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Rational design of new acid-sensitive organogelators

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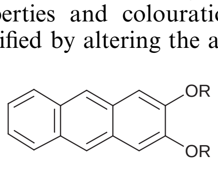
2,3-Di-*n*-alkoxyphenazines were shown to act as acid-sensitive organogelators at ambient temperature in acetonitrile; the protonated yellow species formed in the presence of acid displays stronger aggregative properties and higher temperature resistance than the colourless neutral phenazine; the protonation/deprotonation process is reversible.

Thermoreversible physical gels generated from low molecular mass organic compounds are an active field of research from both an academic viewpoint and because of their practical applications.[1–3] Organogelators not only rigidify the solvents but also create supramolecular networks which could induce specific and unique properties to the resulting materials.[4] Although hydrogen-bonding donor and acceptor groups are necessary for most organogelators which self-aggregate in water and organic solvents, it has been recently shown by us[5] and others[6,7] that small non-hydrogen bonding molecules could also exhibit gelling properties. Amongst the compounds investigated, 2,3-di-*n*-alkoxyanthracenes (DAOA, **1**) were reported to display, at very low concentrations, exceptional aggregative properties in various organic fluids.[5] For these self-assembling systems, van der Waals interactions, dipole–dipole contributions and π-stacking are the main driving forces involved for building the fibrous aggregates.

The gel-to-sol phase transition temperature of an organogelator is usually found to depend on the fluid and the gelator concentration, but it can also be influenced by external stimuli (light, pH *etc.*) as recently observed for some polymer containing hydrogels.[8] Apart from light and cation complexation, which were found to slightly modulate gelling abilities of cholesteric derivatives,[7] such external controls remain quite rare for low molecular mass gelling agents. It occurred to us that the introduction of basic sites on DAOA might provide a new family of pH-sensitive organogelators. From our previous studies, it emerged that long alkyl chains and the oblong shape of the molecule characterized by the anthracene ring system were necessary for gel formation. We therefore decided to investigate the gel-forming abilities of the analogous phenazine derivatives **2a** and **2b**.

In this communication, we report the straightforward synthesis[9] of novel organogelators **2a** and **2b** whose gelling properties and colouration are significantly and reversibly modified by altering the acidity of the solution.



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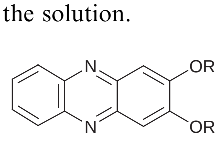


2a R = n-C_9H_{19}
b R = n-$C_{11}H_{23}$

The gelating capacity of **2a** and **2b** was screened at 2×10^{-2} M by means of the inverted test-tube method. Phenazine (**2a**: 9.2 mg; **2b**: 10.2 mg) and solvent (1 ml) were warmed in a septum-capped tube until complete dissolution of the solid. The solution was immersed in a thermocontrolled bath and slowly cooled at 2 °C min^{-1} until the gel formation occurred. The observed gel-to-sol phase transition temperatures (T_{gel}) are reported in Table 1. The data revealed the trend of phenazine derivatives to fairly easily gelify polar solvents; it also indicates that **2b**, possessing two longer alkyl side-chains, acts as a more efficient gelator than **2a**. These compounds are soluble in low polarity solvents (halogenated or aromatic)[11] and hence cannot rigidify such solutions, with the exception of compound **2b**, which can gelify *n*-heptane at low temperature ($T_{gel} = 3$ °C). Under the same conditions, the parent molecules (DAOA, **1**) displayed, in general, similar behaviour and a slightly higher capacity to encage the alcoholic solvents.[4] Thus the replacement of CH groups by nitrogen atoms on the anthracene moiety does not deprive the dialkoxyaromatic from its gelling capacities.

Owing to the presence of basic sites on the phenazine moiety, addition of trifluoroacetic acid (TFA) to solutions of **2a** and **2b** strongly modifies both their ^{1}H and ^{13}C NMR signals, which are shifted upfield, and also the UV-visible absorption spectra, the maxima being bathochromically shifted from 249 and 390 nm to 260 and 413 nm, respectively. The absorption spectra of **2a** and **2b** are superimposable both in the presence or absence of TFA. Taking into account the range of acid concentration used (0 to 2×10^{-2} M) and according to the reported data for neutral, mono- and di-protonated phenazine,[12] the yellow coloured species obtained upon acid addition is consistent with formation of the monoprotonated moiety. More importantly, the gel-forming ability of **2a** and **2b** is significantly enhanced in the presence of acid, resulting in an increase of T_{gel} by much as 60 °C in acetonitrile, as illustrated in Fig. 1. Reinforcement of the gelling properties could be due, in addition to other aggregative factors, to hydrogen-bonding between nitrogen atoms and ammonium centres. As observed by Weiss *et al.*, formation of ammonium groups was shown to influence the gelation in alkyl substrates.[6] The strongest effect for a 10^{-2} M acetonitrile solution of **2b** was recorded using one equivalent of TFA, as displayed in Fig. 2. It was observed that supplementary addition of acid decreases the gelling ability of the material, and that gel formation was totally suppressed in strongly acidic medium; the strengthening of the aggregation through hydrogen-bonding is limited by solubility of the gelling species. The role of the anion, which could be of importance in the construction of the

