

Supramolecular Two-Component Gels: Donor-Acceptor Interaction Promoted Gelation

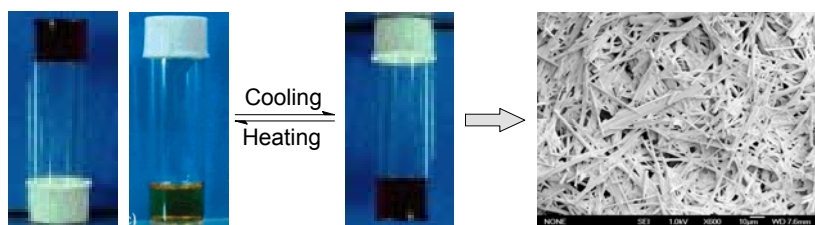
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Received May 5, 2011; accepted November 12, 2011

ABSTRACT

A novel classes of supramolecular gelators formed gels in various organic solvents at low concentrations in presence of electron deficient or electron rich guest. During gelation of these systems, a substantial color change was observed in most of the cases. The charge-transfer interaction of the gel state was established by temperature dependent UV-Visible spectroscopy. The supramolecular assembly of organogels was examined by both microscopy and spectroscopy. This article focuses on the different types of two-component self-assembling gelation systems which have a significant conceptual difference to their one-component analogues.



Keywords: *Gels, Supramolecular chemistry, self-assembly, donor-acceptor interaction, color change, nano-fibers.*

1. Introduction

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.¹⁻² Moreover, the supramolecular structures of various dimensions derived from the organogelators have many potential technological applications³ in structure directing agents, light harvesting materials,⁴ designing thermochromic switches, sensor devices, among others. An organogelator, by definition, is capable of immobilizing varieties of organic solvents usually at a low concentration. The low

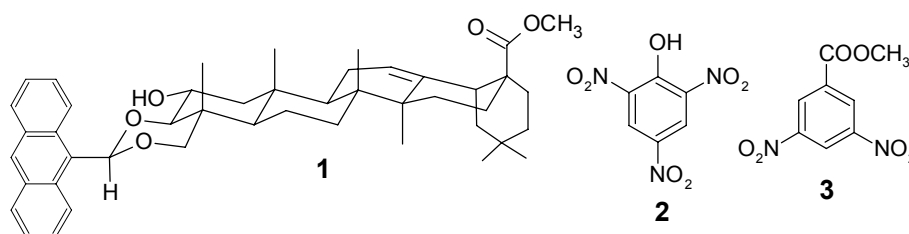
molecular mass organic compounds self-assemble in the solvents to form a three dimensional networks. The solvent molecules are then immobilized inside the network leading to the formation of a soft solid like material called gel. In most cases, these gels are based on a single molecular component. Indeed, using this approach a vast array of organogels and hydrogels based on different molecular building blocks have been reported, and a good understanding is gradually beginning to emerge. The three-dimensional networks are generally formed by means of self-complementary hydrogen bonding, dipole-dipole interaction, π - π interaction, metal coordination, donor-acceptor interaction, van der Waals interaction etc. Various micro or nano-structures including nanofibers, nanotubes, nanotapes, nanoribbons,⁵⁻¹¹ are formed through self-assembling of gelator molecules. Therefore, the molecular self-assembly and network formation of supramolecular gelators has become one of the most active frontiers of the emergent area of nanochemistry.

Recently, the research on multicomponent gelators is active area of research. In two-component systems, an individual component can be present in isotropic solution, and only on addition of the second component will a gel actually form. In some cases, however, two-component gels are reported in which the second component significantly modifies the behavior of a known gelator.¹² Among low molecular mass organogelators studies, dual component gelators have gained increasing importance recently because of the additional level of control over the self-assembly process. Moreover, the ratio of the two components offers another parameter that can be varied to generate new morphologies and tune the materials behavior. The attractive property of two-component donor-acceptor organogels is their ability to assemble organic moieties in close proximity without forming a precipitate.

