An Easy To Prepare Organic Salt as a Low Molecular Mass Organic Gelator Capable of Selective Gelation of Oil from Oil/Water Mixtures

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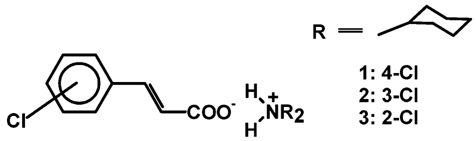
Quite a few low molecular mass organic gelators[1] (LMOGs) and their applications[2] have been reported so far. These physical gels obtained from LMOGs depend on relatively weak interactions, for example, hydrogen bonding, to form a 3-D network that immobilize the solvent molecules, leading to gel formation. During the course of our investigations in the area of crystal engineering of an organic acid−base adduct,[3] we recently found that a simple organic salt[4] can harden few organic solvents. We, therefore, launched an extensive search for new LMOGs based on organic salts. We decided to work on secondary ammonium (dicyclohexylammonium) salt of chloro-substituted monocarboxylic acid (2-, 3-, and 4-chloro cinnamic acid) because of the following reasons: (i) The hydrogen bonding network in such salt is expected to be one-dimensional (through COO$^-$···H−R$_2$N$^+$−H···$^-$OOC hydrogen bonding), which is believed to be one of the prerequisites for a molecule to have potential to become a LMOG,[5] (ii) the presence of conjugated aromatic and alicyclic (cyclohexyl) moieties might help in interacting with nonpolar solvents, and (iii) Cl···Cl nonbonded interactions[6] might play a role in the gelation process. To our delight, we observed that salt **1** (Scheme 1) is an excellent gelator for many organic solvents (nonpolar and polar) and oils (commercial fuels and edible oils). In an attempt to obtain insights into the gelation process, allied salts **2** and **3** were also prepared and investigated (Scheme 1).

Scheme 1



1 is found to be an excellent gelator of many nonpolar and polar organic solvents whereas **2** displayed remarkable gelation ability only with nonpolar solvents. Both **1** and **2** belong to the super-gelator category as the minimum gel concentration (MGC) of these gelators is less than or equal to 1.0 wt %. **1** forms remarkably stable gel (T_{gel} > 100 °C; see Supporting Information) with commercial fuels such as kerosene and diesel. However, salt **3** did not form gel with any solvent studied here (Table 1). SEM of gel of **1** in petrol (Figure 1a) and **2** in toluene (Figure 1b) displayed a typical fibrous network of varying thickness. In a petrol gel of **1**, a population of fibers (ca. 5.5−16 μm) could easily be seen, while in a toluene gel of **2**, an extremely complicated three-dimensional network of fibers (ca. 4−10 μm) is present. Understandably, the solvent molecules get immobilized in such network of fibers, resulting in gel formation.

Selective gelation of oil from an oil/water mixture is considered important in containing an oil spill problem.[7] Interestingly, **1** displays a remarkable ability to gelate selectively an oil (either commercial fuel or edible oil) in a biphasic mixture of oil/water (1 mL/1 mL). **1** is either solubilized in such a mixture by heating with or without the presence of few drops of MeOH and the solution is left to equilibrate. Within a few hours, the oil layer is found to be completely gelled, leaving the water phase unaffected.

The same observation is also seen when the experiment is carried out under vigorous shaking. By this way, **1** is found to gelate petrol, kerosene, cottonseed oil, sunflower oil, and coconut oil in such biphasic system of oil/water mixtures. It is interesting to note that **1** is also capable to gelate petrol from petrol/seawater, meaning that natural ions such as Na$^+$, K$^+$, Ca^{2+}, Br$^-$, SO$_4{}^{2-}$, etc. present in seawater do not affect the gelation process. When the gelator molecule is not soluble in

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Table 1. Gelation Behavior of 1, 2, and 3[a]