Table 1 Gel-forming abilities and gel-to-sol phase transition temperatures (T_{gel}/°C) of phenazines **2a** and **2b** at 2×10^{-2} M[a]

Solvent	2a		2b	
MeOH	15		31	
EtOH	14	(9)	33	(28)
EtOH–H_2O (4:1)	pg		12	
Acetonitrile	−13	(−18)	44	(30)
DMF	p		9	
Acetone	pg		9	
n-Heptane	s		3	

[a] s = soluble at ambient temperature, pg = partial gel, p = precipitate; values in parentheses refer to T_{gel} determined with 1% wt of organogelator (*ca.* 1.75×10^{-2} M and 1.50×10^{-2} M for **2a** and **2b**, respectively).

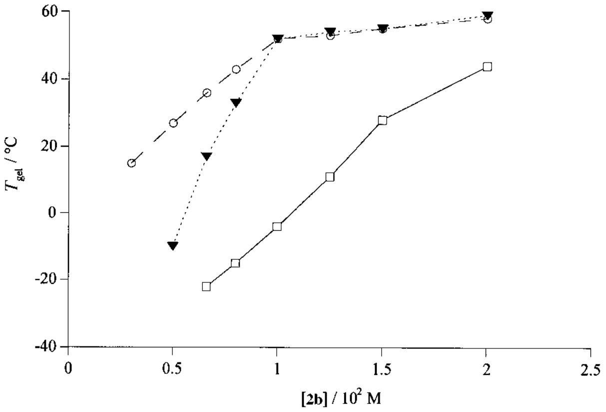


Fig. 1 T_{gel} for **2b** in acetonitrile as a function of organogelator concentration with or without trifluoroacetic acid: (□) [TFA]=0, (▼) [TFA]=[**2b**], (○) [TFA]=10^{-2} M.

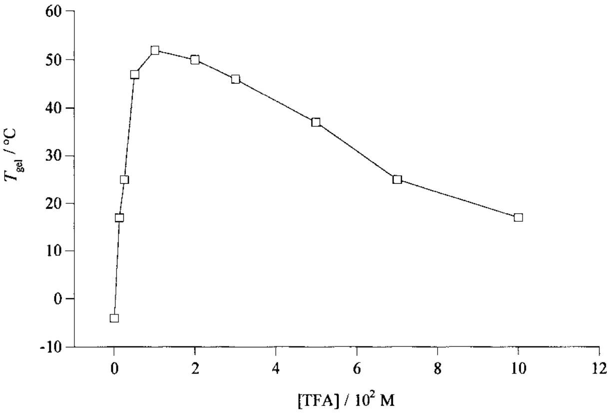
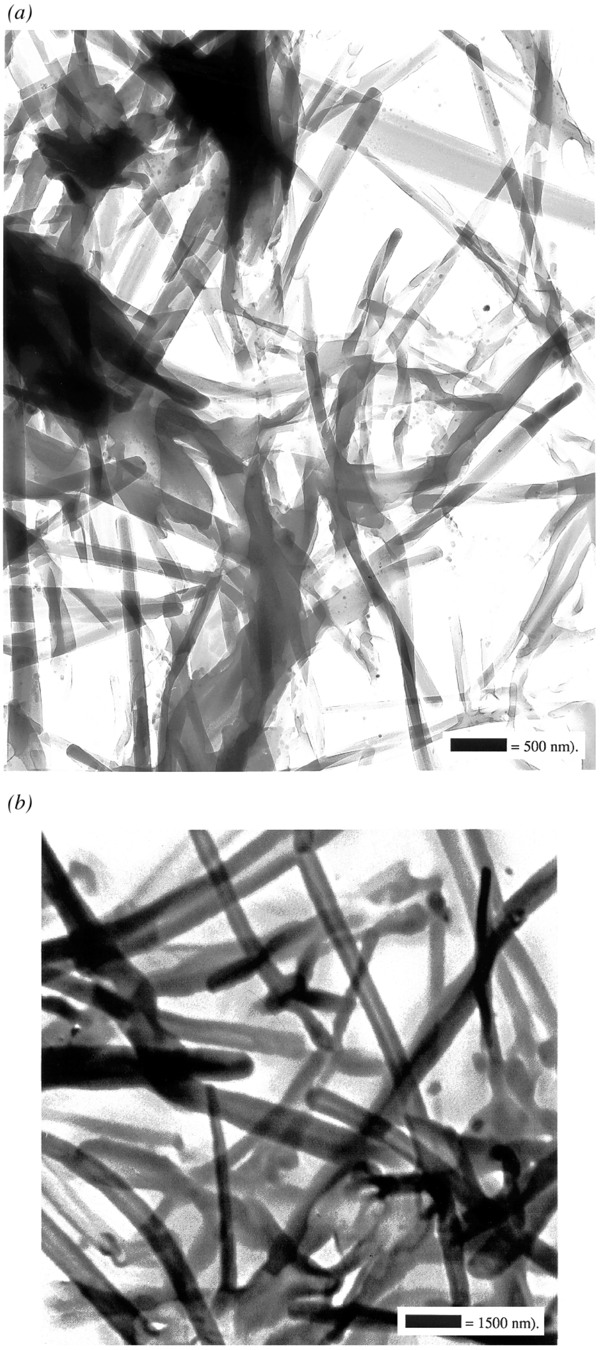


