Nanofibers of asymmetrically substituted bisphenazine through organogelation and their acid sensing properties†

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This paper reports the formation of an organogel of an asymmetric bisphenazine through the growth of one-dimensional nanofibers *via* a coopertive interplay of π–π interaction, hydrogen bonding, and van der Waals interaction and the colorimetric acid sensing property of the nanofibers.

Organogels, a result of trapping solvent in a three-dimensional (3-D) network of one-dimensionally (1-D) grown nanofibers of low molecular weight organogelators (LMOGs), have shown a significant advancement in recent years.[1] Of particular interest have been functional organogels which possess specific utilities such as acid[2] and fluoride sensitivity,[3] energy transfer,[4] color[5] and photoluminescence switching,[6] electrical conduction,[7] drug entrapment,[8] *etc.* π-Conjugated LMOGs have been useful in generating functional organogels owing to their unique optoelectronic properties. As a result, there have been a number of reports regarding π-conjugated LMOGs such as acene,[9] oligo(*p*-phenylenevinylene),[4a,d–g,10] oligo(*p*-phenyleneethynylene),[11] phthalocyanine,[12] phenazine,[2a] perylenebisimide derivatives,[4b] *etc.* Heteroaromatics containing electron-withdrawing imine nitrogens such as quinoline, quinoxaline, anthrazoline, *etc.* have interesting electro-optical properties, *e.g.*, electron transporting abilities in organic light-emitting diodes (OLEDs).[13] However, research on organogelators based on these attractive fused heteroaromatics have not yet been very active.[2a–c] Therefore, we aim to develop a new functional π-conjugated LMOG based on asymmetrically substituted bisphenazine.

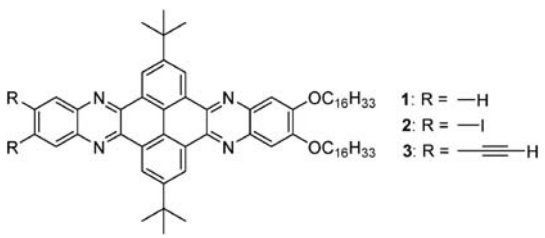
Bisphenazine has demonstrated its self-assembling ability and potential to be a useful n-type semiconductor.[14] Utilization of this interesting moiety requires convenient chemical modification. To that end, we have developed the design strategy and synthetic routes to prepare asymmetrically substituted bisphenazines **1–3** (Scheme 1) such that facile structural tuning to control the assembling property can be possible.

The gelation ability of the compounds was tested by dissolving them in a variety of solvents of varying polarity with gentle heating. After cooling to room temperature, the vial was inverted and the mixture was considered gelled if no flow was observed (Fig. 1). Interestingly, only compound **3** was found to gel in select solvents such as decane, hexadecane and 1,1,1-trichloroethane (TCE). Compounds **1** and **2** in the same solvents showed either precipitation or partial gelation, at best.

The critical gel concentration (CGC) was the highest in TCE (10 mM), while gelation in decane and hexadecane were observed at significantly lower concentrations, 1.3 mM and 1.0 mM, respectively. The results indicate that compound **3** has higher solubility in TCE than in decane or hexadecane. Meanwhile, although the solubility of the whole molecule is lower in decane and hexadecane, the local interaction of the hexadecyloxy side groups with the linear hydrocarbon solvents may be more effective than TCE due to their structural similarity. The gelling temperature (T_{gel}) of compound **3** at CGC, determined by the 'inverse flow' method,[15] were 44 °C (TCE), 77 °C (decane), and 116 °C (hexadecane). Lower T_{gel} of the TCE gel can be in part attributed to the lower boiling point of the solvent. The decane and hexadecane gels were stable for over 1 month at ambient conditions, however a proper measurement of the stability of the TCE gel was difficult due to the volatility of the solvent.

SEM images of xerogels from decane and TCE gels confirmed that the gelation was indeed induced by the formation of a 3-D network of endless 1-D nanofibers. The decane gel (Fig. 2(a)) was composed of homogeneous, interwoven, unusual belt-shaped fiber bundles. Within these bundles, individual fibers vary slightly in width from *ca.* 50 nm. In the case of the TCE gel, similar belt-shaped fibers were observed with additional globules of dense fibers (Fig. 2(b)). Fibers in the globules showed smaller widths starting from *ca.* 15 nm. It is possible that the higher concentration and the fast evaporation of the solvent of the TCE gel caused less lateral growth than in the decane gel.

The mechanism behind only compound **3** forming stable gels was closely investigated with UV-Vis, XRD, and FT-IR spectroscopy. Firstly, the possible formation of a *J*-aggregate in the gel state was substantiated by a red-shift in the absorption maxima at 402 and 422 nm in $CHCl_3$ solution to 410 and 433 nm in the decane gel, respectively, and especially by the appearance of a new sharp peak at 462 nm which was seen as a shoulder at 447 nm in the solution state (Fig. 3(a)). Furthermore, a *d*-spacing



Scheme 1 Structures of asymmetric bisphenazines.