		1		2		
Sr. no.	solvents	MGC wt %	T_{gel} in °C	MGC wt %	T_{gel} in °C	3
1	CCl_4	<1.0	83	ppt		ppt
2	cyclohexane	0.32	75	ppt		FC
3	*n*-heptane	0.31	56	ppt		ppt
4	isooctane	0.25	78	ppt		FC
5	*n*-decane	0.91	91	0.88	80	Ppt
6	kerosene[b]	0.58	114	ppt		ppt
7	petrol[b]	0.42	58	<1.0	58	FC
8	diesel[b]	<1.0	106	ppt		FC
9	paraffin liquid	0.21	103	<1.0	78	FC
10	benzene	0.42	73	FC		FC
11	tolune	0.31	70	0.44	51	Ppt
12	chlorobenzene	0.25	58	FC		FC
13	bromobenzene	0.43	64	FC		FC
14	*o*-xylene	0.26	67	<1.0	60	FC
15	*m*-xylene	0.30	63	0.46	58	FC
16	*p*-xylene	0.29	61	0.36	63	FC
17	mesitylene	0.23	91	FC		FC
18	1,2-di-Cl-benzene	0.39	63	VL		ppt
19	DMF	0.82	RT	S		S
20	ethyl acetate	0.29	69	FC		FC
21	DMSO	1.07	71	S		S
22	nitrobenzene	0.35	84	FC		S
23	ground nut oil[b]	0.45	63	FC		FC
24	cottonseed oil[b]	0.32	70	FC		FC
25	sunflower oil[b]	0.32	85	ppt		FC
26	coconut oil[b]	0.25	95	1.01	62	FC
27	1,4-dioxane	0.39	65	ppt		FC

[a] wt % = g/100 mL of solvent. [b] g/100 g of solvent; FC = fibrous crystals; ppt = precipitate; S = solution.

water, the selective gelation of oil from oil/water mixture by a gelator is expected and not extraordinary. However, in the present case, **1** is completely soluble in water in the presence of a few drops of MeOH and sparingly soluble in water in the absence of MeOH. In fact, when **1** is left to equlibrate in a petrol/water biphasic mixture after heating the mixture at ~70 °C (remains biphasic), the aqueous layer was found to be 0.33 wt %(w/v, with MeOH) and 0.15 wt %(w/v, without MeOH). While **1** gave precipate with water, fibrous crystals were formed in a water/MeOH(few drops) mixture when treated individually. These results clearly suggest that **1** indeed shows preference for oil in such biphasic mixture at least when a few drops of MeOH are added to the mixture. The hydrophobic moieties such as alicyclic and aromatic rings in **1** must be repelling water and help it diffuse to an oil layer to achieve such selective gelation.

The asymmetric stretching of COO^- in FT-IR of **1** in a solid, gelled (CCl_4 and *n*-heptane), and solution (CCl_4, CH_2Cl_2, $CHCl_3$, *n*-heptane, and MeOH) state appeared around 1644 cm^{-1}, meaning that the anion is as strongly hydrogen-bonded with the ammonium cation in its gelled or solution state as in its bulk solid state, suggesting that no further hydrogen bonding is responsible for gel formation. However, the position of the halogen group in the aromatic ring also appears to be crucial in the gelation behavior of the resulting salts. While **1** (4-Cl) is capable of forming a gel with nonpolar as well as polar solvents, **2** (3-Cl) displayed gelation only with a nonpolar solvent. Surprisingly **3** (2-Cl) did not effect any gelation with the solvents studied here. To gain further insights into the gelation process, attempts were made to determine the single-crystal structures of the salts. However, X-ray quality crystals of **3** could only be obtained from an ethyl acetate solution by slow evaporation. Any attempt to obtain X-ray quality crystals either of **1** or **2** turned out to be unsuccessful.

