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Donor–Acceptor Interaction Promoted Gelation: Visual Observation of Color Change

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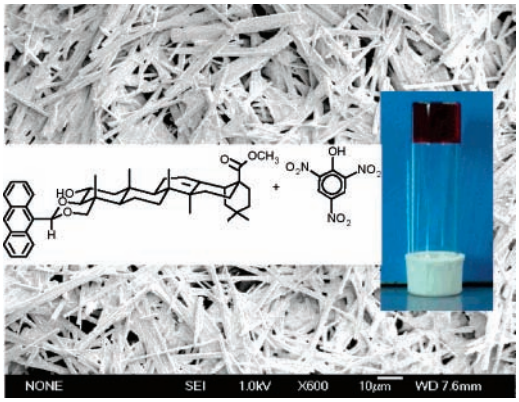
ABSTRACT



An anthrylidene derivative of arjunolic acid could immobilize varieties of organic solvents at low concentrations in the presence of an electron-deficient guest. Gelation in the presence of picric acid in organic solvents could be observed visually with concomitant color change. Electron micrographs of the xerogels showed a fibrous structure having fibers of submicron diameters.

There has been immense interest in recent years in studying *low molecular mass organogelators* for an improved understanding of the self-assembly process in a medium.[1] Moreover, the supramolecular structures of various dimensions derived from the organogelators have many potential technological applications.[2] An organogelator, by definition, is capable of immobilizing varieties of organic solvents usually at a low concentration. The low molecular mass organic compounds self-assemble in the solvents to form a three-dimensional network. The solvent molecules are then immobilized inside the network leading to the formation of a soft solid-like material called gel.[1c] Gels have been classified in different ways based upon their origin, their constitution, the type of cross-linking, and the medium.[2] Low molecular mass organogelators include steroids,[3] carbohydrates,[4] smaller peptides,[5] alkoxy polycyclic hydrocarbons,[6] etc.[7]

Among the low molecular mass organogelators studied, dual-component gelators have gained increasing importance recently because of their additional level of control over the self-assembly process.[8] Two-component organogelation was

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(1) (a) Terech, P.; Weiss, R. G. *Chem. Rev.* **1997**, *97*, 3133. (b) van Esch, J. H.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 263. (c) Estroff, L. A.; Hamilton, A. D. *Chem. Rev.* **2004**, *104*, 1201.
(2) Sangeetha, N. M.; Maitra, U. *Chem. Soc. Rev.* **2005**, *34*, 821.
(3) (a) Mukkamala, R.; Weiss, R. G. *Chem. Commun.* **1995**, 375. (b) Lin, Y. C.; Kachar, B.; Weiss, R. G. *J. Am. Chem. Soc.* **2003**, *125*, 8270. (c) Lin, Y. C.; Weiss, R. G. *Macromolecules* **1987**, *20*, 414. (d) Maitra, U.; Mukhopadhyay, S.; Sarkar, A.; Rao, P.; Indi, S. S. *Angew. Chem., Int. Ed.* **2001**, *40*, 2341. (e) Dastidar, P.; Okabe, S.; Nakano, K.; Iida, K.; Miyata, M.; Tohnai, N.; Shibayama, M. *Chem. Mater.* **2005**, *17*, 741.

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first reported on the basis of a hydrogen bond driven interaction between pyrimidine and barbituric acid derivatives.[9] Donor−acceptor interaction promoted dual-component gelation has been reported on a system consisting of a donor aromatic group attached to a steroid and trinitrofluorinone.[10] A saccharide-based dual-component gelator has been reported where both the donor and the acceptor groups are attached to separate gelators.[11] Dinitrobenzoate derivatives of cholesterol or *n*-octadecanol that are incapable of gelifying the solvent on their own have been shown to assemble a 15−16-fold larger amount of polyaromatic hydrocarbons and form two-component organogels in different solvents.[12]

Functional triterpenes having a rigid lypophilic backbone offer a great opportunity for the construction of molecular receptors, supramolecular architectures, and functional nanomaterials.[13,14] We have recently reported the first example of a triterpene-based organogelator.[15] Herein, we report the significance of electron donor−acceptor (EDA) interaction on the gelation of organic solvents by an anthrylidene derivative of the *triterpenoid*, *arjunolic acid*.

An anthrylidene derivative of arjunolic acid **2** formed weak gel only in methanol.[16] Interestingly, excellent gelation of varieties of organic solvents was observed in the presence of electron-deficient guests such as picric acid or methyl-3,5-dinitrobenzoate (Scheme 1). For example, carbon tetrachloride could be gelled with only 0.38 wt % of compound **2** in the presence of a stoichiometric amount of picric acid.[17] The results of the gelation studies are summarized in Table 1. However, the benzylidene derivative **3** and dimethoxymethyl anthracene **6** did not form gel under identical conditions. This signifies the importance of both the larger aromatic ring and the rigid triterpene backbone of **2** on gelation.

