Journal of Materials Chemistry

Cite this: J. Mater. Chem., 2012, 22, 25277

www.rsc.org/materials

Aggregation induced emission switching and electrical properties of chain length dependent π -gels derived from phenylenedivinylene bis-pyridinium salts in alcohol–water mixtures[†]

Suman K. Samanta^{*a*} and Santanu Bhattacharya^{**ab*}

Received 27th July 2012, Accepted 7th September 2012 DOI: 10.1039/c2jm35012b

Supramolecular π -gels were formed in a mixture of aliphatic alcohols and water for a series of chromophoric phenylenedivinylene bis-N-alkyl pyridinium salts (PPV) appended with terminal aliphatic hydrocarbon chains of different lengths. Gelation could be controlled either by altering the ratio of various alcohol-water mixtures or by changing the aliphatic chain length of the gelator. The temperature- and the ratio-variation in the ethanol-water mixtures exhibited a tunable emission behavior depending on the extent of aggregation which was promoted by aromatic π -stacking, van der Waals and electrostatic interactions among the individual PPV units. Thus, a light-blue emission at higher temperature (>40 $^{\circ}$ C), a reddish-orange emission at low temperature (<20 $^{\circ}$ C) and a white-light emission at room temperature (25-30 °C) were observed in solution. The gelators possessing longer aliphatic chains exhibited a higher gel-melting temperature, increased viscoelasticity and shorter fiber diameter based on a delicate hydrophobic/hydrophilic balance. A semiconducting nature of the electrical conductivity was observed for the individual compounds and the magnitude of the current increased with increasing width of the gel fibers upon decreasing the aliphatic chain length. A reversible one-electron redox behavior was observed for the chromophore and the redox potential decreased with the increase in the chain length. A diffusion-controlled redox behavior was observed for the gelators with shorter aliphatic chains. However, the compounds with longer chains made the process diffusionlimited.

Introduction

Low-molecular-mass gelators (LMMGs) are capable of immobilizing the flow of liquids for the generation of functional softmaterials.¹ The solvents immobilized can be either organic or aqueous or even a mixture of the two.² Supramolecular association among these LMMGs leads to physical gel formation, which represents a macroscopic expression of their self-assembly *via* optimization of various non-covalent interactions, such as hydrogen bonds, π – π stacking, solvatophobic, dipole–dipole, electrostatic, van der Waals forces *etc.*³ Self-association of these LMMGs into three-dimensional aggregates provides a route for the generation of nano- or micro-sized materials for the fabrication of optoelectronic devices.⁴ Thus, rational design of gelator molecules together with a proper understanding of the gelation mechanism and their structure-property relationship remain an important objective.

The self-association of LMMGs depends upon a variety of factors, which includes, solvent, concentration, temperature, and above all the molecular structure.^{1,2,5} A minimal structural alteration such as the length of the flexible aliphatic part of a gelator is often crucial for the manipulation of the gelation induced properties depending on the subtle hydrophobic/ hydrophilic balance.6 Most of the gelators are reported to form a gel in a single solvent entity. However, a mixture of solvents could reflect tuning of the supramolecular organization of the LMMGs.² We have reported previously how the gelation by an amino acid based LMMG in a mixture of two different miscible hydrocarbons controls the self-assembly pattern.⁷ Therefore, an optimum balance between the hydrophilic and hydrophobic groups in the LMMG obtained either by varying the molecular structure or changing the polarity of a solvent mixture could control the gelation assisted properties.

In the field of functional molecular assemblies, achieving supramolecular control over the chromophore-linked molecular systems remains a challenge. Therefore, the design of novel π -conjugated electroluminescent organic materials is important as they show potential applications in organic light emitting diodes

^aDepartment of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India. E-mail: sb@orgchem.iisc.ernet.in; Fax: +91-80-23600529; Tel: +91-80-22932664

^bChemical Biology Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore-560064, India

[†] Electronic supplementary information (ESI) available: Experimental section, synthesis and characterization, supporting figures and tables. See DOI: 10.1039/c2jm35012b

(OLEDs),⁸ enhanced charge transport,⁹ light harvesting and photonic devices *etc.*¹⁰ Furthermore, the gelation process has been shown to be capable of providing novel chromophore assemblies and as a consequence, gelators based on porphyrins,¹¹ phthalocyanines,¹² perylene,¹³ conjugated oligothiophenes¹⁴ and other chromophoric moieties¹⁵ have indeed been developed. In this context, the self-assembly of conjugated systems based on oligo(*p*-phenylenevinylene)s has drawn considerable attention especially for their excellent photophysical properties.^{16,17}

Herein, we report a new class of chromophoric gelator based on phenylenedivinylene bis-pyridinium (PPV) salts with a fixed central PPV core and aliphatic chains of different lengths which are connected to the pyridinium ends (1–7, Chart 1). These compounds can immobilize a mixture of aliphatic alcohol and water through varying propensities of van der Waals interactions at the end functional groups. Such variations of the chain lengths indeed influence their aggregation and gelation properties, such as minimum gelator concentration, morphology, fiber diameter, viscoelasticity, photophysical and electrical properties *etc.* A combination of spectroscopic, microscopic, and diffraction methods were used to probe the influence of the aliphatic chains on the molecular gelation ability and chromophore induced properties.

Experimental

Materials and general methods

All reagents, starting materials and solvents were obtained from the best known commercial sources. Solvents were distilled and dried prior to use. FT-IR studies were performed on a Perkin– Elmer FT-IR Spectrum BX system. ¹H and ¹³C NMR spectra were recorded on a Bruker-400 Avance NMR spectrometer. Chemical shifts were reported in ppm downfield from the internal standard, tetramethylsilane. Mass spectrometry of individual compounds was performed on a MicroMass ESI-TOF MS instrument. Elemental analysis was recorded on a Thermo Finnigan EA FLASH 1112 SERIES instrument.

Synthesis

Syntheses of all the amphiphilic PPV derivatives 1–7 were easily accomplished using two step procedures as summarized in Scheme S1 (see ESI†). Aliphatic chains of desired length were first attached to 4-picoline as a quaternary salt, which in turn increased the reactivity of the $-CH_3$ protons at the para-position. A base promoted aldol-type condensation reaction of the respective 4-picolinium salt with terephthalaldehyde gave rise to



Chart 1 Molecular structures of the PPV based gelators used in the present study.

the desired product. All the new compounds 1–7 were adequately characterized by FT-IR, ¹H NMR, ¹³C NMR, mass spectrometry and elemental analysis (see ESI†). An all-*trans* configuration of the two vinyl moieties was confirmed from the coupling constants in the ¹H NMR spectrum in CD₃OD (*e.g.* $J = \sim 16$ Hz for **5**, Fig. S1a†).

Gelation studies

A weighed amount of a particular compound was added to an excess of the chosen solvent or the solvent mixture and the resulting mixture was heated until the solid was completely dissolved in the closed vial. The clear solution so obtained was left to cool in air at 25 °C without any disturbance. Observations with regard to gelation were recorded from time to time, and each experiment was performed in duplicate. The state of the materials was examined by the "stable-to-inversion of a test tube" method.¹⁷ If a gel was formed, it was evaluated quantitatively by determining the minimum gelator concentration (MGC) which is the minimum amount of the gelator required to form a self-standing gel.

Gel melting temperature

The melting temperatures of the gels were investigated using the dropping ball method. In this method, a steel ball (130 mg) was placed on top of a 0.5 mL volume of gel in a closed glass vial of 8 mm inner diameter. Then the gels were slowly heated (2 °C min⁻¹) in a water bath. The temperature at which the ball reaches the bottom of the vial is recorded as the gel melting temperature (T_{gel}).

