Noncovalent Macromolecular Architectures of Oligo(*p*-phenylenevinylene)s (OPVs): Role of End Functional Groups on the Gelation of Organic Solvents

*Sukumaran S. Babu, Vakayil K. Praveen, Ayyappanpillai Ajayaghosh**

Summary: Self-assembly of a few OPV derivatives having different end functional groups to aggregates, fibrous networks and organogels are discussed. **OPV1** and **OPV2** functionalized with ester moieties form gels in nonpolar hydrocarbon solvents whereas **OPV3** with carboxylic acid groups form gel from THF and dichloromethane. **OPV4** with dicyano moieties form aggregates but could not gelate solvents. AFM and TEM studies revealed considerable difference in the morphology of the self-assembled structures of **OPV1-4**. From the optical, morphological and gelation data it is concluded that the nature of the end functional groups strongly influences upon the self-assembly and gelation properties of OPVs.

Keywords: π-stacking; gels; oligo(*p*-phenylenevinylene); self-assembly; supramolecular structures

Introduction

Self-assembly of small molecules to nano- and microsized supramolecular architectures is of considerable importance.[1] A consequence of molecular self-assembly in many cases is the formation of entangled 3D networks which immobilize a large volume of solvent molecules leading to the formation of soft materials called gels.[2–4] These architectures formed through the cooperative effect of various non-covalent interactions are potential candidates for a wide range of applications.[5] In this context, a class of molecules that has attracted much attention is linear π-conjugated systems due to their inherent optoelectronic properties.[6] In these systems, the organization of the molecular components to ordered self-assembly is a challenging task. An approach towards this goal is the rational use of end functional groups attached to the conjugated backbone. Functional groups give directionality to the self-assembly of chromophores and play a crucial role in gelation.

In recent years, we have been interested in the self-assembly and gelation of linear π-systems such as oligo(*p*-phenylenevinylene)s and oligo(*p*-phenyleneethynylene)s in organic solvents.[7–10] Our design strategy involves the functionalization of the OPV backbone with various end substituents and long hydrocarbon side chains. Extensive studies of various classes of OPVs have revealed that the selection of end functional groups and hydrocarbon chains contribute significantly to the gelation ability. Functional groups that form H-bonds are commonly used for the preparation of molecular gelators. However functional group that enters into dipolar interactions are rarely been used to the design of organogelators. Herein we demonstrate that dipolar functional groups facilitate gelation in combination with other weak interaction such as π-stacking and van der Waals interactions and report

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Photosciences and Photonics Group, Chemical Sciences and Technology Division, National Institute for Interdisciplinary Science and Technology (NIIST), CSIR
Trivandrum - 695019 (India)
Fax: (+91) 471-2491712;
E-mail: ajayaghosh62@gmail.com

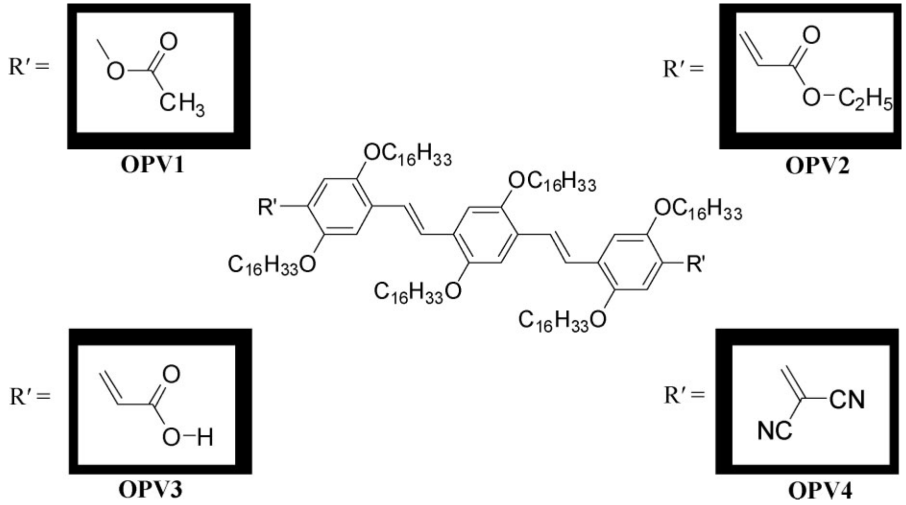

Figure 1.
Structures of OPV derivatives under study.

