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First donor–acceptor interaction promoted gelation of organic fluids

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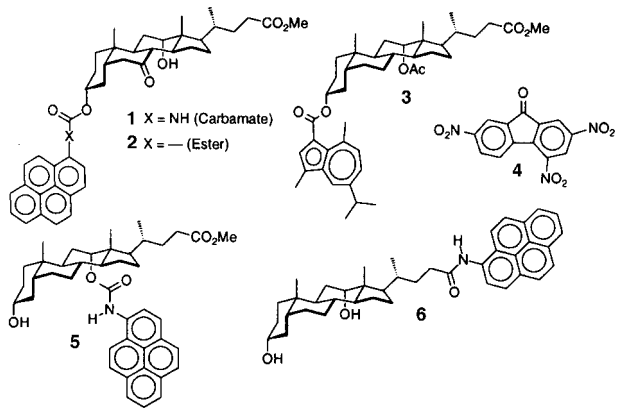
Bile acid derivatives functionalized at the 3-position with an aromatic group formed gels in organic solvents in the presence of trinitrofluorenone.

In recent years there has been considerable interest in developing new types of gelators of organic solvents.[1] Despite the recent advances, *a priori* design of a gelator for gelling a given solvent has remained a challenging task. Various non-covalent interactions like hydrogen-bonding,[2] metal coordination[3] *etc.* have been used as the driving force for the gelation process. A special class of cholesterol-based gelators were reported by Weiss,[4] and by Shinkai.[5] Gels derived from these molecules have been used for chiral recognition/sensing,[6] for studying photo- and metal-responsive functions,[7] and as templates to make hollow fiber silica.[8] Other types of organogels have been used for designing polymerized [9] and reverse aerogels,[10] and in molecular imprinting.[11] Hanabusa's group has recently reported organogels with a bile acid derivative.[12] This has prompted us to disclose our results on a novel electron donor–acceptor (EDA) interaction mediated two-component[13] gelator system based on the bile acid[14] backbone.

During the course of our investigation on bile acid-based molecular tweezers[15] it was discovered that aromatic donor-substituted bile acid derivatives such as **1**–**3**† gelatinized certain organic solvents *in the presence of* trinitrofluorenone **4** as the acceptor.‡ Interestingly, the location of the pyrene unit on the bile acid appeared to be critical, as shown by compounds **5** and **6** which did not form gels in the presence of **4**. The results from the gelation studies are summarized in Table 1. Pyrene derivative **1** in general formed highly stable gels even with less than 1% of the gelator. Compound **4** in the presence of the methyl pyrene-1-carboxylate did *not* form a gel in BuOH and $CHCl_3$.



The stoichiometric requirement of the two components was easily established by measuring the T_{gel}[16] as a function of the ratio of **4**:**1** at a constant concentration of **1**. A steady increase of T_{gel} was observed with increasing amounts of **4** but after 1.25 equiv. were added there was no measurable increase, suggesting the requirement of a 1:1 stoichiometry for effective gelation. This experiment was also carried out in the reverse manner (constant concentration of **4** and variable concentration of **1**) with identical conclusion.

Table 1 Results from gelation studies[a]

Entry	Solvent	1/4	2/4	3/4
1	Bu^nOH	SG[b]	G	G
2	Bu^tOH	SG[b]	SG[b]	G
3	Bu^tOH–$CHCl_3$ (5:1 v/v)	G[c]	SG[c]	G
4	EtOH–$CHCl_3$ (3:1 v/v)	SG[b]	G[b]	G
5	Cyclohexanol	SG	SG	G
6	$CHCl_3$	G	S	S
7	*n*-Octanol	S	S	G
8	$(CH_2OH)_2$–$CHCl_3$ (3:1 v/v)	G	P	G
9	Trigol–$CHCl_3$ (3:1 v/v)	SG	P	G
10	Benzene	S	S	S
11	Cyclohexane	P	P	P
12	Cyclohexanone	S	S	S
13	$(CHCl_2)_2$	S	S	S

[a] SG = super gel (< 1 wt% gelator), G = gel (1–2 wt% of gelators), S = solution, P = precipitate. [b] These gels exhibited thixotrophy. [c] By changing the amount of $CHCl_3$ the T_{gel} could be increased or decreased.

The gels were dried in vacuum[5] and subjected to SEM analysis to examine the morphology.§ The SEM of a dried sample from **3**/**4** (Fig. 1) showed a complex three-dimensional fibrous structure with an average fiber diameter of *ca.* 2 μm. Such fibrous networks have been observed by many others, and appear to be characteristic of most gels. The SEM pictures from the xerogels derived from the other two systems did not show any obvious fibrous structure.

The gels formed from colorless **1** and **2** (and pale yellow **4**) are colored due to a charge-transfer band. The intensity of this band changes substantially during the gelation. The temperature dependence of this absorption band has been examined for **1** and **2** in $CHCl_3$ by UV-VIS spectroscopy (data for **1** are shown in Fig. 2). It is clear from this plot that the gelation process is associated with an increase in the donor–acceptor interaction because of the substantial increase in the charge transfer around

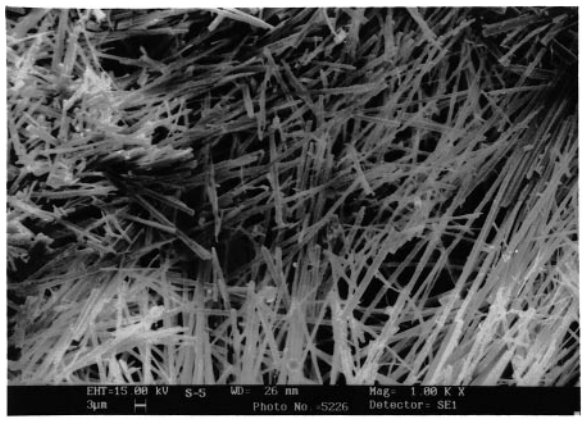


Fig. 1 Scanning electron micrograph of a dried gel derived from **3**/**4** in *n*-octanol (3% w/w) showing a fibrous network.