Variable temperature ¹H NMR

¹H NMR spectra of gels of 4 and 5 were recorded on an AMX 400 MHz (Bruker) spectrometer using 60% CD₃OD/D₂O as the solvent.

UV-vis and fluorescence spectroscopy

The UV-vis and fluorescence spectroscopy of the gelators in solution were recorded on a Shimadzu model 2100 spectrophotometer and Hitachi F-4500 spectrofluorimeter, respectively, both equipped with a temperature-controller bath. Fluorescence spectroscopy of the gels was performed using the front-face geometry in a Jobin Yvon Horiba spectrofluorimeter.

Fluorescence and polarized optical microscopy

Diluted solutions of 2–7 (1×10^{-4} M) in 60% ethanol–water were drop cast on pre-cleaned glass slides and left overnight to air-dry in a dust free environment and finally evacuated. The fluorescence microscopy images were taken on an Olympus IX-71 microscope with a blue excitation range of 340–400 nm. Polarized optical microscopy images were taken of the same samples using polarized light microscopy (Olympus BX51) and the optical textures were recorded using cross-polarizers.

Scanning electron microscopy

The gels in 60% ethanol-water were melted by heating and carefully drop cast onto brass stubs and were allowed to

freeze-dry. The samples were then coated with gold vapor and analyzed on a Quanta 200 SEM operated at 15 kV.

X-ray diffraction

The gel samples prepared in 60% ethanol–water mixtures were individually placed carefully on a pre-cleaned glass slide and were allowed to freeze-dry. This yielded a self-supported cast film of the individual gel on which the measurements were performed using a Bruker Advance D8 instrument. The X-ray beam generated with rotating Cu anode and K_{α} beam wavelength of 1.5418 Å was directed towards the film edge and scanning was carried out up to a 2θ value of 50°. Data were analyzed and interpreted using the Bragg equation.

Rheological studies

An Anton Paar 100 rheometer using a cone and plate geometry (CP 25-2) was utilized. The gap distance between the cone and the plate was fixed at 0.05 mm. The gel was scooped onto the plate of the rheometer. A stress amplitude sweep experiment was performed at a constant oscillation frequency of 1 Hz for the strain range 0.001 to 550 at 20 °C. The rheometer has a built-in computer which converts the torque measurements into either G' (the storage modulus) or G'' (the loss modulus) in oscillatory shear experiments. The values are plotted in the log scale.

Cyclic voltammetry

Cyclic voltammetric measurements were carried out at room temperature (25 °C) on an EG&G PAR 253 VersaStat potentiostat/galvanostat using a three-electrode configuration consisting of a glassy carbon working, platinum wire auxiliary, and saturated calomel reference (SCE) electrode. Each compound was dissolved in DMSO (1 mM) and 100 mM TBAP (tetrabutyl ammonium perchlorate) was used as the supporting electrolyte. All solutions were deoxygenated by passing a stream of prepurified N₂ gas into the solution for at least 10 min prior to recording the voltamograms.

Thermogravimetric analysis (TGA)

Thermal stability of the compounds (2–7) was analysed by thermogravimetric measurements carried out in the presence of air with the heating rate fixed at 10 °C min⁻¹. The samples were heated up to 1000 °C on a TA instrument model SDT Q600 V8.2 Build 100 machine.

Current(I)-voltage(V) measurements

The gels of **2–7** in 60% ethanol–water (2 mg mL⁻¹) were drop-cast on separate gold sputtered glass plates having an electrode gap of 30 µm, and allowed to air-dry in a dust free environment overnight. Finally the samples were further dried *in vacuo* and the *I–V* characteristics of each sample were measured in a two-probe electrode using a semiconductor parameter analyzer 4155C (Agilent).

Results and discussion

One of the main aims of this study is to develop a structureproperty relationship for a closely related new family of gelators based on a PPV backbone that only differs in chain lengths at the termini. Herein, we describe the facile synthesis of these molecules and report physical characterizations of their aggregation induced properties.

Gelation studies

The gelation efficiency of 1-7 was checked towards different aliphatic and aromatic hydrocarbons, aliphatic alcohols and in aqueous medium. Attempted gelation in hydrocarbons such as nheptane or toluene failed due to the lack of solubility. The gelation also failed in a number of solvents including DMF, dioxane, ethyl acetate, DMSO, CHCl₃, acetone, ethanol, and water. However, gelation was observed in acetonitrile for example when compound 5 was used. This implied that the polarity of the solvent plays a specific role in deciding the hydrophilic/hydrophobic balance and hence the resulting gelation. This observation prompted us to check gelation in a mixture of solvents. We selected two solvents i.e., ethanol, where all the compounds remained in solution; and water, where the compounds with longer aliphatic chains (3-7) showed poor solubility. Interestingly, physical gelation was observed in the mixture of ethanol and water in different proportions indicating an optimum polarity has been achieved in the mixture (Fig. 1a). Also, the water molecules in the mixture provide extra stabilization through hydration of the quaternary pyridinium moieties. This result prompted us to check the gelation further in ethylene glycol by imagining HOCH₂CH₂OH as a 1:1 mixture of CH₃CH₂OH and water together. Interestingly, ethylene glycol was also able to gelate the compounds. Following from this result we tried to increase the polarity of the EtOH solution of gelator 5. When we added oxalic acid into the 'sol', it again



Fig. 1 (a) Typical sol-gel phenomena of gelator **5** in 60% ethanol-water mixture under normal light (i) a 'sol', (ii) a 'gel' and under 365 nm UV light (iii) a 'sol', (iv) a 'gel'. (b) Physical gelation efficacies of **4**, **5** and **6** in different ratios of EtOH in H₂O. (c) Comparison of the gelation efficiency of **2–6** in 60% ethanol-water mixture. (d) Physical gelation efficacy of **4**, **5** and **6** in different aliphatic alcohols in the presence of 40% H₂O and also in ethylene glycol.

turned into a gel. Clearly, the stabilization of the repulsive positive charge is key and maintaining an optimum hydrophobic/ hydrophilic balance leads to the physical gelation.

The gelation efficiency of 2-6 was estimated in terms of the minimum gelator concentration (MGC) by increasing the percentage of water in the ethanol-water mixture (Fig. 1b). The MGC decreased progressively with the increasing percentage of water up to 60% ethanol-water and beyond that the MGC again increased (Table S1[†]). Further addition of water rendered these compounds insoluble. Thus, an optimum ratio of 60% ethanol-water showed a minimum value of MGC for 4, 5 and 6 and this was taken as the standard medium for further studies. The gelation efficiency was compared for 1-7 in 60% ethanolwater mixtures. In this medium, while compound 1 remained soluble, compound 7 showed only partial/weak gelation, clearly due to the mismatch in the hydrophilic/hydrophobic balance. Stable gelation was observed for 2-6 (Fig. 1c) and the lowest value of MGC was obtained for 5, which has two tetradecyl chains attached to the central chromophore. Also a trend in the MGC for gelation was observed where, with decreasing chain length, the MGC increased (Table S2[†]).

The gelation efficiency was also checked in different aliphatic alcohols that included MeOH, *n*-PrOH, *i*-PrOH, *t*-BuOH in 60% alcohol-water mixtures for the gelators **4**, **5** and **6**. These compounds were found to be more efficient gelators compared to **2** and **3**. In each alcohol-water mixture, gelator **5** was found to be more efficient compared to **4** and **6** (Fig. 1d). Efficient gelation was observed in EtOH, *i*-PrOH and ethylene glycol by each of **4**–**6** (Table S3[†]).

