Synthesis and self-assembly of dichalcone substituted carbazole-based low-molecular mass organogel

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We report the synthesis and self-assembly of a new π-conjugated dichalcone substituted carbazole-based low molecular mass organogelator. It could form stable gels in most halogen-aromatic solvents. The transmission electron microscopy (TEM) images revealed that the gel formed fibrous structures with diameter of 50–100 nm, which consisted of several thinner fibers. The FT-IR, UV-vis and XRD results suggested that the H-bonds and π–π interactions were the main driving forces for the formation of the self-assembled gel, in which the U-shaped molecules were stacked into lamellar structures. The fluorescent spectra showed that the emission of the xerogel red-shifted markedly compared with the sol state, which resulted from the aggregation of the molecules.

Introduction

Gels are always thought to be generated through the initial assembly of the gelator molecules into fibrous nanostructures which then further organize into a three dimensional lattice, trapping the solvent within the free space of the network. The gels formed from small organic molecules in organic solvents are often called physical gels or supramolecular gels.[1] The following general guidelines for the design principles are accepted: i) the presence of strong self-complementary and unidirectional interactions to enforce one-dimensional self-assembly; ii) control of the interfacial energy between the fibers and solvent to counterpoise the solubility and crystallisation; and iii) some factor to induce fibers to form cross-linking network. In these low molecular mass organogel systems, the three-dimensional network is held together by noncovalent forces, such as hydrogen bonding, π–π stacking, electrostatic forces, and van der Waals interactions. Low molecular mass organogels have received considerable attention recently on account of their unique features and potential applications for new soft organic materials,[2] template synthesis,[3] drug delivery,[4] separations and biomimetics.[5]

Well-known organogelators including, for instance, certain derivatives of carbohydrates,[6,7] amino acids,[8,9] urea[10,11] and cholesterol[12–15] have been prepared and their self-assembling properties have been well studied. Nowadays, there has been increasing interest in the development of functional gels with π-conjugated systems due to their potential applications in various optoelectronic fields, such as enhanced charge transport, fluorescence and sensing abilities.[16] As an attempt to obtain a new functional organogelator with potential photonics applications, we have designed and synthesized a π-conjugated dichalcone substituted carbazole derivative **1**, which can form stable gels in halogen-aromatic solvents, and cannot be destroyed for several months. To the best of our knowledge such a carbazole-based organogel is the firs reported among the limited previous functional organogels.

Compound **1** was synthesized from dialdehyde carbazole **2** and 4-*N*-lauroylamino-acetophenone **4** (Scheme 1). It was found that **1** could form a stable gel in halogen-aromatic solvents *via* the lamellar stacking of the molecules with U-shaped configuration. The fluorescence emission of the xerogel **1** red-shifted markedly

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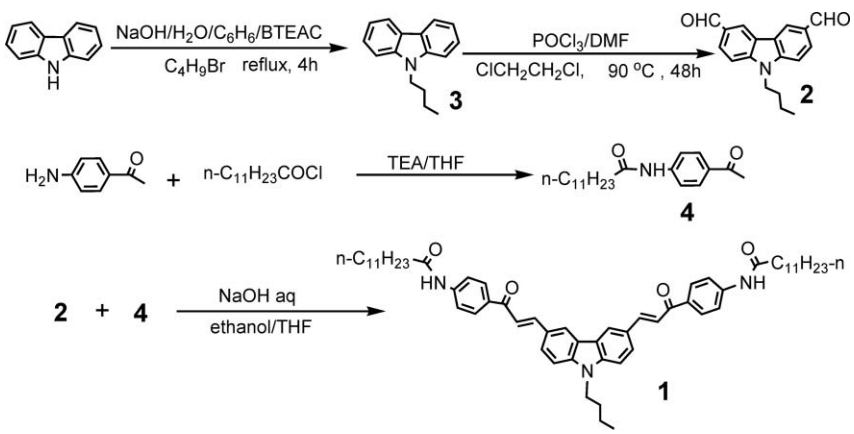


Scheme 1 The synthetic route for the dichalcone substituted carbazole-based organogel.

