2,3-Di-*n*-alkoxyanthraquinones as gelators of organic solvents

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The gelling ability of a series of dialkoxy-9,10-anthraquinone derivatives has been investigated in a number of organic solvents at different concentrations. The most efficient systems were found to be formed from the 2,3-dialkoxy (OC_nH_{2n+1}) derivatives with $n = 8$–11 (compounds **9**–**11**, **14**–**15**). In ethanol, a gel is formed with 2,3-di-*n*-decyloxyanthraquinone (**11**) at a concentration of *ca.* 10^{-2} M (0.65 g/100 g) at 30 °C. The gel-to-sol transition temperatures were determined in ethanol, isopropanol and *n*-heptane as a function of gelling agent concentration. The gel-to-sol transition enthalpies (23–51 kJ mol^{-1}) were found to be in agreement with recent results obtained for other gel forming systems.

Introduction

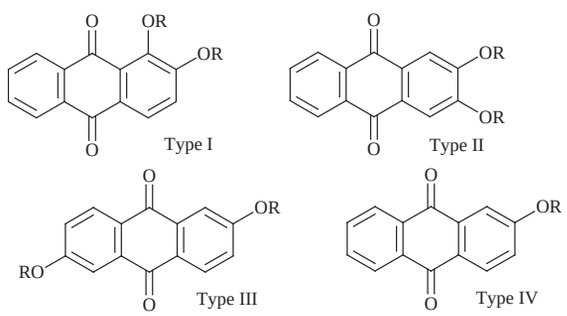
Gels formed from polymers or biomacromolecules have been known for a long time[1] and continue to be an active field of research, reflecting an interest in the gelling process and a wide range of potential applications.[2] Thermoreversible physical gels can also be generated from molecules of low molecular weight (M_w: 300–1000) which form networks by self-aggregation in water and organic solvents.[3] Since the early characterization of the gelation of CCl_4 by 12-hydroxystearic acid,[4] an impressive number of publications have been recently devoted to the discovery of such new organic gels[5–39] extending the field of supramolecular chemistry.[40] According to the driving force responsible for the formation of gels, compounds can be classified in several categories. *i*) For most low-molecular-weight organogelators, hydrogen-bonding donor and acceptor groups are structurally essential, leading to self-aggregation or specific recognition in a two-component organogelator, such as in an amide or amide-like function. *ii*) The driving force may originate through metal–oxygen coordination bonding[5] or metal salts of fatty acids.[6] *iii*) In other systems, dipole–dipole and van der Waals interactions seem to play a major role.[7,18–22,30–32] A subdivision should be made in the latter between those incorporating a steroid skeleton and those without. In the latter group, 2,3-di-*n*-decyloxyanthracene has been reported to form thermoreversible gels with alcohols, and to a lesser extent, with amines and alkanes.[10] Interestingly, some related anthraquinonic compounds were said[10] to display similar behaviour in methanol but have not been studied further.

Anthraquinones are mainly known as dyes[41] and for their pharmacodynamic properties.[42] Hydroxyanthraquinones have also received attention as key intermediates involved in several synthetic routes to anthracyclines and anthracyclones,[43] as for example in the Marschalk reaction.[44] Their current importance stems from their interesting antitumour activities.[45] We thus considered that anthraquinone-based gels deserved a deeper investigation and prepared different anthraquinonic compounds in order to determine the optimal gelling performances by structural variation (position and length of the chains) and solvent screening. In this paper, we report their gel-forming properties and the gel-to-sol transition temperatures at various concentrations.

Results and discussion

Synthesis

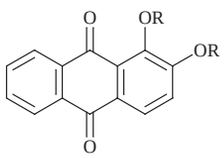
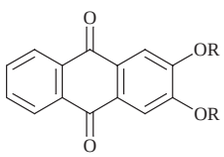
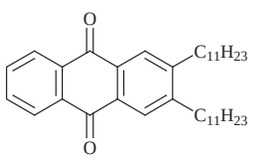
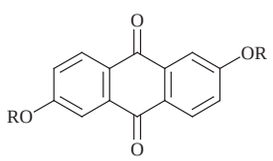
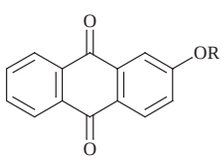
Because 2,3-di-*n*-decyloxyanthraquinone (Type II, Scheme 1) was briefly mentioned[10] as forming a gel in methanol, it was taken as a starting point to investigate other symmetrically dialkoxy-substituted anthraquinones such as 1,2-dialkoxy (Type I) and 2,6-dialkoxy (Type III). Monoalkoxy-substituted anthraquinone (Type IV) was selected in analogy with gels obtained by Weiss *et al.*[7] from 2-substituted anthraquinones incorporating a cholesterol skeleton. Our study did not systematically encompass the other dialkoxy derivatives because the attempts with Type I and Type III derivatives failed in contrast to the gelation experiments conducted with a series of 2,3-di-*n*-alkoxyanthraquinones (Type II); it thus appeared that a prerequisite for gel formation was an oblong molecular shape.



Scheme 1 Substitution pattern of the anthraquinones investigated.

Hydroxyanthraquinone derivatives are the obvious precursors for the desired organogelator molecules. Starting materials such as alizarin (1,2-dihydroxyanthraquinone) or anthraflavic acid (2,6-dihydroxyanthraquinone) are commercially available. Preparations of 2-hydroxyanthraquinone and hystazarone (2,3-dihydroxyanthraquinone) have been described elsewhere.[47–48] For these latter compounds, we recently reported an improved method avoiding cumbersome set up and work up.[49] The syntheses of the various alkoxyanthraquinones were achieved according to the classical procedure using potassium carbonate as a base and alkyl halides in refluxing dimethylformamide. A typical experiment involved a 1:5:4.5 molar ratio of diphenols, base and alkyl halides respectively. Alkyl bromides were preferred to alkyl chlorides. When not commercially available, they could be easily obtained by halogen exchange (Finkelstein reaction). No marked difference in alkylation yield was observed for the different anthraquinones. This reflects a weak difference in both acidities and nucleophilicities whatever the positions of the phenol functions. We also prepared anthraquinones with $(ethyleneoxy)_n$ sidearms and anthraquinoyloxy alkanoates. The preparation of compounds **1**, **4**, **7**, **11**–**13**, **15**–**20** is described elsewhere.[48]

Table 1 Gel-forming ability using Method 1 at ambient temperature (conc. 10^{-2} M) of the anthraquinones studied