2. Anthracene appended arjunolic acid derivative

First donor-acceptor interaction promoted gelation of organic liquids were reported by us based on aromatic donor substituted triterpenoid derivative (*Scheme 1*).¹³ A triterpenoid, arjunolic acid derivatives functionalised with an anthracene unit (**2**) formed gels in organic solvents in presence of electron deficient guest such as picric acid **2** or methyl-3,5-dinitrobenzoate **3** (*Table 1*). Interestingly, the most effective *thermochromic supermolecular gelation* was achieved using a 1:1 stoichiometry of the two components. The stoichiometric requirement of the two components was easily established by measuring the T_{gel} as a function of the ratio of **1:2** at a constant concentration of **1**. In the presence of picric acid, the gelation and melting can be observed visually. The deep red colored gel transformed thermoreversibly into yellowish colored solution on heating (Figure 1). By using variable-temperature UV-visible spectroscopy, it became clear that the gelation process was associated with a general increase in the donor-acceptor interaction because a charge-transfer band was formed at 490 nm. The intensity of the band decreases substantially during melting around melting temperature. Indeed, whilst

the two individual components are pale yellow, the two-component gel is deep red colored due to the charge-transfer band.



Scheme 1: Arjunolic acid derivative and electron deficient guest.

Table 1: Results of gelation studies

Solvent	1/2	1/3
Methanol	P	P
Ethanol	G	PG
n-propanol	G	PG
2-Propanol	G	G
n-butanol	G	G
2-Butanol	G	G
^t Butanol	P	P
Cyclohexanol	G	G
n-octanol	G	G
Diethylene glycol	G	P
CHCl ₃	WG	S
CCl ₄	G	P
CHCl ₃ / CCl ₄ (1:20)	G	S
P.E./CHCl ₃ (6:1)	G	P

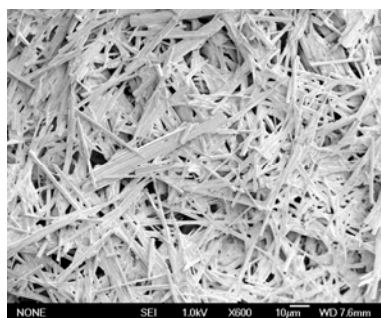


Figure 2: SEM image of dried gel obtained from 1.1: 1 mixture of **1** and **2**.

G = gel, PG = partial gel, WG = weak gel,
S = solution, C = crystal, P = precipitate.

The thermal stability of gels was examined by measuring the gel to sol temperature, T_{gel} . It is clear that T_{gel} increases with increasing in gelator concentration. This observation allowed to calculate thermodynamic parameters at 298 K of gel melting in various organic solvents. The importance of both large aromatic ring and triterpene backbone of **1** on gelation was established. Entangled fibrous networks having submicron diameter fibers formed by self-assembly of the molecules were observed in scanning electron microscopy (SEM) study (Figure 2).

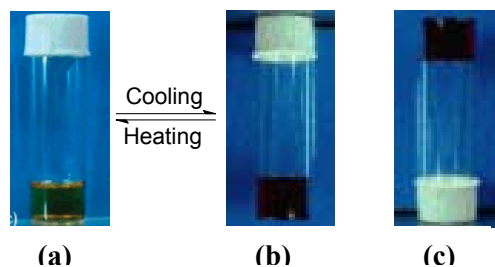
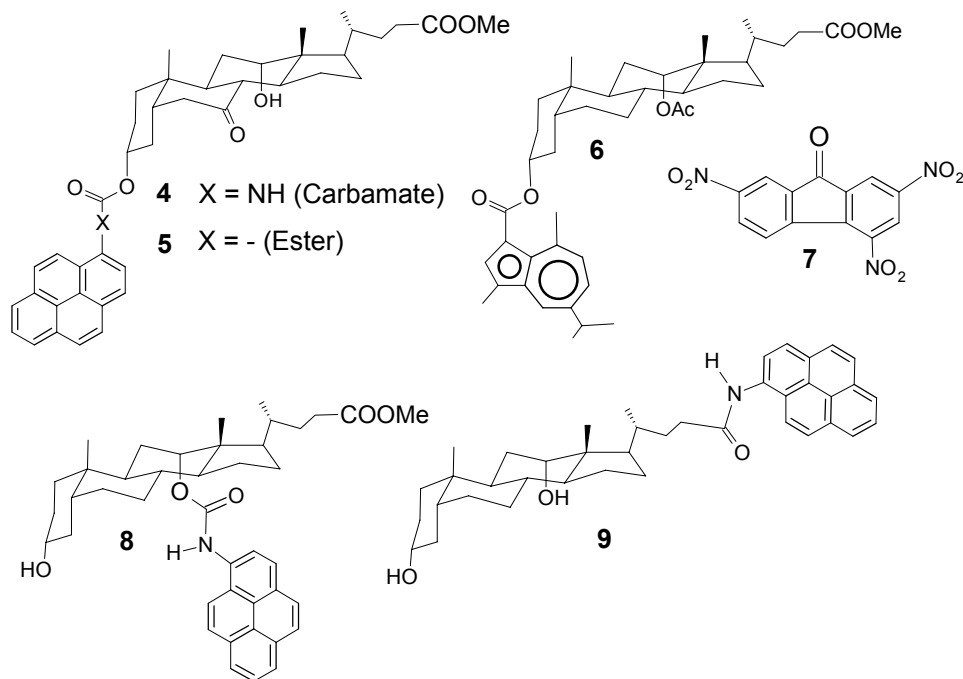