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† Electronic supplementary information (ESI) available: Synthetic procedures, gelling abilities in a variety of solvents, additional SEM images, acid sensing experiment, picture of color change of xerogel of **3** upon the exposure to TFA vapor. See DOI: 10.1039/b806084c

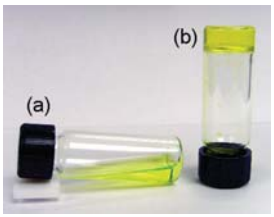

Fig. 1 Pictures of (a) chloroform solution and (b) organogel of compound **3** in decane (1.3 mM).

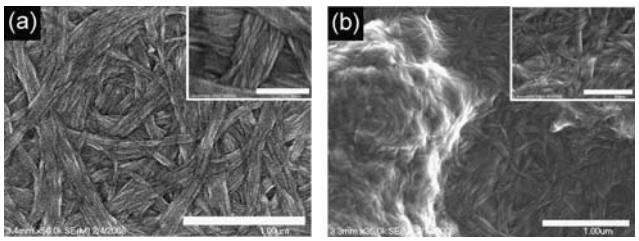

Fig. 2 SEM images of the xerogel of compound **3**: (a) from decane gel (1.3 mM), scale bar: 1 μm (inset: 300 nm), (b) from TCE gel (10 mM), scale bar: 1 μm (inset: 500 nm).

of 3.73 Å similar to the typical π–π stacking distance (3.5 Å), was observed with X-ray diffraction, supporting that π–π stacking drives gel formation. A key element that only compound **3** enabled gel formation, revealed by FT-IR spectroscopy, was that the terminal acetylene moieties were heavily involved in hydrogen bonding (Fig. 3(b)). In CCl_4 solution, the free terminal acetylene showed only one characteristic acetylenic C–H stretching at 3311 cm^{-1}. Meanwhile, the xerogel showed two acetylenic C–H stretching vibrations, one with stronger intensity at 3247 cm^{-1} and another at 3318 cm^{-1}. The remarkable low frequency shift to 3247 cm^{-1} (Δ = 64 cm^{-1}) is reminiscent of a previous observation for hydrogen-bonded acetylene with electronegative atoms.[16] This result implies that the intermolecular interaction of terminal acetylenes with nitrogens in the neighboring bisphenazine ring is predominant in the xerogel. With respect to the peak at 3318 cm^{-1}, when one of two acetylenes in compound **3** is engaged in hydrogen bonding, it is reasonable to assess that the remaining acetylene experiences an electron-withdrawing substituent effect[17] due to the *o*-disubstitution nature causing a shift to a higher wavenumber.

This result strongly supports the fact that only compound **3** is an effective gelator since a hydrogen bonding motif is absent

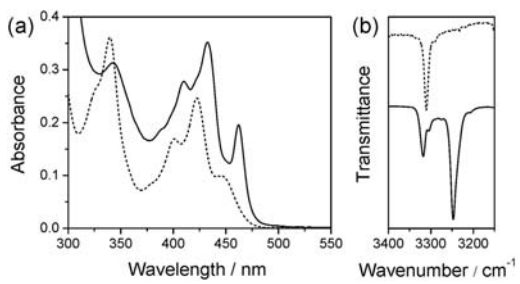

Fig. 3 (a) UV-Vis spectra of chloroform solution (dotted line) and organogel in decane (solid line) of compound **3**. (b) Transmission FT-IR spectra of CCl_4 solution (dotted line) and xerogel of compound **3** (solid line).

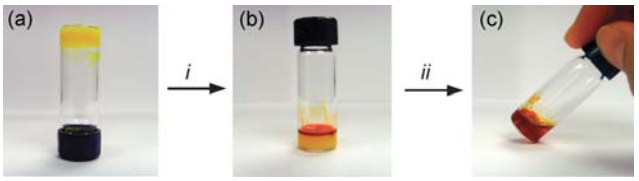

Fig. 4 Pictures of (a) TCE gel of **3**, (b) immediately after the addition of one drop of TFA on TCE gel of **3**, and (c) disrupted gel by TFA (*i*; addition of one drop of TFA, *ii*; standing for 4 h).

in compounds **1** and **2**. The existence of hydrogen bonding was further manifested by the disruption of the gel upon the addition of a drop of trifluoroacetic acid (TFA) (Fig. 4). It can be deduced that TFA intercalates the hydrogen bonding between the nitrogen and acetylene, thus breaking the gel.

As shown in Fig. 4, there was a significant color change from yellow to red upon the addition of TFA. This result implied that the nanofibers of **3** could be a potential colorimetric acid sensor. Therefore, we first tested such function in solution. The change in the absorption behavior was monitored with UV-Vis spectroscopy immediately after TFA was added to the chloroform solution of compound **3**. The absorbances at 422 and 402 nm decreased gradually while new absorptions at 493 and 435 nm increased, and eventually an absorption at 482 nm with a prominent shoulder at *ca.* 530 nm became dominant as the amount of TFA increased (Fig. 5(a)). However, it required a substantial excess of the acid to saturate the spectral change. Note that there was no further spectral change even after overnight standing, indicating that the process is thermodynamic rather than kinetic.