Gelator		R	Solvent				
			CH_3OH	C_2H_5OH	CH_3CN	n-C_7H_{16}	n-C_5H_{12}
	**1**	$C_{10}H_{21}$	P	T	S	SS	SS
	2	$C_{12}H_{25}$	T (P)	T	SS	SS	
	3	$C_{16}H_{33}$	SS	S	SS (P)	S	S
	**4**	CH_3	I	I	I	SS	SS (P)
	5	$(CH_2CH_2O)_2CH_3$	P	T (P)	SS	SS	
	6	C_6H_{13}	S (T)	S (T)	SS-Th	S (T)	
	7	$CH_2CH(C_2H_5)C_4H_9$	SS	SS	SS	S	S
	8	C_7H_{15}	T	S (G)	S (G)	S (G)	
	9	C_8H_{17}	*G*	S (G)	*G*	S (G)	
	10	C_9H_{19}	T (G)	*G*	T	T (G)	
	11	$C_{10}H_{21}$	T (G)	*G*	S (T)	T (G)	SS (T)
	12	$(CH_2CH_2O)_3CH_3$	T	T	SS	SS	
	13	COC_9H_{19}	T	P	S	P	P
	14	$C_{11}H_{23}$	*G*	*G*	P	T (G)	
	15	$C_{12}H_{25}$	SS-Th	T (G)	S (T)	*G*	
	16	$C_{16}H_{33}$		SS		S	S
	**17**		I	I	SS (P)	SS (P)	SS
	**18**	$C_{10}H_{21}$	P	T (P)	S	SS	SS
	19	$C_{12}H_{25}$	P	T (P)	S	SS	—
	**20**	$C_{10}H_{21}$	SS-P	SS	SS	T	SS
	21	$C_{12}H_{25}$	SS	T	T	T	SS
	22	$C_{16}H_{33}$	SS	T	T	S (T)	
	23	$(CH_2)_2O$–Steroid[a]	I	I	SS	*G*	P
	24	$COCH_2O$–Steroid[a]	I	I	SS	*G*	P

I: Insoluble at the boiling temperature, P: soluble but precipitated upon cooling, S: dissolved but remained soluble upon cooling, SS: sparingly soluble at boiling temperature but gel not formed upon cooling, Th: thickening upon cooling, T: turbidity manifested upon cooling, G: gel formed, *G*: gel formed at ambient temperature. Values in parentheses refer to behaviour at *ca.* −18 °C when this differs from that at ambient temperature. [a] Taken for comparison from the work of Weiss *et al.*;[7] the steroid used was the cholesterol skeleton with natural configuration (*S*-chirality).

Gel-forming properties

General screening. The gelling properties of all the available anthraquinones were systematically investigated at the arbitrary usual concentration (10^{-2} M) in five solvents (methanol, ethanol, acetonitrile, *n*-heptane and *n*-pentane) typical of protic, non-protic polar and aprotic apolar solvents (Table 1).[49] Gelation tests were performed by means of the inverted test-tube method (Method 1, see Experimental section).

With a view to determining the most efficient organogelators, we decided to limit our investigations to temperatures ≥−18 °C and at concentrations ≤10^{-2} M which represent useful conditions for potential application. We tested the gelators at lower concentration (Table 2) and performed the extensive gelation test for a variety of organic solvents (Table 3). In general, the gels obtained were found to be pale yellow, mostly transparent, or, rarely, opalescent.

Although numerous systems that aggregate and form gels have been discovered, examples remain quite rare that involve only van der Waals interactions or dipole–dipole interactions as driving forces for the gel formation as appears to be the case for the tested derivatives in non-protic solvents. A gel-forming molecule requires a moderate affinity with solvent and a moderate self-aggregation ability. Results from solvent screening at 5×10^{-3} M (Table 3) show that the anthraquinones tend to gelify solvents for which their solubility is very low at room temperature but high at boiling temperature. Upon cooling, the mutual interactions between molecules become more effective resulting in the advent of aggregates and fibres which will intertwine to constitute the network for the gel-structure.

Table 2 Gel-forming ability using Method 1 at ambient temperature (conc. 5×10^{-3} M) of gelators **8**–**11** and **14**–**15**

Gelator	Solvent				
	CH_3OH	C_2H_5OH	CH_3CN	n-C_7H_{16}	n-C_5H_{12}
8	S (T)	S (G)	S (T)	S (T)	S
9	*G*	S (G)	S (T)	S	S
10	*G*	*G*	SS	S	S
11	T (G)	*G*	T	SS (T)	—
14	T (G)	T (G)	S (T)	T (G)	SS
15	SS-Th	T (G)	S (T)	*G*	—

Symbols used here are identical to those used in Table 1.

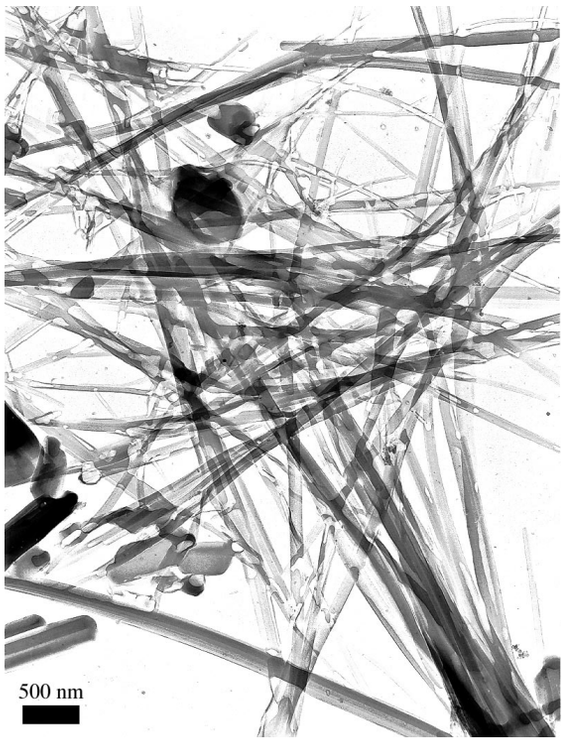


Fig. 1 Transmission electron micrograph of a dried *n*-hexanol gel of **11**. (10 mg cm^{-3}, carbon coated, ■ = 500 nm).

Electron microscopy structure investigation. A photograph obtained by transmission electron micrography (TEM) of a dried *n*-hexanol gel of **11** (Fig. 1) provides direct evidence for a network of numerous straight thin fibres. The latter, with a length of several microns, occasionally fuse and intertwine. The diameter of the smallest fibres is approximately 50 nm which represents several gelator molecular lengths.