Gel-melting temperatures

The melting temperature (T_{gel}) of the gels of **3–6** in 60% ethanol– water were measured using the dropping ball method (Fig. 2).¹⁸ T_{gel} increases progressively with increasing concentration of the individual gelators. This indicates that with increasing concentration of the gelator, the density of the gel assembly increases to ensure participation of a greater number of gelator molecules per unit volume in the thermally induced transitions.^{17a} Above a certain concentration, the T_{gel} reached a plateau. In the case of **6**, when the concentration reached 10 mg of compound in 1 mL solvent, this quantity of compound could not be solubilized, indicating a saturation was reached. The T_{gel} increased gradually upon increasing the length of the hydrocarbon chain of the



Fig. 2 Melting temperatures of different gelators (3, 4, 5, 6) with increasing concentrations in a 60% ethanol-water mixture.

gelators at a particular concentration. For example, at 8 mg mL⁻¹ the T_{gel} for 4 was 47 °C. At the same concentration, as much as an 8 °C increase for 5 (55 °C) and another 15 °C for 6 (70 °C) were observed. At 14 mg mL⁻¹, the T_{gel} for 3 was 37 °C, and 52 °C for 4 and 57 °C for 5 were observed. Clearly, greater van der Waals interactions were experienced for the thermally induced transitions with increasing chain length, giving rise to a progressively greater T_{gel} .¹⁹

Variable temperature ¹H NMR study of the gels

¹H NMR spectra of the gels in 60% CD₃OD in D₂O at different temperatures provide an insight into the self-assembly process of the thermoreversible gelation. As a gel (at 25 °C), the ¹H NMR signals of 5 were broadened and almost quenched due to the restriction of the molecular tumbling to produce zero-average dipolar coupling (Fig. 3).²⁰ The broadening and subsequent disappearance of the proton signals suggest intervention of the strong intermolecular interactions leading to the aggregation of the PPV units and subsequent self-organization of the molecules leading to gelation. On gradual increase of the temperature, as the gel melts, an isotropic distribution of the molecules was achieved in solution and their NMR signals appeared gradually, indicating a disruption of the self-organization. The protons which appeared broadened in the gel phase became well-resolved as the gel melted on increasing the temperature. Above 45 °C, there was a dramatic sharpening of all the resonance lines upon complete gel melting.²¹

Similar behavior of line-broadening was also observed for **4** in 60% CD₃OD in D₂O (Fig. S1b†). This kind of observation has been made for various other types of LMMG gel,²² which provide evidence of the manifestation of self-assembly in the gel phase.

Rheological properties

The mechanical stability and the flow behavior of gels were measured by rheological studies.²³ In an oscillatory frequency



Fig. 3 Variable temperature ¹H NMR spectra of the gel of 5 (7 mg mL⁻¹) in 60% CD₃OD in D₂O. The spectrum is assigned to the protons in the molecular structure for convenience.

sweep experiment, the storage (*G'*) and loss moduli (*G''*) were measured as a function of angular frequency (ω) at a fixed strain (0.01%). The *G'* and *G''* of the gels of **3–6** in 60% ethanol–water mixtures showed a plateau region over the entire angular frequency range (1–100 rad s⁻¹) (Fig. S2a and b†). At a particular concentration (10 mg mL⁻¹), *G'* showed greater values with increasing length of the aliphatic chain *i.e.* **6** (1040 Pa) > **5** (610 Pa) > **4** (230 Pa). Increasing the concentration (20 mg mL⁻¹) of the gelators showed a significant increase in the *G'* for individual gelators although the trend remained the same *i.e.* **5** (5600 Pa) > **4** (2950 Pa) > **3** (1270 Pa). In each case a greater *G'* over *G''* suggested a substantial elastic response of the gels and the ratio of *G'/G''* was found to be 7.5 for **4**, 9.7 for **5** and 12.2 for **6** at 10 mg mL⁻¹. Also ~7-fold higher *G'* than *G''* was observed when the concentration was raised to 20 mg mL⁻¹.

In an oscillatory amplitude sweep experiment, the complex modulus (G^*) is composed of two components: (i) G', representing the ability of the deformed material to restore its original geometry, and (ii) G'', representing the tendency of a material to flow under stress. For the gels, G' is generally an order of magnitude greater than G'', showing the dominant elastic behavior of the system. An applied stress above which the gel starts to flow (G'' > G') is called the yield stress where the viscousliquid-like behavior dominates. Under applied stress the gels of **3–6** in 60% ethanol–water showed 6–7 times higher values of G'over G'' indicating a dominating viscoelastic-solid-like behavior (Fig. S2c and d[†]). When the gels succumbed to the applied stress, they began to flow at 1.0 Pa for 4, 3.1 Pa for 5 and 7.2 Pa for 6 at 10 mg mL $^{-1}$. With increasing concentration the yield stress values increased and became 5.7 Pa for 3, 11.1 Pa for 4 and 33.2 Pa for 5. Therefore, the viscoelastic-solid-like behavior (G') and the yield stress were increasingly dominant with increasing chain length and also with increasing concentration of the gelators (Fig. 4). Clearly, the aliphatic chains play a significant role in modifying their mechanical properties.

Morphological characterization of the gels

Microscopic studies were undertaken to observe the morphology of the gel network. The luminescent nature of the gelator molecules allowed us to observe the superstructures created in the selfassemblies using fluorescence microscopy (FM).^{17b-d} When



Fig. 4 A bar diagram showing the *G'* and yield stress values of different gels at different concentrations. A 60% ethanol–water mixture was used in each experiment.

excited at the near UV region (340–400 nm), the thin-films of 2–7 obtained from 60% ethanol–water mixtures showed yellowishorange emission and the presence of three-dimensional fiber bundles was clearly visible (Fig. S3†). In the case of 2–5, fibers of high aspect ratios were observed with diameters within the range \sim 4–5 µm. However, with increase in the hydrocarbon chain length, the aspect ratio decreased and the fibrous nature started to diminish. Fibers with lower aspect ratio were observed in the case of compound 6 and even smaller fibers were seen for 7.

To discern the superstructures and the gel fiber morphologies, scanning electron micrographs (SEM) of the freeze-dried gels derived from the different gelators were recorded. The gels (2–7) showed the presence of three-dimensional fibrillar networks with uniform fiber diameters in all instances (Fig. 5). Progressively decreasing fiber diameter and aspect ratio were observed with increasing aliphatic chain length. The fiber diameters of the xerogels ranged from 4–5 μ m for 2, 2–3 μ m for 3, 1–2 μ m for 4, 1–1.5 μ m for 5, 700–800 nm for 6 and 300–400 nm for 7. Clearly, a lateral association of the individual nano-fibers resulted in a collation of themselves to form tape-like fibers for the shorter-chain analogues. This means that the gel fibers probably consist of hierarchical structures and growth of the monomeric entity into the superstructure depends on the fine balance between the aromatic and aliphatic parts.

X-ray diffraction studies (XRD)

X-ray diffraction studies were undertaken to acquire information about the packing patterns of the gelator molecules in the supramolecular self-assemblies. The diffraction pattern of the xerogel of 2 obtained from 60% ethanol-water shows five peaks corresponding to the d-values of 2.57 nm, 1.25 nm (which is in the ratio of 1 : 1/2), 0.82 nm (1 : 1/3), 0.61 nm (1 : 1/4) and 0.49 nm (1:1/5) (Fig. 6). This indicates a lamellar arrangement of the $aggregates^{24}$ of the xerogel of 2 with an interlayer spacing of 2.57 nm. The diffraction patterns of each of these xerogels showed sharp Bragg's reflection peaks ensuring highly ordered lamellar organization was present in each case (Table 1). It may be noted that with increasing hydrocarbon chain length, the higher order Bragg's reflections become weaker and eventually they disappear. This indicates that the crystallinity decreases with increasing aliphatic chain length of the gelators, which is in line with the microscopic images. However, in each case the first



Fig. 5 Scanning electron microscopy images of the freeze-dried samples of (a) 2, (b) 3, (c) 4, (d) 5, (e) 6 and (f) 7.



