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A new Example of Small Molecular Non-Hydrogen Bonding Gelators for Organic Solvents

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Abstract: Two novel low molecular weight gelling agents 1 and 2 for organic sovents are presented. These molecules, which do not contain hydrogen bonding groups, can gelify reversibly a great variety of solvents. © 1997 Published by Elsevier Science Ltd.

It has been shown that small organic molecules can form thermoreversible gels with various organic solvents.[1] These low molecular weight gelling agents are of interest for practical purposes (hardening oils or organic fluids) and also for the design of novel organic materials. For the development of new molecular gels displaying specific and required applications (e.g. photochemistry, cation or molecular recognition, electrolytes, etc.) it is necessary to find correlations between the molecular structure and the organizing capabalities of the gelator. It is recognized that the driving forces for weaving the 3D network usually involve hydrogen bonds and Van der Waals interactions.[2] However, the literature also suggests some examples of efficient gelators in which no hydrogen bonding groups are available. Thus, cholesteryl and cholestanyl esters of anthracene derivatives have been shown to aggregate organic solvents at room temperature.[3] In this case, the gelling abilities of the compounds probably originate in the well-known mesogenic properties of the steroid subunit. Meanwhile, we have discovered in our laboratory the uncommon behaviour of DDOA[4] (2,3-bis-*n*-decyloxyanthracene) which forms luminescent gels with alcohols, hydrocarbons, amines, etc. at very low concentrations. For instance, a molecule of DDOA is able to aggregate 40,000 molecules of methanol! The gelling properties were assigned to the rectangular shape and the rigidity[5] of the aromatic moiety of DDOA (three linearly aromatic fused rings[5] substituted with two long alkoxy chains on the 2, 3 positions) which allow, in addition to dipolar forces, specific π-π intermolecular interactions for constructing the three dimensional pattern. As large spectroscopic modifications of the medium were recorded along the phase transition related to the microscopic organization (stacking of anthracene groups of DDOA)[4], it appeared of interest to investigate the influence of the latter on the chemical reactivity of the material.[6] With this intention, the catalytic hydrogenation of DDOA was selected since this reaction is known to produce two main products with anthracene derivatives[7] and their ratio could be sensitive on the local structure of the molecular

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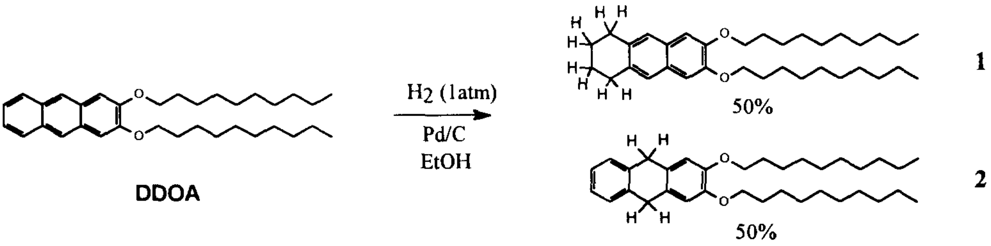
assemblies. Moreover, these hydrogenated products in which the oblong structure of the aromatic core is strongly perturbed appear to be good candidates for testing the validity of the hypotheses regarding the gelling abilities of DDOA.

Results and discussion

The hydrogenation of DDOA was conducted in methanol with Pd/C, at room temperature under 1 atmosphere of H_2.[8] The isotropic and gel phases gave the same products **1** and **2** in a 1:1 ratio (100% yield). The structure of the products fully characterized by the usual spectrometric techniques and elemental analysis[8] indicates that no specific control on the reaction route occurs in the organized phase. Moreover, the same ratio of reduction products was obtained with solutions of the non-gelating 2,3-bis-n-hexyloxyanthracene.[4] This could result from the high local mobility of the species strengthening the gel, thus preventing the type of topochemical control of the reaction observed in crystals[9] or in more static molecular assemblies (e.g. Langmuir-Blodgett films[10]).



