

# Strong fluorescence emission induced by supramolecular assembly and gelation: luminescent organogel from nonemissive oxadiazole-based benzene-1,3,5-tricarboxamide gelator†

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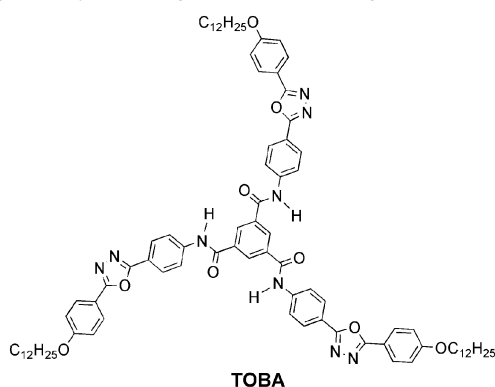
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**Supramolecular aggregation of a novel nonfluorescent gelator yields highly luminescent organogels in aprotic organic solvents through intermolecular hydrogen bonding, which is a key motif for both self-assembly and photophysical process control.**

Organogels are a new class of materials in supramolecular chemistry, composed of a self-assembled superstructure of low molecular weight organogelators through specific interactions and a large volume of organic liquid immobilized therein.<sup>1</sup> In addition to the academic importance, optical and electronic applications of organogels are being actively investigated particularly with  $\pi$ -electron conjugated organogelators<sup>2,3</sup> or anisotropic gel medium like liquid crystals.<sup>4</sup> As an attempt to obtain a new functional organogelator with potential photonics applications, we have designed and synthesized a benzene-1,3,5-tricarboxamide derivative (TOBA) with three 2,5-diphenyl[1,3,4]oxadiazole arms. Interestingly, TOBA showed an unusual optical property related to the supramolecular assembly and gelation: the monomer state is totally nonfluorescent, whereas hydrogen (H)-bonded ones are highly luminescent. This phenomenon is a novel supramolecular version of the aggregation-induced enhanced emission that is of growing interest in organic nanoscience.<sup>5</sup> Here we report the supramolecular assembly and gelation of TOBA in some organic solvents accompanied by a striking fluorescence change.



TOBA† is insoluble in nonpolar hydrocarbon solvents, alcohols and also in poor solvents for macromolecules such as diethyl ether, ethyl acetate, acetone, and acetonitrile. However, it showed robust gelating capabilities for THF, 1,4-dioxane, and most chlorinated solvents including chloroform, dichloroethane, and *o*-dichlorobenzene. In chloroform, for example, TOBA is still insoluble at room temp. but turns into a clear solution by heating vigorously to the boiling point in a capped vial. Upon cooling to room temp., immobile gels are readily formed within several minutes at TOBA contents as low as 0.05 wt%. Addition of a small drop of methanol

completely dissolved TOBA gels into clear solutions, suggesting that the intermolecular H bonding between amide groups is a key motif for the gel formation.

The X-ray diffractogram (XRD) of a TOBA xerogel obtained by drying a 0.1 wt% chloroform gel showed a distinct small-angle peak and a wide-angle broad halo.† Only one small-angle peak at  $2\theta \approx 2.2^\circ$  suggests that the gel contains one-dimensional columnar structures with a diameter of  $\sim 4.0$  nm. Moreover, the absence of higher order diffractions in the small-angle region means that this one-dimensional structure does not possess intercolumnar structural coherence. On considering the simulated size of the fully extended planar geometry of TOBA ( $\sim 6$  nm, MM+, HyperChem 5.0), it can be mentioned that disk-shaped TOBA molecules stack in the face-to-face manner through axial H bonding, similar to the stacking of other benzene-1,3,5-tricarboxamides.<sup>6</sup> The difference between column diameter and calculated molecular size is most probably due to the presence of long flexible dodecyl groups and the possible geometry change of the core scaffold by axial H bonding of amide groups.<sup>6b</sup> It is also noted from the wide-angle halo that rigid order is not promoted between TOBA molecules within a column and the average interdisk distance is 3.5–4.4 Å which is compatible with the values for H-bonded benzene-1,3,5-tricarboxamide strands.<sup>6b,c</sup> Actually, the xerogel sample showed no birefringence between the crossed polarizers. A scanning electron microscopy (SEM) image (Fig. 1a) shows the morphology of the TOBA xerogel that consists of intertwining bundles of fibrils, which further intertwine to form a large rope elongated over hundreds of micrometers. A transmission electron microscopy (TEM) image of a 0.005 wt% sample in chloroform (containing a small part of fibrillar precipitate) offers a closer look at the self-assembled structures of TOBA. As shown in Fig. 1b, highly elongated fibrillar aggregates with various diameters are occasionally fused and split to form a network with junction zones. The smallest aggregate with a diameter of  $\sim 5$  nm can be assigned as a single strand fibril, based on good accordance with the column diameter and the absence of intercolumnar structural coherence from the XRD result.