Figure 1: Color change during cooling (a to b) and melting (b to a), inverted vial containing gel (c).



Scheme 2: Bile acid derivative and electron deficient guest (TNF).

3. Aromatic donor substituted bile acid derivatives

U. Mitra and co-workers were the first group to report a two-component gelation system based on a specific donor-acceptor pi-pi interaction based on aromatic donor substituted bile acid derivatives (*Scheme 2*).¹⁴ Bile acid derivatives functionalised at the C-3 position with an aromatic group (**4**, **5**, and **6**) gelatinized organic liquids in the presence of trinitrofluorenone (**7**, TNF) as the acceptor (*Table*

2). The location of the pyrene unit on the bile acid appended to be critical as shown compound **8** and **9** which did not form gels in the presence of **7** in organic solvents. The nature of the linkage between the bile acid and the pyrene unit was explored. The pyrene derivative **4** in general formed highly stable gels even with less than 1% of the gelator. To determine the stoichiometric requirements of the two components on gelation, T_{gel} was measured with increasing concentration of **7** at a constant concentration of **4**. Interestingly, a steady increase T_{gel} values was observed with increasing amounts of **7** but after 1.25 equivalent were added there was no measurable increase, suggesting the requirement of a 1:1 stoichiometry for effective gelation. The gels formed from colorless **4** or **5** in presence of trinitrofluorenone are colored due to a charge-transfer band. The temperature-dependent UV-visible spectroscopy also indicates the charge-transfer interaction between the aromatic unit (donor) attached at bile acid and TNF (acceptor).

Table 2: Results of gelation studies

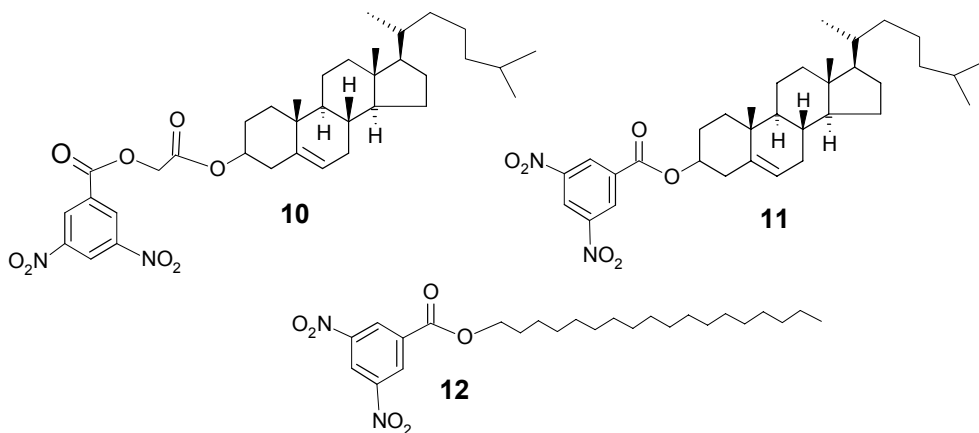
Entry	Solvent	4/7	5/7	6/7
1	ⁿ BuOH	SG	G	G
2	^t BuOH	SG	SG	G
3	^t BuOH-CHCl ₃ (5:1 v/v)	G	SG	G
4	EtOH-CHCl ₃ (3:1 v/v)	SG	G	G
5	Cyclohexanol	SG	SG	G
6	CHCl ₃	G	S	S
7	n-Octanol	S	S	G
8	(CH ₂ OH) ₂ -CHCl ₃ (3:1 v/v)	G	P	G
9	Trigol- CHCl ₃ (3:1 v/v)	SG	P	G
10	Benzene	S	S	S
11	Cyclohexane	P	P	P
12	Cyclohexanone	S	S	S
13	(CHCl ₂) ₂	S	S	S

