Design of Metastable Solid $\pi$-Assemblies for Stimuli-Responsive Fluorescent Materials

Shiki Yagai,* Yu Hirai, Satoru Okamura and Yujiro Nakano

Department of Applied Chemistry and Biotechnology, Graduate School of Engineering
Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

Keywords : stimuli-responsive materials, photoluminescence, self-assembly, metastable phase

1. Introduction

Recently, organic, $\pi$-conjugated compounds that show tunable luminescent properties in the solid state have attracted considerable attention because they have the unique ability to tune their molecular physical or chemical properties via macroscopic stimulation [1-3]. A number of solid organic compounds that exhibit these mechano-responsive luminescent properties have been reported [4-12]. However, no rational designs have been proposed that impart these interesting functional properties to $\pi$-conjugated compounds. In this study, we demonstrate a rational strategy for the synthesis of mechano-responsive luminescent materials by designing metastable assemblies of functional $\pi$-conjugated compounds that can be transformed through mechanical stimulation to a more stable structure [13].

2. Experimental

We designed oligo($p$-phenylenevinylene) luminophore 1 with amphiphilic and dipolar characteristics. The amphiphilic property is imparted by didodecyl groups and tri(ethylene glycol) ester group, whereas dipolar property is given by amino and ester groups. The didodecylamino group at one end and a tri(ethylene glycol) ester group at the other end yields segregated solid structures consisting of hydrophobic and hydrophilic segments. Generally dipolar $\pi$-conjugated systems favor antiparallel stack due to attractive dipolar interactions (Fig. 1B). However, the segregated structures of 1 could force the dipolar $\pi$-conjugated systems to align in the same direction, thereby generating a conflict between the side-chain aggregation and dipolar stabilisation of the $\pi$-system (Fig. 1C). We expect that the resulting metastable assemblies undergoes mechano-responsive phase transition to more stable assemblies, thus exhibiting a change in its luminescent property.

Fig. 1 (A) Chemical structure of amphiphilic dipolar oligo($p$-phenylenevinylene) luminophore 1. (B) A reasonable packing structure of dipolar $\pi$-systems. (C) Schematic representation of the molecular packing in the various luminescent phases formed by the amphiphilic dipolar $\pi$-system.
3. Results and discussion

Luminophore 1 initially exhibited yellow photoluminescence in the aggregated state (Agg) after being drop cast onto a glass substrate (Fig. 2). When Agg was pressed, the luminescence became orange which was accompanied by the formation of liquid crystalline mesophase (LC). A mechanical stimulus (rubbing) applied to LC triggered a phase change to a crystalline material (Cryst) with green photoluminescence. Even when the rubbing area was small, the phase conversion spontaneously propagated across the entire sample area. An analysis of the structural and optical properties of the phases revealed that the variable luminescence originates from the alteration of the intermolecular interaction and the conformation of the \( \pi \)-conjugated luminophores upon the mechanical induction of phase transitions from aggregate to mesophase to crystal.

We obtained thin film aggregates (Agg) that exhibited yellow photoluminescence (fluorescence quantum yield, \( \Phi_F = 0.19 \)) after casting aqueous acetonitrile solutions of 1 (Fig. 2). Optical microscopy and polarized optical microscopy showed the formation of birefringent, sheet-like micro-objects (microsheets). After being pressed or gently ground, Agg became a waxy, fluidic, highly birefringent mesophase (LC). The Agg→LC phase transition was accompanied by a change in the photoluminescence from yellow to orange (\( \Phi_F = 0.25 \)). The mesomorphic phase LC could be reverted to Agg by exposure to acetonitrile vapour. To our surprise, vigorous grinding of LC triggered a crystallisation and a further change in the photoluminescence to yellowish green (Cryst, \( \Phi_F = 0.22 \)).

The PXRD measurements of three distinct phases of 1 indicated that the mechanical stimuli induced explicit transformations in the material’s molecular packing. The PXRD pattern of Agg was characterised by numerous reflections with a reciprocal spacing ratio 1:2:3:4:6:7 for 42.7 Å, suggesting the formation of multilamellar structures with a tilted molecular arrangement (Fig. 3). The in-plane molecular ordering in the Agg was further revealed by two-dimensional (2D) wide-angle X-ray diffraction (WAXD) analysis. Transmission mode 2D WAXD analysis using the X-ray beam perpendicular to the multilamellar structure showed diffractions assignable to an oblique lattice with lattice parameters \( a = 11.6 \) Å, \( b = 5.09 \) Å, and \( \gamma = 94^\circ \). The short lattice parameter \( b \) indicates the presence of cofacially \( \pi \)-conjugated moieties.