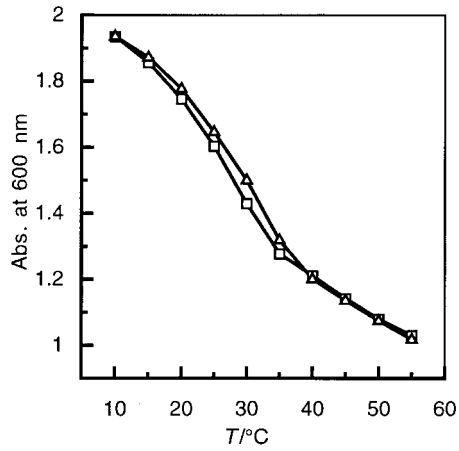


Fig. 2 Plot of A_{600} (1 mm cuvette) *vs.* temperature for gel obtained from **1** and **4** in $CHCl_3$ (62 mM each; this corresponds to 2.8% w/w of **1**): (□) cooling and (△) heating.

T_{gel}. With a true solution of **1** and **4** (in a 1 : 1 ratio) in $CHCl_3$ a monotonous increase in the absorbance was observed as the temperature was decreased in the same range. This, and the observation that no gelation occurs in the absence of **4**, suggest that the donor–acceptor interaction between the pyrene unit on the steroid and **4** is the primary driving force responsible for gelation.

Since **1** formed good gels in $CHCl_3$ (entry 6, Table 1), ^{1}H NMR spectroscopy was used to investigate the temperature dependence of the chemical shifts in $CDCl_3$. A 2.8 wt% sample was prepared in $CDCl_3$ and NMR spectra were recorded from 22 (gel) to 42 °C (fluid). Significant changes in chemical shifts were observed for the protons from **4** and the carbamate NH. A plot of the chemical shift against temperature for the C_3-H of **4** is shown in Fig. 3.[17] It is satisfying to observe that the T_{gel} determined from UV (35 °C) and NMR spectra (*ca.* 38 °C) of the same sample were comparable to that measured by the method of Takahashi *et al.*[16] (*ca.* 35 °C). The existence of hysteresis is also clear from this plot. It was also observed that the T_1 value (^{1}H) for the methoxycarbonyl group decreased from 1.48 s in the gel phase (3.8 wt %) to 1.08 s in the fluid phase (1.2 wt%) at 22 °C, suggesting reduced segmental motion of the sidechain in the gel in $CDCl_3$.

In conclusion, we have demonstrated for the first time a two-component organic gelator system which can gelatinize several organic fluids (primarily alcohols) through *donor–acceptor interaction*. The requirement of EDA for the gelation has been established from our studies, but the role of the bile acid backbone is yet to be uncovered. These systems are currently being extensively investigated to understand their structure–property relationships, three dimensional structures and material properties. We believe that these novel phases will expand our understanding of the gelation of organic fluids, and will also lead to the development of new materials for futuristic applications.[18]

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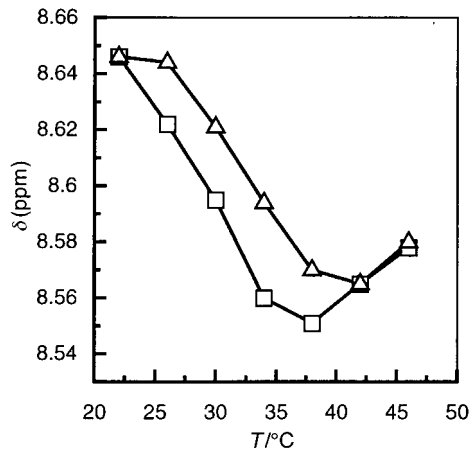

Fig. 3 Plot of chemical shift of C_3-H of **4** *vs.* temperature (the gel composition is the same as in Fig. 2): (□) cooling and (△) heating.

Notes and references

† *Selected data* of **1**: Mp 198 °C; δ_H(300 MHz, $CDCl_3$) 7.85–8.5 (m, 9H), 7.79 (br, 1H), 4.78 (m, 1H), 3.85 (m,1H), 3.67 (s, 1H), 2.73 (m, 1H), 1.1–2.4 (steroidal CH and CH_2), 1.05 (s, 3H), 0.89 (d, *J* 4.5, 3H), 0.57 (s, 3H); δ_C(75 MHz, $CDCl_3$) 211.74, 174.7, 154.4, 131.26, 130.78, 128.32, 127.57, 127.21, 126.4, 126.0, 125.17, 125.12, 125.01, 124.76, 124.64, 120.44, 74.15, 71.84, 34.76, 34.49, 33.76, 33.6, 33.43, 31.05, 30.75, 29.06, 27.42, 24.91, 24.07, 22.56, 17.31, 12.68; *m/z* 663 (M^+), 243 (100%). Compounds **2** and **3** were prepared by the direct acylation of the corresponding alcohols with the appropriate acid halides in 75 and 60% yields, respectively.

‡ *Gelation studies:* The gelator (**1**–**3**) was taken in a stoppered test tube along with an equivalent amount of **4,** the solvent (0.25 ml) was added and the mixture was heated until the solid dissolved. The solution was allowed to come to room temperature and the appearance was noted.

§ *Scanning electron micrographs:* To observe the morphology of the xerogels, 200 Å thick gold films were deposited by dc sputtering, and were examined using a Leica 440*i* SEM with a LaB_6 emitter.

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