the self-assembly of OPV derivatives functionalised with ester, carboxylic acid and dicyano groups. For this purpose, **OPV1-4** were synthesised using standard synthetic protocols and characterised by spectral data.[7a,7b]

Aggregation Behavior

Absorption and emission properties of **OPV1-4** exhibited significant changes in chloroform and dodecane. The absorption and emission maxima along with quantum yield (Φ_f) values in different solvents at a concentration of 1×10^{-5} M are shown in Table 1. The optical spectral features in chloroform and dodecane are compared in Figure 2. In nonpolar aliphatic solvents, these molecules form stable aggregates as indicated by a red shifted absorption shoulder and the long wavelength shifting of the emission with significant quenching. For example, **OPV1** in dodecane showed an absorption maximum at 399 nm with a red shifted shoulder at 470 nm and emission maxima at 478, 512 and 550 nm with fluorescence quantum yield of 0.59. **OPV2** showed an absorption maximum of 427 with a shoulder at 515 nm in dodecane and

Table 1.
Photophysical parameters of **OPV1-4** in different organic solvents at a concentration of 1×10^{-5} M.

Compound	Solvent	Absorption	Emission	Φ_f
		γ_{max} (nm)	γ_{max} (nm)	
OPV1	Chloroform	410	467, 496	0.90[a]
	Dodecane	399, 470	478, 512, 550	0.59[b]
OPV2	Chloroform	450	527, 562	0.94[b]
	Dodecane	427, 515	530, 568, 615	0.51[b]
OPV3	Chloroform	448	534, 562	0.90[b]
	Dodecane	475, 517	588	0.21[b]
OPV4	Chloroform	521	626	0.85[b]
	Dodecane	507, 590	566, 614, 680	0.12[b]

[a] Fluorescence quantum yields were determined using quinine sulphate as the standard ($\Phi_f = 0.546$ in 0.1 N H_2SO_4), ±5% error.
[b] Fluorescence quantum yields were determined using rhodamine 6G as the standard ($\Phi_f = 0.9$ in ethanol), ±5% error.

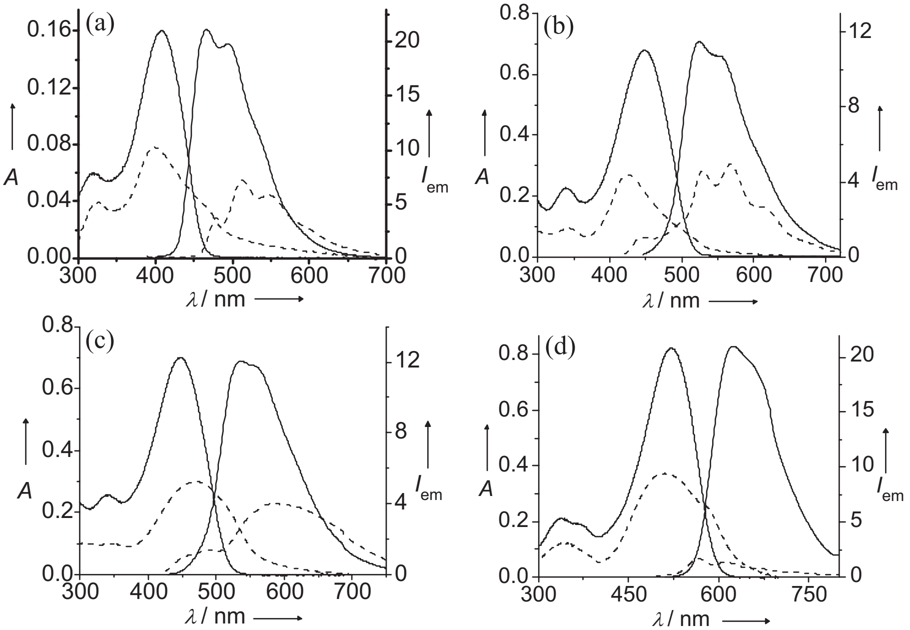

Figure 2.
Absorption and emission spectra of a) **OPV1** ($\lambda_{ex} = 380$ nm), b) **OPV2** ($\lambda_{ex} = 410$ nm), c) **OPV3** ($\lambda_{ex} = 460$ nm) and d) **OPV4** ($\lambda_{ex} = 490$ nm) in chloroform (—) and dodecane (- - -) at a concentration of 1×10^{-5} M.

emission maxima of 530, 568 and 615 nm ($\Phi_f = 0.51$). **OPV3** in dodecane showed an absorption maximum at 475 and a shoulder band at 517 nm, with a broad emission spectrum having maximum of 588 nm ($\Phi_f = 0.21$). **OPV4** in dodecane showed an absorption maximum of 507 nm with shoulder band at 590 nm and emission maxima of 566, 614 and 680 nm with a fluorescence quantum yield of 0.12. From the optical studies it was clear that these molecules form aggregates in cyclohexane and dodecane whereas in chloroform they exist as molecularly dissolved state.