Table 1 Gelation test of **1** in different solvents

Entry	Solvent	Gelation[a]	Entry	Solvent	Gelation[a]
1	Toluene	I	5	Chlorobenzene	G
2	THF	S	6	Bromobenzene	G
3	Benzene	I	7	Acetonitrile	P
4	Xylene	G	8	Ethyl acetate	I

[a] Gelator = 2.0% (wt/vol); G, stable gel formed at room temperature; S, soluble; I, insoluble; P, precipitate.

compared with the sol state, which resulted from the aggregation of the molecules.

Results and discussion

The gelation ability of compound **1** was estimated in different solvents. As summarized in Table 1, we found that **1** could form stable gels in xylene and halogen-benzene, and the self-assembled gels were thermoreversible in these solvents, for example, the gelator was insoluble at room temperature, and then turned into a clear solution by heating to reflux, upon cooling to room temperature, the immobilized gels appeared. The morphologies of the gels were examined by TEM, which showed fibers with diameters of 50–100 nm and the fibers consisted of several thinner fibers with diameters of 15–20 nm (as shown in Fig. 1). In the previous gel system, hydrogen bonding-directed self-assembly is a well studied mechanism for the formation of the superstructure in an arranged system, whereas for compound **1**, π–π interactions may also play a key role on the formation of the organogel due to the extended π-conjugated moiety. To study the driving forces for the self-organization of organogelator **1**, FT-IR and UV-vis spectra were measured.

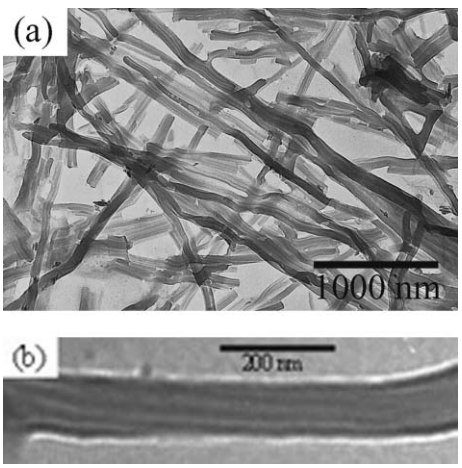


Fig. 1 TEM images of **1** in chlorobenzene gel at 2.0 (wt/vol)%. (a), the whole image; (b), the magnified image of a single fiber.

The FT-IR spectra (as shown in Fig. 2) for the xerogel **1** from chlorobenzene showed an absorption at 3355 cm^{-1} for the N–H stretching vibration, 1650 cm^{-1} for amide I and 1564 cm^{-1} for amide II, which suggested that weak hydrogen bonding between amide units was formed in the gel state.[17] Fig. 3 shows the UV-vis absorption of the gel and the corresponding dilute solution at the concentration of 1×10^{-6} M, in which the molecules may be considered as monomers. The absorption band of **1** red-shifted

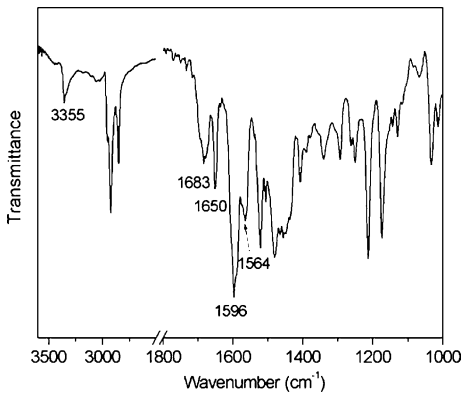


Fig. 2 The FT-IR spectra of xerogel **1** from chlorobenzene.