Scheme 1. Arjunolic Acid **1**, Its Derivatives **2** and **3**, the Electron-Deficient Guests **4** and **5**, and the Model Compound **6**

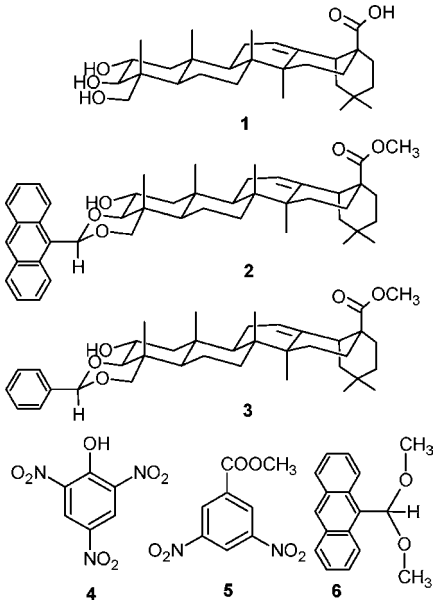

Table 1. Results of the Gelation Studies for Compound **2** and the Effect of the Addition of Electron-Deficient Guests **4** and **5** in Various Solvents[a]

entry	solvent	2/4	2/5	2
1	methanol	P	P	WG
2	ethanol	G	PG	S
3	*n*-propanol	G	PG	P
4	2-propanol	G	G	C
5	*n*-butanol	G	G	C
6	2-butanol	G	G	P
7	*t*-butanol	P	P	S
8	cyclohexanol	G	G	S
9	*n*-octanol	G	G	S
10	diethylene glycol	G	P	S
11	petroleum ether	I	I	I
12	DMF	S	S	S
13	benzene	S	S	S
14	CH_2Cl_2	S	S	S
15	$CHCl_3$	WG	S	S
16	CCl_4	G	P	P
17	$CHCl_3/CCl_4$ (1:20)	G	S	S
18	P.E./$CHCl_3$ (6:1)	G	P	S

[a] G = gel, PG = partial gel, WG = weak gel, S = solution, C = crystal, P = precipitate, I = insoluble.

To determine the stoichiometric requirements of the two components on gelation, T_{gel} was measured with increasing concentration of picric acid at a constant concentration of **2**. A plot of T_{gel} vs the molar ratio of picric acid is given in Figure 1. Interestingly, the T_{gel} was maximum at a 1:1 molar ratio of picric acid. Such a behavior was also observed with a mixture of **2** and **5**.

Figure 1. Plot of T_{gel} vs molar ratio of **4** and **2**.

(4) (a) Vassil, P.; Simanek, E. E.; Wood, M. R.; Wong, C.-H. *Chem. Commun.* **1998**, 1865. (b) Hafkamp, R. J. H.; Feiters, M. C.; Nolte, R. J. M. *J. Org. Chem.* **1999**, *64*, 412.

(5) (a) Maji, S. K.; Malik, S.; Drew, M. G. B.; Nandi, A. K.; Banerjee, A. *Tetrahedron Lett.* **2003**, *44*, 4103. (b) Suzuki, M.; Owa, S.; Yumoto, M.; Kimura, M.; Shirai, H.; Hanabusa, K. *Tetrahedron Lett.* **2004**, *45*, 5399.

(6) Reichwagen, J.; Hopf, H.; Guerzo, A. D.; Belin, C.; Bouas-Laurent, H.; Desvergne, J.-P. *Org. Lett.* **2005**, *7*, 971.

(7) (a) Kato, T. *Science* **2002**, *295*, 2414. (b) Murata, K.; Aoki, M.; Nishi, T.; Ikeda, A.; Shinkai, S. *Chem. Commun.* **1991**, 1715. (c) Srivastava, A.; Ghorai, S.; Bhattarajya, A.; Bhattacharya, S. *J. Org. Chem.* **2005**, *70*, 6574. (d) Ajayaghosh, A.; Vijayakumar, C.; Varghese, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 456.

In the presence of picric acid, the gelation and melting can be observed visually. A yellowish solution of a 1:1 mixture of **2** and **4** in carbon tetrachloride is transformed into a deep red colored gel on keeping at room temperature in ca. 5 min. The deep red colored gel transformed thermoreversibly into a yellowish colored solution on heating (Figure 2).

