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Remarkably simple small organogelators: di-*n*-alkoxy-benzene derivatives

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Abstract

A series of symmetrically substituted di-*n*-alkoxy-benzene derivatives are shown to act as effective gelators for a range of organic liquids. These readily accessible compounds form thermoreversible gels which do not involve H bonds and open up new prospects for larger scale applications.

Keywords: benzene; gels; supramolecular chemistry; aggregation.

Over the last decade, the field of low molecular mass gelators has attracted considerable research interest.[1] It is now well accepted that gelation of organic liquids stems from the self-aggregation of gelator molecules leading to the formation of a three-dimensional network of intertwined, elongated fibres that immobilize the solvent molecules on the macroscopic scale.[1a] A large diversity of chemical families of gelators was discovered and the properties of their gels were investigated in order to have an insight into structural and mechanistic aspects of network formation. Yet the necessary and sufficient structural factors at the molecular level that govern gelation ability are not well identified, and the elaboration of design strategies towards tailor-made systems remains a challenging goal.

Besides this fundamental approach, organic gels with low molecular mass gelators are becoming very attractive as self-assembled supramolecular templates for the generation of mesoporous or functional materials. Recently, elegant examples of polymerization reactions in gels were indeed reported to lead to new polymeric systems, organic[2] or inorganic,[3] with remarkable properties. Organogels are thus promised to far-reaching perspectives provided that there will be the possibility to produce low-mass organogelators economically and from simple synthetic procedures. Up to now, examples of such simple gelators remain quite rare, exceptions such as tetraalkyl ammonium halides[2a] or cyclic bis-urea compounds[4] could be cited. Although one can note that most of the reported gelators possess plural hydrogen bonding sites that provide self-complementarity or self-aggregative properties, some of us focused on the gelation propensities of various dialkoxy polycyclic arenes.[5] In that connection, we report

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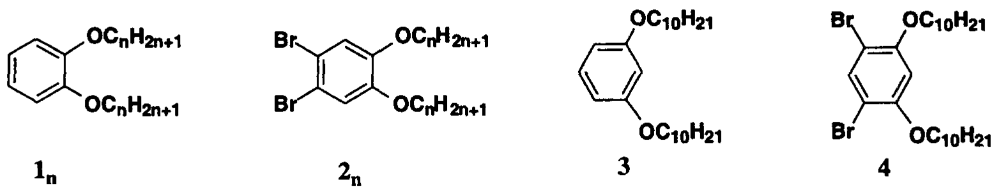

Figure 1.

Table 1

Gel-to-sol phase transition temperatures of **1**–**4** in organic fluids at 5×10^{-2} M

Solvent	$\mathbf{1_8}$	$\mathbf{1_{10}}$	$\mathbf{1_{16}}$	$\mathbf{2_8}$	$\mathbf{2_{10}}$	$\mathbf{2_{16}}$	**3**	**4**
Acetonitrile	15	26	32	25	38	p	28	31
Propylene Carbonate	1	22	9	28	-2	4	-20	43
Dimethylformamide	s	7	45	-15	6	p	17	14
Dimethylacrylamide	s	5	30	s	-8	-8	s	11
Methanol or Ethanol	c	c	c	c	c	c	c	c

s = soluble, p= soluble at solvent reflux temperature but precipitate upon cooling
c = crystallization

therein the ability of a series of very simple compounds, symmetrically substituted di-*n*-alkoxy-benzene derivatives, $\mathbf{1_n}$, $\mathbf{2_n}$, **3**, **4** (Fig. 1), to gelate several organic solvents.

According to our previous studies, a range of linear chain lengths was selected (*n*=8–16). The synthesis of these compounds (except that of compound **4**) was already reported in literature but their gelation ability was never mentioned.[6] Gelators $\mathbf{1_n}$ and **3** were obtained by direct alkylation of catechol and resorcinol, respectively, under classical conditions. Multi-gram amounts of these compounds can be easily obtained with high purity in one step from low cost commercially available starting materials. For the preparation of the dibromo analogues, $\mathbf{2_n}$ and **4**, catechol and resorcinol were dibrominated with Br_2 in CCl_4 at room temperature, and then alkylated according to the same procedures as above.[7]

At ambient temperature, 1,2- and 1,3-dialkoxy-benzenes form isotropic solutions even concentrated in heptane, ethyl acetate, toluene, diethyl ether or chloroform. In contrast, they are sparingly soluble in dimethylformamide, dimethylacrylamide, acetonitrile and propylene carbonate. They gradually dissolve upon heating and gel formation occurs upon cooling. Gelation properties were systematically investigated at 5×10^{-2} M using the inverted test-tube method[8] and are summarized in Table 1. The gels obtained were translucent to opalescent, and were found to be stable for weeks.

