A Novel Small Molecular Luminescent Gelling Agent for Alcohols

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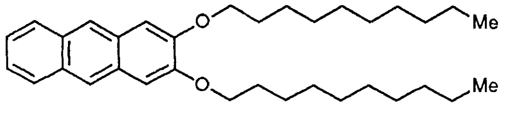
2,3-Bis-n-decyloxyanthracene can form thermoreversible gels with alcohols at very low concentrations; electronic absorption spectra and fluorescence emission studies suggest that the network of the gel consists of head-to-tail assemblies of the aromatic component coexisting with the alcohol, the organization of the system essentially relying upon dipolar forces and van der Waals interactions.

In the course of an investigation of substituted anthracenes[1] arising from their photochromic properties,[2] we discovered by chance the gelling properties of 2,3-bis-n-decyloxyanthracene,† DDOA. Surprisingly, at room temperature, aliphatic alcohols (and to a lesser extent aliphatic amines) are readily and reversibly transformed into translucent gels‡ in the presence of a small amount of DDOA; at room temperature, one molecule of the gel-forming agent can confine up to 25 000 molecules of methanol, the most suitable solvent for gelation (Fig. 1). As shown in Fig. 1, the sol–gel process is temperature dependent, since cooling the alcoholic solution lowers the



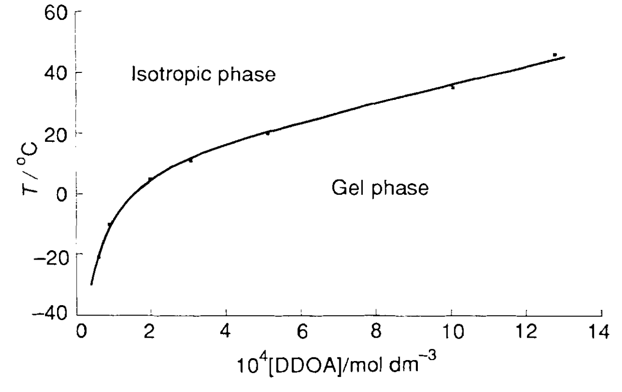


Fig. 1 Gelation temperature of methanolic solutions of DDOA *vs.* DDOA concentration

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† DDOA was synthesized by a two-step reduction (NaBH$_4$ in propan-2-ol) of 2,3-bis-n-decyloxyanthraquinone which was readily obtained by alkylation of 2,3-dihydroxyanthraquinone[3] with n-bromodecane [K$_2$CO$_3$, dimethyl formamide (DMF), 80 °C]; DDOA: white crystals, m.p. 84 °C, ^{1}H NMR (CDCl$_3$): δ 0.88 ('t,' 6H), 1.2–1.6 (m, 28H), 1.90 (m, 4H), 4.10 ('t,' 4H), 7.14 ('s,' 2H), 7.35 (m, 2H), 7.88 (m, 2H) and 8.15 ('s,' 2H). Satisfactory elemental analyses were obtained. 't' and 's' denote apparent triplet and singlet states.

‡ Their macroscopic properties fit any of the several definitions applied to gels.[4]

Fig. 2 Freeze–fracture electron micrograph of gels from DDOA in propanol (10^{-3} mol dm^{-3})

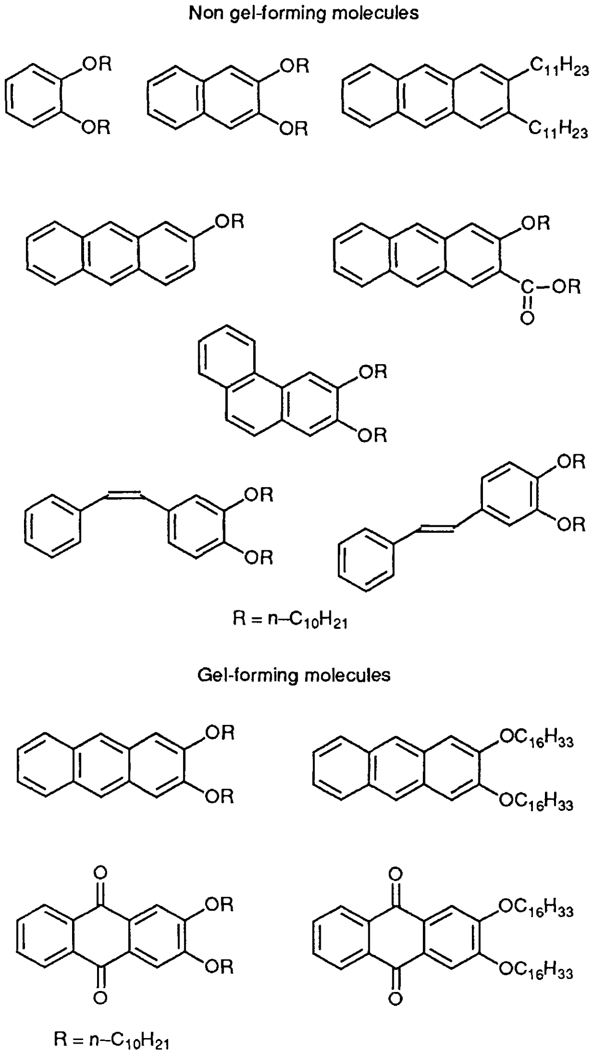
minimum concentrations of DDOA necessary to construct the gel network ([DDOA] = *ca.* 10^{-3} and 10^{-4} mol dm^{-3} at 40 and −20 °C, respectively).