Fig. 6 X-ray diffraction patterns of the freeze-dried gels of **2–7** in 60% ethanol–water mixtures.

diffraction peak appeared more intense compared to the higher order reflection peaks. Only the alternate peaks appeared for **3–5**. Depending upon the aliphatic chain length, the Bragg's reflections also vary for how the peaks corresponding to the planes 1/3 (marked by '*') and 1/5 (marked by '**') appear in Fig. 6.

Interestingly another set of peaks appeared invariably in each of the gelators. These can be assigned due to the presence of an aromatic segment which is identical in every instance (Table 1). These peaks provide valuable information about the arrangement of the aromatic segment in the self-assembly. The π - π stacking distance emerged at 0.39 nm, which is slightly above the reported values²⁵ and this could be due to the presence of two positive charges at the end of the aromatic segment. The lengths of the appended alkyl chains were obtained from the ground state geometry of compounds 2–7 optimized through B3LYP/6-31G* level computations (Fig. S4†). A model has been proposed by considering the above mentioned results (Fig. 7).

XRD analysis reveals a periodic lamellar organization with the repeat distances being slightly less than double the alkyl chain length. This indicates that the hydrophobic chains are interlocked with each other so that they introduce strong van der Waals interactions among the long chains. A J-type aggregation in the aromatic segments may give rise to the *d*-spacing of 0.85 nm. The thickness of a single layer could be assigned to 0.41 nm (as obtained from the breadth of the optimized molecular structure) and the distance between the successive layers is 0.79 nm. The XRD pattern of **5** obtained from only ethanol revealed similar Bragg's peaks, indicating a similar self-assembly pattern remained in the thin film (Fig. S5†).

 Table 1
 Bragg's reflection peaks (d-values)^a obtained from XRD studies for the xerogels of 2–7 in 60% ethanol–water mixture

	1	1/2	1/3	1/4	1/5	R^b	2 nd se	et of pe	aks	
2 3 4 5 6 7	2.57 2.74 2.93 3.33 3.64 3.74	1.25 1.75 1.84	0.82 0.89 0.97 1.06 1.15 1.22	0.61	0.49 0.53 0.58	1.11 1.36 1.62 1.87 2.13 2.39	0.87 0.85 0.84 0.85 0.85	0.80 0.79 0.78 0.79 0.79	$\begin{array}{c} 0.42 \\ 0.42 \\ 0.41 \\ 0.41 \\ 0.41 \\ 0.40 \end{array}$	0.39 0.39 0.39 0.39 0.39 0.39 0.39

 a All the *d*-spacing values are expressed in nm. b *R* represents the length of the hydrocarbon chain from the quaternary N.



Fig. 7 Proposed model depicting the probable self-assembly motif of **5** in the gel as evidenced from the XRD studies.

The crystalline lamellar nanofibers were further examined under a polarized optical microscope (POM) in order to confirm the presence of birefringent textures. Thin films obtained from solutions of the gelators in 60% ethanol–water mixtures indeed showed the presence of birefringent textures in every instance. This indicates an anisotropic growth of the three-dimensional aggregates of the PPV molecules leading to the formation of nanofibers (Fig. S6†).¹⁷ Also, the fiber diameters decreased progressively with increase in the aliphatic chain length, which agrees well with the FM and SEM studies. As observed under XRD, the thin film obtained from EtOH is also crystalline in nature which again showed the presence of birefringent texture although the aspect ratio is smaller (Fig. S7†). The birefringent textures were also evident in the gel of **5** in 60% ethanol–water mixture.

UV-vis and fluorescence spectroscopy

The chromophoric nature of this class of molecules allows manifestation of interesting optical and photophysical properties.²⁶ The absorption maxima (λ_{max}) of each of **2–7** (1 × 10⁻⁵ M) in ethanol at 25 °C appeared at 400 nm (S₀ \rightarrow S₁) in addition to a small band at 250 nm (S₀ \rightarrow S₂) due to the presence of the same chromophore unit (Fig. S8†). The λ_{max} did not shift when the absorption spectrum was recorded for example with compound **5** in 60% ethanol–water where it transformed into a physical gel. The emission maximum appeared at 470 nm when excited at 380 nm for each of **2–7** (1 × 10⁻⁵ M) in ethanol.

The aggregation leading to the gelation in ethanol-water mixture exhibited a drastic visual color change under normal daylight as well as under a 365 nm UV lamp (Fig. 1a). The color changed from intense light-blue to yellowish-orange upon sol-to-gel transformation, as observed under the UV-light. The self-assembly of the gelators clearly depends on the polarity (the hydrophobic/hydrophilic balance) of the medium as they formed a 'sol' in ethanol and an 'aggregate' in water. Thus, by varying the ratio of ethanol-water it may be possible to modulate their aggregation. Snapshots of the solution of 5 (1×10^{-5} M) in different ratios of ethanol-water mixtures were viewed under a 365 nm UV lamp (Fig. 8a) and also under normal daylight (Fig. S9†). The solution in ethanol alone

(100%) and up to 40% of ethanol-water mixture showed highly fluorescent light-blue emission representing a 'monomeric' emission. But at the ratio of 30–0% ethanol-water, a yellowish-orange emission appeared indicating an aggregated emission. This suggests that the aggregation of the gelator molecules in the mixed solvent system is assisted by intermolecular π - π stacking and van der Waals interactions. These solutions were then analyzed using UV-vis and fluorescence spectroscopies.

Under UV-vis, the λ_{max} appeared at 400 nm when the ratio of ethanol-water was between 100 and 50% (Fig. 8b). However, the intensity of the λ_{max} decreased when the ratio became 40% although there was no significant shift in the λ_{max} . Beyond this ratio, the absorption patterns changed drastically. A new band appeared at 370 nm followed by a broad band at 430 nm and a hump-like shoulder band at 480 nm. Also the small band at 250 nm experienced a red-shift. Under fluorescence, the solutions showed intense monomeric emission at 470 nm up to the ethanol-water ratio of 50% (Fig. 8d). The intensity decreased at 40% ethanol-water without any change in the emission maxima and beyond that a significantly hypochromic, red-shifted emission maximum at 575 nm was observed for 30-0% of ethanolwater, indicating an aggregated emission.²⁷ These studies indicate that the monomeric species form self-assembled species when the amount of ethanol is below 40% in the ethanol-water mixture.



Fig. 8 (a) Snapshots showing solutions of **5** $(1 \times 10^{-5} \text{ M})$ in different ethanol–water mixtures (% of EtOH) (A) 100%, (B) 90%, (C) 80%, (D) 70%, (E) 60%, (F) 50%, (G) 40%, (H) 30%, (I) 20%, (J) 10%, (K) 0%. (b) UV-vis and (d) fluorescence emission spectra of **5** $(1 \times 10^{-5} \text{ M})$ at different ratios of ethanol–water mixtures ($\lambda_{ex} = 380 \text{ nm}$). Variable temperature (c) UV-vis and (e) fluorescence spectra of **5** $(2 \times 10^{-5} \text{ M})$ in 35% ethanol–water mixture ($\lambda_{ex} = 380 \text{ nm}$).

To imitate a thermoreversible sol-gel transition, a 35% ethanol-water solution of 5 was subjected to temperature variation. At higher temperature (50 °C) the λ_{max} appeared at 400 nm in addition to a small band at 250 nm which resembled the monomeric absorption (Fig. 8c). When the temperature was lowered, the intensity of the λ_{max} decreased gradually and a redshifted band appeared at 480 nm. The generation of an aggregated state was also accompanied by a gradual loss of the shape and intensity of the 250 nm band along with a ~ 10 nm red-shift of the λ_{max} which is suggestive of a possible J-type aggregation.²⁸ Under fluorescence, at higher temperature (50 °C) the emission was observed at 470 nm due to the molecularly dissolved species (Fig. 8e). On decreasing the temperature the intensity of the band decreases progressively with the gradual generation of a red-shifted band at 575 nm indicating that an aggregated state has been reached. The presence of clear isosbestic points in the UV-vis spectra and an isoemissive point (565 nm) in the fluorescence emission spectra indicated a thermal equilibration between the aggregated and non-aggregated states, which is approximately reversible irrespective of whether the temperature was varied in the low-to-high or highto-low direction.

