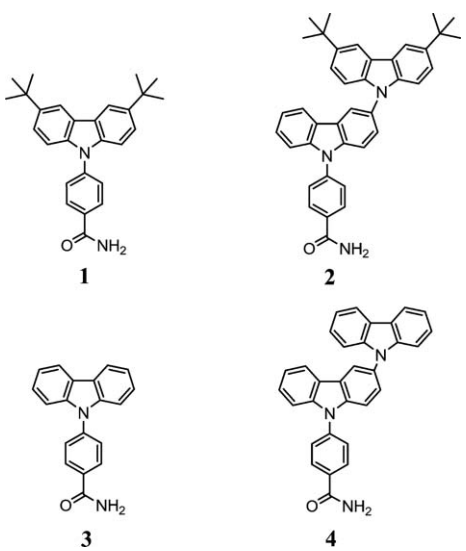
Novel carbazole-based organogels modulated by *tert*-butyl moieties†

Xinchun Yang, Ran Lu,* Tinghua Xu, Pengchong Xue, Xingliang Liu and Yingying Zhao

Received (in Cambridge, UK) 6th September 2007, Accepted 19th November 2007
First published as an Advance Article on the web 28th November 2007
DOI: 10.1039/b713734f

***tert*-Butyl groups can modulate the self-assembling properties of carbazole derivatives; organogel fibers with a bright blue emission are generated, directed by the cooperation of hydrogen bonding as well as π–π interactions.**

Recently, low molecular mass organogels have received much attention due to their unique supramolecular architectures and potential applications in optoelectronic devices, template syntheses, drug delivery and biomimetics systems.[1] A good number of organogelators have been designed, including derivatives of perylene, phenylene, porphyrin, tetrathiafulvalene, carbohydrates, amino acids, *etc.*,[2] and most of them bear long carbon chains or steroidal groups, favoring a balance between their solubility and crystallization.[3,4] Organogelators without steroidal units or long alkyl chains, in which π–π interactions have important effects on the self-assembling process, are rarely reported.[5] It is well known that carbazole is a typical π-conjugated system[6] and a promising candidate for optoelectronic materials due to its intense luminescence and electron efficiency.[7] In this Communication, we present two novel carbazole-based organogelators, 4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)benzamide (**1**) and 4-(3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)benzamide (**2**) (Scheme 1), containing two *tert*-butyl groups instead of long alkyl or steroidal chains, that can self-assemble into fibers with a strong fluorescent emission.



Scheme 1 The molecular structures of carbazole derivatives.

State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, P. R. China. E-mail: luran@mail.jlu.edu.cn; Fax: +86 431-88923907; Tel: +86 431-88499179

† Electronic supplementary information (ESI) available: Synthetic methods and characterization data for relevant compounds, SEM images, and FT-IR and XRD spectra. See DOI: 10.1039/b713734f

Compound **1** was synthesized *via* the hydrolyzing of 4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)benzonitrile in a yield of 62%, which itself was obtained from 4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-benzaldehyde.[7] Under similar conditions, compound **2** was obtained from 4-(3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9*H*-carbazol-9-yl)benzaldehyde, which could be prepared *via* a two-step Ullmann condensation reaction. In order to evaluate the effect of *tert*-butyl units on gelation behaviour, compounds **3** and **4**, whose molecular structures are similar to compounds **1** and **2**, respectively, were synthesized.

The gelation ability of **1–4** in various organic solvents was investigated by the "stable to inversion in a test tube" method.[8] As summarized in Table 1, we found that **1** showed robust gelation capabilities in some apolar alkane liquids, such as cyclohexane, hexane and petroleum ether. For example, a semi-transparent cyclohexane gel was formed less than two minutes after a hot solution was placed in room temperature surroundings with a concentration as low as 0.2 wt% (Fig. 1(a)). In benzene, toluene, chloroform, ethyl acetate, ethanol, THF and DMSO, compound **1** had a good solubility, while it precipitated from acetonitrile, so no organogel could be obtained in these solvents. On the other hand, compound **2** only formed an organogel in cyclohexane, and it required more than 5 h for gel formation under the same concentration as **1** (Fig. S2†). This indicates that compound **1** exhibits a better gelation ability than **2**. However, compounds **3** and **4**, with similar molecular structures to **1** and **2**, respectively, except for the absence of *tert*-butyl moieties, could not self-assemble into gels in organic liquids, indicating that the *tert*-butyl units play a key role in the formation of the organogels of **1** and **2**.

