x*-axis is logarithmic scale.

In conclusion, we evaluated the optical chirality of aggregates in high concentration and opaque solution using perylene derivative **1** by the epi-illumination CPL measurement system. While the chloroform solution of (*R*)- and (*S*)-**1** was condensed from 5×10^{-6} to 2×10^{-3} mol dm^{-3}, emission intensity from individual molecules at 555 nm decreased due to energy migration within aggregated particles, and the emission intensity at around 630 nm increased. In addition, while the g_{lum} value of monomer emission stayed constant, those from aggregates at around 630 nm markedly increased with a concentration above 3×10^{-4} mol dm^{-3}. These results indicate the change in local environment of the chromophores in the aggregated particles upon growth of aggregated structures with higher optical chirality. The present molecule seems to form aggregates with intermolecular interactions such as $\pi-\pi$ interaction, which would not give a precisely organized structure. In this sense, the present marked enhancement in the optical dissymmetry would also be observed in many other molecular aggregates of chiral molecules, and further enhanced CPL dissymmetry should be observed in well-organized fluorescent molecular systems which are currently being studied extensively.

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Supporting Information Available: Schematic diagram of the CPL measurement system, detailed spectral study of compounds **1** and achiral perylene derivative, fitting equation for the concentration dependent g_{lum}, and photoluminescence and CPL spectra of an achiral perylene derivative. This material is available free of charge via the Internet at http://pubs.acs.org.

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