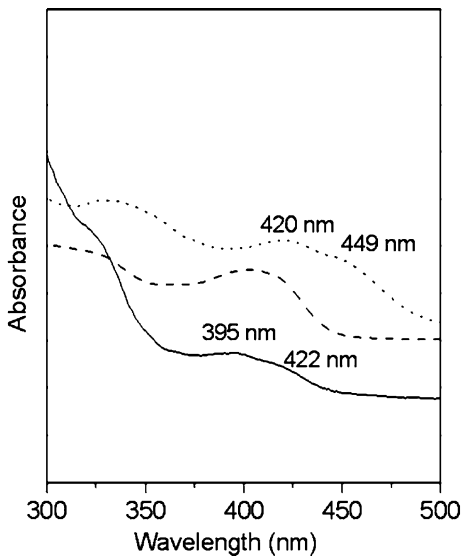


Fig. 3 The UV-vis spectra for the chlorobenzene solution at 10^{-6} M (the solid line), and at 10^{-5}M (the dashed line), and the chlorobenzene gel at 2.0 (wt/vol)% (the dotted line).

to 420 nm with a shoulder at 449 nm in the gel phase compared with that at 395 nm (with a shoulder at 422 nm) for the sol state. It illustrated that π–π interactions happened and J-aggregation was formed in the gel state.[18] Therefore, it indicated that the H-bonds and π–π interactions were the main driving forces for the formation of self-assembled gel.

To reveal how the molecules packed into the fibrous self-assemblies, XRD was investigated for the xerogel **1** obtained from chlorobenzene. In Fig. 4, the small-angle diffraction pattern of the xerogel showed two peaks at a d-spacing of 3.35 nm and 1.64 nm, which is close to $1 : \frac{1}{2}$, indicating the layered stacking of the molecules with a period of 3.35 nm. The optimized structure for the molecule by CPK molecular modeling showed that the molecule was present as a U-shaped configuration with a length of 3.4 nm, which was similar to the result from XRD. Therefore, we could conclude that the U-shaped molecules formed lamellar packing of J-aggregates in favor of H-bonding and π–π interactions. The stacking model is shown in Scheme 2 (edge-on view and top-on view) based on the above results and the optimized molecular structure.

Fluorescence spectra also provide important information on the molecular organization of fluorophores.[19] Fig. 5 shows the

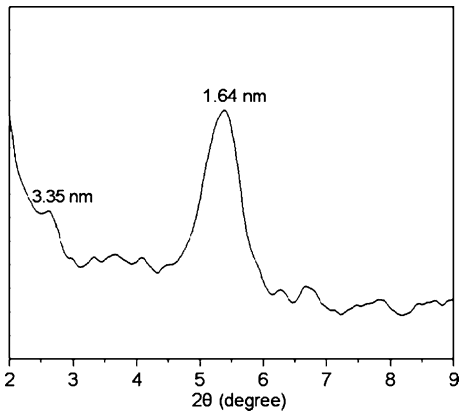
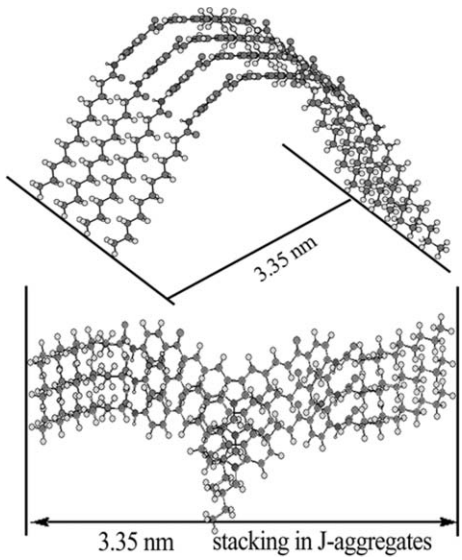


Fig. 4 The XRD diffraction of the xerogel **1** from chlorobenzene.



Scheme 2 The stacking model for **1** in the gel state based on the CPK optimized configuration from the edge-on view and top-on view, respectively.