Very surprisingly and contrary to all expectations, these two compounds were found to gelify a large variety of organic solvents (see list in Table 1). Indeed, at relatively high concentrations (conc.≈ 2% weight) **1** or **2** form a white opaque gel and at more dilute solutions a transluscent sample is obtained. The samples are characteristic of gels as no significant flow was observed when a test tube filled with the materials was turned upside down and apparently display the same characteristic as those given by DDOA.

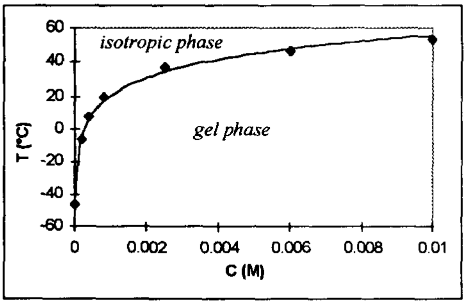


Fig.1a : Phase transition temperature of methanolic solutions of **1** *vs* gelator concentration

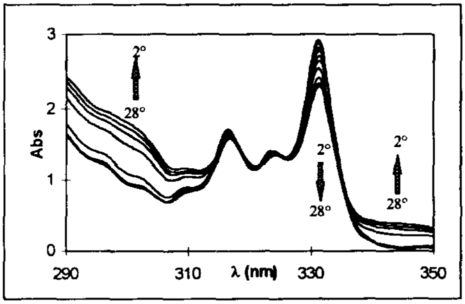


Fig.1b : Electronic absorption spectra of **1** in methanol as a function of temperature

As indicated in Fig. 1a, 2 and 3 the sol-gel transformation is temperature dependent.[11] Cooling the solutions significantly lowers the effective concentration of **1** and **2** required to form a gel. It also emerges that compound **1** (which is a tetrasubstituted naphthalene) is at least as efficient as DDOA (Fig. 2), in contrast to compound **2** which hardly gives gels at low concentrations. Whilst this point is of interest for applications (naphthalenes being less toxic than anthracenes) it makes questionable the parameters taken into account (*vide supra*) to explain the gelling capacity of DDOA and its derivatives.

Table 1: Gelling Properties of **1** and **2** for Different Organic Solvents

	1		**2**	
solvent	Tgel (°C)	Conc. x10^2(M)	Tgel (°C)	Conc. x10^2(M)
chloroform	no gel	3.0	no gel	3.0
tetrahydrofuran	-50	1.3	no gel	3.0
methylene chloride	-45	4.6	-70	1.8
toluene	-45	1.4	-70	1.2
carbon disulfide	-40	2.5	-50	2.5
diethyl ether	-30	1.4	-40	3.0
ethyl acetate	-20	0.7	-30	0.8
pentane	-15	0.2	-20	0.7
acetone	-5	0.4	-20	0.7
acetonitrile	>20	0.7	10	0.6
2-propanol	>20	1.0	>20	0.9
methanol	53	1.0	20	1.0

In contrast to DDOA where large spectral shifts occur in relation to strong π-π intermolecular interactions, the electronic absorption spectra of **1** and **2** display only moderate changes during the sol-gel transition (Fig. 1b) suggesting no specific or marked orientations between the aromatic parts of the gelator units.

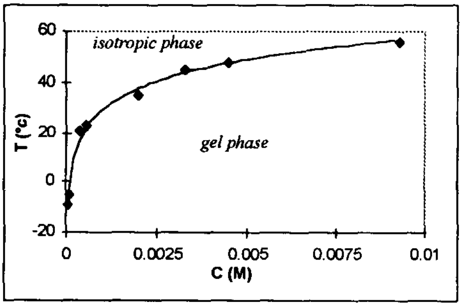


Fig.2 : Phase transition temperature of methanolic solutions of **DDOA** *vs* gelator concentration

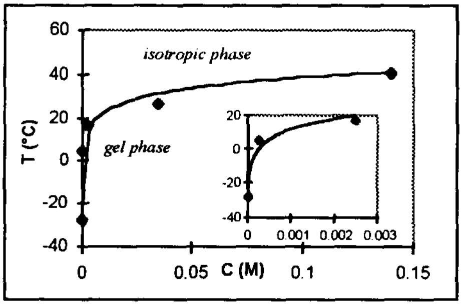


Fig.3 : Phase transition temperature of methanolic solutions of **2** *vs* gelator concentration

Although spectra display the transition characteristics in the fluid solution of compounds **1** and **2**, they present in the gel a large diffusion contribution revealing the microheterogeneity of the medium.