Fig. 2 Schematic representation of mechano-induced phase transition of 1.

Fig. 3 Packing structure of Agg phase of 1 revealed by PXRD analysis.
In contrast, the PXRD patterns of LC were fairly simple and were attributed to a lamellar mesophase with a 34.2-Å interlayer spacing. The absence of reflections for in-plane ordering may reflect the dynamic nature of the individual molecules in this phase; the π-conjugated chromophores were rotating around their long molecular axis. When LC was thermally generated on a glass substrate via slow cooling of the isotropic melt, a four-brush schlieren texture was observed by POM. For thinner LC samples prepared by sandwiching two glass substrates, a focal-conic fan texture was observed with extinction brushes that were inclined by 45° with respect to the crossed polarisers. These POM textures are typical of smectic C liquid crystalline mesophases with homeotropic (schlieren) and planar orientations (focal-conic fan), respectively. The 2D WAXD pattern of sheared LC showed no diffraction peaks in the small-angle region, suggesting the absence of in-plane molecular ordering.

The crystalline phase Cryst exhibited the most complicated diffraction pattern, which contained an intense diffraction at 38.6 Å and a number of weak diffractions indicative of crystallisation-induced, three-dimensional molecular order. Although a clear assignment of the diffraction pattern could not be made, the appearance of the major diffraction at around 40 Å suggests that the inclination of the molecules within the layers is also preserved upon crystallisation of LC.

The emission properties of the three distinct phases were studied via steady-state, and time-resolved fluorescence spectroscopy, and the fluorescence quantum yield (Φ_F), average fluorescence lifetime (τ_F), and radiative rate constant (k_F) are estimated (Fig. 4). We also measured the fluorescence properties of 1 dissolved in various solvents with different polarities and compared the values with those of the solid phase. All the solid phases displayed smaller Φ_F and k_F values compared to those in the solution phases; these smaller values can be attributed to possible energy transfer in the bulk materials. In contrast to the nearly \( \lambda_{\text{em-max}} \)-independence of \( \tau_F \) (1–2 ns) in the solution phases, the \( \tau_F \) of the solid phases exhibited a large dependence on \( \lambda_{\text{em-max}} \). This observation suggests that the geometrical freedom and/or intermolecular interaction of luminophores are responsible for the emission wavelength in the solid states.

The H-aggregated phase Agg had a maximum emission at 545 nm with a 3.24-ns lifetime and a radiative rate constant of \( 5.9 \times 10^7 \text{ s}^{-1} \). In general, H-type aggregation causes strong fluorescence quenching, as is typically observed for dipolar merocyanine dyes. If the largest Stokes shift (11681 cm\(^{-1}\)) among the three phases is taken into consideration, the fluorescence from Agg could arise from an imperfect H-type stacking with a rotational displacement around the stacking axis, thereby allowing the radiative decay to originate from the lower-lying exciton state.

![Fig. 4](A) UV/vis absorption (left axis) and fluorescence spectra (right axis, \( \lambda_{\text{ex}} = 400 \) nm) of Agg, LC and Cryst. The dotted curve represents the UV/vis spectrum of the acetonitrile solution (c = 1.0 × 10\(^{-3}\) M). (B) Fluorescence decay profiles of Agg, LC and Cryst with their fluorescence lifetimes (\( \tau_F \)).

The mesomorphic phase LC exhibited a more red-shifted emission that reached a maximum at 587 nm (Stokes shift = 8539 cm\(^{-1}\)) and was unchanged after transformation into isotropic phase Iso. The longest \( \tau_F \) but the same approximately \( k_F \) value as that of Agg indicates that the intermolecular energy transfer was suppressed in LC compared to in Agg because of the absence of the excitonic interaction between the luminophores. Importantly, the crystal of 2 involving distorted π-conjugated moieties exhibited an orange fluorescence with emission properties analogous to those of LC, except for a higher \( \phi_F \) (0.46). Therefore, similar geometric distortion of the π-conjugated systems occurs in this fluid phase’s excited state, which may facilitate intramolecular charge-transfer interactions to generate a relatively long-lived,
red-shifted emission. In contrast, the crystalline phase Cryst exhibited an emission maximum at the shortest wavelength (498 nm) with the smallest Stokes shift (6090 cm⁻¹) among the three phases. These emission properties are analogous to those of the toluene solution: the polar excited state was weakly stabilised by the solvent. Therefore, the bluish-green emission from Cryst could be derived from monomeric luminophores packed in a rigid crystalline phase.