SG = super gel (<1 wt% gelator, G = gel (1-2 wt% of gelator), S = solution, P = precipitate.

4. Aromatic acceptor substituted cholesterol derivatives

The concept of donor-acceptor gelators has been further extended by O. Lev, A. Melman and their groups.¹⁵ They synthesised cholesterol -based gelators containing a acceptor moiety (3,5-dinitrobenzoate) (*Scheme 3*). The ester, cholesteryl[(3,5 dinitrobenzoyl)oxy]acetate **10**, cholesteryl 3,5-Dinitrobenzoate **11** and **12** (*Scheme 3*) gelify different solvents in presence of large excess of polyaromatic hydrocarbons (PAHs). The ionization potentials of polyaromatic hydrocarbons were reported as a measure for their electron donating aptitude.

Polyaromatic hydrocarbons with ionization potentials lower than or equal to 7.43 eV, that is, those having higher electron donation power than anthracene such as **13**, **14**, **15**, **16** and **17**, gelified mixtures of ester **10** in acetonitrile solvent. In contrast, aromatics that are poorer electron donors, such **18**, **19** and **20**, did not form gels with **10** or **11**. The minimal gelation concentration (5.2 mg/mL) of **10** was observed in presence of anthracene with 1:6 molar ratio of **10** and anthracene. It is speculated that the ability to sustain *pi-pi* stacking plays a more significant role in cogelation than the stability of the donor-acceptor complex. The charge-transfer complex formation between 3,5-dinitrobenzoyl ester derivatives and polyaromatic hydrocarbons in gel state was established by temperature dependent UV-visible spectroscopy. Indeed, the intensive yellow color of the organogels formed from faintly yellow ester **10** and anthracene suggests strong donor-acceptor interactions. Donor-acceptor complexes composed of PAHs and dinitrobenzoate esters can self-assemble a many fold larger amount of PAHs. Full incorporation of the PAH molecules into the gel was established by ^1H NMR spectroscopy, X-ray, and time-resolved fluorescence. The thermodynamics of the gelation process was described on the basis of temperature dependent ^1H NMR studies.

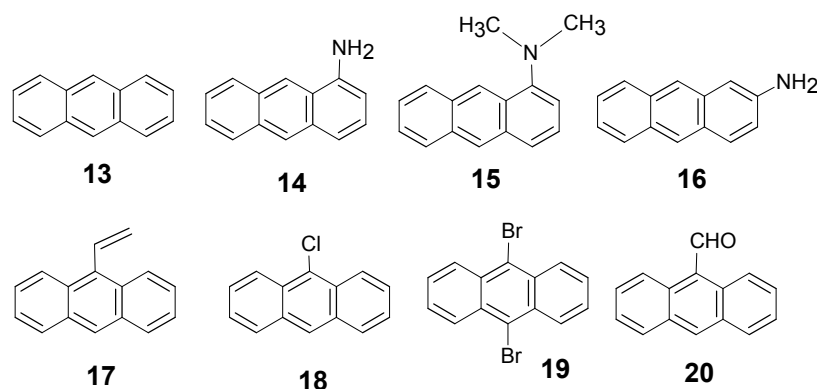


Scheme 3: Cholesterol derivatives and octadecyl 3,5-dinitrobenzoate

5. Alkyl-chain appended pyrene derivatives

Uday Mitra and co-workers also reported two-component gelators based on alkyl-chain appended pyrene derivative as one of the component.¹⁶ They synthesized a new class of compounds (**21-23**, **27**), incorporating long chain alkyl group into pyrene unit via ester group or ether group (Scheme 5). They also synthesized compounds (**24-26**) incorporating alkyl group into the pyrene unit. The compounds (**21-27**) formed gel in various organic solvents in presence of trinitrofluorenone (TNF) owing to a charge-transfer (CT) interaction between the pyrene (donor) unit and TNF (acceptor) (*Table 4*). The derived from these compounds were stable at