Interestingly, the xerogel of compound **3** showed a drastically enhanced response. Significant spectral change was observed within a few seconds after exposing the xerogel to the vapor of TFA (Fig. 5(b)). This enhanced response can be attributed to a massive surface area created by the fibrous network of the xerogel for the TFA to react. We also tested the sensing ability of the xerogel film to H_2SO_4 and HCl. Only HCl caused a color change upon exposure. No visible color change was detected upon exposure to H_2SO_4 even after 24 h. This can be explained by the low volatility of H_2SO_4 which would make it difficult to obtain a saturated atmosphere of acid vapors, causing no recognition to occur. As a control, we conducted the same experiment with the cast film of compound **3** prepared by the rapid evaporation of a TCE solution on a hot glass substrate.

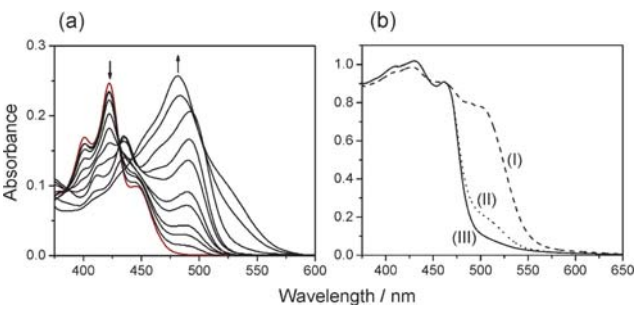

Fig. 5 Acid responsiveness of compound **3**. (a) UV-Vis in $CHCl_3$ with increased amount of TFA (0 (red curve), 3, 4, 6, 8, 10, 15, 20, 60, 150, 300 μL). (b) UV-Vis of xerogel (I) after 3 s exposure to the vapor of TFA, (II) 30 min standing after the exposure, (III) 1 h standing after the exposure (The spectrum is identical to that before exposure to TFA vapor).

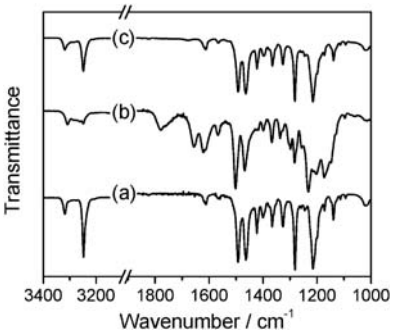

Fig. 6 FT-IR spectra of (a) xerogel of **3**, (b) after exposure to the vapor of TFA for 1 min, and (c) 1 day standing after the exposure.

However, only a subtle color change was noticeable. This result demonstrates a unique applicability of the xerogel to sense acids while other forms of the same compound, solution and amorphous film, are ineffective.

FT-IR spectroscopy was used to investigate the color change of the xerogel film upon exposure to TFA (Fig. 6). Two important observations were made from FT-IR spectroscopy: (1) when the film was exposed to the vapor of TFA for 1 min, a new peak at 1655 cm^{-1} was observed due to protonation of an imine nitrogen;[18] (2) the intensity of the peak at 3247 cm^{-1} was reduced significantly. Upon protonation, the alteration of conjugation through resonance can be expected which will cause a color change. In that process, the resonance occurs to delocalize the positive charge on the nitrogen extending to the acetylene side group resulting in less acetylenic character causing the noteworthy reduction of the acetylenic C–H stretching. In addition, initial hydrogen bonding between the nitrogen and acetylenic proton would be lost upon protonation of the imine nitrogen. It is interesting to note that the protonation was reversible, indicated by the return of the original character after 1 day standing at ambient conditions (Fig. 6(c)). This indicates that the imine and acetylene remained in close proximity such that the original hydrogen bonding can be restored after evaporation of the acid. The possibility of an addition reaction of a strong acid to the acetylene may exist, however the reversibility without adding any base suggests that such a reaction with HCl or TFA under the conditions presented is highly unlikely. It is worthwhile to comment that the IR study corroborates with the collapse of the organogel upon the addition of TFA, which further supports that the hydrogen bonding between the imine nitrogen and acetylene moieties is necessary for organogel formation.

In conclusion, we have reported here the first example of an asymmetric bisphenazine based π-LMOG. UV-Vis, XRD, FT-IR and SEM analyses revealed that effective gelling was possible only through the harmonious interplay of π–π interaction, hydrogen bonding, and van der Waals interaction producing unusual belt-like fibers. In addition, the remarkable acid sensing abilities of the xerogel film of compound **3** was demonstrated. More detailed studies on the electronic properties of the nanofibers of **3** are in progress along with controlling the morphology and physical properties with different types of substituents on the bisphenazine ring. The presented strategy of chemical modification of this attractive heteroaromatic moiety may generate well-defined 1-D nanofibers with many interesting electro-optical applications.

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