Multicolor fluorescence from aggregated perylene

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Fluorescence properties of fluorescent organic molecules are often affected by molecular aggregation. This is mainly due to interaction between molecules in excited state, including excimer formation between the ground state molecule and an excited molecule. For systematic understanding of the effect of aggregation on fluorescence properties such as spectral shape, lifetime (τ_F) and quantum yield (Φ_F), perylene would be a suitable molecule. This is because various aggregate forms such as excimer in solution, two crystal polymorphs, highly doped polymer film and molten liquid can be prepared. Fig. 1 schematically shows such aggregate forms.

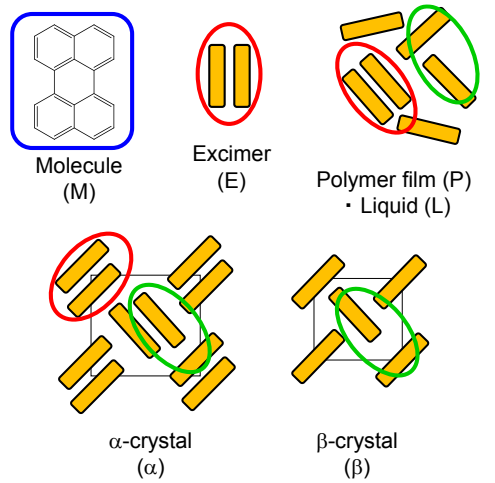

Fig. 1 Aggregated perylene

Fig. 2 summarizes fluorescence spectra of various aggregate forms of perylene, solution, crystal, polymer film and molten liquid. Blue fluorescence is observed from a dilute solution (M) with high Φ_F (0.95). At high concentrated solutions (> 10^{-3} M), orange fluorescence from an excimer can also be observed. From detail kinetic analysis of the fluorescence, Φ_F and τ_F of the excimer fluorescence were estimated to be 0.02 and 17.6 ns, respectively [1]. Accordingly, the radiative lifetime (τ_R) of the excimer is evaluated to be 880 ns ($\tau_R = \tau_F / \Phi_F$). This long τ_R indicates that the excimer fluorescence is optically forbidden transition caused by the sandwich configuration of the excimer.

Orange fluorescence is also observed in α-phase crystal, which has a dimer herring-bone structure. This is reasonable because structure of the dimeric pair in the crystal is similar to that of the sandwich configuration of the excimer in solution. Similarity of the electronic structure of these excimer has also been studied by using transient absorption spectroscopy [2]. Relative high Φ_F (0.3) could be obtained [3]. The large difference between the Φ_F values of the excimer in solution and in the α-phase crystal suggests that differences in the extent to which molecular motion is restricted lead to large differences in fluorescence properties.

Perylene has a different polymorph, β-phase crystal, which has a monomer herringbone structure. β-phase crystal shows green fluorescence and Φ_F and τ_F of the fluorescence were evaluated to be 0.6 and 12.3 ns, respectively [4]. Relative short τ_R (20 ns) indicates that it arises from the excimer in which the two molecules are in a nonparallel configuration, which is optically allowed transition.

It has been known that β-phase crystal undergoes to phase transition into α-phase crystal at around 140°C. This phase transition can be easily identified by observing fluorescence color from green to orange as shown in Fig. 3.

Green fluorescence is also observed in a polymer film doped with large amounts of perylene [5]. Again, this green fluorescence can be attributed to the excimer with the nonparallel configuration, which is formed by randomly oriented molecules in the polymer film.

For molten state of perylene, green fluorescence with low Φ_F (0.05) is observed and spectral shape was very broad. As shown in the bottom of Fig. 2, the spectra could be divided into two contributions, green (L_1) and orange (L_2) components. We conclude that the green fluorescence is emitted from the excimer with the nonparallel configuration populated by thermal activation of the excimer with the stable parallel configuration [6].

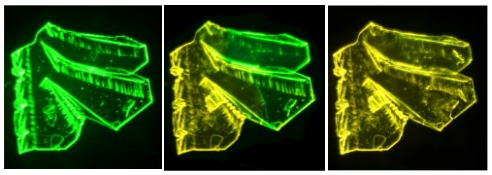

Fig. 3 Fluorescence color change during phase transition.

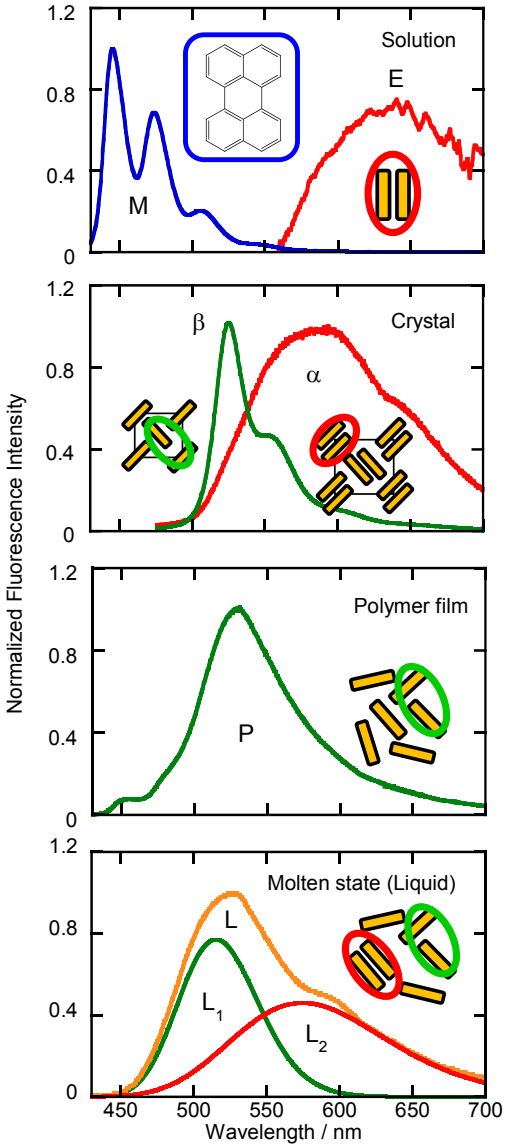

Fig. 2 Fluorescence spectra of perylene in various aggregate states.

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