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Organogel based on *β*-diketone-boron difluoride without alkyl chain and H-bonding unit directed by optimally balanced π–π interaction†

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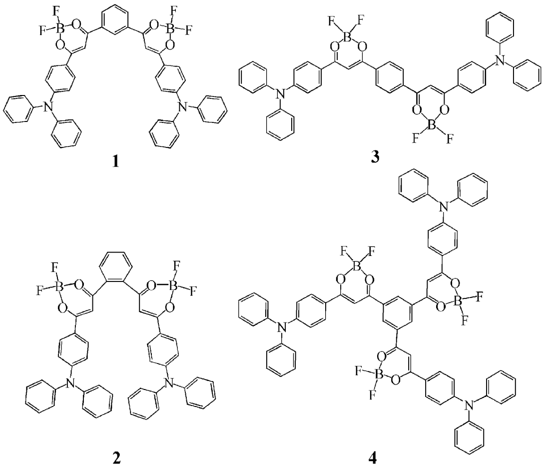
Rigid boomerang shaped triphenylamine functionalized bis-*β*-diketone-boron difluoride without alkyl chain and H-bonding unit exhibits good gelation ability in some mixed organic solvents directed by optimally balanced π–π interactions.

Recently, π-conjugated low molecular mass organic gelators (LMOGs), especially with rigid functional moieties, have attracted substantial interest from the viewpoint of acting as building blocks of supramolecular assemblies due to their unique optical and optoelectronic properties, such as multi-color emission, enhanced fluorescence, and sensing abilities.[1] In general, most of the π-gelators bear long carbon chains or steroidal groups, which prefer to balance their solubility and crystallization but might be unimportant in the functionality of the organogels. Therefore, the strategy to design rigid π-gelators without long carbon chains or steroidal groups is consistent with the current point of view of atom economy in green chemistry. Until recently, only a few such rigid LMOGs have been reported. Hisaki *et al.* have synthesized an organogelator derived from dehydrobenzoannulene with methyl ester groups.[2a] An *et al.* have designed a gelator of a trifluoromethyl based cyanostilbene.[2b] Ishi-I *et al.* have reported the gelators based on discotic hexaazatritriphenylene with six aromatic side chains.[2c] Our group have found that *tert*-butyl substituted carbazole derivatives can self-assemble into organogels directed by π–π interaction and H-bonding, and the tuning of the strength of π–π interaction appropriately is helpful for the fabrication of functional gels.[2d,e] Therefore, we deem that π-conjugated compounds without alkyl group and H-bonding unit would arrange into organogels driven by balanced π–π interactions.

In addition, *β*-diketone-boron difluoride compounds have been extensively studied in recent years due to their intriguing spectroscopic properties, such as large molar absorption coefficients, two-photon absorption activity, controllable emission wavelength and high fluorescence quantum yields.[3] Many applications have been found in sensors, OLED, and OFET, *etc.*[4] Therefore, the construction of an organogel based on *β*-diketone-boron difluoride will be significant not only in the concept of designing new π-gelators but also in extending gel-phase material with appealing photonic and electronic functionality. In this communication, we synthesized a series of new bis- and tri-*β*-diketone-boron difluorides linked to the benzene ring in different positions using triphenylamine as the terminal groups. This would induce increased solubility in organic solvents due to the umbrella conformation (Scheme 1). It was found that only the boomerang shaped compound **1**, which has two *β*-diketone-boron difluoride moieties linked to benzene in *meta*-positions, could form a stable gel with strong red emission in some mixed solvents.

The synthetic routes for **1–4** were shown in Scheme S1 (see ESI†). Claisen condensation between 1-(4-(diphenylamino)-phenyl) ethanone and the corresponding dimethyl phthalates or trimethyl benzene-1,3,5-tricarboxylate catalyzed by sodium hydride in dry THF afforded *β*-diketones,[5] which were complexed with $BF_3{\cdot}Et_2O$ in dry CH_2Cl_2 under an atmosphere of nitrogen to give **1–4** in the yields of 45–70%.[3c] Their molecular structures were characterized with FT-IR, ^1H NMR, elemental analysis, and MALDI/TOF mass spectroscopy, and the detailed synthetic methods and the characterizations were shown in the ESI.†

The gelation properties of **1–4** were tested in various solvents by means of the "stable to inversion of a test tube" method. It was found that **2–4** could not form gel in the tested solvents, such as cyclohexane, hexane, $CHCl_3$, THF, and some mixed solvents by typical heating-cooling processes (see Table S1 ESI†). As for **1**, it could not form a gel in THF, toluene, 1,2-dichloroethane or



Scheme 1 Molecular structures of compounds **1–4**.