Stability of the aggregates of **OPV1-3** could be compared from the plots of the fraction of aggregates (α) vs. temperature (Figure 3). For **OPV1** and **OPV2** the plots of fraction of aggregates (α) vs. temperature showed sigmoidal transitions within short temperature range indicating the cooperative nature of the self-assembly process. In the case of **OPV3** a broad transition is observed for a wide range of temperature. The carboxylic acid groups of **OPV3** form two point hydrogen bonds between them resulting in one dimensional supramolecular polymeric chains. These polymeric chains may undergo π-stacking to form higher order aggregates with increased melting transition temperature. With increase in temperature, initially, the π-stacking of the stable H-bonded aggregates may break, resulting in single poly-

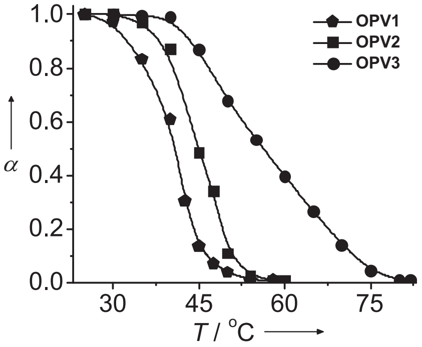

Figure 3.
Plot of the fraction of aggregate (α) vs. temperature of **OPV1-3** indicating the stability of the aggregates in solution (data points were obtained from the variable temperature absorption spectra in dodecane).

Table 2.
Critical gelator concentration[a] (CGC) [mM] of **OPV1-4** in different organic solvents.

Solvent	OPV1	OPV2	OPV3	OPV4
n-Decane	1.61 (s, tr)	1.04 (s, tr)	ppt	ppt
n-Hexane	3.21 (s, tr)	2.08 (s, tr)	ppt	ppt
Cyclohexane	4.01 (s, tr)	2.60 (s, tr)	ppt	ppt
Methylcyclohexane	4.11 (s, tr)	2.69 (s, tr)	ppt	ppt
Toluene	4.28 (th, tr)	3.38 (th, tr)	ppt	ppt
p-Xylene	4.32 (th, tr)	3.41 (th, tr)	ppt	ppt
Dichloromethane	s	s	3.38 (s, tr)	s
Tetrahydrofuran	s	s	3.41 (s, tr)	s

[a] CGC is the minimum concentration required for the formation of a stable gel at room temperature. In parenthesis, s = stable, th = thixotropic, tr = transparent, s = soluble, ppt = precipitate.

meric chains which subsequently dissociate into monomers through a noncooperative fashion. Surprisingly **OPV4** does not form gel in any of the solvents analysed, however shows tendency to form stable aggregates.

Gelation Properties

Detailed gelation studies of **OPV1-4** were carried out in various organic solvents by dissolving different amounts of the respective compound in definite volume of the solvents in a glass vial with 0.5 cm diameter. Heating and cooling of the solution resulted in the gelation of the solvent as indicated by its inability to flow. Details of the gelation properties are tabulated in Table 2. **OPV1** and **OPV2** form strong gels in aliphatic nonpolar solvents such as *n*-decane or *n*-hexane when compared to aromatic solvents such as toluene and *p*-xylene. For example, the critical gelator concentration (CGC) of **OPV1** in *n*-decane is 1.61 mM which is much lower than in *p*-xylene (4.32 mM) whereas for **OPV2** the CGC values are 1.04 and 3.41 mM in *n*-decane and *p*-xylene respectively. In chloroform and tetrahydrofuran, no gelation occurred for both compounds due to high solubility of the molecules. **OPV3** is found to be partially soluble in nonpolar and less polar solvents due to the presence of more polar carboxylic acid end functional group. Therefore, in nonpolar hydrocarbon solvents **OPV3** resulted in aggregation induced precipitation. However, in polar solvents like dichloromethane and tetrahydrofuran stable gels were formed. The CGC value of **OPV3** is 3.38 and 3.41 in dichloromethane and THF, respectively. In **OPV3** the carboxylic acid groups may form directional hydrogen bonds with adjacent molecules resulting in linear polymeric assembly which precipitates out in solvents such as hexane, decane and dodecane. In THF due to better solubility, the H-bonded polymeric assemblies may result in three dimensional network structures through π-stacking. As mentioned earlier, **OPV4** forms aggregates and precipitates out from nonpolar and less polar solvents. These aggregates are soluble in polar solvents such as dichloromethane and tetrahydrofuran and were unable to gelate any of the solvents tested.