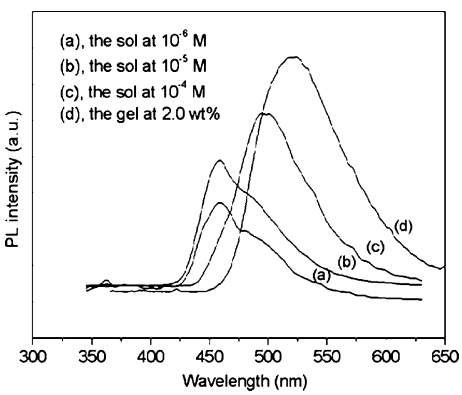


Fig. 5 The fluorescent spectra for **1** at different concentrations (a), 10^{-6} M; (b), 10^{-5} M; (c), 10^{-4} M; and (d), gel state at 2.0 (wt/vol)% in chlorobenzene.

fluorescence spectra of compound **1** in chlorobenzene solutions at different concentration and in the chlorobenzene gel state, respectively. When excited at 325 nm, compound **1** showed an emission peak at 460 nm under lower concentrations at 10^{-6} M and 10^{-5} M, and gave a red-shifted emission peak (around 500 nm) at 10^{-4} M and a more red-shifted emission peak (around 520 nm) in the gel state. The UV-vis spectra depending on the concentration in the Fig. 3 also showed a red-shift, which suggested that the molecules would aggregate when the concentration increased, and the large degree of π-aggregations induced the great red-shift of the fluorescence emission for the gel. Therefore, the fluorescence could be modulated by controlling the aggregated degree of the molecules, which may be useful for some sensors and some other optical devices.

Conclusion

A new organogelator with good gelated capability in halogen-aromatic solvents based on dichalcone substituted carbazole derivative was prepared. From the TEM images, FT-IR and UV-vis results, it suggested that the molecules stacked into a fibrous structure in favour of H-bonds and π–π interactions, and J-aggregates formed. Combining the XRD result and the optimized molecular configuration, the U-shaped molecules were stacked into lamellar structures. The fluorescent spectra indicated that the emission could red-shift obviously with increasing of the aggregated degree of molecules, which provided a simple way to modulate the emission band by controlling the aggregated degree of the molecules.

Experimental

The dry tetrahydrofuran (THF) was distilled after refluxing in Na–benzophenone for 3 h. The lauroyl chlorides were prepared according to the general procedure and were used without any further distillation. Other chemicals were used as received.

Measurements

^{1}H nuclear magnetic resonance (^{1}H NMR) spectra were determined with a Varian-300 EX spectrometer. UV-visible absorption spectra were recorded with a Shimadzu UV-2201 UV-visible spectrophotometer. Fourier transform infrared (FT-IR) spectra were measured at room temperature on a Nicolet Impact 410 FT-IR spectrometer. X-Ray diffraction (XRD) patterns were carried out on a Japan Rigaku D/max-γA instrument. XRD was equipped with graphite monochromatized Cu-Kα radiation ($\lambda = 1.5418$ Å), employing a scanning rate of 0.02° s^{-1} in the 2θ range from 0.7° to 10°. Transmission electron microscopy (TEM) was taken with a Hitachi modes H600A-2 apparatus by wiping the samples onto a 200-mesh copper grid followed by naturally evaporating the solvent. Fluorescence spectra were measured on a Japan Hitachi 850 fluorescence spectrophotometer at room temperature.

Synthesis of compounds

4-*N*-Lauroylamino-acetophenone (4). A mixture of 4-amino-acetophenone (1.62 g, 0.012 mol) and triethylamine (4 mL, 0.03 mol) in dry THF (10 mL) was added dropwise to a solution of lauroyl chloride (2.6 g, 0.012 mol) in THF (10 mL) at 0 °C. After stirring overnight at room temperature the solution was poured into water (100 mL), and the precipitate was filtered and recrystallized in ethanol. Yield: 3.2 g, 85%. Mp 109.0–110.0 °C. FT-IR (cm^{-1}): 3324, 2917, 2848, 1678, 1658, 1606, 1536;

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 0.87 (t, 3H, CH_3), 1.26 (m, 16H, CH_2), 1.73 (m, 2H, CH_2), 2.58 (s, 3H, $COCH_3$), 2.90 (m, 2H, CH_2), 7.63 (d, 2H, ArH), 7.94 (d, 2H, ArH).