Table 1 Gelation test of **1**, **2**, **3** and **4** in organic solvents

Solvent	**1**[a]	**2**[a]	**3**[a]	**4**[a]
Cyclohexane	G	G	I	I
n-Hexane	G	P	I	I
Petroleum ether	G	I	I	I
Benzene	S	S	S	S
Toluene	S	S	S	S
THF	S	S	S	S
Chloroform	S	S	S	S
Dichloromethane	S	S	S	S
Acetonitrile	P	I	I	I
Ethyl acetate	S	S	S	S
Ethanol	S	S	S	S
Methanol	S	S	S	S
1-Octanol	S	S	S	S
DMF	S	S	S	S
DMSO	S	S	S	S

[a] Gelator = 0.2 wt%; G: stable gel; S: soluble; I: insoluble; P: precipitate.

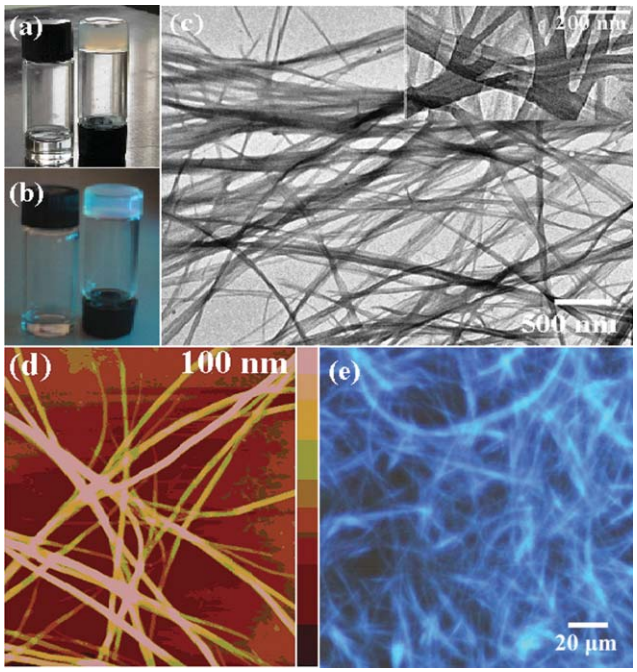


Fig. 1 (a) Daylight and (b) 256 nm fluorescence emission-irradiated photos of **1** in a cyclohexane solution at 70 °C (left vial) and gel at 25 °C (right vial) at a concentration of 0.2 wt%. (c) TEM image, (d) AFM height image (7.5 × 7.5 μm^2) and (e) fluorescence microscopy image of a dried gel of **1** obtained from cyclohexane.

The morphologies of the organogels were determined by SEM, TEM and AFM. The SEM images (Fig. S1†) of the cyclohexane gels of **1** and **2** show three-dimensional networks, consisting of entangled bundles of fibres. From the TEM image (Fig. 1(c)) of the cyclohexane gel of **1**, we find that a great deal of the long fibres consist of thin fibrils, which juxtapose or interwind with each other, preventing the flow of solvent molecules. As shown in Fig. 1(d), the AFM image of the cyclohexane gel of **1** shows that the fibre bundles are built up from thin fibrils of 40–50 nm width and several micrometers length. The AFM image of the cyclohexane gel of **2** (Fig. S2†) shows many thicker and shorter fibrils compared with those of the gel of **1**, which also suggests that compound **1** is a better organogelator than **2**.

In order to investigate the driving forces leading to the formation of the organogels, FT-IR and UV-vis absorption investigations were performed. Taking compound **1** as an example, Fig. S3† shows the IR spectrum of **1** in THF in a gel state. In THF solution, the vibration absorption bands arising from the free amide groups appear at 3448 (N–H bond stretching vibration band) and 1682 cm^{-1} (amide I band). For the cyclohexane gel of **1** (0.2 wt%), the band at 3448 cm^{-1} disappears, while new bands at 3379 and 3209 cm^{-1} are found, and the amide I band shifts from 1682 to 1651 cm^{-1}, suggesting the formation of hydrogen bonds between the amide groups in the gel phase.[8] Fortunately, in the mass spectrum of compound **1**, we found a strong peak at *m*/*z* = 797.4 (Fig. S13†), indicating the formation of a hydrogen-bonded dimer. In addition, a small drop of methanol destroys the gel completely into a transparent solution, which further confirms that hydrogen bonding has an effect on the formation of the organogel of **1**.[9] This is because a new peak at 1670 cm^{-1} appears in the IR spectrum of such a destroyed gel system, suggesting that some hydrogen bonds were cleaved (Fig. S4†).