Thermotropic behavior of the *n*-hexane gel of **OPV1**, **OPV2** and the THF gel of **OPV3** are determined by dropping ball method[7b]. Plots of the gel melting tem-

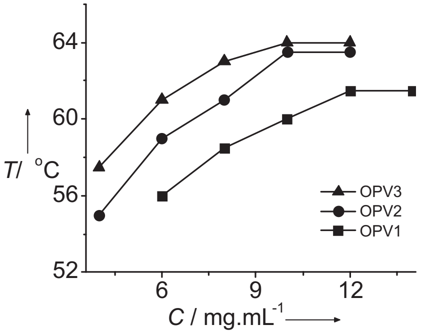

Figure 4.
Plots of T_{gel} versus concentration of **OPV1** and **OPV2** in *n*-hexane and **OPV3** in tetrahydrofuran (data points were obtained by dropping ball method).

perature (T_{gel}) at different concentrations are shown in Figure 4. The T_{gel} value increases with increase in concentration of the gelator and reaches a platue. Since **OPV3** form stable gels only in polar solvents, a direct comparison of the thermotropic behavior in same solvent was not possible. Dichloromethane and tetrahydrofuran gels of **OPV3** showed higher T_{gel} values than that of **OPV1** and **OPV2** in n-hexane which is clear from the binary phase diagram. The reduced T_{gel} values of **OPV1** and **OPV2** in n-hexane indicates that although the dipolar interactions are sufficient for gel formation, they are weaker than hydrogen bonded network of **OPV3**. Among the gels of **OPV1** and **OPV2**, the latter showed better stability as indicated by the higher T_{gel} values. This observation indicates that the dipolar interaction is stronger in **OPV2** due to the conjugation of the ester moiety with the OPV backbone.