Molecular structure of the organogelator. From the data in Table 1, it may be concluded that the gel-forming anthraquinones are disubstituted in positions 2 and 3, this property being restricted to linear alkoxy chains. The replacement of the oxygen atoms by methylene groups (compound **17**) deprived the molecule of its gelling properties. This structural change led to a poorly soluble or insoluble material; one could speculate that, unlike the benzylic CH_2, the phenolic oxygen induces an open conformation more favourable to solvation of the chains. Moreover, branching (as in **7**) suppresses the gelling ability shown by the linear counterpart. Compound **7** has been designed in analogy with the surfactant property of AOT [sodium di(2-ethylhexyl)sulfosuccinate][17] which is known to generate inverse micelles. In **7**, the non-gelling behaviour could be ascribed to an increase of solubility, the branched alkyl chains filling a larger space than the linear one. This prevents the stacking of this unit and further aggregation responsible for the formation of the network. Finally, gels were not observed either with ester (**13**) or with polyethyleneoxy sidearms (**5**, **12**) which led to precipitates or isotropic solutions in similar conditions.

Regarding the chain length (OC_nH_{2n+1}), one can note that the gelation was observed at ambient temperature for $6 < n < 16$; the most efficient derivatives being **9**–**11** ($n = 8$, 9, 10) and **14**–**15** ($n = 11$, 12). From the foregoing gelation tests no *odd–even* effect[50] within the series such as those observed for homologous alkanes could be detected.

Search for the most efficient compounds. A more precise evaluation of the efficiencies of anthraquinone derivatives **9**–**11** and **14**–**15** could be made at lower concentrations (5×10^{-3} M). From these studies, compounds **10** (in alcohols) and **15** (in *n*-heptane) seem to emerge. It is remarkable that at ambient temperature one molecule of **10** is statistically able to gelify *ca*. 5000 molecules of methanol or *ca*. 3500 molecules of ethanol whereas one molecule of **15** can imprison 1400 molecules of *n*-heptane at ambient temperature. Obviously, this number of molecules is higher at lower temperatures.

Table 3 Organic solvents tested for gelation at 5×10^{-3} M of gelator at ambient temperature

		Gelator		
Solvent	E_N^T	**10**	**11**	**15**
n-Pentane	0.009	T	S (G)	S (G)
n-Hexane	0.010	*G*	*G*	*G*
n-Heptane	0.012	*G*	*G*	*G*
Isooctane	0.015	*G*	*G*	*G*
Light oil		S (P)	S (P)	S (P)
Olive oil		SS	SS	SS
Toluene	0.099	S	—	S
Styrene		S	S	S
Benzene	0.111	S	S	S
Diethyl ether	0.117	SS	S	S
Tetrahydrofuran	0.207	T	T	T
Chloroform	0.259	T	T	T
Dichloromethane	0.309	T	T	T
Acetone	0.355	S (G)	S (G)	*G*
Dimethylformamide	0.404	—	S (G)	S (G)
Acetonitrile	0.460	T	T	T
Propan-2-ol	0.546	S (G)	S (G)	S (G)
n-Hexanol	0.559	*G*	*G*	*G*
Propan-1-ol	0.617	*G*	*G*	*G*
Ethanol	0.664	*G*	*G*	*G*
Ethanol–water (4:1)	0.710	*G*	*G*	*G*
Methanol	0.762	*G*	*G*	T (G)

Symbols are identical to those used for Table 1. E_N^T values are extracted from ref. 49.

Solvent screening. The most effective gelators **10**, **11** and **15** were tested at lower concentration in an attempt to extend the scope of the solvents which could be used to form a gel. Twenty solvents or a mixture of solvents and two natural oils were arbitrarily selected (Table 3). In order to establish more precisely the relationship between the chain structures and gelation ability, we used a larger range of organic fluids as mentioned in Table 3. Obviously the gel phase appears on the border of the solution phase and the solid phase, so that organogelators are required to possess both slight self-aggregation ability and moderate affinity with organic fluids. These conditions are not respected for aromatic hydrocarbons, ethers and halogen solvents. The data in Table 3 reveal that primary alcohols are efficiently gelified. The gelation of an ethanol–water (4:1) mixture suggests their possible use for drug delivery. Besides alcohols, aprotic polar solvents like acetone and dimethylformamide are also gelified even if the gel-to-sol transition occurs at a lower temperature when the same concentration is used: indeed, a more significant amount of gelator is needed to observe identical T_{Gel}. Several alkanes are also gelified under those conditions. These latter experimental data signify that the formation of the gel should be essentially driven by dipole–dipole interactions and van der Waals interactions. This also leads us to conclude that the aromatic part and the alkoxy chain play complementary roles for the formation of the gel phase. In keeping with the dipolar character of the disubstituted anthraquinones studied, the empirical parameter of dipolarity E_N^T was tentatively used for a possible correlation, but no fit was observed with gel formation, the latter occurring in saturated hydrocarbons and in alcohols which are at the extremes of this scale. To discuss the role of solvents in the gel formation, further data such as the gel-to-sol temperatures are needed.

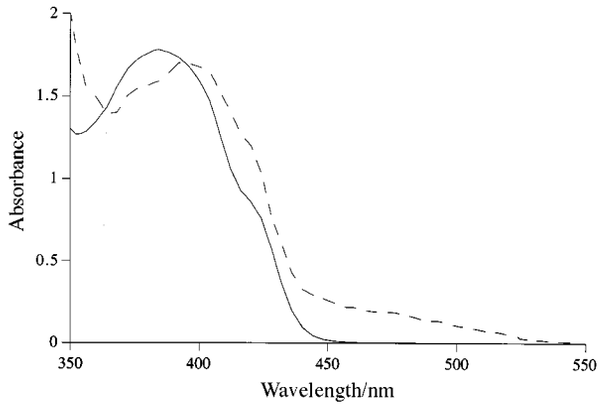


Fig. 2 Electronic absorption spectra of anthraquinone **11** (conc. 5×10^{-3} M) in ethanol at −5 °C (gel phase, – – –) and at 35 °C (isotropic phase, ———).

T_{Gel} measurements

Method 1. To determine the gel-to-sol phase transition temperatures, the inverted test-tubes (see Experimental section) containing the gel were warmed in a thermocontrolled bath. The T_{Gel} values were determined when the gel melted down; they could be reproduced with an accuracy of ±1 °C.

Method 2. The preceding method is based on a visual inspection whereas Method 2 involves a spectrophotometric technique. This phase transition could be also followed in some cases by UV–VIS measurements owing to the remarkable absorption of anthraquinones which display two strong absorption bands centred at 250 and 380 nm respectively. The transition at lower energy is markedly changed when decreasing the temperature as depicted in Fig. 2. A red shift is observed when gels are formed, compared to corresponding isotropic solutions. These changes are observed frequently for aggregates in comparison with monomers.[51] Taking advantage of clear spectral changes, the transition temperatures in anthraquinone-based organogelators could be readily 'read-out' by an electronic absorption technique, scanning the spectra at different temperatures, as depicted for **11** in ethanol at 5×10^{-3} M (Fig. 2). In view of the concentration needed for gelation (*ca.* 10^{-2} M) and the molar absorptivities of such compounds, this is restricted to efficient gelling agents which are able to form gels at low concentration to maintain absorbance within reasonable limits.