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† Electronic supplementary information (ESI) available: Synthetic methods and characterization data for new compounds, gelation properties, fluorescence spectra, optimal geometry configurations. Experimental details for the structural determination of single crystal are presented in the cif file. CCDC 790916. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc03448g

chlorobenzene in which the solubility was too large. It could not gel the solvents of hexane, cyclohexane or ethanol due to poor solubility. In order to balance the precipitate and solubility a series of mixed solvents were employed. It was found that organogel **1** could be generated in $CHCl_3$/cyclohexane (v/v = 2/3), and some mixed solvents (see Table S1 ESI†). The critical gelation concentration (CGC) values were in the range of 1.9 and 2.7 mM. Moreover, we found that 1,2-dichloroethane/cyclohexane gel and chlorobenzene/hexane gel formed from **1** could be preserved for several weeks at room temperature, while $CHCl_3$/cyclohexane gel **1** could be stable for serval days. The above results suggested that the molecular conformation had a significant effect on the self-assembling properties of compounds **1–4**.[6] Accordingly, the optimal geometry configurations were calculated by the semi-empirical quantum mechanical method (AM1 force field). As shown in Fig. S1 (see ESI†), **1** possessed a boomerang shape in which the dihedral angle between the benzene rings connected to the *β*-diketone-boron difluoride groups was small so that the extended π-conjugated system favoured molecular self-assembly *via* π–π interaction.[7] This could be further confirmed by the change in the absorption spectrum of **1** in gel phase compared with that in solution. As shown in Fig. 1a, the absorption band of **1** appeared at 494 nm in dilute solution, which might be partly attributed to charge-transfer (CT) transitions due to its solvent dependence (see Fig. S5 ESI†).[8] It blue-shifted to 484 nm in the gel phase, meaning that the gelator molecules **1** might self-assemble into *H*-aggregates in the gel state.[9] As for **2**, the dihedral angle between the benzene rings connected to *β*-diketone-boron difluoride groups was much larger than that in **1** (see Fig. S2 ESI†) due to steric hindrance, leading to a smaller degree of π-conjugation in **2** than in **1**. For example, the absorption band of **2** was located at 473 nm (see Fig. S6 ESI†), which emerged in the high-energy region compared with **1**. Hence, it is understandable that **2** cannot form gels in organic solvents on account of its good solubility resulting from very weak or minimal π–π interactions (see Table S1 ESI†). On the contrary, the conjugated degree of **3** and **4** is larger than **1** (see Fig. S3 and S4 ESI†). On the one hand, the conjugated degree would be enhanced for the compounds with the functional groups in *para*-positions compared with those bearing the groups in *meta*-positions, so the absorption of **3** appeared at 522 nm (see Fig. S6 ESI†). On the other hand, the conjugated degree of **4** can be extended due to more *β*-diketone-boron difluoride units connected to *meta*-positions on the central benzene ring compared with **1**, and the absorption of **4** was located at 511 nm (see Fig. S6 ESI†). As a result, **3** and **4** preferred to precipitate from organic solvents because of strong π–π interactions. Thus, it is reasonable that the gelation ability of the rigid conjugated molecules could be tuned by the degree of conjugation. Moreover, the "boomerang" shape might be another factor, which might favour the gelation of **1**.[2a]

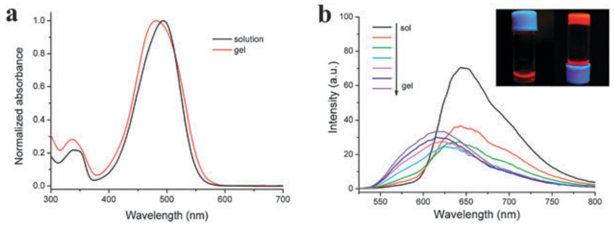

Fig. 1 (a) Normalized UV/Vis spectra of **1** in solution (black, 1.0 μM) and in gel (red) in $CHCl_3$/cyclohexane (v/v = 2/3, 3.5 mM). (b) Variational fluorescence spectra of **1** with cooling the hot solution to room temperature in $CHCl_3$/cyclohexane (v/v = 2/3, 3.5 mM) excited at 490 nm. The inset in (b) shows the photograph of **1** in sol (left) and gel (right) states illuminated by 365 nm light.