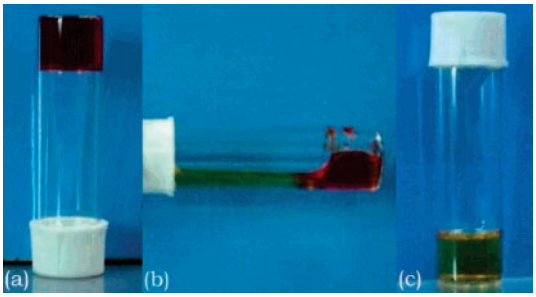

Figure 2. Color change during melting of a gel from **2** (0.83%) in carbon tetrachloride in the presence of an equivalent amount of picric acid: (a) gel obtained at room temperature; (b) melting of the gel at 49 °C on heating; (c) solution above 49 °C.

Temperature-dependent UV−vis spectra obtained for a gel in carbon tetrachloride is shown in Figure 3a. The charge-transfer band was formed at 490 nm. A plot of absorbance at 490 nm vs temperature is shown in Figure 3b. The intensity of the band decreases substantially during melting around the melting temperature (T_{gel} = 39.5 °C). However, for a solution of concentration (0.11%) below the minimum gel concentration, no significant change of intensity was observed. This observation indicates that the charge-transfer interaction between the anthrylidene part of the triterpene derivative and picric acid is the major driving force for gelation.

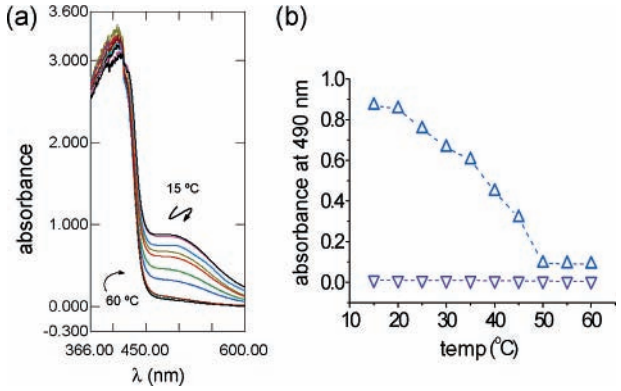

Figure 3. (a) UV−vis absorption spectra of a 1:1 mixture of **2** and **4** at different temperatures. (b) Plot of absorption at 490 nm for the gel (Δ) and for a solution (▽).

To determine the thermal stability of the gels, the gel to sol melting temperature, T_{gel}, was plotted against the gelator concentration (Figure 4). The increase in T_{gel} with an increase in the concentration of the gelator and also the remarkably low minimum gel concentration for **2** in the presence of picric acid support the above conclusion that self-assembly is driven by an EDA interaction. The model anthracene derivative **6** afforded mostly crystals with picric acid which indicates that the lypophilic triterpene backbone helps the molecules to assemble in one dimension.

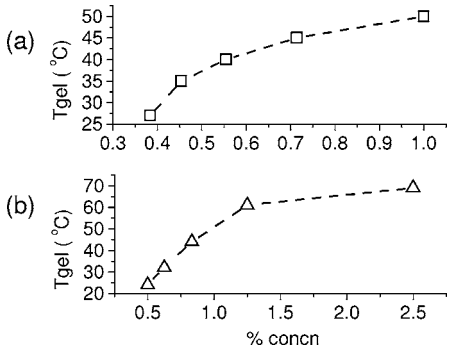

Figure 4. Plot of T_{gel} vs % concentration of the gelator: (a) 1:1 mixture of **2** and **4** in carbon tetrachloride and (b) 1:1 mixture of **2** and **5** in cyclohexanol.

Increase of T_{gel} with increasing gelator concentration allowed us to calculate the thermodynamic parameters ($\Delta H°$, $\Delta S°$) and free energy ($\Delta G°$) at 298 K of gel melting in various solvents (Table 2).[12] For the two-component gel in three alcoholic solvents having **2** and **4** in a (1:1) molar ratio, the importance of both entropic and enthalpic contributions to the overall free energy change was evident.

Table 2. Thermodynamic Parameters ($\Delta H°$, $\Delta S°$) and Free Energy ($\Delta G°$) at 298 K of the Two-Component Gel Melting in Various Solvents

components/solvents	$\Delta H°$ kJ/mol	$\Delta S°$ J/mol/K	$\Delta G°$ kJ/mol
2 and **4** in *n*-butanol	94.8	242.1	22.6
2 and **4** in 2-butanol	58.2	133.7	18.4
2 and **4** in *n*-octanol	40.5	88.6	14.1
2 and **5** in cyclohexanol	40.6	54.9	24.3

(8) For a review article, see: Hirst, A. H.; Smith, D. K. *Chem.−Eur. J.* **2005**, *11*, 5496.
(9) Hanabusa, K.; Miki, T.; Taguchi, Y.; Koyama, T.; Shirai, H. *Chem. Commun.* **1993**, 1382−1384.
(10) Maitra, U.; Vijay Kumar, P.; Chandra, N.; D'Souza, L. J.; Prasanna, M. D.; Raju, A. R. *Chem. Commun.* **1999**, 595.
(11) Friggeri, A.; Gronwald, O.; van Bommel, K. J. C.; Shinkai, S.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **2002**, *124*, 10754.
(12) Rizkov, D.; Gun, J.; Lev, O.; Sicsic, R.; Melman, A. *Langmuir* **2005**, *21*, 12130.
(13) Tamminen, J.; Kolehmainen, E. *Molecules* **2001**, *6*, 21.
(14) For the first *arjunolic acid* derived crown ether, see: Bag, B. G.; Pramanik, S. R.; Maity, G. C. *Supramol. Chem.* **2005**, 297.