room temperature for several months. Compounds **24-27**, were found to show better gelation ability than compound **21**, **22** in the presence of TNF. The compounds **21**, **22** were capable of gelling only hydroxylic solvents to form opaque gels, whereas compounds (**24-26**) and **27** formed transparent red colored and black gels in hydrocarbon and hydroxylic solvents, respectively. Interestingly, the most effective gelation was achieved using a 1:1 stoichiometry of the two components. At a 1:1 ratio of donor (**22**) to acceptor (TNF), the T_{gel} values increased with increasing gelator concentration. It was also established that the length of the hydrocarbon chain did not affect the thermal stability of the gels in hydroxylic solvents.

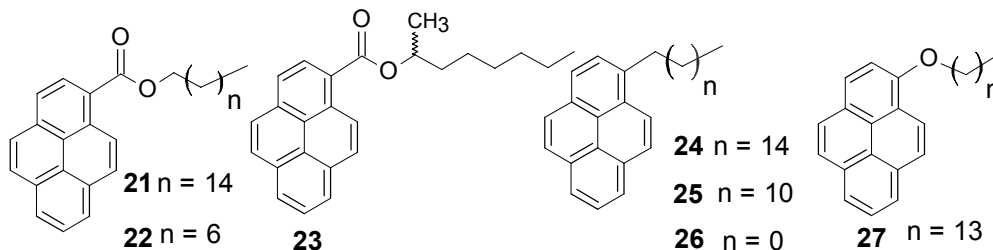


Scheme 4: polyaromatic hydrocarbons (PAHs)

Table 3: Anthracene-Derived Gel Precursors and Their Ionization Energy

Cogelator	Ionization energy	Gel formation	Minimal gelation concentration of 10
Anthracene	7.43	Yes	5.2
1-aminoanthracene	6.24	Yes	11.0
1-dimethylamino anthracene	-	Yes	9.0
2-aminoanthracene	6.24	Yes	9.4
9-vinylanthracene	7.33	Yes	8.2
9-chloroanthracene	7.47	No	-
9,10-dibromo anthracene	7.54	No	-
9-formyl anthracene	7.68	No	-

During the gelation of these systems, a substantial color change was observed. This observation suggests that the formation of gel aggregates is driven by a charge-transfer interaction. Indeed, the charge-transfer interaction was also established by variable temperature dependent UV-Visible spectroscopy. In the UV-Visible spectroscopy, a charge transfer band was formed at 540 nm (for **24-27**) in gel state. The long alkyl chain could only be playing a secondary role in modulating the solubility/crystallinity of the molecule in the given solvent.



Scheme 5: Alkyl-chain appended pyrene derivatives

A chiral gelator **23** formed orange gel in cyclohexanol solvent in the presence of TNF. The chiral aggregation of compound **23** in gel state was examined by circular dichroism (CD) spectroscopy. The CD spectra of the compound **23** showed positive/negative cotton effects with high molar ellipticity at $\lambda = 375$ and 310 nm. These results suggest that the aggregation formed in the gel were possibly helical.

Table 4: Results of gelation studies

Entry	Solvent	21/2	24/2	27/2
1	Cyclohexanol	G	G	G
2	n-Octanol	G	S	G
3	n-butanol	G	G	G
4	Tert-butyl alcohol	G	G	G
5	n-hexane	P	G	G
6	n-dodecane	P	G	G
7	n-decane	P	G	G
8	Cyclohexane	P	G	G

G = gel, S = solution, C = crystal, P = precipitate.

6. Saccharide based gelators

Reinhoudt, Shinkai and their groups have also reported the first example of donor-acceptor interactions in dual-component systems, where both donor and acceptor moieties are confined to separate gelators (*Scheme 6*).¹⁷ They synthesised two saccharide-based gelators (**28**, **29**) —one containing a donor moiety (p-aminobenzylidene), the second containing an acceptor group (p-nitrobenzylidene). The results of gelation are given in the Table 5. The mixture of the two compounds **28** and **29**, formed gels in various solvents in different molar ratios of the two compounds (*Table 6*).