The fluorescence emission spectral changes of **1** from sol to gel phases were shown in Fig. 1b. It was clear that **1** gave an emission band at 646 nm in solution, which blue-shifted to 618 nm in gel state. In order to reveal the origin of the emission of **1**, the fluorescence spectra in solvents with different polarity were recorded (see Fig. S7 ESI†). The emission band was broadened and red-shifted significantly with increasing solvent polarity, for example, from 530 nm in cyclohexane to 642 nm in $CHCl_3$. Based on the evidence of a large Stokes shift (142 nm in $CHCl_3$) and the obvious broadening of the emission bands in polar solvents, we suggested that the gelator **1** gave a twisted intramolecular charge-transfer (TICT) emission.[8] In addition, from the plotting of the emission maximum energy as a function of the Lippert solvent polarity (see Fig. S9 ESI†), we could find a deviation of the emission maximum energy in cyclohexane from the linear relationship followed by those in other solvents. This means that a locally excited (LE) state was responsible for the emission in nonpolar solvents and the TICT state contributed to the emission in polar solvents.[10] Therefore we deduced that the blue-shift of the emission of **1** in $CHCl_3$/cyclohexane gel compared with that in solution could be attributed to the suppression of TICT since conformational rotation might be inhibited when the molecules are packed into an ordered superstructure in the gel phase.[11] Moreover, the concentration dependent fluorescence spectra of **1** in $CHCl_3$/cyclohexane (v/v = 2/3) further proved this point because the aggregation of **1** at high concentration could lead to a red-shift of the emission (see Fig. S10 ESI†), suggesting that π–π interaction was irrelevant to the blue-shift of the emission in the gel state. Meanwhile, the fact that the emission intensity of **1** decreased with increasing concentration, when the concentration was higher than 10 μM, illustrated that the lower emission intensity of gel **1** compared with that of the solution at the same concentration (Fig. 1b) were due to the formation of *H*-aggregates in a gel state.[12] Although the emission intensity of the gel was lower than that of the solution, the gel can still emit intense red light as shown in the inset in Fig. 1b as well as in the fluorescence microscopy (FM) image of the gel (see Fig. S8 ESI†).

The morphology of the organogel **1** was determined by SEM, TEM and AFM techniques. From the SEM image, we can find a three-dimensional network consisting of lots of entangled fibres (Fig. 2a). These fibre bundles are built up from thin fibrils, which intertwine around each other as shown in TEM image (Fig. 2b). The AFM image revealed that the thin fibrils were of 80–90 nm in width, 20–25 nm in height and several micrometres in length (Fig. 2c).

To illustrate how the molecules pack, we obtained the single crystal of **1** (see ESI †). Crystallographic analysis revealed that two molecules packed into *J*-aggregate in each unit cell (Fig. 3a), which was confirmed by the red-shift of the absorption of **1** the single crystal compared with that in dilute solution (see Fig. S12 ESI†). However, from the results of absorption

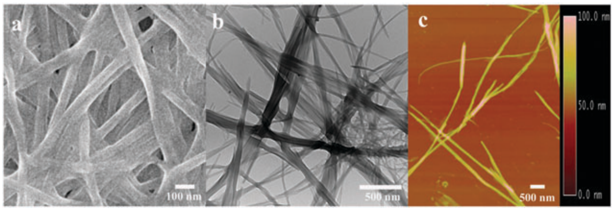

Fig. 2 SEM (a), TEM (b) and AFM (c) images for the dried gel **1** obtained from $CHCl_3$/cyclohexane (v/v = 2/3, 3.5 mM).

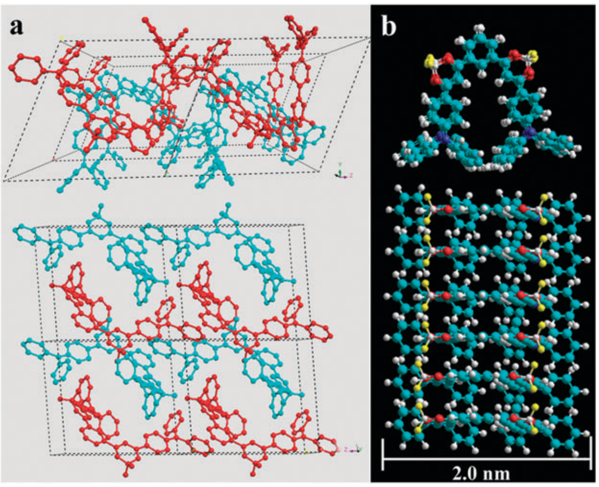

Fig. 3 (a) Schematic illustration of molecular conformations and packing diagrams of **1** in crystal structure. The hydrogen atoms are omitted. (b) Proposed molecular packing model with a period of 2.0 nm in gel **1** (top and side views).

and fluorescence spectra, the molecules are packed into *H*-aggregates in gel state. The XRD pattern of the dried gel of **1** obtained from $CHCl_3$/cyclohexane (v/v = 2/3, 3.5 mM) is given in Fig. S11†. One peak at *d*-spacing of 2.0 nm emerged in small-angle region. Combined with the length of 1.9 nm for molecule **1** calculated by the semi-empirical quantum mechanical method (AM1 force field, see Fig. S1 ESI†), the molecular packing model was proposed as shown in Fig. 3b, in which the bis-β-diketone-boron difluoride moieties formed *H*-aggregates with a period of 2.0 nm.

In conclusion, a series of rigid β-diketone-boron difluoride derivatives have been synthesized, and it is found that only the boomerang shaped compound **1** exhibits good gelation ability in some mixed solvents. It suggests that the balanced π–π interaction, which can be tuned by the molecular conjugation, can lead to the gel formation from rigid π-conjugated molecules without alkyl chain and H-bonding unit. This strategy provides a new perspective not only in designing new rigid π-gelators from the point of view of atomic economy but also in extending gel-phase material with appealing photonic and electronic functionality.

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