When we looked at the variable temperature emission spectra of 5 in 35% ethanol-water closely, we found that at room temperature ($\sim 25-30$ °C) the spectra covered the whole visible range of emission (~450-650 nm). This prompted us to observe the solution under UV light (365 nm) at room temperature. Interestingly, the solution showed a white-light emission under this condition (Fig. 9). However, the same solution when cooled $(\sim 10 \ ^{\circ}\text{C})$, showed a yellowish-orange emission and when heated $(\sim 50 \,^{\circ}\text{C})$, it showed a light-blue emission. We have recorded the emission spectra of these three solutions after pre-adjusting their emission colors visually under the UV lamp. The emission spectra were consistent with the previous observations and resembled that of a 'monomeric' emission (470 nm) at high temperature, aggregated emission (575 nm) at low temperature and a wide-range emission (~450-650 nm) at room temperature. The CIE chromaticity diagram exhibited the coordinates for the white-light emission (0.32, 0.39) which are quite close to pure white-light emission (0.33, 0.33). The excitation spectra of these three solutions resembled the spectral patterns as observed under the variable temperature absorption spectra (Fig. S11[†]). Therefore, it may be assumed that, at room temperature a certain proportion of the monomeric and aggregated species exist



Fig. 9 Variable temperature fluorescence spectra of 5 (2×10^{-5} M) in 35% ethanol–water mixture (excited at 380 nm).

together in the mixture which could cover the whole visible emission spectral range. This depends upon the temperature, ratio of ethanol-water in the mixture and most importantly the concentration of the gelator. Thus, when a gel of 5 (10 mg mL⁻¹) in 60% ethanol-water was heated and then cooled it did not show white-light emission, instead it showed a direct transformation from light-blue to yellowish-orange emission. This is due to the direct and fast transformation from the monomeric to the aggregated species as the concentration was very high (Fig. S12[†]). Thus, white-light emission can be observed from a single component depending on the aggregate fraction in the mixture, unlike the other white-light emitting substances reported in the literature which generally contain more than one chromophore.29

Cyclic voltammetry

25

The structural features of such compounds prompted us to examine their electronic redox behavior. Accordingly, the cyclic voltamograms (CV) were recorded for a freshly prepared solution of 2–7 (10^{-3} M) in DMSO at 100 mV s⁻¹ scan rate and using a glassy carbon working electrode. The cyclic voltammograms exhibited a cathodic peak (reduction) with a directly associated anodic peak (oxidation) in the reverse scan (Fig. 10a). In each case only one oxidation-reduction wave was observed throughout the scan range +1 to -2 V (Fig. S13a[†]). Corresponding reduction (E_{red}) and oxidation (E_{ox}) potentials were obtained from the CV plots (Table 2). The potentials were found to be greater for the compounds with shorter aliphatic chains (2 and 3). Interestingly, a sudden jump in E_{ox} was observed for 4 (with $-C_{12}H_{25}$ chain) and after that a gradual decrease in the E_{red} and E_{ox} was observed with the increase in the aliphatic chain length (Fig. 10b). Clearly, the electron transfer is strongly influenced by the length of the alkyl chains.

The ratio of the reduction (I_{pc}) and the oxidation (I_{pa}) currents (I_{pc}/I_{pa}) is close to 1, which indicates the electrochemical reversibility of the electron transfer process (Table 2).30 The $E_{\rm red}$ and $E_{\rm ox}$ for 2 appeared at -0.853 and -0.787 V, respectively, and show a sudden jump for compound 5 ($E_{\rm red}$ -0.832 V and $E_{\rm ox}$ -0.717 V) as observed clearly in Fig. 10a. The experimental ΔE value $(E_{red} - E_{ox})$ for **2** is 0.066 V which is close to 0.059 V (theoretically expected for an electrochemically reversible one-electron redox process).³¹ Using the ΔE value, the number of electrons (n) involved in the redox process is calculated from the equation $\Delta E = 0.059/n$, which indicates a one

Fig. 10 Cyclic voltammogram of 1 mM solution of (a) 2 and 5 and (b) comparison of 2-7 in DMSO at a scan rate 100 mV s⁻¹.

Table 2 Cyclic voltammetry peak potentials (E_{red}, E_{ox}) and redox potentials (E) obtained from differential pulse voltammetry for 2–7^a

	$E_{\rm red}$ (V)	$E_{\mathrm{ox}}\left(\mathrm{V}\right)$	$\Delta E\left(\mathrm{V}\right)$	$I_{\rm pc}/I_{\rm pa}$	$E_{1/2}$ (V)	<i>E</i> ⁰ (V) from DPV
_						
2	-0.853	-0.787	0.066	1.2	-0.820	-0.804
3	-0.853	-0.787	0.066	1.2	-0.820	-0.804
4	-0.853	-0.721	0.132	1.1	-0.787	-0.806
5	-0.832	-0.717	0.115	1.2	-0.774	-0.783
6	-0.813	-0.705	0.108	0.9	-0.759	-0.771
7	-0.803	-0.695	0.108	0.8	-0.749	-0.761

^a Conditions: scan speed 100 mV s⁻¹, temperature 25 °C, supporting electrolyte 100 mM TBAP, solvent DMSO, three electrode system; SCE as reference, Pt wire counter and glassy carbon working electrode. $E_{1/2}$ is the half-wave potential = $(E_{red} + E_{ox})/2$.

electron exchange process.³² However, the ΔE value for the compounds with longer aliphatic chain length departed from the constant value (0.059 V) suggesting that probably structural reorganization and aliphatic chain reorientation take place on reduction.³⁰ The half-wave potential $(E_{1/2})$ can be obtained from a voltammogram by calculating the average value of the anodic and cathodic peaks. The subscript 1/2 indicates that the potential is obtained approximately at the half-height of the cathodic and anodic peaks and at these points the concentrations of the reduced and oxidized species on the electrode are equal.³³ The redox potentials (E^0) were also obtained from the differential pulse voltammetry (DPV) measurements (Fig. S13b-g[†]). $E_{1/2}$ decreases progressively with increasing aliphatic chain length in the series and is consistent with the E^0 values obtained from DPV.

The peak current (I_p) for compound **2** increases linearly as a function of square root of the scan rates $(v^{1/2})$ ranging from 25– 300 mV s^{-1} indicating that the electrode reactions are diffusion-controlled for the redox process (Fig. S14[†]).³⁴ However, a deviation from linearity in the $I_{\rm pc}$ vs. $v^{1/2}$ is observed for 5, a member with longer aliphatic chains, indicating that at sufficient overpotential, the reaction is diffusion-limited.35 In both the cases, compounds 2 and 5 display larger peak separations at higher scan rates, which may be due to a relatively slow electron transfer rate between the oxidized species and the electrode.³⁶ The plot of I_{pc} vs. $v^{1/2}$ for **2** shows a linear fit passing through y = 0. Using the 'slope', the diffusion coefficient (D) for reduction can be calculated using the well known Randles-Sevcik eqn (1).37

$$I_{\rm pc} = (2.687 \times 10^5) \ n^{3/2} \ v^{1/2} \ D^{1/2} \ A \ C \tag{1}$$

$$Slope = (2.687 \times 10^5) n^{3/2} D^{1/2} A C$$

where, n = the number of electrons appearing in the halfreaction for the redox couple, A is the electrode area (0.2827) cm^2) and C is the concentration of the electrolyte solution (10⁻⁶) mol cm⁻³). Using the magnitude of slope (5.1909 \times 10⁻⁵ A $s^{1/2} V^{-1/2}$) and considering a one-electron transfer reaction, the diffusion coefficient (D) of 2 is calculated to be 4.67×10^{-7} $cm^2 s^{-1}$.