Method 3. In general, the gel-to-sol transition could be also followed by the spectroscopic turbidity method. The transmittance was measured at a wavelength where the anthraquinone chromophore does not absorb in isotropic solution (for example at 475 or 550 nm) while varying the temperature. At low temperatures, the values are due to a diffusion phenomenon if a network is formed. A typical experiment is presented in Fig. 3. The maximum of the first derivative of the absorbance *versus* temperature curve was taken as the gel-to-sol transition phase temperature (T_{Gel}) of the solution (Method 3). This is illustrated for compound **10** in *n*-heptane (Fig. 3). T_{Gel} values obtained at different wavelengths are identical. They were found to be close to those determined by the inverted test-tube method (Method 1).

Gel-to-sol phase transition temperatures *versus* gelling agent concentration

Using Methods 1 and 3, the T_{Gel} values were plotted as a function of concentration for the best gelling agents (**10**, **11** and **15**) in ethanol (Fig. 4a), *n*-heptane (Fig. 4b) and isopropanol (Fig. 4c) respectively. The upper phase above each curve is the sol whereas the phase below is the gel. The concentration has been limited to *ca.* 10^{-2} M for solubility reasons.

Table 4 ΔH (kJ mol^{-1}) calculated using data of Fig. 5a–c

Gelator	*n*-Heptane	Ethanol	Propan-2-ol
10	30	39	—
11	23	51	32
15	32	41	—

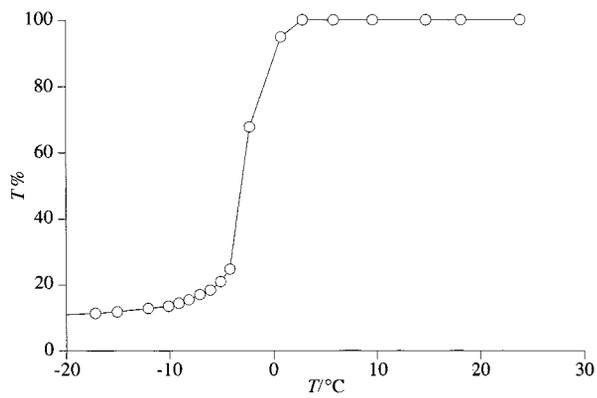


Fig. 3 Transmittance at $\lambda = 550$ nm of compound **10** in *n*-heptane at 5×10^{-3} M as a function of temperature (Method 3).

Anthraquinone derivatives form fibrillar aggregates (see Fig. 1) in the gel phase whereas they are discrete molecules in the isotropic phase. A simplified picture of the gel-to-sol phase transition is a process like dissolution of a solid into a solvent to form an ideal solution; the latter obeys the following equation:[52]

$$\ln C = -\frac{\Delta H_f}{R}\left(\frac{1}{T} - \frac{1}{T_f}\right) \quad (1)$$

When ΔH_f is the melting enthalpy, T_f is the solid melting point and C its molar concentration, the equation can be rewritten as follows:

$$\ln C = -\frac{\Delta H}{RT_{Gel}} + \text{const.} \quad (2)$$

The same relationship, derived by Ferry,[53] is often used to determine ΔH values in polymer gels.[1c] In the case of small molecular gels, eqn. (2) and the enthalpy data obtained thereof were recently discussed by Shinkai *et al.*[18] ΔH values of the present study, listed in Table 4, were determined from the slopes of the [ln C *vs.* $1/T_{Gel}$] plots in ethanol (Fig. 5a), *n*-heptane (Fig. 5b) and isopropanol (Fig. 5c) respectively. The slope of the lines affords the change of enthalpy associated with the gel-to-sol transition. The data are of the same order of magnitude as those found by Shinkai for a different system,[18] based on cholesterol aggregation.

Although the interpretation of ΔH data is delicate[18] because the gel melting is more complex than a crystal melting, the values could be related to the strength of the aggregates which form the gel [this is on average 8.5 kcal mol^{-1} (equivalent to eight van der Waals interactions)].

Gel-to-sol transition temperature variation as a function of chain length

The foregoing T_{Gel} values were plotted *versus* chain length ($n = 7$–12) for ethanol and *n*-heptane (Fig. 6). The values are given in mass% (here 0.65 g of gelling agent per 100 g of solvent) which is useful for applications and in molar concentration related to thermodynamic data. In molar concentration, compound **11** ($n = 10$) is the more efficient in the alcohol but not in the saturated alkane. For this latter solvent, two maxima

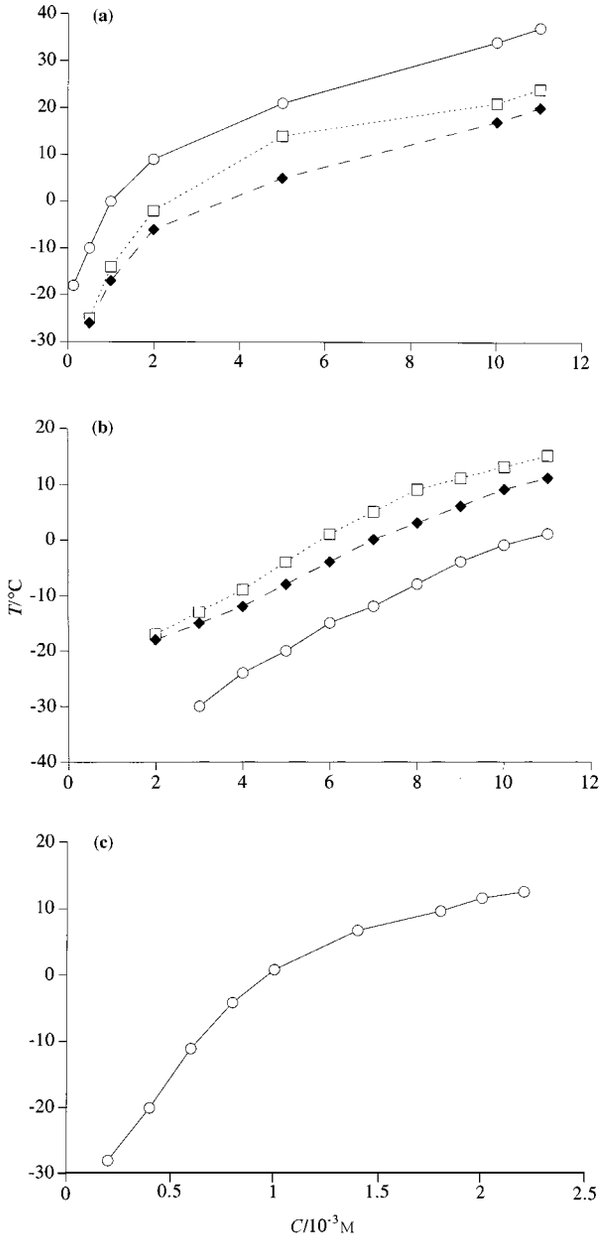


Fig. 4 (*a*) Gel-to-sol transition temperatures as a function of concentration in ethanol (Method 1) for compounds **10** (---□---), **11** (–○–) and **15** (– ◆- -). (*b*) Gel-to-sol transition temperatures as a function of concentration in *n*-heptane (Methods 1 and 3) for compounds **10** (---□---), **11** (–○–) and **15** (– ◆- -). (*c*) Gel-to-sol transition temperatures as a function of concentration in isopropanol (Method 1) for compound **11** (–○–).