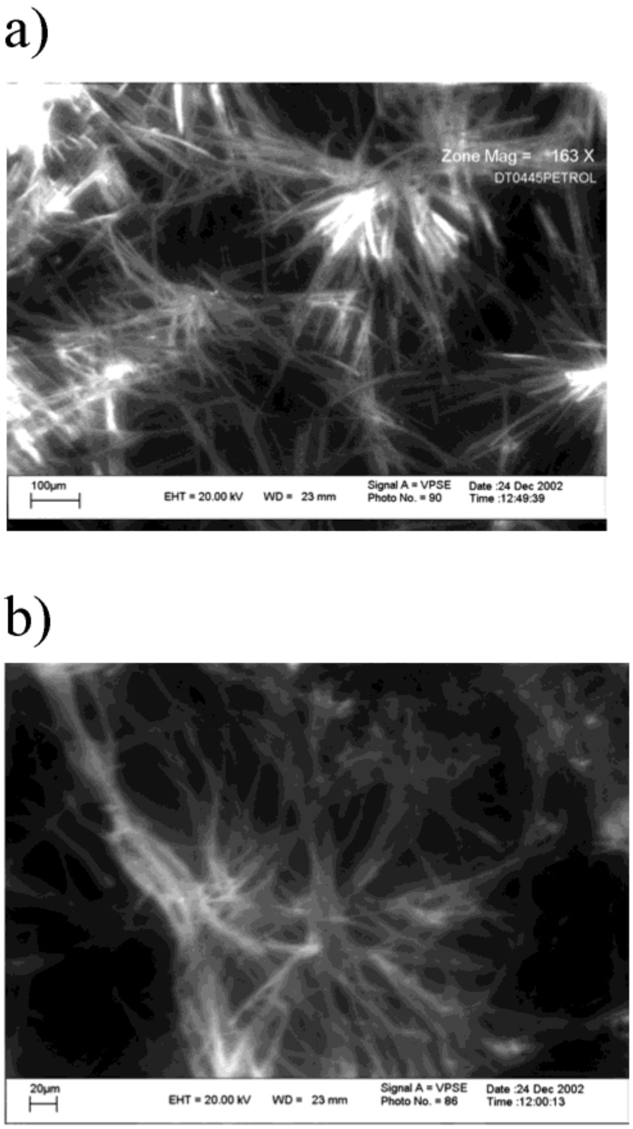

Figure 1. SEM micrograph of 2.5 wt % gel of (a) **1** in petrol (scale bar = 100 μm) and (b) **2** in toluene (scale bar = 20 μm).

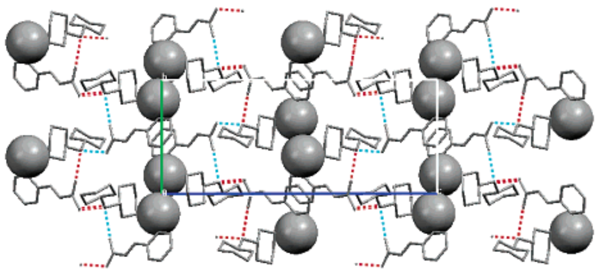

Figure 2. Packing of **3** in its crystal structure displaying a 1D hydrogen-bonded network of anions and cations and Cl···Cl nonbonded contact. Hydrogen atoms are not shown and Cl atoms are represented in a CPK model to show the short contacts.

As expected, the molecular aggregate in the crystal structure (see Supporting Information) of **3** (Figure 2) is a 1D hydrogen-bonded network between anions (COO^-) and cations ($H-R_2N^+-H$). Two O atoms of COO^- anion is involved in hydrogen bonding with two symmetry-related dicyclohexylammonium cations through N−H···O hydrogen bonding (N···O = 2.748(2) and 2.710(4) Å), leading to a 1D chain. Such 1D chains, which are running parallel to the crystallographic *b*-axis, are further stabilized in the crystal lattice through reasonably significant Cl···Cl (3.393 Å) interactions. Shinkai et al. and collaborator's recent findings propose that a 1D hydrogen-bonded network promotes gelation whereas the 2D and 3D networks either produce a weak gel or do not promote gelation at all.[8] Considering significant Cl···Cl interactions and hydrogen bonding together in **3**, the overall assembly can be regarded as a 2D network propagating through a b−c plane, which may be the reason behind **3** being a nongelator. Although in the absence of crystal structures of **1** and **2** it is unclear why **1** and **2** go to metastable gelled states instead of thermodynamically more stable crystalline states, it may be reasonable to assume that the 1D network arising from $COO^{-}\cdots H-R_2N^{+}-H\cdots {}^{-}OOC$ hydrogen bonding between cations and anions is the main supramolecular motif that is responsible for the metastable gelled states in salts **1** and **2**. A change in position of Cl from 2 (in salt **3**) to 3 (in salt **2**) and 4 (in salt **1**) in the aromatic ring must be playing a crucial role in the gelation process.

The ability of **1** to gel commercial fuels and edible oils from a biphasic mixture of oil/water is significant. Overall, salts **1** and **2** represent a new type of LMOGs that are easy to prepare, quite efficient, and versatile. The present system is definitely attractive because of its easy preparation and simplicity of the gelator molecules. Work on related systems is underway.

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Supporting Information Available: Preparation of all new compounds **1**−**3** and their analytical data (melting points, IR, ^{1}H NMR, and elemental analysis), T_{gel} measurement, data collection, crystallographic parameters, ORTEP diagram, and hydrogen-bonding parameters of **3** (PDF). Crystallographic information (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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