(b)

Thermogravimetric analysis (TGA)

The decomposition behavior of 2-7 was elucidated using TGA. A typical weight-loss profile shows a two-step decomposition pathway for this class of molecules (Fig. S15[†]). A sharp decomposition between 250 and 340 $^\circ C$ with $\sim 60\%$ mass loss followed by another comparatively slower decomposition between 340 and 600 °C with more than 95% weight loss. The derivative plots of the TGA curves show the peak of the mass loss (the peak degradation temperature) between 299 and 330 °C for the first step followed by 481-535 °C for the second step of decomposition (Fig. S16[†]). The weight loss in the first step is due to the degradation of the alkyl chains and the second step corresponds to the loss of aromatic residue of the gelators.³⁸ The peak degradation temperatures are listed in Table 3. The decomposition temperatures and hence the thermal stability increased progressively with increasing aliphatic chain length appended to the PPV core.

Electrical conductivity (I-V) measurements

Since the gelators 2–7 have π -electron conjugation in their backbones and also carry two cationic charges, it would be interesting to investigate their electrical conductivity across the fibers created by the intermolecular stacking interactions through the aromatic surface in the xerogel matrices. The I-Vmeasurements for the dried gels of 2-7 were measured in a two probe electrode. In the low voltage region ($\sim 1-10$ V) the curve followed Ohm's law (V/I = R) (the linear region of the curve) and the corresponding resistance (R) was calculated from the I-V curve (Fig. 11).³⁹ However, in the higher voltage region, the I-V curves show deviation from the linearity which is characteristic of a typical semiconducting nature of the gels.⁴⁰ On increasing the voltage, the current increased in a nonlinear fashion. Notably, the device did not collapse even after applying 100 V, which showed the robustness of the system comprising the nanoassembly. The current at voltages of 10 V, 50 V and 100 V and the calculated resistance at 10 V are recorded (Table S4[†]). The magnitude of current increases with the decrease of the length of the aliphatic hydrocarbon chains. It has been observed from the microscopic studies that the fiber diameter increases with the decrease in the aliphatic chain length. Thus, with larger fiber diameter and higher aspect ratio, the electrical conductivity increases. It is also possible that with increasing chain length the weight fraction of the semiconducting chromophore in the gelator decreases and hence the conductivity decreases.

 Table 3
 Peak degradation temperatures of 2–7 in the two-step decomposition profiles based on thermogravimetric analysis

	Loss of aliphatic parts (°C)	Loss of aromatic parts (°C)		
2	299	481		
3	295	502		
4	300	503		
5	300	505		
6	306	505		
7	330	535		



Fig. 11 Electrical conductivity studies showing I-V characteristics of 2–7 in a two-probe electrode. Inset shows a magnified plot for easier comparison.

Conclusions

We have described the synthesis and aggregation properties exhibited by a new family of PPV derivatives tailored with different aliphatic chains on the periphery. With increasing length of the aliphatic chain, their gelation ability increases. However, the presence of excess hydrophobic moiety at the periphery weakens the gelation ability. Spectroscopic studies unravel a thermoreversible self-assembly leading to emission switching depending on the temperature and a white-light emission at room temperature. A high degree of crystallinity and the presence of lamellar structures in the self-assembly of the gelators were evident from the X-ray diffraction studies. Microscopic studies suggest that the shorter alkyl chains favor the self-assembly of PPVs leading to a greater aspect ratio of the fibrillar networks. The electrical conductivity increases progressively with larger fiber diameter *i.e.* with the shorter aliphatic chains. Also, the redox reaction at the electrode surface depends on the aliphatic chain length on the PPV core and the redox potentials decrease with increasing aliphatic chain length. However, their mechanical and thermal stabilities increase gradually with the increase in the chain length. Clearly, the subtle balance between the hydrophobic and hydrophilic groups in the PPV backbone holds the key in tuning the gelation phenomenon assisted with the modulation of the ethanol-water solvent polarity. These systems therefore provide a convenient way for the modulation of macroscopic properties of the resulting soft materials. This study thus provides opportunities for the development of nanostructured advanced materials from the gelation of a variety of linear, π -conjugated systems and organic semiconductors, which may find applications in the emerging field of supramolecular electronics.

Notes and references

- (a) P. Terech and R. G. Weiss, *Chem. Rev.*, 1997, **97**, 3133–3159; (b)
 T. Ishi-I and S. Shinkai, *Top. Curr. Chem.*, 2005, **258**, 119–160; (c)
 S. Bhattacharya and S. K. Samanta, *Langmuir*, 2009, **25**, 8378– 8381; (d) S. Bhattacharya and S. N. G. Acharya, *Chem. Mater.*, 1999, **11**, 3504–3511.
- 2 (a) I. Furman and R. G. Weiss, *Langmuir*, 1993, 9, 2084–2088; (b)
 N. M. Sangeetha and U. Maitra, *Chem. Soc. Rev.*, 2005, 34,

821–836; (c) P. Terech, N. M. Sangeetha and U. Maitra, J. Phys. Chem. B, 2006, **110**, 15224–15233; (d) J. Cui, J. Zheng, W. Qiao and X. Wan, J. Colloid Interface Sci., 2008, **326**, 267–274; (e) G. Wang, H. Yang, S. Cheuk and S. Coleman, Beilstein J. Org. Chem., 2011, 7, 234–242.