The morphology of the xerogels was studied under scanning electron microscopy. Entangled fibrous networks having submicron diameter fibers formed by self-assembly of the molecules were observed (Figure 5).

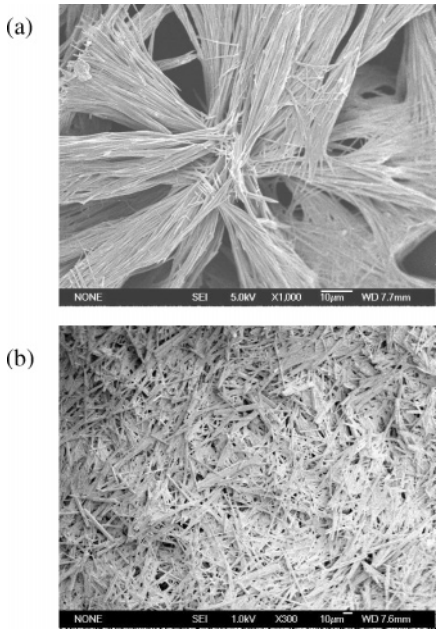

Figure 5. Scanning-electron micrographs of the dried gels: (a) gel from a 1:1 mixture of **2** and **4** in *n*-octanol and (b) gel from a 1.1:1 mixture of **2** and **4** in *n*-propanol.[18]

In summary, we have demonstrated the first example of a triterpene-based dual-component gelator. The presence of picric acid makes the otherwise weak gelator **2** a more efficient gelator of varieties of organic solvents. Moreover, the *color change* during gelation and melting makes the system even more interesting.[19] Formation of charge-transfer complexes by picric acid with varieties of electron-rich aromatic compounds is well-known.[20] Indeed, the model compound **6** formed a charge-transfer complex with picric acid in most of the solvents studied. Moreover, a picric acid mediated solvent extraction protocol has been utilized for the determination of association constants.[21,22] Our result is also the first example of the use of picric acid in organogelation. Thermodynamic parameters and the free energy change data derived from the phase-transition diagrams afforded an insight into the stability of the gels. The *thermochromic supramolecular gelation* demonstrated here may find applications in, e.g., designing thermochromic switches, sensor devices, etc. Current investigations in our laboratory are focusing on the systematic variation of the donor aromatic moieties on the triterpene and the effect of varieties of acceptor compounds for gelation.

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Supporting Information Available: Synthesis of **2**, spectroscopic data, ^{1}H and ^{13}C NMR of **2**, gelation test results, and thermodynamic parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) (a) Bag, B. G.; Maity, G. C.; Pramanik, S. R. *Supramol. Chem.* **2005**, 383. (b) Bag, B. G.; Maity, G. C.; Pramanik, S. R. *Pramana* **2005**, 925.

(16) The anthrylidene derivative **2** was synthesized from methyl arjunolate[14] by reacting with 9-anthraldehyde in dry benzene in the presence of perchloric acid in 85% yield.

(17) Dry picric acid is explosive, and safety protection is necessary while using it.

(18) A thin layer of gel was taken on a small glass plate, and the sample was initially allowed to dry at room temperature for 3−4 days. Then it was dried under reduced pressure for several hours and sputter coated with platinum before SEM analysis.

(19) Intensification of the yellow color during sol-gel transition has been observed for a two-component gelator based upon a dinitrobenzoate derivative and anthracene (ref 12). However, no visual color *change* has been observed in this case.

(20) For electron donor−acceptor (EDA) complexes involving picric acid, see: (a) Briegleb, G. *Electronen-Donator-Acceptor-Komplexe*; Springer-Verlag: Göttingen, 1961. (b) Briegleb, G.; Czekalla, J.; Hauser, A. *Z. Phys. Chem. Neue Folge.* **1959**, *21*, 99.

(21) (a) Maitra, U.; Rao, P.; Vijay Kumar, P.; Balasubramanian, R.; Mathew, L. *Tetrahedron Lett.* **1998**, *39*, 3255. (b) Vijay Kumar, P.; Maitra, U. *J. Org. Chem.* **2000**, *65*, 7764.

(22) For the use of metal picrates for the determination of association constants of crown ethers with metal ions, see: Moore, S. S.; Tarnowski, T. L.; Newcomb, M.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 6398.