The UV-vis absorption spectra of compounds **1** and **2** in cyclohexane solution and in their gel phase are shown in Fig. 2(a). Compared with the cyclohexane solution of **1** (1 × 10^{-6} M), in which the molecules may be considered to be in a monomeric state, the absorption bands of the cyclohexane gel of **1** are red-shifted from 296, 331 and 342 nm to 300 and 335 nm, accompanied by a broad shoulder at around 348 nm. A red shift of the absorption bands of the cyclohexane gel of **2** also took place, compared to the corresponding solution. These results indicate that π–π stacking interactions between the aromatic moieties play an important role in the formation of the gels, and might induce the formation of J-aggregation.[10]

To reveal how the molecules packed into fibrous self-assemblies, the XRD pattern of a dried gel of **1**, obtained from cyclohexane, was obtained (Fig. S5†). The small angle X-ray diffraction pattern gave two peaks at *d*-spacings of 2.41 and 1.20 nm, and exactly in the ratio 2 : 1, suggesting perfect lamellar organization with a period of 2.41 nm in the aggregates of the gel of **1**. The optimized CPK model showed that the molecular length of **1** was 1.25 nm. It is notable that the *d* value of 2.41 nm from the XRD pattern is approximately twice the evaluated molecular length obtained from the CPK model. We deduce that the molecules might form bimolecular lamellar packing in the gel phase,[11] which could be supported by the formation of a hydrogen-bonded dimer, as mentioned above. Therefore, we propose the molecular packing model in the gel phase shown in Fig. 3. Bimolecular layers are easily formed *via* hydrogen bonding, and the aromatic moieties are enforced by π–π interactions to adopt the J-aggregation mode, and further develop into 3-D superstructures.

Fluorescence spectra may provide important information on the molecular organization of fluorophores.[12] Fig. 2(b) shows the fluorescence emission spectra of **1** and **2** in cyclohexane solutions and gel phases, respectively. When excited at 297 nm, **1** showed two emission bands at 352 and 368 nm in dilute solution (fluorescence quantum yield, Φ_F = 0.37), and gave a broadened band at around 402 nm in the gel state (Φ_F = 0.75). Such red-shifting of the emission bands results in a bright blue emission from the gel phase, which could be confirmed by fluorescence microscopy upon illumination with UV light (Fig. 1(e)), while the emission of the solution was very weak (Fig. 1(b)). Compound **2** also showed a significant red-shift emission band at 456 nm in its gel phase compared to those in solution (373 and 388 nm). Such remarkable red-shifting of the emission could be ascribed to the formation of π-aggregations in the gel phase. Therefore, the

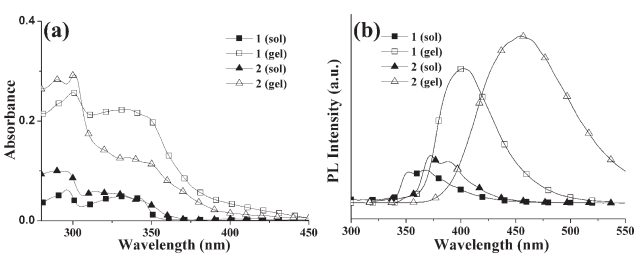


Fig. 2 (a) UV-vis absorption and (b) PL emission (excited at 297 nm) spectra of **1** and **2** in cyclohexane solution (1 × 10^{-6} M) and as gels (0.2 wt%).

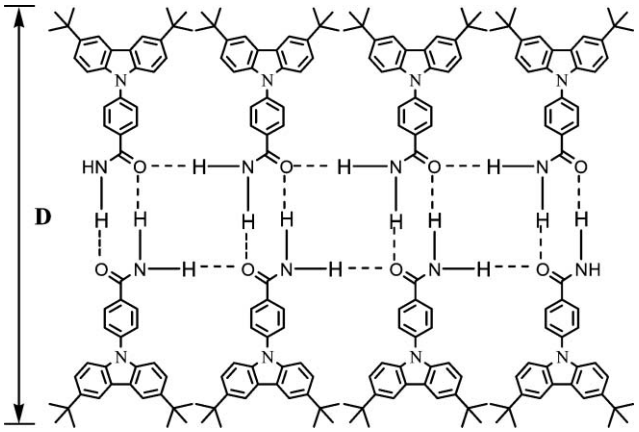


Fig. 3 The proposed biomolecular layer microstructure of **1** in an organogel.

fluorescence could be tuned by a reversible sol–gel transformation (Fig. S6†).

In conclusion, we have found that *tert*-butyl groups can modulate the gelation behavior of carbazole derivatives. The fluorescence of compound **1** can be tuned by a reversible sol–gel transformation, and an aggregation-induced bright blue emission can be observed in the gel phase. Such unique organogelators may have potential applications in sensor, switch and soft optical materials.

This work was financially supported by the National Natural Science Foundation of China (NNSFC, no. 20574027) and the Program for New Century Excellent Talents in University (NCET).

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