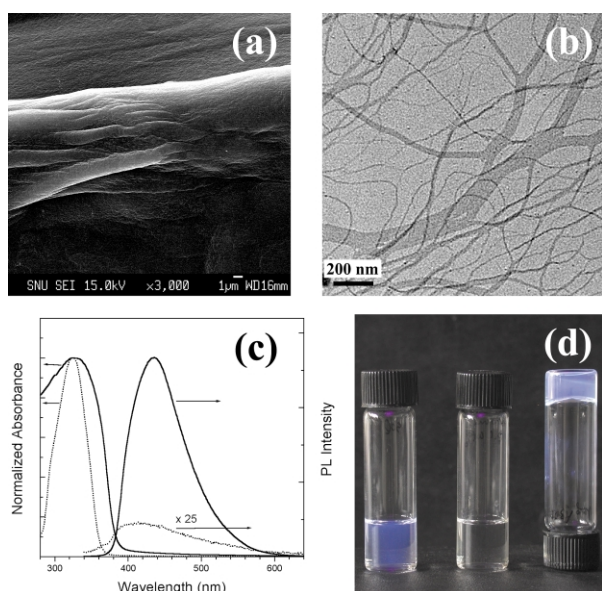
To study optical properties arising from the partly conjugated oxadiazole arms, the gel-state absorption spectrum of a xerogel cast sample was measured and compared with that of the monomer state in a H-bond-disturbing protic cosolvent (20  $\mu$ M in  $\text{CHCl}_3$ /methanol = 9/1 by volume).† Regardless of the thickness, xerogel samples gave a markedly broadened band relative to that of the monomer state, with almost the same peak position at 324 nm (Fig. 1c). This absorption broadening was also observed in a homogeneous chloroform solution (20  $\mu$ M),† suggesting that TOBA molecules readily self-assemble, even in extremely dilute aprotic conditions, to form a H-bonded aggregate.<sup>3</sup> Sources for spectral broadening are quite complex in the supramolecular system, possibly including intra- and interfibrillar chromophore interactions, spectral shifts in H-bonded complexes, and a geometrical distribution of monomer units within each self-assembled fibril.

More profound changes by self-assembly of TOBA were found in the photoluminescence (PL) spectra (Fig. 1c). When excited at 330 nm, the monomer state was almost nonfluorescent (the middle

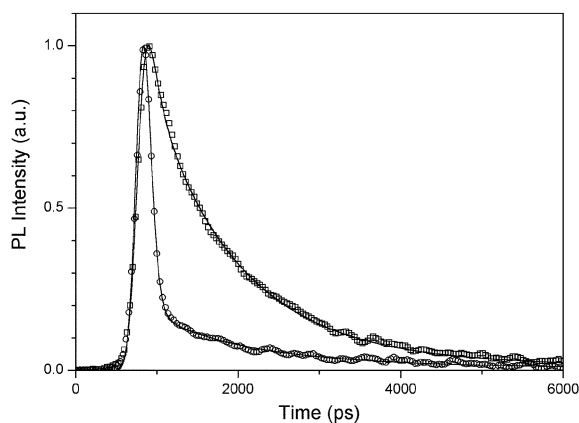
† Electronic Supplementary Information (ESI) available: Synthetic and experimental details, X-ray diffractograms, H-bonded aggregate-state absorption and emission spectra, and original data for Fig. 1c and 2. See <http://www.rsc.org/suppdata/cc/b3/b311648d/>

sample in Fig. 1d), while the chloroform gel of the same concentration emitted 100 times stronger fluorescence (on the right side of Fig. 1d). To the best of our knowledge, this PL enhancement of TOBA is unique and also the amplitude of modulation is the largest among the reported organogels showing PL changes usually arising from excimer formation.<sup>2e,f,3</sup> Judging from the similar blue luminescence observed from the H-bonded aggregate sample (on the left side of Fig. 1d), it is concluded that the luminescence of TOBA is turned on by supramolecular aggregation into H-bonded fibrils.<sup>†</sup>