To elucidate the unexpected properties of compounds **1** and **2**, theoretical and further experimental investigations are needed. With this intention, spectroscopic measurements (far IR, fluorescence: dynamic and stationary regimes) and molecular mechanics simulations are planned. The results and a complete description of the gelling properties of **1** and **2** will be presented in the full paper.

ACKNOWLEDGMENTS

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4. Brotin, T.; Utermöhlen, R.; Fages, F.; Bouas-Laurent, H.; Desvergne, J.-P. *J. Chem. Soc. Chem. Commun.* **1991**, 416-418.
5. Other aromatic nuclei such as benzene, naphthalene, phenanthrene, stilbene were found to be inefficient with these two alkoxy chains. Moreover, the substituents have to be on both the 2 and 3 vertices of anthracene. The related 2,3-substituted anthraquinone is also a gelator.
6. DDAO was found to not give a photodimer as usually observed with anthracenes. see: Brotin, T.; Waluk, J.; Desvergne,J.-P.; Bouas-Laurent, H.; Michl, J. *Photochem. Photobiol.* **1992**, *55*, 335-347 and Brotin, T.; Desvergne, J.-P.; Fages, F.;Utermöhlen, R.; Bonneau, R.; Bouas-Laurent, H. *Photochem. Photobiol.* **1992**, *55*, 349-359.
7. See for instance: Garlock Jr, E. A.; Mosettig, E; *J. Am. Chem. Soc.* **1945**, *67*, 2255-2269.
8. **1** and **2** are obtained as follows: DDOA (0.3 g, 0.6 mmol) and Pd/C (0.015 g) in ethanol (0.5 L for isotropic conditions and 0.05 L for the gel phase, respectively) are stirred (only for isotropic solution) under hydrogen atmosphere (1 bar) for 3 days. After filtering the catalyst and removing the solvent *in vacuo*, a white solid is isolated as a ≈ 1:1 mixture of compounds **1** and **2** (≈ 0.3 g, 100%). **1** and **2** are separated upon chromatography on silica gel (petroleum ether/ dichloromethane 4/1).

   1 (white xerogel) m.p. 74°C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.90 (6H,t); 1.29-1.51 (28H, m); 1.86 (8H, m); 2.92 (4H, m); 4.08 (4H, t); 7.01 (2H, s); 7.36 (2H, s); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 14.1; 22.7; 23.5; 26.1; 29.1; 29.4; 29.4; 29.4; 29.5; 29.6; 31.9; 68.8; 107.1; 125;2; 127.2; 133.9; 148.9; HRMS 494.4124(M^+) calc: 494.4123; Elem. Anal. calc: C 82.5%, H 11.0%, found: C 82.1%, H 11.1%.

   2 (white xerogel) m.p. 76-78°C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.90 (6H,t); 1.29-1.53 (28H, m); 1.82 (4H, m); 3.88 (4H, s); 4.00 (4H, t); 6.83 (2H, s); 7.23 (4H, s) ; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 14.1; 22.7; 26.0; 29.4; 29.4; 29.4; 29.5; 29.6; 31.9; 35.4; 68.6; 113.8; 125;9; 127.4; 136.6; 147.6; HRMS 492.3964(M^+) calc: 492.3967; Elem. Anal. calc: C 82.9%, H 10.6%, found: C 82.6%, H 10.7%.
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11. The Tgel were determined using UV spectrometry. Indeed, the gel formation is characterized by a hypochromic effect and the emergence of a background diffusion contribution. The accuracy of Tgel measurement is *ca* 2-3°.

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