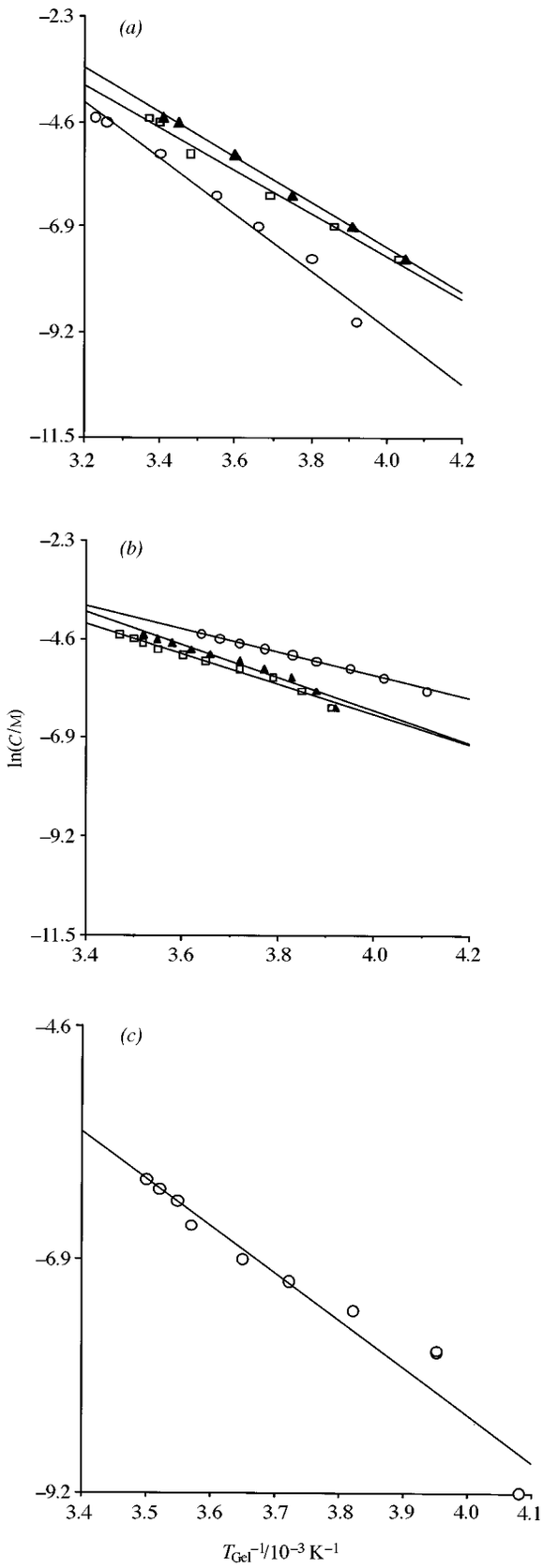


Fig. 5 (*a*) Plots of ln *C versus* T_{Gel}^{-1} in ethanol: compounds **10** (–□–), **11** (–○–) and **15** (–▲–). (*b*) Plots of ln *C versus* T_{Gel}^{-1} in *n*-heptane: compounds **10** (–□–), **11** (–○–) and **15** (–▲–).(*c*) Plot of ln **[11]** *versus* T_{Gel}^{-1} in isopropanol.

were found, both expressed in terms of mass% or in molar concentration, which are at the extrema of the studied series. The observed differences reflect the subtle balance between the propensity to self-aggregation and the affinity for solvent molecules. In this series, the range is narrow.

Conclusion

We have shown for the first time that 2,3-dialkoxyanthraquinones form yellow coloured thermoreversible gels with a large set of organic solvents; the gels in *n*-heptane do not involve H bonding for the network formation. The presence of 2,3-dialkoxy substituents is both structurally and electronically a prerequisite, emphasizing the necessity for an elongated structure. The shape of the entire alkyl chain might adopt a conformation inducing an in-between ability for crystallization and solubilization, by filling a larger space than the rigid anthraquinonic moiety. As shown by electron microscopy, the network is formed of entwined fibres liable to encage the solvent molecules. The most efficient gelators were found to incorporate 9 to 12 methylene groups in the linear chains. The

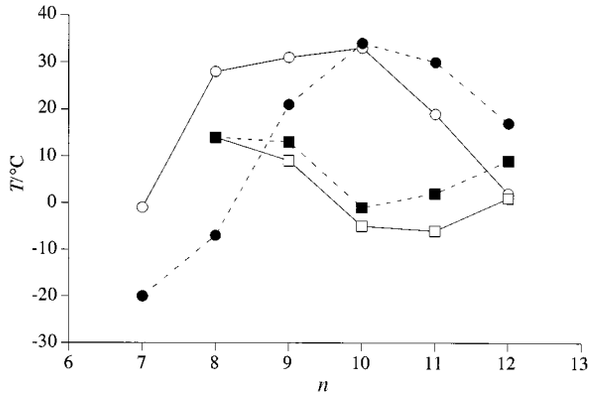


Fig. 6 Gel-to-sol transition temperature (Method 1) variation as a function of chain length. Ethanol 0.65 mass% (–○–); *n*-heptane 0.65 mass% (–□–); ethanol $c = 10^{-2}$ M (--●--); *n*-heptane $c = 10^{-2}$ M (--■--). n = 7–12: Compounds **8**–**11** and **14**, **15**.

concentration limits are *ca.* 5×10^{-3} M to 2×10^{-2} M. Further structural studies involving small angle neutron scattering (SANS) and X-ray scattering analyses, and differential scanning calorimetry (DSC) measurements are under way.

