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Unusual emission properties of a triphenylene-based organogel system†

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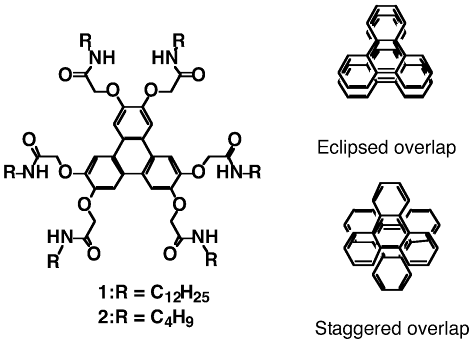
We have found that compound 1 forms organogels in appropriate organic solvents and the resultant gel phase exhibits unusual emission properties arising from the excimer formation.

Recently, a low molecular weight organogel system has offered a new methodology to assemble molecules into the supramolecular array using practical procedures.[1] Organogelators comprised of disk-shaped molecules have attracted increasing attention, because they are promising candidates for photo- and electrochemical materials.[2] Here, we designed compound **1** as a new organogelator, which has six long alkyl chains as tail groups and six amide groups as hydrogen-bonding sites for aligning the core aromatic units. Compound **1** formed organogels in appropriate organic solvents and the supramolecular structures were assessed by using UV-Vis, static and dynamic fluorescence, FT-IR, and XRD spectroscopies and SEM and POM microscopies. Very interestingly, we have found that compound **1** in the gel phase exhibits unusual emission properties arising from the excimer formation, which is novel and totally different from those of conventional triphenylene-based liquid crystals (LCs).[3]



1:R = $C_{12}H_{25}$
2:R = C_4H_9

Compounds **1** and **2** were synthesized from 2,3,6,7,10,11-hexahydroxytriphenylene and 2-bromo-*N*-alkylacetoamide. The products were identified by ^{1}H NMR and MALDI-TOF-MS spectral evidence and elemental analyses. The gelation test was carried out as follows. The powder of **1** or **2** was dispersed in solvent (13.4 wt/vol%: 10 mmol dm^{-3}), and the mixture was heated in a septum-capped test tube. By this treatment, we found that **1** is soluble in most solvents, however gelates some hydrocarbon solvents such as *n*-hexane, *n*-octane, cyclohexane and *p*-xylene. In contrast, **2** was not able to gelate such hydrocarbon solvents except cyclohexane (partially gelated). Compound **1** gave the relatively low critical gelation concentration, *e.g.*, *ca.* 3.0 mmol dm^{-3} (4.0 wt/vol%) for *n*-hexane and 2.0 mmol dm^{-3} (2.7 wt/vol%) for cyclohexane. The results indicate that **1** acts as an efficient and specific gelator for hydrocarbon solvents.

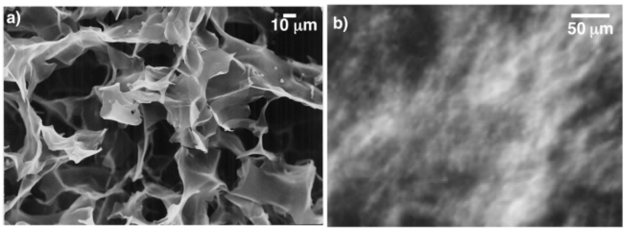


Fig. 1 (a) Scanning electron micrograph of a xerogel and (b) polarized optical microscope image (cross polarizers, 40×) of the cyclohexane gel **1**.

To obtain a visual image of the cyclohexane gel **1** ([**1**] = 5.0 mmol dm^{-3}) the xerogel sample was subjected to SEM analysis. The SEM image shows a three-dimensional sponge-like structure with average sheet thickness of 5 µm (Fig. 1 (a)). As shown in Fig. 1 (b), we found that the sheet shows a birefringent character, indicating that a high degree of molecular ordering structure is developed in these aggregates.