9-Butylcarbazole (3). Carbazole (6 g, 0.036 mol), benzyltriethylammonium chloride (BTEAC, 0.2 g), and 1-bromobutane were dissolved in benzene (20 mL), then NaOH aqueous (50%, 10 mL) was added, the obtained mixture was stirred and refluxed for 3 h. Then the solvent benzene was removed under the reduced pressure, and water (200 mL) was added to the flask and a white solid formed. The white solid was collected by filtration and washed with water. The solid was recrystallized from a mixture of ethanol and water and gave white needle crystals. Yield: 6.4 g, 80%. Mp 58.0–62.0 °C. IR (cm^{-1}): 3043, 2972, 2953, 2929, 2869, 2858, 1625, 1592, 1483, and 1378. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 0.95 (t, 3 H, CH_3), 1.39 (m, 2 H, CH_2), 1.86 (m, 2 H, CH_2), 4.31 (t, 2 H, NCH_2), 7.19–7.48 (m, 6 H, ArH), 8.00 (d, 2 H, ArH).

9-Butyl-3,6-diformylcarbazole (2). A solution of *N*,*N*-dimethylformamide (12.5 g, 0.17 mol) in 1,2-dichloroethane (10 mL) was added dropwise to phosphoryl chloride (21.9 g, 0.145 mol) at 0 °C. Then the reaction mixture was heated to 35 °C, and 9-butylcarbazole **3** (2.23 g, 0.01 mol) was added. After being stirred for 48 h at 90 °C, the mixture was poured into water (200 mL), extracted with chloroform, and the organic layer was washed with water, dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate–hexane, 1 : 3 as an eluent). Yield: 0.98 g, 35%. Mp 153.0–156.0 °C. IR (KBr): 2806, 2722 (mC–H stretching), 1685 (mC=O aromatic aldehyde), 1592, 1487 (mC=C aromatic stretching) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 0.96 (t, CH_3), 1.35–1.70 (m, 4H, CH_2), 4.25 (t, 2H, NCH_2), 7.40 (d, 2H, ArH), 7.85 (d, 2H, ArH), 8.36 (s, 2H, ArH), 9.98 (s, 2H, CHO).

9-Butyl-3,6-di[3-(4-dodecanoylamino-phenyl)-3-oxo-propenyl]-carbazole (1). A mixed solution of THF–ethanol (10 mL–30 mL) containing 9-butylcarbazole-3,6-dicarbaldehyde **2**(0.56 g, 0.002 mol), 4-*N*-lauroylamino-acetophenone (1.4 g, 0.0044 mol), and NaOH aq. (3 g, 25 mL) was reacted at 70 °C for 6 h, and then most of the solvent was removed under the reduced pressure and orange solid was formed. The orange solid was collected by filtration and washed with water. The solid was purified by silica gel column chromatography (ethyl acetate–hexane, 1 : 1 as an eluent). Yield: 0.57 g, 35%. Mp 238.0–240.0 °C. IR (KBr): ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 0.87 (t, 6H, CH_3), 0.96 (t, 3H, CH_3), 1.25–1.42 (m, 34H, CH_2), 1.74–1.80 (m, 6H, CH_2), 2.45 (t, 4H, CH_2), 4.30 (t, 2H, CH_2), 7.40 (d, 2H, ArH), 7.62 (d, 2H, CH=CH), 7.67 (s, 2H, ArH), 7.73 (d, 4H, ArH), 7.76 (d, 2H, ArH), 8.08 (d, 4H, ArH), 8.12 (d, 2H, CH=CH).

Gelation test in solvents

The weighed gelator **1** in solvents was heated in sealed test tubes in an oil bath until the solid was dissolved. After the solution was allowed to stand at room temperature for 5 h, the state of the mixture was evaluated by the "stable to inversion of a test tube" method.[20]

Acknowledgements

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