Other organic liquids are rather resistent towards gelation but methylcyclohexane (MCH) displays gel behaviour for low concentrations of DDOA ($\leqslant 10^{-5}$ mol dm^{-3}) and at low temperatures (−60 and −70 °C for MCH), the process being in competition with the crystallization of the aromatic gelling agent.

These observations are unusual as most organic gels need either a polymeric gelling agent in large concentrations or a gelling agent bearing groups acting as hydrogen bond donors.[4] Apart from fluorinated alkanes,[5] which, in large concentrations, are recognized to form gels with hydrocarbons, only a few examples of gelling agents developing only van der Waals type interactions were known up to now, except for the recent discovery[6] of the gelling properties of an anthracene substituted (in the β position) by a cholesteryl group. Interestingly, this substrate, which is needed in higher concentrations than DDOA (at least one order of magnitude), is effective for various hydrocarbons but is ineffective with alcohols of small dimensions such as methanol or ethanol; its gelling properties could be related to the well known mesogenic influence of the steroid pendant group.[7]

An electron micrograph of a gel formed between DDOA and n-propanol (Fig. 2), obtained by the freeze–fracture technique, shows a dense three-dimensional pattern composed of randomly oriented and intertwined fibrous bundles (average section of the smallest: 60–70 nm, the thickness being mainly due to the aggregation of tubular filaments and, probably, a too abundant platinum/carbon coating) which delimits meshes of variable sizes encaging the isotropic fluid (immobilized by surface tension). It emerges from the size of the fibres, which requires, for the smallest of them, several extended gelling agent units to be arranged linearly, that they are the result of several molecular threads joined together.

Inspection of the gelling abilities of some structurally related molecules (Scheme 1) suggests that the gelling agent framework has to display together the following characteristics: (*i*) Three linearly fused rings, *e.g.* anthracene and anthraquinone nuclei. (*ii*) Two alkoxy substituents located on positions 2 and 3 of the ring (the other isomers are inactive); the replacement of the oxygen atoms by methylene groups or the presence of only one alkoxy group makes the molecule inactive. (*iii*) Two long aliphatic chains: 2,3-dimethoxyanthracene is not a gelling agent.



Scheme 1

Gel formation can easily be scanned by recording electronic absorption and emission fluorescence spectra of the anthracene chromophore (Fig. 3) which display large changes along the sol–gel transition; thus the gel-forming agent acts as