To investigate the origin of the PL enhancement by H-bonded supramolecular aggregation, TOBA samples in different states were examined by a picosecond time-resolved fluorescence study.<sup>†</sup> As shown in Fig. 2,<sup>†</sup> a monomer sample (20  $\mu\text{M}$  in  $\text{CHCl}_3/\text{methanol} = 9/1$  by volume) without H bonds gave a very short-lived component of 90 ps,<sup>‡</sup> indicating that its lowest-excited singlet state ( $S_1$ ) undergoes a facile nonradiative relaxation process such as



**Fig. 1** SEM (a) and TEM (b) images of TOBA xerogel formed from 0.1 wt% chloroform gel (a) and precipitate sample from 0.005 wt% chloroform solution (b). (c) Absorption and PL spectra of TOBA : xerogel film (solid absorption), 20  $\mu\text{M}$  solution in  $\text{CHCl}_3/\text{methanol} = 9/1$  (dotted absorption), 0.1 wt% gel in  $\text{CHCl}_3$  (solid PL), and 0.1 wt% solution in  $\text{CHCl}_3/\text{methanol} = 9/1$  (dotted PL). (d) Fluorescence image of TOBA taken under 365 nm illumination: (from left) 20  $\mu\text{M}$  solution in  $\text{CHCl}_3$ , 0.1 wt% solution in  $\text{CHCl}_3/\text{methanol} = 9/1$ , and 0.1 wt% gel in  $\text{CHCl}_3$ .



**Fig. 2** Fluorescence kinetic profiles for monomer (○) and H-bonded aggregate (□) states of TOBA. Samples were excited at 386 nm and monitored above 420 nm. Solid lines are convoluted fits for the profiles.

intersystem crossing (ISC) or twisted intramolecular charge transfer, both of which are often observed in benzanilide derivatives.<sup>7</sup> In contrast, a H-bonded aggregate sample (20  $\mu\text{M}$  in  $\text{CHCl}_3$ ) gave mainly a long-lived component of 1.1 ns,<sup>‡</sup> inferring that such a nonradiative process is suppressed to elongate the lifetime of the  $S_1$  state. At this stage, the most plausible mechanism of nonradiative relaxation in the monomer state is suggested to be ISC on the basis of the observation of very long-lived transients (in microseconds) instead of any Stokes-shifted fluorescing ones. We also found from experiments and semiempirical quantum chemical calculations that the H bonding between TOBA molecules plays an important role in aggregation-induced luminescence generation by providing significant singlet–triplet splitting to reduce the rate of ISC. This is a totally different mechanism from those of other reported aggregation-induced emitting systems.<sup>5</sup> The semiempirical quantum chemical calculation and the full results studied by time-resolved fluorescence and transient-absorption spectroscopy will be reported elsewhere in detail.

In conclusion, a novel chromophoric but nonfluorescent benzene-1,3,5-tricarboxamide (TOBA) has been proven to be a powerful organogelator for some aprotic organic solvents. It has been demonstrated that the face-to-face intermolecular H bonding is a key motif for inducing strong fluorescence as well as supramolecular aggregation. It was inferred that the nonradiative relaxation process is inactivated in the H-bonded supramolecular assembly and gel states leading to the enhanced fluorescence emission.

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## Notes and references

<sup>‡</sup> Actually, the fluorescence decay of the monomer state has an additional long-lived component, speculated to come from a small contribution of a H-bonded state. In turn, the short-lived component (90 ps), presumably arising from a monomer state, also contributes to the fluorescence decay of the H-bonded aggregate state.

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