Table 5: Results of gelation studies

Entry	Solvent	28	29	28/29 (1:1)
1	Benzene	G	G	P
2	Toluene	G	P	P
3	p-xylene	G	P	P
4	Carbon tetrachloride	G	P	G
5	Carbon disulfide	G	G	G
6	Diphenyl ether	G	G	G
7	Ethanol	P	P	P
8	n-propanol	G	P	S
9	n-butanol	G	S	S
10	n-hexanol	G	-	S
11	Octanol	G	P	G
12	n-decanol	G	-	G
13	Glycerol	G	S	-
14	Hexanoic acid	G	Reaction	-
15	Water	G	S	S

G = gel, S = solution, C = crystal, P = precipitate.

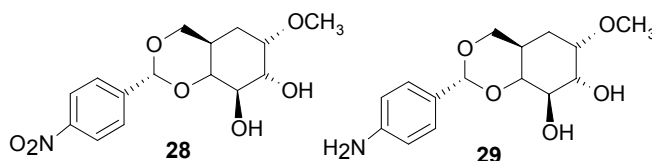
The gel formed from colorless mixture of **28** and **29** in octanol or diphenyl ether was yellow colored due to charge-transfer interaction. This was thought to be caused by an increase in the charge-transfer interaction (CT) during gelation and, therefore, the gelation of these compounds was investigated by variable-temperature absorption spectroscopy by monitoring changes in the charge-transfer band during gelation. The charge-transfer interactions were maximized in samples containing a higher molar ratio of **29**. To determine whether the donor-acceptor interactions between **28** and **29** induce stabilization of the dual-component gel, T_{gel} measurements with different ratios of the two gelators were carried out. The T_{gel} measurements showed that in diphenyl ether, the two-component gel exhibited increased thermal stability at a 1:1 molar ratio, independent of the solvent.

Table 6: Gelation Tests for Different Molar Ratios of **28** and **29** in Water, Octanol, and Diphenyl Ether, with corresponding Gel Colors

28:29	H ₂ O (1wt%)	color	Octanol (3 wt %)	color	Diphenyl ether (3 wt%)	color
100:0	G	none	G	white	G	none
90:10	G	none	G	white	G	yellow 1
80:20	G	none	WG	yellow 1	PG	yellow 1
70:30	G	none	WG	yellow 1	G	yellow 1
60:40	PG	none	WG	yellow 1	G	yellow 1
50:50	S	none	G	yellow 2	G	yellow 1
40:60	S	none	G	yellow 2	G	yellow 2
30:70	S	none	P	yellow 2	G	yellow 2
20:80	S	none	P	yellow 1	G	yellow 2
10:90	S	none	P	yellow 1	G	yellow 2
0:100	S	none	P	white	G	none

G = gel, PG = partial gel, WG = weak gel, Yellow 1 is a paler yellow than yellow 2.

Indeed, the two-component system was 30–38°C more stable than the single-component analogues. In diphenyl ether, however, while Transmission electron microscopy (TEM) images of the single component gels showed networks of straight fibers (**28**, 30-150 nm; **29**, 20-110 nm in diameter), the images of the dual-component gel revealed very large, helical bundles (250-500 nm in diameter) of intertwined fibers. The intertwined fibrous structure of the dual-component gel in contrast to the straight-fiber networks of the single-component gels seem to reflect the increased thermal stability and intermolecular cohesiveness of the former with respect to the latter.