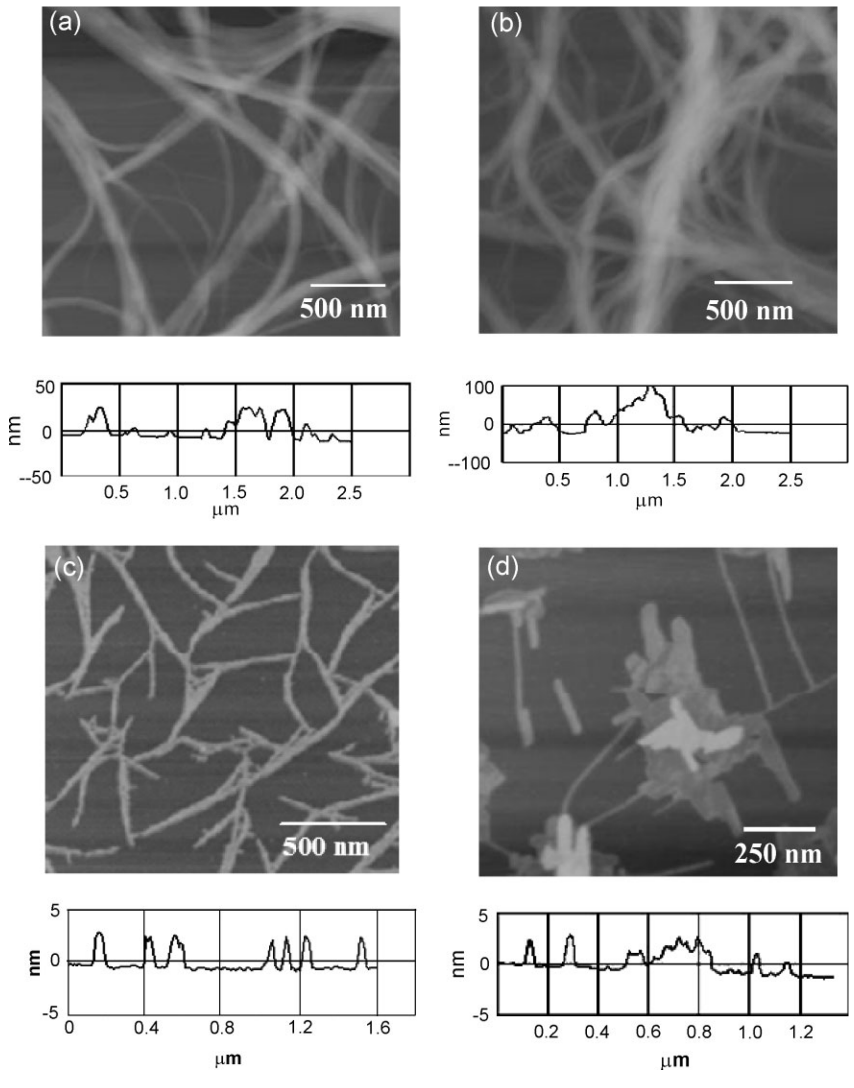

Figure 5.
AFM tapping mode height images and corresponding section analysis of a) **OPV1**, b) **OPV2**, c) **OPV3** and d) **OPV4** (5 × 10^{-5} M in toluene). Sample of **OPV3** is prepared from dodecane-chloroform mixture (16:1).

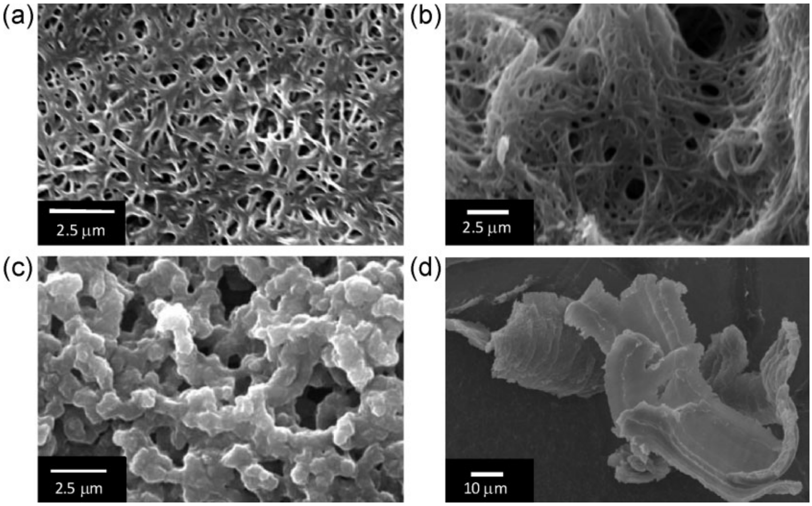

Figure 6.
SEM images of the aggregates of a) **OPV1**, b) **OPV2** and d) **OPV4** in toluene and c) **OPV3** in tetrahydrofuran. In all studies concentration of OPV is 4×10^{-3} M.

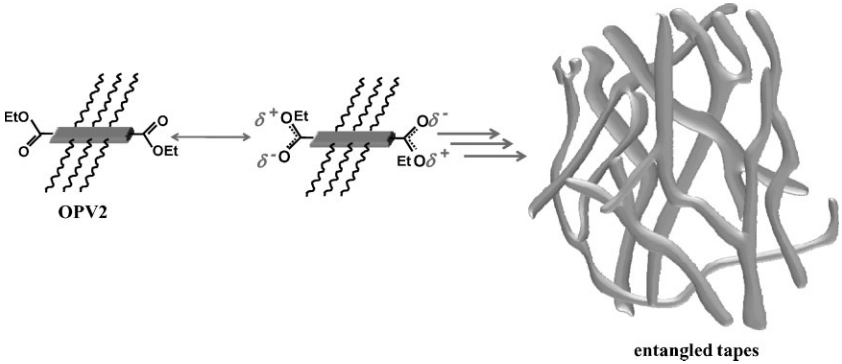

Figure 7.
Schematic representation showing the aggregation pattern of the supramolecular aggregates of **OPV2**.