- (a) M. Ikeda, M. Takeuchi and S. Shinkai, *Chem. Commun.*, 2003, 1354–1355;
 (b) L. A. Estroff and A. D. Hamilton, *Chem. Rev.*, 2004, **104**, 1201–1217;
 (c) J.-H. Ryu and M. Lee, *J. Am. Chem. Soc.*, 2005, **127**, 14170–14171;
 (d) E. Lee, J.-K. Kim and M. Lee, *Angew. Chem., Int. Ed.*, 2008, **47**, 6375–6378;
 (e) L. Chen, S. Revel, K. Morris and D. J. Adams, *Chem. Commun.*, 2010, **46**, 4267–4269.
- 4 (a) T. Goodson III, W. Li, A. Gharavi and L. Yu, Adv. Mater., 1997,
 9, 639–643; (b) F. Wurthner, Chem. Commun., 2004, 1564–1579; (c)
 K. Sugiyasu, N. Fujita and S. Shinkai, Angew. Chem., Int. Ed., 2004, 43, 1229–1233; (d) M. Llusar and C. Sanchez, Chem. Mater., 2008, 20, 782–820; (e) K. Sugiyasu, S. Kawano, N. Fujita and S. Shinkai, Chem. Mater., 2008, 20, 2863–2865.
- 5 (a) K. Murata, M. Aoki, T. Suzuki, T. Harada, H. Kawabata, T. Komri, F. Ohseto, K. Ueda and S. Shinkai, *J. Am. Chem. Soc.*, 1994, **116**, 6664–6676; (b) K. J. C. van Bommel, A. Friggeri and S. Shinkai, *Angew. Chem., Int. Ed.*, 2003, **42**, 980–999.
- 6 (a) T. Kunitake, Y. Okahata, M. Shimomura, S. Yasunami and Takarabe, J. Am. Chem. Soc., 1981, 103, 5401-5413; (b) Y. C. Lin, B. Kachar and R. G. Weiss, J. Am. Chem. Soc., 1989, 111, 5542-5551; (c) K. Hanabusa, Y. Maesaka, M. Kimura and H. Shirai, Tetrahedron Lett., 1999, 40, 2385-2388; (d) G. Mieden-Gundert, L. Klein, M. Fischer, F. Vogtle, K. Heuze, J. L. Pozzo, M. Vallier and F. Fages, Angew. Chem., Int. Ed., 2001, 40, 3164-3166; (e) H. Koshima, W. Matsusaka and H. Yu, J. Photochem. Photobiol., A, 2003, **156**, 83–90; (f) M. George, S. L. Snyder, P. Terech, C. J. Glinka and R. G. Weiss, J. Am. Chem. Soc., 2003, 125, 10275-10283; (g) A. Pal, Y. K. Ghosh and S. Bhattacharya, Tetrahedron, 2007, 63, 7334-7348; (h) M. Cote, T. Nicholls, D. W. Knight, I. R. Morgan, P. G. A. Rogueda, S. M. King, R. K. Heenan and P. C. Griffiths, Langmuir, 2009, 25, 8678-8684; (i) A. Ghosh and J. Dey, Langmuir, 2009, 25, 8466-8472; (j) B. G. Bag, S. K. Dinda, P. P. Dey, V. A. Mallia and R. G. Weiss, Langmuir, 2009, 25, 8663-8671; (k) A. G. L. Olive, G. Raffy, H. Allouchi, J. M. Leger, A. D. Guerzo and J. P. Desvergne, Langmuir, 2009, 25, 8606-8614; (1) J. Cui, Y. Zheng, Z. Shen and X. Wan, Langmuir, 2010, 26, 15508-15515.
- S. Bhattacharya and A. Pal, J. Phys. Chem. B, 2008, 112, 4918–4927.
 (a) M.-Y. Lai, C.-H. Chen, W.-S. Huang, J. T. Lin, T.-H. Ke, L.-Y. Chen, M.-H. Tsai and C.-C. Wu, Angew. Chem., Int. Ed., 2008, 47, 581–585; (b) A. Liedtke, M. O'Neill, A. Wertmoller, S. P. Kitney and S. M. Kelly, Chem. Mater., 2008, 20, 3579–3586.
- 9 (a) A. J. Zucchero, J. Tolosa, L. M. Tolbert and U. H. F. Bunz, *Chem.-Eur. J.*, 2009, **15**, 13075–13081; (b) S. M. Kim, J. H. Jang, K. K. Kim, H. K. Park, J. J. Bae, W. J. Yu, I. H. Lee, G. Kim, D. D. Loc, U. J. Kim, E.-H. Lee, H.-J. Shin, J.-Y. Choi and Y. H. Lee, *J. Am. Chem. Soc.*, 2009, **131**, 327–331.
- (a) T.-Q. Nguyen, J. Wu, V. Doan, B. J. Schwartz and S. H. Tolbert, *Science*, 2000, **288**, 652–656; (b) S. Hecht and J. M. J. Frechet, *Angew. Chem.*, *Int. Ed.*, 2001, **40**, 74–91; (c) K. Becker, J. M. Lupton, J. Feldmann, S. Setayesh, A. C. Grimsdale and K. Mullen, *J. Am. Chem. Soc.*, 2006, **128**, 680–681; (d) Y. Sun, N. C. Giebink, H. Kanno, B. Ma, M. E. Thompson and S. R. Forrest, *Nature*, 2006, **440**, 908–912.
- 11 (a) S.-i. Tamaru, M. Takeuchi, M. Sano and S. Shinkai, Angew. Chem., Int. Ed., 2002, 41, 853–856; (b) M. Shirakawa, S.-I. Kawano, N. Fujita, K. Sada and S. Shinkai, J. Org. Chem., 2003, 68, 5037–5044; (c) H. Jintoku, T. Sagawa, T. Sawada, M. Takafuji, H. Hachisako and H. Ihara, Tetrahedron Lett., 2008, 49, 3987–3990.
- 12 H. Engelkamp, S. Middlebeek and R. J. M. Nolte, *Science*, 1999, 284, 785–788.
- 13 (a) K. Sugiyasu, N. Fujita and S. Shinkai, Angew. Chem., Int. Ed., 2004, 43, 1229–1233; (b) K. Sugiyasu, S.-i. Kawano, N. Fujita and S. Shinkai, Chem. Mater., 2008, 20, 2863–2865.
- 14 (a) F. S. Schoonbeek, J. H. van Esch, B. Wegewijs, D. B. A. Rep, M. P. de Haas, T. M. Klapwijk, R. M. Kellogg and B. L. Feringa, *Angew. Chem., Int. Ed.*, 1999, **38**, 1393–1397; (b) P. Pratihar, S. Ghosh, V. Stepanenko, S. Patwardhan, F. C. Grozema, L. D. A. Siebbeles and F. Würthner, *Beilstein J. Org. Chem.*, 2010, **6**, 1070–1078.