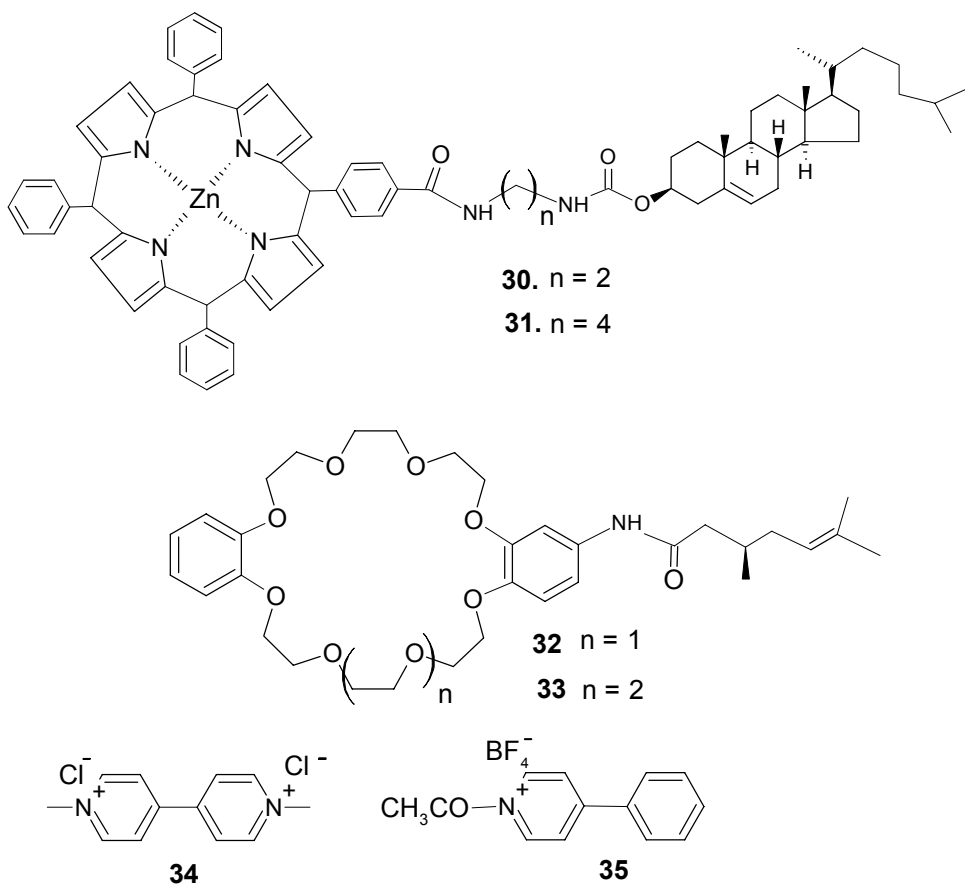


Scheme 6: Methyl 4,6-O-benzylidene α -D-glucopyranoside derivatives.

7. Porphyrin unit appended cholesterol derivative

Shinkai and co-workers have reported a donor-acceptor promoted gelators based on porphyrin unit appended cholesterol derivative.¹⁸ The compound **30** forms gel with certain aromatic hydrocarbon solvents (benzene, toluene, and p-xylene) at 5°C but the compound **30** did not form gel with these solvents at 20°C whereas the compound **31** did not form gel with these solvents at 20°C or at 5°C. The gelation ability of compound **30** or **31** for these solvents was efficiently improved by addition of [60]fullerene due to donor-acceptor interaction between porphyrin unit and fullerene. It was reported that the presence of fullerene could stabilize the gel

formed. The evidence for the Zn(II) porphyrin-[60]fullerene interaction was obtained from UV-vis and CD spectra.



8. Crown ether based gelators

Shinkai and co-workers have incorporated crown ether derivative into their two-component gelation system and importantly illustrated the generality of their two-component approach to gelation. The compounds **32** and **33** formed stable complex with bipyridinium cations (**34** or **35**) during gelation.¹⁹ The formation of complex was driven by charge-transfer, hydrogen-bonding and hydrophobic interaction. The stability of gel was determined by measuring the T_{gel} values at different concentrations. The host-guest interaction stabilized gelation was established by the ^1H NMR and IR spectroscopy and XRD.

9. Conclusions

This results focus on the different types of two-component self-assembling gelation systems, which have a significant conceptual difference to their one-component analogues. During gelation of these systems, a substantial color change was observed in most of the cases. It is shown that charge-transfer interactions to build self-assembling two-component systems confer tunability and responsiveness to different stimuli. It should, however, be noted that in some of the two-component gels discussed here, one of the components forms a gel in its own right and the addition of the second component modifies the gelation process as a consequence of complex formation with the first component. In two-component systems, structural modifications of either one of the two components readily enable the introduction of functional behavior into the materials. Finally, the ratio of the two-components offers another parameter that can be varied to generate new morphologies and tune the materials behavior.

Acknowledgement

GCM thanks to Dr. B. G. Bag for introducing me into this active frontiers of the emergent area of supramolecular chemistry.