When we were preparing sols, gels and xerogels of **1** and **2**, we noticed that their emission colour changes very sensitively: that is, the cyclohexane gels of **1** and **2** showed the yellow colour and the greenish blue colour, respectively, whereas the cyclohexane sols of **1** and **2** both showed the blue colour (for the visual image see Fig. 2). The xerogels of **1** and **2** showed colours similar to those of the corresponding gels. We thus examined the origin of their novel colour changes by several spectroscopic methods.

X-ray powder diffraction (XRD) of a dried sample prepared from the cyclohexane gel of **1** (5.0 mmol dm^{-3}) showed the peaks, spacing of 36.1, 27.2, 4.4 and 3.6 Å (ESI: Fig. S1 (a))†. The low angle diffraction peaks (36.1 and 27.2 Å) are attributed to the intermolecular distance between columns. The peak pattern is characteristic of the lateral rectangular columnar phase of LC.[3] In the large angle range, we observed two broad

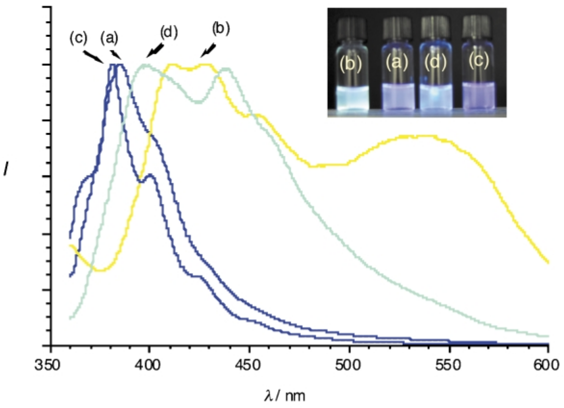


Fig. 2 Fluorescence spectra of (a) chloroform solution, [**1**] = 5.0 × 10^{-5} mol dm^{-3}, (b) cyclohexane gel, [**1**] = 5.0 × 10^{-5} mol dm^{-3}, (c) chloroform solution, [**2**] = 5.0 × 10^{-5} mol dm^{-3}, and (d) cyclohexane gel, [**2**] = 5.0 × 10^{-5} mol dm^{-3} (λ_{ex} = 350 nm). Inset photograph was taken for the sample excited by a UV lamp at λ_{ex} = 365 nm.

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† Electronic supplementary information (ESI) available: Characterization data for **1** and **2**. Fig. S1: UV-Vis spectra of **1** and **2**. Fig. S2: X-ray powder diffractograms of xerogels **1** and **2**. Fig. S3: Transient fluorescence spectra and fluorescence decays of cyclohexane gel **1**. See http://www.rsc.org/suppdata/cc/b3/b302415f/

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peaks around 2θ = 20 °(4.4 Å) which is a typical angle for diffraction from disordered alkyl chains and a peak around 2θ = 25 °(3.6 Å) which is attributed to the average distance between disks. In contrast, XRD of a dried sample prepared from the cyclohexane gel of **2** (5.0 mmol dm^{-3}) showed a very different pattern from that of **1**. It shows two sharp peaks, spacing of 19.9 and 3.6 Å, with a small peak, spacing of 11.0 Å (ESI: Fig. S1 (b))†. The low angle diffraction peak pattern is characteristic of the lateral hexagonal columnar phase of LC.[3] These results indicate that compounds **1** and **2** form the stacked aggregates (the average distance between disks = 3.6 Å) in cyclohexane, however, there is a large difference between their packing modes. Judging from the structural difference between **1** and **2**, one can presume that the van der Waals interaction among alkyl chains should have a significant effect on their packing modes.