- 15 (a) P. Mukhopadhyay, Y. Iwashita, M. Shirakawa, S.-i. Kawano, N. Fujita and S. Shinkai, Angew. Chem., Int. Ed., 2006, 45, 1592– 1595; (b) T. Shu, J. Wu, M. Lu, L. Chen, T. Yi, F. Li and C. Huanga, J. Mater. Chem., 2008, 18, 886–893; (c) J. W. Chung, S.-J. Yoon, S.-J. Lim, B.-K. An and S. Y. Park, Angew. Chem., Int. Ed., 2009, 48, 7030–7034; (d) R. Abbel, R. van der Weegen, W. Pisula, M. Surin, P. Leclere, R. Lazzaroni, E. W. Meijer and A. P. H. J. Schenning, Chem.–Eur. J., 2009, 15, 9737–9746; (e) K. V. Rao, K. Jayaramulu, T. K. Maji and S. J. George, Angew. Chem., Int. Ed., 2010, 49, 4218–4222.
- 16 (a) A. El-ghayoury, A. P. H. J. Schenning, P. A. van Hal, J. K. J. van Duren, R. A. J. Janssen and E. W. Meijer, Angew. Chem., Int. Ed., 2001, 40, 3660–3663; (b) A. Ajayaghosh and S. J. George, J. Am. Chem. Soc., 2001, 123, 5148–5149; (c) A. P. H. J. Schenning, J. V. Herrikhuyzen, P. Jonkheijm, Z. Chen, F. Wurthner and E. W. Meijer, J. Am. Chem. Soc., 2002, 124, 10252–10253; (d) F. J. M. Hoeben, M. Wolffs, J. Zhang, S. D. Feyter, P. Leclere, A. P. H. J. Schenning and E. W. Meijer, Angew. Chem., Int. Ed., 2004, 43, 1976–1979; (e) J. F. Hulvat, M. Sofos, K. Tajima and S. I. Stupp, J. Am. Chem. Soc., 2005, 127, 366–372; (f) M. Mba, A. Moretto, L. Armelao, M. Crisma, C. Toniolo and M. Maggini, Chem.-Eur. J., 2011, 17, 2044–2047.
- 17 (a) S. K. Samanta, A. Pal and S. Bhattacharya, Langmuir, 2009, 25, 8567–8578; (b) S. K. Samanta, A. Pal, S. Bhattacharya and C. N. R. Rao, J. Mater. Chem., 2010, 20, 6881–6890; (c) S. K. Samanta, A. Gomathi, S. Bhattacharya and C. N. R. Rao, Langmuir, 2010, 26, 12230–12236; (d) S. K. Samanta, K. S. Subrahmanyam, S. Bhattacharya and C. N. R. Rao, Chem.– Eur. J., 2012, 18, 2890–2901; (e) S. Bhattacharya and S. K. Samanta, Chem.–Eur. J., 2012, DOI: 10.1002/chem.201201940.
- 18 (a) J. W. Chung, B.-K. An and S. Y. Park, *Chem. Mater.*, 2008, 20, 6750–6755; (b) N. Mohmeyer, P. Wang, H.-W. Schmidt, S. M. Zakeeruddin and M. Gratzel, *J. Mater. Chem.*, 2004, 14, 1905–1909; (c) R. Schmidt, M. Schmutz, M. Michel, G. Decher and P. J. Mesini, *Langmuir*, 2002, 18, 5668–5672.
- 19 (a) N. Zweep, A. Hopkinson, A. Meetsma, W. R. Browne, B. L. Feringa and J. H. van Esch, *Langmuir*, 2009, 25, 8802–8809; (b) Low Molecular Mass Gelators: Design, Self-Assembly, Function; Topics in Current Chemistry, ed. F. Fages, Springer, New York, 2005, vol. 256.
- 20 (a) T. M. Duncan and C. Dybowski, *Surf. Sci. Rep.*, 1981, 1, 157–250;
 (b) D. C. Duncan and D. G. Whitten, *Langmuir*, 2000, 16, 6445–6452.
- 21 The ¹H NMR signals due to the aliphatic $-CH_2$ protons adjacent to the quaternary *N* merged with the H-D-O signals of the solvent. However, the signal can be observed for the spectra taken in only CD₃OD (Fig. S1a[†]).
- 22 (a) M. Tata, V. T. John, Y. Y. Waguespack and G. L. McPherson, J. Am. Chem. Soc., 1997, 116, 9464–9470; (b) J. H. Jung, G. John, M. Masuda, K. Yoshida, S. Shinkai and T. Shimizu, Langmuir, 2001, 17, 7229–7232; (c) H. Basit, A. Pal, S. Sen and S. Bhattacharya, Chem.-Eur. J., 2008, 14, 6534–6545; (d) A. Pal, H. Basit, S. Sen, V. K. Aswal and S. Bhattacharya, J. Mater. Chem., 2009, 19, 4325–4334.
- 23 (a) H. A. Barnes, in A Handbook of Elementary Rheology, University of Wales, Institute of Non-Newtonian Fluid Mechanics, Aberystwyth, 2000, pp. 55–61; (b) F. M. Menger and K. L. Caran, J. Am. Chem. Soc., 2000, **122**, 11679–11691; (c) P. Terech, D. Pasquier, V. Bordas and C. Rossat, Langmuir, 2000, **16**, 4485– 4494.
- 24 (a) D. J. Abdallah, S. A. Sirchio and R. G. Weiss, *Langmuir*, 2000, 16, 7558–7561; (b) M. Caffrey, J. Hogan and A. S. Rudolph, *Biochemistry*, 1991, 30, 2134–2146; (c) J. Kadam, C. F. Faul and J. U. Scherf, *Chem. Mater.*, 2004, 16, 3867–3871.
- 25 C.-X. Yuan, X.-T. Tao, Y. Ren, Y. Li, J.-X. Yang, W.-T. Yu, L. Wang and M.-H. Jiang, J. Phys. Chem. C, 2007, 111, 12811–12816.
- 26 (a) B. Juskowiak, M. Ohba, M. Sato, S. Takenaka, M. Takagi and H. Kondo, *Bull. Chem. Soc. Jpn.*, 1999, **72**, 265–277; (b) J. Tang, C. Wang, Y. Wang, J. Sunb and B. Yang, *J. Mater. Chem.*, 2001, **11**, 1370–1373; (c) E. P. Petrov, F. Cichos, F. Wagner, St. Spange and C. von Borczyskowski, *Photochem. Photobiol.*, 2005, **81**, 898– 907; (d) C.-X. Yuan, X.-T. Tao, Y. Ren, Y. Li, J.-X. Yang, W.-T. Yu, L. Wang and M.-H. Jiang, *J. Phys. Chem. C*, 2007, **111**, 12811–12816.
- 27 When the emission spectrum of the gel of 5 in 60% ethanol-water was recorded under the front-face geometry, it showed excitation and

emission maximum at 470 and 590 nm respectively. Therefore, the emission maximum at 575 nm ensured the aggregated emission (see Fig. $S10^+$).

- 28 (a) S. Ghosh, X.-Q. Li, V. Stepanenko and F. Wurthner, *Chem.-Eur.* J., 2008, 14, 11343–11357; (b) F. Wurthner, T. E. Kaiser and C. R. Saha-Moller, *Angew. Chem., Int. Ed.*, 2011, 50, 3376–3410; (c) M. Shirakawa, S.-i. Kawano, N. Fujita, K. Sada and S. Shinkai, *J. Org. Chem.*, 2003, 68, 5037–5044; (d) H. Wu, L. Xue, Y. Shi, Y. Chen and X. Li, *Langmuir*, 2011, 27, 3074–3082; (e) X.-Q. Li, X. Zhang, S. Ghosh and F. Wurthner, *Chem.-Eur. J.*, 2008, 14, 8074–8078.
- 29 (a) C. Vijayakumar, V. K. Praveen and A. Ajayaghosh, Adv. Mater., 2009, 21, 2059–2063; (b) Y.-L. Liu, Y.-H. Wu and C.-Y. Hsu, Nanotechnology, 2009, 20, 235704; (c) X. Wang, J. Yan, Y. Zhou and J. Pei, J. Am. Chem. Soc., 2010, 132, 15872–15874; (d) C. Vijayakumar, K. Sugiyasu and M. Takeuchi, Chem. Sci., 2011, 2, 291–294; (e) C. Giansante, G. Raffy, C. Schafer, H. Rahma, M.-T. Kao, A. G. L. Olive and A. D. Guerzo, J. Am. Chem. Soc., 2011, 133, 316–325; (f) M. R. Molla and S. Ghosh, Chem.-Eur. J., 2012, 18, 1290–1294.
- 30 S. Perez, C. Lopez, A. Caubet, A. Roig and E. Molins, J. Org. Chem., 2005, 70, 4857–4860.

- 31 E. R. Brown and J. R. Sandifer, in *Physical Methods in Chemistry*. *Electrochemical Methods*, ed. B. W. Rossiter and J.H. Hamilton, Wiley, New York, 1986, vol. 4, ch. 4.
- 32 S. Petrovic, Chem. Educ., 2000, 5, 231-235.
- 33 N. G. Tsierkezos, J. Solution Chem., 2007, 36, 289-302.
- 34 X. H. Zhang and S. F. Wang, Sensors, 2003, 3, 61-68.
- 35 S. Ershad and J. Khodmarz, Int. J. Electrochem. Sci., 2010, 5, 1302– 1309.
- 36 (a) R. Nicholson, Anal. Chem., 1965, 37, 1351–1355; (b) C. N. Myer and C. W. Allen, Inorg. Chem., 2002, 41, 60–66.
- 37 B. L. Funt and P. M. Hoang, J. Electrochem. Soc., 1984, 131, 2295– 2298.
- 38 (a) J. M. Cervantes-Uc, J. V. Cauich-Rodriguez, W. A. Herrera-Kao, H. Vazquez-Torres and A. Marcos-Fernandez, *Polym. Degrad. Stab.*, 2008, **93**, 1891–1899; (b) J. Liu, W. Yang, L. Tao, D. Li, C. Boyer and T. P. Davis, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 425– 433.
- 39 Y. Yao, C. Liu and S. Fan, Nanotechnology, 2006, 17, 4374-4378.
- 40 (a) Q. Zheng, B. J. Jung, J. Sun and H. E. Katz, J. Am. Chem. Soc., 2010, 132, 5394–5404; (b) S. Ahn, Y. Kim, S. Beak, S. Ishimoto, H. Enozawa, E. Isomura, M. Hasegawa, M. Iyoda and Y. Park, J. Mater. Chem., 2010, 20, 10817–10823.