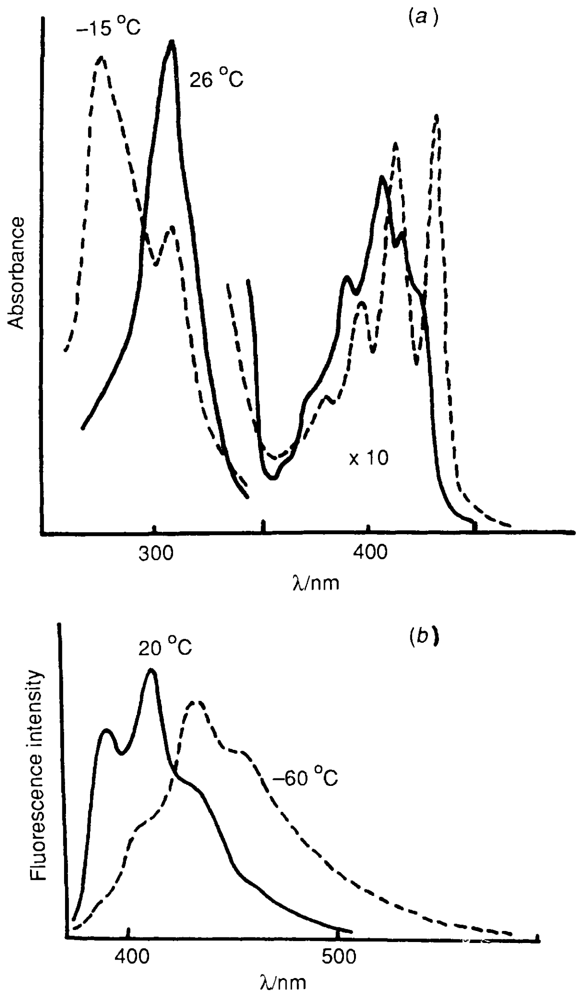


Fig. 3 (*a*) Isotropic (——) and gel (- - - -) absorption spectra of 10^{-3} mol dm^{-3} DDOA in methanol; (*b*) isotropic (——) and gel (- - - -) corrected emission of 10^{-4} mol dm^{-3} DDOA in methanol (λ_{exc} = 370 nm)

an internal sensor of the microscopic structural modifications of the medium.

Upon gelation the low energy band (300–400 nm), which originates[8] from both the ^1L_a and ^1L_b transitions, is smoothly transformed§ (in methanol and all other gelling liquids, with several isosbestic points) into a net red-shifted and well structured band exhibiting a pure ^1L_a character as demonstrated by linear dichroism.[8] The high energy transition (200-300 nm, ^1B_l band[8]) is still more perturbed; in the gel a strong transition appears at ≈ 220 nm at the expense of that occurring in the isotropic solution (258 nm). These spectral changes may be attributed[9] to intermolecular interactions between the anthracenes with a marked degree of antiparallelism between their long axes.

The maximum intensity of the fluorescence emission is red-shifted with large changes in the spectral shape when an isotropic solution of DDOA (in alcohols) is progressively cooled and forms a gel¶ (Fig. 3). The excitation spectra scanned at all wavelengths closely match the electronic absorption spectra recorded for the gel.

If the fluorescence decay of the isotropic solution (of DDOA in alcohols) is exponential ($\approx$4.2 ns), the gel phase emission¶ can be fitted to a sum of two exponentials at all the wavelengths investigated. The two decay times smoothly increase and the contribution of the slow component decreases with increasing analysis wavelengths. At −45 °C in methanol: λ(420 nm): $\tau_1 = 5.0$ ns, $A_1 = 0.40$; $\tau_2 = 14$ ns, $A_2 = 0.14$; λ(440 nm): $\tau_1 = 8.0$ ns, $A_1 = 0.37$; $\tau_2 = 19$ ns, $A_2 = 0.07$; λ(480 nm): $\tau_1 = 11.3$ ns, $A_1 = 0.44$; $\tau_2 = 37$ ns, $A_2 = 0.04$. The success of the fits was evaluated by reduced χ^2 values (range from 0.95 to 1.3), the randomly distributed weighted residuals about zero, and the autocorrelation function of weighted residuals.[10]

The above-mentioned results are in agreement with the occurrence of different excited species displaying nearly identical emission spectra (as recently discussed by De Schryver[11] for anthracene chromophores in Langmuir–Blodgett films); these discrete fluorescent entities could result from the various mutual orientations of the anthracene moieties in the gel and could be the precursors of excited complexes as detected by time-resolved fluorescence spectroscopy (a non structured emission spectrum peaking at 460 nm was revealed 40 ns after the exciting pulse, in accordance with the formation of excimer type complexes with partially overlapped monomers[12]).

Attempts to probe the microscopic structure of the gel by correlating the packing arrangement of DDOA with the geometry of anthracenyl photodimers met with failure, since DDOA was found to be photostable in fluid solutions as well as in the gel phase.

In conclusion, it emerges that the gelling agent forms assemblies where anthracene units display *anti*-orientation (head-to-tail) with partial overlap between aromatic rings. The solvent associated with DDOA by hydrogen bonds, involving the oxygen atoms of the alkoxy substituents, forms and strengthens the network which involves dipolar forces (the calculated dipole moment[8] of DDOA in the ground state is 3.3 Debyes) and van der Waals interactions.

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§ From the spectroscopic measurements, a tentative evaluation of thermodynamic data of gel formation in methanol provides $\Delta H^\circ \approx -105$ kJ mol^{-1} and $\Delta S^\circ \approx -375$ J mol^{-1} K^{-1}.

¶ The spectra displayed by the core of the gel were recorded using the right angle method (conc. $< 10^{-4}$ mol dm^{-3}), since the frontal illumination technique (conc. $> 10^{-3}$ mol dm^{-3}) was shown to exhibit isotropic solution behaviour owing to the quartz–alcohol interface.

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