To obtain more detailed information about the self-assembled structures, UV-Vis and FT-IR spectra were measured. The UV-Vis spectra of homogeneous chloroform solutions **1** and **2** were typical for triphenylene chromophores (ESI: Fig. S2)†.[3,4] In the cyclohexane gel **1**, the peak assignable to transition $S_0 \rightarrow S_4$ (276.0 nm in chloroform) shifted to shorter wavelength (259.5 nm) with *significant* peak broadening.[4] In contrast, the red shift (from 343.0 nm to 347.0 nm) was observed for transition $S_0 \rightarrow S_1$.[4] These results consistently support the view that the triphenylene moiety of **1** forms a stacked aggregate in the gel phase. In the cyclohexane gel phase of **2**, almost similar spectral change, but *slight* peak broadening compared to cyclohexane gel **1**, was observed. The UV-vis spectra of triphenylene-based LCs[3] are similar to that of the cyclohexane gel **2**, but not that of the cyclohexane gel **1**, indicating that the stacking mode of **1** in the gel phase is very novel. In the FT-IR spectra, the characteristic peaks appeared at 3278 and 1657 cm^{-1} for **1** and 3278 and 1656 cm^{-1} for **2**. These peaks are assignable to N–H and C=O stretching vibrations, respectively. These FT-IR spectral data suggest that the hydrogen-bonding interaction among the amide groups is operative in the aggregations of both **1** and **2**.

Fluorescence spectroscopy provides important information on the molecular organization of fluorophores, in the present system, triphenylene moieties.[5] Fig. 2 shows fluorescence spectra of **1** and **2**. All fluorescence spectra were obtained by excitation at 350.0 nm. As shown by (a) and (c) in Fig. 2, the fluorescence spectra of freshly prepared chloroform solutions show a similar spectral pattern. In the cyclohexane gel phases of **1** (b) and **2** (d), the fluorescence maxima shifted to longer wavelength. The red shift is due to a stabilization effect on the excited state in the aggregates.[4] In general, triphenylene derivatives in the LC phase show similar fluorescence spectra. The more noteworthy difference is a strong new emission peak at around 525.0 nm observed only for the cyclohexane gel **1**. The large shift and the peak broadening suggest that the new peak is attributed to *excimer emission*.[5] As far as we are aware, such an emission peak has never been observed for triphenylene-based LCs.[3] Furthermore, the new peak also appeared in the cast film evaporated from the cyclohexane gel, indicating that the stacked aggregation, which is the origin of the new peak, is firmly maintained even in the absence of solvents.

To estimate photochemical features of this emission process, we measured the transient fluorescence spectra and fluorescence decays. The fluorescence decay in chloroform solution was well fitted with a single exponential component yielding a lifetime of 6.9 ns (± 0.06 ns), which is consistent with that reported in the previous literature.[3] Fig. S3 (ESI)† shows the transient fluorescence spectra and fluorescence decays in the cyclohexane gel **1**. The fluorescence decays cannot be fitted with a single exponential component. This implies that the decays in the gel phase consist of a few different components. Interestingly, we found that the spectrum at the initial stage (after 7 ns) is mainly related to the emission around 400 nm. In contrast, the spectrum at the later stage (after 18 ns) is mainly related to the emission around 525 nm. The results thus establish that the component of the 525 nm emission has a longer lifetime than that of the 400 nm emission. It is known that this type of dynamic photochemical process is generally characteristic of excimer-forming fluorophores.[5] The finding supports the view that the band at around 525 nm is attributable to *excimer emission*.

These results demonstrate that, differently from those of the conventional triphenylene-based LC phase, the gel system would contain some new electron overlapping mode, which should be a unique molecular arrangement suitable to the excimer emission in the cyclohexane gel **1**. To yield the excimer emission among the triphenylene moieties, *it is indispensable to adopt the eclipsed overlaps of triphenylene moieties*.[5] In contrast, in the cyclohexane gel phase of **2** which did not show such excimer emission, the triphenylene moieties adopt the staggered or helical overlaps, which are basically the same as conventional triphenylene-based LC phase reported so far.[3] Hence, the hydrogen-bonding interaction among amide moieties as well as the van der Waals interaction among long alkyl chains would play an important role to construct the unique but unstable eclipsed overlaps of triphenylene moieties in the supramolecular assembly.

In conclusion, we have demonstrated that a triphenylene derivative, which is rationally designed for supramolecular assembly acts as an efficient gelator of some hydrocarbon solvents and yields excimer emission arising from unique eclipsed overlaps of triphenylene moieties. We believe, therefore, that the present organogel system, which differs entirely from the LC or crystal systems bearing conventional 'staggered' or 'helical' π-electron overlaps, has high and wide potential in the development of new photo- and electrochemical properties.

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