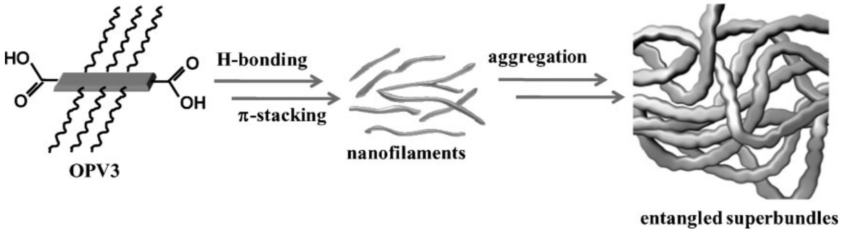

Figure 8.
Schematic representation showing the aggregation pattern of the supramolecular aggregates of **OPV3**.

Morphological Studies

Atomic force microscopy (AFM) studies were performed on samples casted from dilute solutions of **OPV1-4** on freshly cleaved mica surface. AFM images of **OPV1** and **OPV2** in toluene and **OPV3** in dodecane-chloroform mixture (16:1) at a concentration of 5×10^{-5} M are shown in Figure 5. They form supramolecular tapes consisting of bundles of fibers having 50–150 nm width and several micrometers length. The smallest fibers obtained was having a width of 95–115 nm and a height of 12 ± 2 nm. However, **OPV3** showed the formation of relatively short interconnected rod like assemblies of 1–2 μm in length, 50-100 nm in width. Section analysis of these structures showed a uniform height of 3–4 nm when compared to the variable heights of the fibers of **OPV1** and **OPV2**. The aggregates of **OPV4** exhibit isolated rod like structures with 20–47 nm width, 2.8 ± 0.5 nm in height and a few micrometers in length. These aggregates were not able to gelate any of the solvents tested. Morphological studies indicate that the formation of supramolecular tapes are due to the self-assembly of OPV units through H-bonding (for **OPV3**), and dipolar interactions (for **OPV1**, **OPV2** and **OPV4**), assisted π-stacking, van der Waals forces.

Further evidence for the formation of fibrous assemblies was obtained from the scanning electron microscopy (SEM) studies of the gels in various solvents at a concentration of 4×10^{-3} M. In the xerogel state, highly dense entangled fibrous network structures could be seen in the SEM images. For example, a toluene gel of **OPV1** showed entangled supramolecular tape like structures with 100–300 nm width and several micrometers in length. In toluene **OPV2** also formed fibrous aggregates having a width of 100–250 nm and length in several micrometers. In the case of **OPV3**, SEM image of a gel in THF showed the formation of super bundles with micrometer size, the morphology of which are significantly different from those of **OPV1** and **OPV2**. The morphology of **OPV4** appears to be like large sheets (Figure 6d) which are formed by layer-by-layer stacking of large aggregates and is significantly different from the entangled network structures of **OPV-3.** Thus the AFM and SEM analyses indicate that the morphology of the self-assembled structures in dilute solutions and of gels of **OPV1-4** is strongly influenced by the end functional groups of the respective OPVs.

From AFM and SEM morphological data it is obvious that **OPV1-2** form supramolecular structures through weak noncovalent interactions. In the case of **OPV1** and **OPV2** the dipolar interactions of the ester moieties and π-stacking of the OPV backbones may be responsible for the self-assembly as shown in Figure 7. In this case, in the gel state the molecules are in the form of supramolecular tapes of 50–200 nm in width. In the case of **OPV3**, H-bonded 1D supramolecular assemblies are formed, which form entangled nanobundles and microstructures leading to gels as shown in Figure 8. In this case the f-assembled structures are of several micrometers in width in contrast to that of **OPV1** and **OPV2**.

Conclusion

The present study reveals that the end functional groups play a significant role in the self-assembly and gelation of OPVs. It has been established that weak dipolar interactions are capable of facilitating gelation as noticed in the case of the ester functionalised OPVs. Due to the directional two point H-bonding, **OPV3** facilitates the formation of supramolecular polymeric structures which further self-assembles to form gels from THF and not from nonpolar solvents in contrast to **OPV1** and **OPV2**. The dicyano group attached OPV could not gelate both nonpolar and polar solvents. AFM and SEM analyses indicate significant difference in the morphology of the self-assemblies of **OPV1-4**. These data reveal that by choosing appropriate end functional groups it is possible to control the morphology of the self-assembly and the gelation of OPVs.

[1] [1a] J.-M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, VCH, Weinheim, Germany **1995**; [1b] D. N. Reinhoudt, M. Crego-Calama, *Science* **2002**, *295*, 2403; [1c] G. M. Whitesides, B. Grzybowski, *Science* **2002**, *295*, 2418; [1d] F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning, *Chem. Rev.* **2005**, *105*, 491; [1e] A. Ajayaghosh, S. J. George, A. P. H. J. Schenning, *Top. Curr. Chem.* **2005**, *258*, 83.