Experimental

Physical measurements

Mps were determined in capillary tubes on a Buchi 510 apparatus and are uncorrected. FTIR spectra were recorded on a Perkin Elmer Paragon 1000 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 250 AC instrument for solutions in $CDCl_3$ unless stated otherwise. Chemical shifts are given in ppm and J values are given in Hz. Chromatography separations were performed on SDS Silica Chromagel (70–210 μm). Mass spectra were obtained on an AutoSpeq EQ spectrometer. Elemental analyses were performed by the Microanalytical Service, Institut du Pin, University Bordeaux I. Electronic absorption spectra and transmission spectra were measured on an Hitachi U-3300 spectrophotometer equipped with a thermocontrolled cell monitored by a Lauda thermostat. The measurements were realized using cells having 10 mm optical pathlength and a platinum temperature sensor.

Transmission electron microscopy

The gels were deposited on formvar copper grids in sufficiently thin slices which were prepared by ultracryomicrotomy. Then the samples were recovered by a carbon-coated film before exploration with a GEOL 2000.

Gelation tests

In a typical gelation experiment, 1 cm^3 of solvent of special grade was added to a weighed amount of anthraquinone in a septum-capped test tube in order to have a concentration *ca.* 10^{-2} or 5×10^{-3} M as desired. The mixture was warmed to the boiling point until the solid was dissolved and then was allowed to cool down to room temperature. In those cases when a gel was formed, which generally occurred within several minutes and was confirmed by observing that the sample did not flow when the test tube was inverted, the tube was weighed to quantify the amount of gelatinized solvent. When the solution was turbid but the solvent was not entirely gelatinized, the mixture was warmed again and then cooled in a freezer (−18 °C) for 24 h. Some gelation tests were realized with 0.65 wt% gelator with similar equipment.

T_{Gel} measurements

Method 1. To determine the gel-to-sol phase transition temperature, we set up an inverted septum-capped glass tube (*ca.* 4 cm length and 0.7 cm diameter) containing the gel immersed in a thermocontrolled bath (ethanol or water were used as fluids depending on the temperature range), the temperature being raised at 2 °C min^{-1}. The T_{Gel} measurements were taken when the gel began to melt down. The reported values are the average of several measurements and have been found to be reproducible within ±1 °C.

Method 2. The electronic spectra were measured at 380 nm, using 10 mm cells and the temperature was varied at a constant rate (1.2 °C min^{-1} for a temperature increase and 3 °C min^{-1} for a temperature decrease).

Method 3. All the transmittances were measured at 475 and 550 nm, using 10 mm cells and the temperature was varied at a constant rate (1.2 °C min^{-1} for a temperature increase and 3 °C min^{-1} for a temperature decrease).

Reactions of hydroxy-9,10-anthraquinones with alkyl halides

Typical procedure. Anthraquinone and potassium carbonate (2.5 amount per hydroxy group) were dispersed in freshly distilled DMF (10 ml per 1 mmol). The solution being warmed until complete dissolution, the alkyl bromide (2.25 amount per hydroxy group) was then added within 20 min and the reaction mixture was refluxed for 12 h. After concentration, the remaining solid was hydrolysed with water and the aqueous layer was extracted continuously with dichloromethane. The organic layers were combined, dried ($MgSO_4$) and then filtered. Subsequent elution from silica with petroleum ether–dichloromethane as the eluent [percentage of dichloromethane, solvent system **A**: 20%, **B**: 40%, **C**: 50%] gave the desired product. After concentration, the crystalline residue was recrystallized from the appropriate solvent (*vide infra*).

1,2-Di-n-decyloxy-9,10-anthraquinone **2** was obtained as yellowish needles (84%); mp 101 °C (from heptane; Found: C, 78.37; H, 9.34. Calc. for $C_{34}H_{48}O_4$: C, 78.42; H, 9.29; O, 12.29); [Solvent System **B**]; δ_H (250 MHz) 8.20–8.15 (2 H, m, 5-H and 8-H), 8.02 (1 H, d, J 8.9, 4-H), 7.70–7.65 (2 H, m, 6-H and 7-H), 7.09 (1 H, d, J 9.0, 3-H), 4.05 (4 H, m, OCH_2), 1.90–1.85 (4 H, m, OCH_2CH_2), 1.50 [4 H, m, (CH_2)], 1.30–1.20 [24 H, m, (CH_2)] and 0.92 (6 H, m, CH_3); δ_C (62.9 MHz) 182.6, 182.4 (9-C and 10-C), 158.7 (2-C), 149.4 (1-C), 135.1 (8a-C), 133.3, 132.9 (6-C and 7-C), 132.7 (10a-C), 126.9 (8-C), 126.7 (4a-C), 126.5 (5-C), 125.0 (4-C), 122.9 (9a-C), 116.3 (3-C), 74.3 (OCH_2), 70.9 (OCH_2), 31.9 (t), 31.8 (t), 30.3 (t), 29.6 (d), 29.4 (t), 29.2 (t), 26.1 (t), 22.7 (t) and 13.9 (CH_3); ν_{max} (KBr)/cm^{-1} 2953, 2917, 2849, 1670, 1576, 1465, 1338, 1309, 1272 and 713; *m*/*z* 520.6 (M$^+$, 60%), 380.4 (16), 240.1 (100).

1,2-Di-n-hexadecyloxy-9,10-anthraquinone **3** was obtained as yellowish prisms (69%); mp 52 °C (from heptane); [Solvent System **A**]; δ_H (250 MHz) 8.20–8.15 (2 H, m, 5-H and 8-H), 7.99 (1 H, d, J 9.0, 4-H), 7.70–7.65 (2 H, m, 6-H and 7-H), 7.10 (1 H, d, J 9.0, 3-H), 4.09 (4 H, m, OCH_2), 1.92–1.86 (4 H, m, OCH_2CH_2), 1.50 [4 H, m, (CH_2)], 1.33–1.16 [48 H, m, (CH_2)] and 0.98 (6 H, m, CH_3); δ_C (62.9 MHz) 182.7, 182.6 (9-C and 10-C), 158.5 (2-C), 149.6 (1-C), 134.9 (8a-C), 133.2, 133.0 (6-C and 7-C), 132.5 (10a-C), 127.2 (8-C), 126.6 (4a-C), 126.3 (5-C), 125.2 (4-C), 123.4 (9a-C), 116.7 (3-C), 74.9 (OCH_2), 71.8 (OCH_2), 70.9 (t), 31.9 (t), 31.8 (t), 30.5–29.0 (d, nC), 26.4 (t), 26.2 (t), 22.7 (t) and 14.1 (CH_3); ν_{max} (KBr)/cm^{-1} 2960, 2921, 1672, 1581, 1464, 1330, 1309, 1271 and 715; *m*/*z* 688.8 (M$^+$, 32%), 240.0 (100).