While parent molecules having an anthracene or an anthra-9,10-quinone unit as an aromatic part were reported to display outstanding gelling abilities in alcoholic solvents,[5] here ethanol was found to be a very efficient solvent for recrystallization. This shows that the most difficult task in developing new organogelators is prevention of the transformation from the metastable gel to a crystalline state. In our series, the driving force for gel formation may originate through a subtle counterbalance between π–π stacking, dipole–dipole and van der Waals interactions. The length of the alkyl chain causes clear differences in solvent compatibility and gelation efficiencies. No optimal carbon number of the alkoxy substituents has been found, suggesting a balance between the propensity to self-aggregation and the affinity for solvent molecules. In contrast to bis-ureido phenyl compounds,[4] the *meta*-substituted benzene derivatives **3**–**4** are also potent organogelators. Furthermore, the packing abilities brought by the bromine atoms reinforce the strength of the network for the latter compound. The *para*-substituted analogue (1,4-

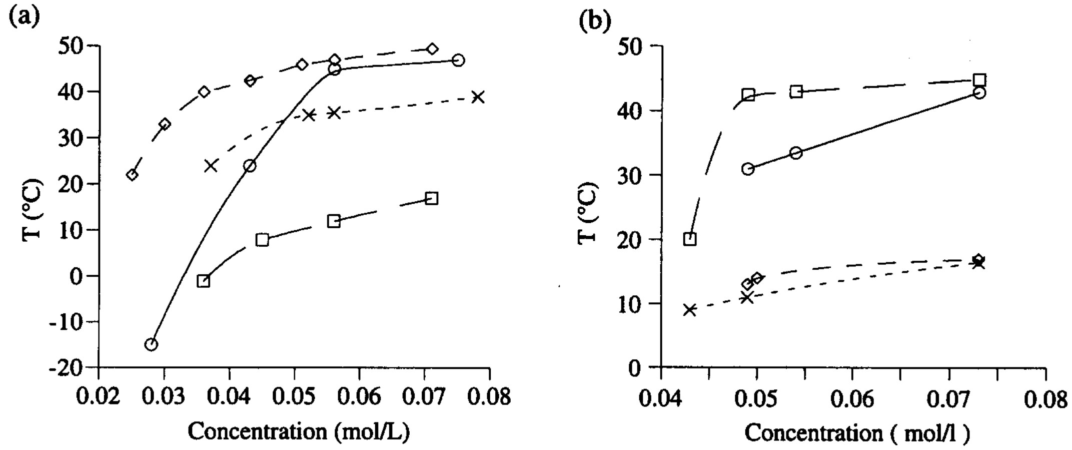

Figure 2. Gel-to-sol transition temperatures as a function of concentration in acetonitrile (—○—), propylene carbonate (—□—), dimethylformamide (—◇—) and dimethylacrylamide (—×—) for compounds: (a) **1**$_{16}$ and (b) **4**

bis-decyloxybenzene) synthesized from hydroquinone, failed to gelate any solvent investigated and led to a precipitate or to crystalline platelets. Even if several questions remain unanswered, the gelation phenomenon seems not to be restricted to dialkoxy arene molecules possessing an oblong shape although the symmetry of the building blocks seems to play a major role.[5]

The gel-to-sol transition temperatures as a function of concentration plots (Fig. 2a,b) clearly demonstrate that thermoreversible gels can be formed over an important range of concentrations and that efficient gelation requires a minimum concentration of ca. 3×10^{-2} M (i.e. 10–20 g L^{-1}), which is higher in most cases than for polycyclic aromatic gelators.[5] This may represent a positive feature with regard to network imprinting by gel polymerization as a high density of fibers is needed. The gelation ability of polymerizable monomers such as dimethylacrylamide opens up such a prospect, and low-temperature polymerization experiments are underway. The easy synthetic access to large amounts will favor further studies and applications at a larger scale.

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7. Compound **4**: mp 53°C (methanol); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.63 (s, 1H, H-5), 6.44 (s, 1H, H-2), 3.94 (t, 4H, O-CH_2), 1.82 (m, 4H, O-CH_2-CH_2), 1.60–1.20 (m, 4H, CH_2), 0.82 (t, 6H, CH_3); ^{13}C NMR (82.5 MHz, $CDCl_3$) 155.6 (C-1, C-3), 135.7 (C-5), 102.9 (C-6), 99.7 (C-4, C-6), 69.6 (O-CH_2), 31.9, 29.6, 29.5, 29.4, 29.1, 25.9 (CH_2), 22.7 (CH_2-CH_3) and 14.1 (CH_3).
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