[2] [2a] P. Terech, R. G. Weiss, *Chem. Rev.* **1997**, *97*, 3133; [2b] R. G. Weiss, P. Terech, Eds., Kluwer Press, Dordrecht, The Netherlands **2005**.

[3] [3a] J. H. van Esch, B. L. Feringa, *Angew. Chem. Int. Ed.* **2000**, *39*, 2263; [3b] N. M. Sangeetha, U. Maitra, *Chem. Soc. Rev.* **2005**, *34*, 821.

[4] L. A. Estroff,, A. D. Hamilton, *Chem. Rev.* **2004**, *104*, 1201.

[5] [5a] M. Sano, J. Okamura, S. Shinkai, *Langmuir* **1999**, *15*, 7890; [5b] J. D. Hartgerink, E. Beniash, S. I. Science. Stupp, **2001**, *294, 1684;* [5c] E. D. Sone, E. R. Zubarev, S. I. Stupp, *Angew. Chem. Int. Ed.* **2002**, *41*, 1706.[5d] K. J. C. van Bommel, A. Friggeri, S. Shinkai, *Angew. Chem. Int. Ed.* **2003**, *42*, 980; [5e] J. C. Tiller, *Angew. Chem. Int. Ed.* **2003**, *42*, 3072; [5f] L. Li, E. Beniash, E. R. Zubarev, W. Xiang, B. M. Rabatic, G. Zhang, S. I. Stupp, *Nat. Mater.* **2003**, *2*, 689; [5g] T. Ishii, S. Shinkai, *Top. Curr. Chem.* **2005**, *258*, 119.

[6] [6a] A. Ajayaghosh, V. K. Praveen, C. Vijayakumar, *Chem. Soc. Rev.* **2008**, *37*, 109; [6b] A. Ajayaghosh, V. K. Praveen, *Acc. Chem. Res.* **2007**, *40*, 644.

[7] [7a] A. Ajayaghosh, S. J. George, *J. Am. Chem. Soc.* **2001**, *123*, 5148; [7b] S. J. George, A. Ajayaghosh, *Chem. Eur. J.* **2005**, *11*, 3217; [7c] R. Varghese, S. J. George, A. Ajayaghosh, *Chem. Commun.* **2005**, 593; [7d] V. K. Praveen, S. J. George, A. Ajayaghosh, *Macromol. Symp.* **2006**, *241*, 1.

[8] [8a] A. Ajayaghosh, S. J. George, V. K. Praveen, *Angew. Chem. Int. Ed.* **2003**, *42*, 332; [8b] V. K. Praveen, S. J. George, R. Varghese, C. Vijayakumar, A. Ajayaghosh, *J. Am. Chem. Soc.* **2006**, *128*, 7542; [8c] A. Ajayaghosh, C. Vijayakumar, V. K. Praveen, S. S. Babu, R. Varghese, *J. Am. Chem. Soc.* **2006**, *128*, 7174; [8d] A. Ajayaghosh, V. K. Praveen, S. Srinivasan, R. Varghese, *Adv. Mater.* **2007**, *19*, 411.

[9] [9a] S. J. George, A. Ajayaghosh, P. Jonkheijm, A. P. H. J. Schenning, E. W. Meijer, *Angew. Chem. Int. Ed.* **2004**, *43*, 3422; [9b] A. Ajayaghosh, R. Varghese, S. J. George, C. Vijayakumar, *Angew. Chem. Int. Ed.* **2006**, *45*, 1141; [9c] A. Ajayaghosh, C. Vijayakumar, R. Varghese, S. J. George, *Angew. Chem. Int. Ed.* **2006**, *45*, 456.

[10] [10a] A. Ajayaghosh, R. Varghese, V. K. Praveen, S. Mahesh, *Angew. Chem. Int. Ed.* **2006**, *45*, 3261; [10b] A. Ajayaghosh, R. Varghese, S. Mahesh, V. K. Praveen, *Angew. Chem. Int. Ed.* **2006**, *45*(7729); [10c] S. Yagai, S. Mahesh, Y. Kikkawa, K. Unoike, T. Karatsu, A. Kitamura, A. Ajayaghosh, *Angew. Chem. Int. Ed.* **2008**, *47*, 4691.