2,3-Di-(3,6-dioxoheptyloxy)-9,10-anthraquinone **5**. 7-Tosyl-2,5-dioxoheptane was used in place of alkyl bromide. (19%); mp 59 °C (from methanol); [Solvent System **C**]; δ_H (250 MHz) 8.51 (2 H, m, 5-H and 8-H), 8.06 (2 H, m, 6-H and 7-H), 7.95 (2 H, s, 1-H and 4-H), 4.65 (4 H, t, 1′-H), 4.32 (4 H, t, 2′-H), 4.10 (4 H, t, 4′-H), 3.96 (4 H, t, 5′-H) and 3.78 (6 H, s, 7′-H); δ_C (62.9 MHz) 182.2 (9-C and 10-C), 153.3 (2-C and 3-C), 133.6

(6-C and 7-C), 133.4 (8a-C and 10a-C), 128.2 (4a-C and 9a-C), 126.8 (5-C and 8-C), 109.6 (1-C and 4-C), 72.0 (1′-C), 70.9 (5′-C), 69.3 (2′-C), 68.8 (4′-C) and 59.1 (7′-C); *m*/*z*: 444.3 (M^+, 20%), 240.1 (100).

2,3-Di-n-hexyloxy-9,10-anthraquinone **6** was obtained as yellow needles (88%); mp 89 °C (from methanol; Found: C, 76.37; H, 8.01. Calc. for $C_{26}H_{32}O_4$: C, 76.44; H, 7.90; O, 15.67); [Solvent System **B**]; δ_H (250 MHz) 8.17 (2 H, m, 5-H and 8-H), 7.66 (2 H, m, 6-H and 7-H), 7.60 (2 H, s, 1-H and 4-H), 4.12 (4 H, t, *J* 6.5, O*CH*$_2$), 1.82 (4 H, m, OCH$_2$*CH*$_2$), 1.44 (4 H, m, OCH$_2$CH$_2$*CH*$_2$), 1.27 (8 H, m, *CH*$_2$*CH*$_2$CH$_3$) and 0.85 (6 H, t, *J* 6.7, *CH*$_3$); δ_C (62.9 MHz) 182.5 (9-C and 10-C), 153.8 (2-C and 3-C), 133.6 (6-C and 7-C), 133.4 (8a-C and 10a-C), 128.1 (4a-C and 9a-C), 126.9 (5-C and 8-C), 109.3 (1-C and 4-C), 69.4 (O*CH*$_2$), 31.5 (*CH*$_2$CH$_2$CH$_3$), 28.9 (OCH$_2$*CH*$_2$), 25.6 (OCH$_2$CH$_2$*CH*$_2$), 22.6 (*CH*$_2$CH$_3$) and 14.0 (CH$_3$); ν_{max} (KBr)/cm^{-1} 3075, 2953, 2927, 2856, 1668, 1576, 1513, 1465, 1375, 1333, 1309, 1219, 1110, 1087, 713, 621; *m*/*z* 408.3 (M^+, 71%), 324.3 (23), 240.1 (100).

2,3-Di-n-heptyloxy-9,10-anthraquinone **8** was obtained as yellow needles (88%); mp 96 °C (from methanol; Found: C, 76.92; H, 8.21. Calc. for $C_{28}H_{36}O_4$: C, 77.02; H, 8.30; O, 14.68); [Solvent System **B**]; δ_H (250 MHz) 8.16 (2 H, m, 5-H and 8-H), 7.65 (2 H, m, 6-H and 7-H), 7.55 (2 H, s, 1-H and 4-H), 4.11 (4 H, t, *J* 6.5, O*CH*$_2$), 1.85 (4 H, m, OCH$_2$*CH*$_2$), 1.47 (4 H, m, OCH$_2$CH$_2$*CH*$_2$), 1.21 (12 H, m, *CH*$_2$) and 0.87 (6 H, t, *J* 6.7, *CH*$_3$); δ_C (62.9 MHz) 182.4 (9-C and 10-C), 153.7 (2-C and 3-C), 133.6 (6-C and 7-C), 133.5 (8a-C and 10a-C), 128.0 (4a-C and 9a-C), 126.8 (5-C and 8-C), 109.2 (1-C and 4-C), 69.3 (O*CH*$_2$), 31.8 (*CH*$_2$CH$_2$CH$_3$), 29.0 (t), 28.9 (t), 25.9 (t), 22.6 (*CH*$_2$CH$_3$) and 14.0 (CH$_3$); ν_{max} (KBr)/cm^{-1} 3076, 2956, 2924, 2854, 1669, 1577, 1513, 1466, 1377, 1332, 1312, 1219, 1111, 1087, 713, 621; *m*/*z* 436.3 (M^+, 100%), 338.3 (38), 240.1 (60).

2,3-Di-n-octyloxy-9,10-anthraquinone **9** was obtained as yellow needles (85%); mp 97 °C (from methanol; Found: C, 77.41; H, 8.77. Calc. for $C_{30}H_{40}O_4$: C, 77.50; H, 8.70; O, 13.80); [Solvent System **B**]; δ_H (250 MHz) 8.15 (2 H, m, 5-H and 8-H), 7.65 (2 H, m, 6-H and 7-H), 7.55 (2 H, s, 1-H and 4-H), 4.11 (4 H, t, *J* 6.5, O*CH*$_2$), 1.85 (4 H, m, OCH$_2$*CH*$_2$), 1.47 (4 H, m, OCH$_2$CH$_2$*CH*$_2$), 1.30–1.20 [16 H, m, (*CH*$_2$)] and 0.86 (6 H, t, *J* 6.7, *CH*$_3$); δ_C (62.9 MHz) 182.4 (9-C and 10-C), 153.7 (2-C and 3-C), 133.6 (6-C and 7-C), 133.5 (8a-C and 10a-C), 128.0 (4a-C and 9a-C), 126.8 (5-C and 8-C), 109.2 (1-C and 4-C), 69.3 (O*CH*$_2$), 31.8 (t), 29.4 (t), 29.3 (t), 29.0 (t), 25.9 (OCH$_2$CH$_2$-*CH*$_2$), 22.7 (O*CH*$_2$CH$_3$) and 14.1 (*CH*$_3$); ν_{max} (KBr)/cm^{-1} 3076, 2921, 2851, 1671, 1576, 1515, 1465, 1377, 1332, 1315, 1220, 1111, 1087 and 712; *m*/*z*: 464.3 (M^+, 100%), 353.1 (44), 240.0 (85).