REFERENCES

1. P. Terech, R.G. Weiss, 1997, 'Low molecular Mass gelators of Organic Liquids and the Properties of Their Gels,' *Chem. Rev.*, 97, 3133.
2. L.A. Estroff, A.D. Hamilton, 2004, 'Water Gelation by Small Organic Molecules,' *Chem. Rev.* 104, 1201.
3. N. M. Sangeetha, U. Mitra, 2005, 'Supramolecular gels: Functions and uses,' *Chem. Soc. Rev.* 34, 821.
4. K. Sugiyasu, N. Fujita, S. Shinkai, 2004, 'Visible-Light-Harvesting Organogel Composed of Cholesterol-Based Perylene Derivatives,' *Angew Chem. Int. Ed.* 43, 1229.
5. J. H. Jung, Y. Ono, K. Hanabusa, S. Shinkai 2000, 'Creation of Both Right-Handed and Left-Handed Silica structure by Sol-Gel transcription of Organogel Fibers Comprised of Chiral Diaminocyclohexane Derivatives,' *J. Am. Chem. Soc.*, 122, 5008-5009
6. U. Maitra, V. K. Potluri, N. M. Sangeeta, P. Babu, A. R. Raju, 2001, 'Helical aggregates from a chiral organogelators,' *Tetrahedron Asymmetry*, 12, 477-480
7. K. J. C. van Bommel, A. Friggeri, S. Shinkai, 2003, Organic Templates for the Generation of Inorganic Materials,' *Angew.Chem.Int.Ed.*, 42, 980
8. B. G. Bag, G. C. Maity, S. R. Pramanik, 2005, A Terpenoid-based Gelator: The First Arjunolic Acid-derived Organogelator for alcohols and Mixed Solvents,' *Supramol. Chem.* 17, 383.
9. B. G. Bag, G. C. Maity, S. R. Pramanik, 2005, 'Arunolic acid: A promising new building block for nanochemistry,' *Pramana*, 65.

10. G. C. Maity 2007 'Low molecular Mass Gelators of Organic Liquids,' *Journal of Physical Sciences*, 11, 156-171.
11. G. C. Maity 2008 'Supramolecular Hydrogels,' *Journal of Physical Sciences*, 12, 173-186.
12. R. Anarew, David. K. Smith, 2005, 'Two-Component Gel-Phase Materials-Highly Tunable self-Assembling Systems,' *J. Chem. Eur.* 11, 5496 –5508
13. B. G. Bag, G. C. Maity, S. Dinda, 2006, Donor-Acceptor Interaction Promoted Gelation: Visual Observation of Color Change,' *Organic Letter* 8, 5457.
14. U. Mitra, P. Vijay Kumar, N. Chandra, L. J. D'Souza, M. D. Prasanna, A. R. Raju, 1999, 'First donor-acceptor interaction promoted gelation of organic fluids,' *Chem. Commun.*, 595.
15. D. Rizkov, J. Gun, O. Lev, R. Sicsic, A. Melman, 2005, 'Donor acceptor-Promoted Gelation of Polyaromatic Compounds,' *Langmuir*, 21, 12130-12138.
16. P. Bablu, N. M. Sengeetha, P. Vijaykumar, U. Mitra, K. Rissanen, A. R. Raju, 2003, 'Pyrene-Derived Novel one- and Two-component Organogelators,' *Chem. Eur. J.* 9, 1922-1932
17. A. Friggeri, O. Gronwald, K. J. C. van Bommel, S. Shinkai, D. N. Reinhoudt, 2002, 'Charge-Transfer Phenomena in Novel, Dual-Component, Sugar-Based Organogels,' *J. Am. Chem. Soc.* 124, 10754 – 10758.
18. T. Ishi-i, R. Iguchi, E. Snip, M. Ikeda, S. Shinkai, 2001, '[60]Fullerene Can Reinforce the Organogel Structure of Porphyrin-appended Cholesterol Derivatives: Novel Odd-Even Effect of the (CH₂) Spacer on the Organogel Stability,' *Langmuir*, 17, 5825 –5833
19. J. H. Jung, S. J. Lee, J. A. Rim, H. Lee, T. S. Bae, S. S. Lee, S. Shinkai, 2005, 'Stabilization of Crown-Based Organogelators by Charge_transfer Interaction,' *Chem. Mater.* 17, 459 – 462.