The mechanically induced phase conversion from LC to Cryst was found to be caused by the nucleation and propagation of a crystalline phase in a mesomorphic state. After an edge of the LC sample was rubbed on a glass substrate, the crystallisation developed toward the surrounding area at approximately 1.0 mm/h at r.t. (Fig. 5A). The same phase transformation was triggered by touching a small “seed” of Cryst to LC, similar to crystal growth in solution. The phase conversion could be halted by heating the sample to 50 °C; this temperature is higher than the isotropisation temperature (Tiso) of LC (47 °C) but lower than that of Cryst (54 °C). The process was restarted when the sample was cooled to r.t.. Therefore, the phase conversion does not transmit to Iso. On the basis of these observations, we conclude that subjecting the metastable LC to strong mechanical stimulation generates a small nucleus of thermodynamically stable Cryst.

When the seeding experiment was performed for LC film prepared on a copier paper, the spontaneous crystallization randomly stopped (Fig. 5B). This observation implies that proper processing of LC phase on a smooth surface such as glass is prerequisite for the LC→Cryst transition. Probably, microscopically rough fibrous surface of the paper hampers the formation of a continuous liquid crystalline structure of LC.

The spontaneous phase transition from LC to Cryst was suppressed by the treatment with CF₃SO₃Li. When a LC film were immersed in an n-butanol solution of CF₃SO₃Li solution (~10 wt%) for a few seconds, the immersed area of the film continued to exhibit orange emission with almost the same fluorescence colours. Upon grinding or seeding this CF₃SO₃Li-treated LC film, no transition from LC to Cryst was observed. The concentration of CF₃SO₃Li is critical: the use of excess amount of CF₃SO₃Li resulted in the reconversion into Agg. The PXRD analysis revealed that LC was converted to more stable mesophase (Li⁺-LC) with higher melting temperature (120 °C) than that of LC (47 °C) by forming chelation complexes in the TEG moieties (Fig. 6A). The interlayer distance was extended from ca. 34 Å in LC to ca. 60 Å in Li⁺-LC; this change could be ascribed to the cancellation of the molecular tilt due to the loss of the interdigitation of the TEG moieties upon chelation with the salt. The cancellation of the molecular tilt was further supported by POM observation, which displayed a focal-conic fan texture with extinction brushes parallel to the polarisers.

![Fig. 5 (A) Photographs showing a spontaneous propagation of Cryst on LC on glass substrate under UV light. (B) Photographs showing a spontaneous propagation of Cryst on LC on a copier paper substrate under UV light.](image_url)
clearly discernible under room light or even under UV illumination (Fig. 6C) because the resulting Li+-LC has an emission maximum identical to that of LC. However, when small crystallites of Cryst were seeded onto several parts of the films, only the background LC was converted into Cryst after several hours. In contrast, Li+-LC in the imaged area remained unchanged, thereby revealing the printed images as orange emissions on the green-emitting background under UV illumination (Fig. 6D). Fluorescence microscopy observations revealed that the diffusion of the lithium salt on LC was suppressed within approximately 30 μm, which ensures a high resolution for imaging on the micrometer scale. Because the use of an aqueous solution of CF3SO3Li resulted in more unambiguous images, the selection of the solvent system for the inkjet procedure is important to minimise the diffusion of the salt within the mesophase.

We demonstrated that amphiphilic dipolar π-conjugated systems can form several metastable self-assembled phases with distinct molecular packing and emission properties. The designed metastable state was converted to a more stable packing state by the application of both weak and strong mechanical stimuli. The rationale for this behavior involves unfavorable parallel orientation of the molecular dipole moments that become kinetically trapped upon segregation between incompatible molecular segments. The present study provides one of the basic molecular strategies for the design of new mechano-responsive materials with various π-conjugated luminophores.

References