2,3-Di-n-nonyloxy-9,10-anthraquinone **10** was obtained as yellow prisms (85%); mp 103–104 °C (from methanol; Found: C, 77.95; H, 8.89. Calc. for $C_{32}H_{44}O_4$: C, 78.01; H, 8.99; O, 13.00); [Solvent System **B**]; δ_H (250 MHz) 8.17 (2 H, m, 5-H and 8-H), 7.66 (2 H, m, 6-H and 7-H), 7.59 (2 H, s, 1-H and 4-H), 4.13 (4 H, t, *J* 6.5, O*CH*$_2$), 1.82 (4 H, m, OCH$_2$*CH*$_2$), 1.45 (4 H, m, OCH$_2$CH$_2$*CH*$_2$), 1.30–1.20 [20 H, m, (*CH*$_2$)] and 0.83 (6 H, t, *J* 6.7, *CH*$_3$); δ_C (62.9 MHz) 183.1 (9-C and 10-C), 153.5 (2-C and 3-C), 133.6 (6-C and 7-C), 129.5 (8a-C and 10a-C), 127.7 (4a-C and 9a-C), 126.9 (5-C and 8-C), 109.3 (1-C and 4-C), 69.4 (O*CH*$_2$), 31.9 (t), 29.6 (t), 29.4 (t), 29.3 (t), 28.9 (t), 25.9 (OCH$_2$CH$_2$*CH*$_2$), 22.7 (O*CH*$_2$CH$_3$) and 14.1 (*CH*$_3$); ν_{max} (KBr)/cm^{-1} 3078, 2957, 2920, 2850, 1670, 1575, 1514, 1466, 1332, 1220, 1111, 712 and 621; *m*/*z*: 492.3 (M^+, 100%), 367.1 (24), 240.0 (53).

2,3-Di-n-undecyloxy-9,10-anthraquinone **14** was obtained as yellow prisms (79%); mp 97 °C (from heptane–benzene; Found: C, 79.88; H, 9.64. Calc. for $C_{36}H_{44}O_4$: C, 79.79; H, 9.55; O, 11.65); [Solvent System **A**]; δ_H (250 MHz) 8.26 (2 H, m, 5-H and 8-H), 7.74 (2 H, m, 6-H and 7-H), 7.67 (2 H, s, 1-H and 4-H), 4.18 (4 H, t, *J* 6.9, O*CH*$_2$), 1.89 (4 H, m, OCH$_2$*CH*$_2$), 1.48 (4 H, m, OCH$_2$CH$_2$*CH*$_2$), 1.25 [28 H, m, (*CH*$_2$)] and 0.87 (3H, t, *J* 6.6, *CH*$_3$); δ_C (62.9 MHz) 182.7 (9-C and 10-C), 153.5 (2-C and 3-C), 133.7 (6-C and 7-C), 133.5 (8a-C and 10a-C), 128.0 (4a-C and 9a-C), 126.9 (5-C and 8-C), 109.3 (1-C and 4-C), 69.4 (OCH$_2$), 32.0 (t), 29.8 (t), 29.7 (t), 29.6 (t), 29.4 (t), 28.9 (t), 26.0 (d, 2C), 22.7 (*CH*$_2$CH$_3$) and 14.2 (CH$_3$); ν_{max} (KBr)/cm^{-1} 2955, 2922, 2849, 1669, 1576, 1515, 1466, 1378, 1329, 1221, 1113, 713 and 621; *m*/*z*: 540.3 (M^+, 100%), 389.1 (37), 240.0 (59).

2-n-Dodecyloxy-9,10-anthraquinone **21** was obtained as pale yellow needles (86%); mp 143 °C (from heptane–benzene; Found: C, 79.67; H, 8.11. Calc. for $C_{26}H_{32}O_3$: C, 79.56; H, 8.22; O, 12.23); [Solvent System **B**]; δ_H (250 MHz) 8.17 (2 H, m, 5-H and 8-H), 8.09 (1 H, d, *J* 8.7, 4-H), 7.62 (2 H, m, 6-H and 7-H), 7.53 (1 H, d, *J* 2.5, 1-H), 7.14 (1 H, dd, *J* 8.7, 2.6, 3-H), 4.05 (2 H, t, *J* 6.6, OCH$_2$), 1.84 (2 H, m, OCH$_2$*CH*$_2$), 1.43 (2 H, m, CH$_2$), 1.30–1.25 [16 H, m, (CH$_2$)] and 0.88 (3 H, t, *J* 6.7, CH$_3$); δ_C (62.9 MHz) 183.2, 181.3 (9-C and 10-C), 160.7 (2-C), 134.8 (s), 133.6 (s), 133.0 (s), 132.5, 132.0 (6-C and 7-C), 127.1 (4-C), 126.3, 126.0 (5-C and 8-C), 124.7 (4a-C), 119.8 (1-C), 116.0 (3-C), 68.8 (OCH$_2$), 31.7 (*CH*$_2$CH$_2$CH$_3$), 29.8 (OCH$_2$*CH*$_2$), 29.4 (t), 29.1 (t), 29.0 (t), 28.8 (t), 26.1 (t), 25.8 (t), 22.8 (*CH*$_2$CH$_3$) and 14.2 (CH$_3$); ν_{max} (KBr)/cm^{-1} 2917, 2845, 1671, 1592, 1576, 1470 and 719; *m*/*z* 392.4 (M^+, 56%), 240.1 (100); HRMS (FAB^+) MH^+ Found 393.2438, Calc. 393.2431.

2-n-Hexadecyloxy-9,10-anthraquinone **22** was obtained as pale yellow needles (41%); mp 69 °C (from benzene); [Solvent System **A**]; δ_H (250 MHz) 8.19 (2 H, m, 5-H and 8-H), 8.11 (1 H, d, *J* 8.7, H4), 7.67 (2 H, m, 6-H and 7-H), 7.59 (1 H, d, *J* 2.5, H1), 7.15 (1 H, dd, *J* 8.7, 2.6, H3), 4.10 (2 H, t, *J* 6.6, OCH$_2$), 1.88 (2 H, m, OCH$_2$*CH*$_2$), 1.46 (2 H, m, CH$_2$), 1.32–1.18 [24 H, m, (CH$_2$)] and 0.93 (3 H, t, *J* 6.7, CH$_3$); δ_C (62.9 MHz) 183.2, 181.3 (9-C and 10-C), 160.7 (2-C), 134.8 (s), 133.6 (s), 133.0 (s), 132.5, 132.0 (6-C and 7-C), 127.1 (4-C), 126.3, 126.0 (5-C and 8-C), 124.7 (4a-C), 119.8 (1-C), 116.0 (3-C), 68.8 (OCH$_2$), 31.7 (t), 30–28.5 (t, nC), 26.3 (t), 25.8 (t), 22.4 (*CH*$_2$CH$_3$) and 13.2 (CH$_3$); ν_{max} (KBr)/cm^{-1} 2916, 2848, 1674, 1591, 1577, 1471 and 713; *m*/*z* 448.3 (M^+, 100%), 225.0 (82).

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