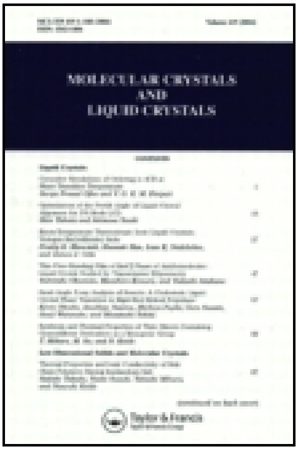

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# Photochromic Guests in Organogels

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# Photochromic Guests in Organogels

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3,3-Diphenyl-9,10-di-*n*-undecyloxypyrano[3,2-a]phenazine **3** was designed to be incorporated into fibres of 2,3-di-*n*-undecyloxyphenazine which display gel-forming ability in various fluids. A spectrokinetic study and the determination of the temperatures of gel-to-sol phase transition, give evidence of the insertion of the photochromic chromene into the organogelator network. Under continuous irradiation, the photochromic reaction induces a decrease of the gel strength which can be used to trigger the gel-to-sol phase transition.

*Keywords:* 2*H*-chromene; phenazines; self-aggregation; gels; supramolecular chemistry

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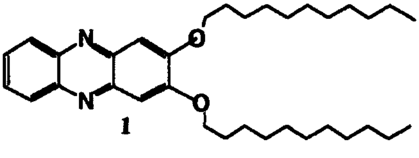
## Introduction

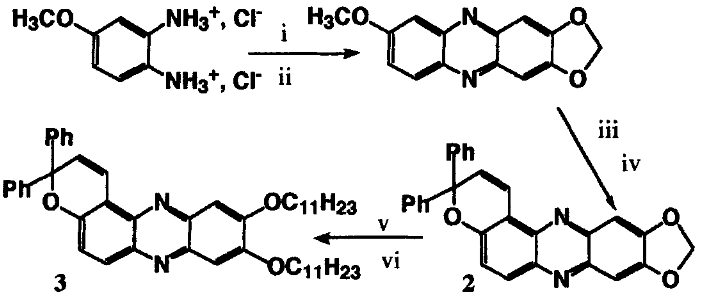
Thermoreversible physical gels generated from low molecular mass organic compounds are an active field of research for both their fundamental interest and their potential applications.[1-3] Organogelators imprison the solvent molecules creating supramolecular networks which could confer specific and unique properties onto the resulting materials. Although hydrogen-bonding donor and acceptor groups are necessary for most organogelators that self-aggregate in water and organic solvents, it has been recently shown by us[4] and others[1] that small non-hydrogen bonding molecules could also exhibit gelling properties. Amongst the compounds investigated, 2,3-di-*n*-alkoxyanthracenes, 2,3-di-*n*-alkoxyphenazines and to a lesser extent dialkoxybenzenes were reported to display aggregative properties in various organic fluids *at very low concentrations.*[4] The gel-to-sol phase transition temperature of an organogelator is usually found to depend on the fluid and the gelator concentration, but can be also influenced by external stimuli (light, p*H*,...). It occurred to us that the mixing of structurally similar photochromic compounds with organogelators might provide a light-controlled gelling system. From our previous studies, it emerged that long alkyl chains and an oblong shape of the molecule formed by a polycyclic system were necessary for gel formation. We therefore decided to investigate the gel-forming ability of phenazine **1** mixed with the analogous photochromic phenazine derivative **3**.



**1**

## Results and discussion

As adapted from a literature procedure[5], the phenazine skeleton was obtained by refluxing 2,5-dihydroxybenzoquinone and 4-methoxy-*o*-phenylenediamine in ethanol. Then, the adjacent hydroxy groups were blocked using a methylene bridge as protecting group. *Specific deprotection* of the methoxy group using 9-bromo-9-borabicyclo [3.3.1]nonane provided the desired phenol.



i) NEt$_3$ then 2,5-dihydroxybenzoquinone, EtOH (95%); ii) CH$_2$Br$_2$ DMF, CsF (76%); iii) 9-Br BBN, CH$_2$Cl$_2$ 24h, 0°C (79%); iv) β-phenylcinnamaldehyde, Ti(OEt)$_4$ Toluene (54%); v) BBr$_3$ , CH$_2$Cl$_2$ (76%); vi) K$_2$CO$_3$, C$_{11}$H$_{23}$Br, DMF, 120°C (82%). **2** and **3** gave satisfactory spectroscopic and elemental analysis data.