Fig. 2 T_{gel} for **2b** in acetonitrile as a function of TFA concentration ([**2b**]=10^{-2} M).

tridimensional supramolecular network, is under current investigation and will be discussed in the forthcoming full paper.

Moreover, it was also shown that the gel-forming ability of the system can be fine controlled by the reversible protonation of the phenazine ring. For example, bubbling ammonia through the gel provoked fading of the coloured protonated species and led to an optically translucent gel, the process being reversible upon addition of acid. The magnitude of the increase in T_{gel} obtained by addition of acid was found to depend on both fluid and concentration of organogelator. As shown in Fig. 1 for acetonitrile solution, the effect is less pronounced at higher concentrations and most dramatic at concentrations below 10^{-2} M.

Direct evidence of the microscopic organization of the gel formed in acetonitrile was obtained from transmission electron micrographs (TEM, Fig. 3). Numerous juxtaposed, fused, and intertwined thin straight fibres (several microns length) are formed by entanglement of long, slender aggregates with a width of *ca.* 150 nm woven in a three-dimensional architecture. The diameter of the smallest fibres represents several gelator molecular lengths. Of note is the formation of nodes corresponding to areas of large gelator concentration where no diffraction pattern could be recorded, suggesting a non-microcrystalline environment. These intertwined fibres are able to encage the solvent molecules. At 10^{-2} M, with one equivalent of TFA, TEM [Fig. 3(b)] shows the occurrence of longer elongated fibre-like structures without nodes, indicating that the molecules are apparently more efficiently packed. Compounds **2a** and **2b** differ from other hydrogen-bond based organogelators in that the neutral species already form gels through self-aggregation *via* dipole–dipole and van der Waals interactions, and that addition of acid induces a structural reorganization of the molecular rearrangement within the fibres. Presumably, this latter is necessary to accommodate hydrogen-bonding interactions formed upon protonation of the phenazine ring.


(a)

(b)

Fig. 3 Transmission electron micrographs of a dried acetonitrile gel of **2b** (*a*) in the absence and (b) in the presence of TFA.

In conclusion, the present study has demonstrated that the gelling abilities and colouration of low molecular mass organic compounds can be fine-tuned by variation in pH. Further studies are in progress, devoted to the elucidation of the microscopic arrangement of these supramolecular assemblies. We believe that these and other systems would open up new prospects for signal-responsive chemistry in molecular assembly systems.

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9 As adapted from a literature procedure (ref. 10), *o*-phenylenediamine and 2,5-dihydroxybenzoquinone in refluxing ethanol yielded 2,3-dihydroxyphenazine, which was subsequently etherified into **2a** and **2b** using K_2CO_3 and alkyl bromides (1/4.5/3.5). The new compounds purified by flash chromatography (light petroleum–dichloromethane) were fully characterized by ^1H and ^{13}C NMR, IRFT, mass spectra and elemental analyses.

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