Scheme 1: Synthesis of 3,3-diphenyl-9,10-di-*n*-undecyloxypyrano[3,2-a]phenazine **3**.

*2H*-Chromene **2** was obtained by reaction of β-phenylcinnamaldehyde with the appropriate titanium (IV) phenolate prepared by treatment of the conveniently substituted hydroxyphenazine with titanium (IV) ethoxide. The methylene bridge was removed by treating with boron tribromide and further dietherification which was achieved according to the classical procedure using potassium carbonate as a base and 1-bromoundecane in hot dimethylformamide, to afford **3** as depicted in scheme1.

The photochromic behavior in toluene and acetonitrile was quantified by the absorption spectrum of the colored form (photomerocyanine) and by the thermal bleaching rate ($k_\Delta$). The spectra of the photomerocyanines of **2** and **3** in a set of solvents were determined using the flash photolysis technique. The spectrokinetic parameters, including those in the gel phase are listed in Table 1.

**Table 1** Spectrokinetic properties of pyrano[3,2-a]phenazines **2** and **3** in various solvent at ambient temperature.

| | toluene | | acetonitrile | | gelled acetonitrile | |
|---|---|---|---|---|---|---|
| **Compound** | $\lambda_{max}$ | $k_\Delta$ | $\lambda_{max}$ | $k_\Delta$ | $\lambda_{max}$ | $k_{\Delta 1}$ $k_{\Delta 2}$ |
| **2** | 494 | 0.33 | 494 | 0.37 | 494 | 0.36 |
| **3** | 498 | 0.29 | 501 | 0.33 | 502 | 0.33/**0.06** |

$\lambda_{max}$ values are given in nm, $k_\Delta$ are expressed in $s^{-1}$

When the photochromic compound **3** has been mixed with **1** in the conditions where a gel is formed, a second and slower kinetic rate constant ($k_{\Delta2}$) is observed. The latter is attributed to the presence of **3** intercalated or associated to the fibre network. For **2**, no changes in terms of thermal bleaching rate were observed between sol and gel phase. It *indicates that* **2** *remains within the bulk solvent encaged inside the* network, whereas the biexponential decay of **3** suggests that the chromene at least partially participates in the aggregation to form to the gel network.

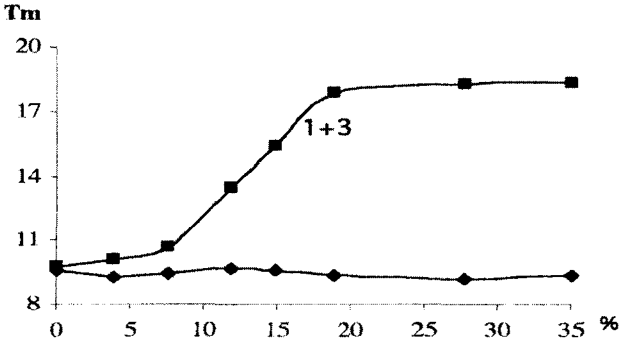


Fig 1. Gel-to-sol phase transition temperatures of **1+2** and **1+3** in acetonitrile at [**1**]=1.3 $10^{-2}$ M, [**2**] and [**3**]=0 to 4$10^{-3}$ M.

The gelling ability of mixtures composed of 1.3 × $10^{-2}$ M of **1** and variable amounts **2** and **3** was investigated by means of the inverted test-tube method. Phenazine **1** and chromenes **2** or **3** and acetonitrile were warmed in a septum-capped tube using the usual procedure.[4] Then, melting temperatures ($T_m$) were determined for each tube; the results are reported on Figure 1. One observes first that compound 2 has no effect on $T_m$, in agreement with the kinetic data. In contrast, the gel-forming ability of **1** is significantly enhanced in the presence of chromene **3**, resulting in an increase of $T_m$ by much as 8°C in acetonitrile. Reinforcement of the gelling properties could be due to the incorporation of **3** within the gel filaments or on their surface. Preliminary experiments have shown that continuous irradiation (medium pressure lamp, $\lambda>300$ nm) at *ca.* 18°C induces a structural reorganization of the network molecular arrangement leading to the loss of gelation.

In conclusion, the present study has shown that the gelling ability of low molecular mass organic compounds can be affected by incorporation of photochromic antenna and subsequent irradiation. Further studies are in progress, devoted to the elucidation of the microscopic arrangement in these supramolecular assemblies and their signal-responsive chemistry.

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