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## COMMUNICATION

#### Role of Synergistic $\pi$ - $\pi$ Stacking and X—H····Cl (X = C, N, O) H-Bonding Interactions in Gelation and Gel Phase Crystallization

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Self-assembly of *p*-pyridyl ended oligo *p*-phenylenevinylenes (OPVs) in ethanol leads to the formation of either hollow or solid microrods. The corresponding protonated OPVs with *n*butyl chains induce transparent gelation and also gel phase <sup>10</sup> crystallization owing to various synergistic noncovalent interactions. Chloride ion-selective gelation, AIEE and stimuli responsiveness of the gel are also observed.

Self-assembly of certain low molecular-mass organic molecules and/or macromolecules yields various functional soft materials <sup>15</sup> like micelles, <sup>1a</sup> vesicles, <sup>1b</sup> lipoplexes, <sup>1c</sup> nanoparticles, <sup>1d,e</sup> gels, <sup>2</sup> liquid-crystals, <sup>3</sup> etc. Towards this end, the design of oligo (*p*phenylenevinylene) (OPV) based assemblies including gels has become a fascinating area of research during the last few years because of their superior optoelctronic properties, liquid-<sup>20</sup> crystallinity, potential candidacy as artificial light harvesting materials and for numerous other applications.<sup>4</sup> Therefore tuning the morphology of  $\pi$ -gels is challenging as well as important in the field of supramolecular electronics and other areas.<sup>5</sup>

- On the other hand, weak X—H···Cl (X = C, N, O) H-bonding <sup>25</sup> interactions have been mostly encountered in the solid state through crystal engineering<sup>6a</sup> and anion-recognition processes<sup>6b</sup> in solution. However, reports comprising their involvement on the construction of supramolecular gel are rather rare.<sup>2q</sup> Only recently, hydrogelation induced by C—H···X (Cl, O) H-bonding <sup>30</sup> among the  $\pi$ - $\pi$  stacked aromatic-units has been reported.<sup>2q</sup> One of the possible ways to probe such interactions inside a gel is to grow single-crystals of the gelator within the gel matrix, which is of course a challenging task.<sup>7</sup> Rare instances include crystallization of a hydrogelator from its gelling solvents,<sup>7c</sup> or fast <sup>35</sup> cooling of a two-component system that triggered gelation by halogen-bonding but slow cooling of the same afforded only co-
- crystals instead of a gel.<sup>7d</sup> NMR studies of the gel phase can also shed light on the existence of such interactions.<sup>2q</sup>
- Herein, we show the important role of the alkyl chain length <sup>40</sup> in the self-organization of non-protonated OPV derivatives in ethanol to fabricate either hollow or solid rods with rectangular cross-sections. Further, we demonstrate that the cooperative  $\pi$ - $\pi$ and multiple X—H···Cl (X = C, N, O) H-bonding interactions are sufficient to trigger supramolecular polymerization leading to the
- <sup>45</sup> formation of a robust gel from the protonated *p*-pyridyl ended OPVs. We also report for the first time that the gel matrix of such protonated OPV-based gelator comprising *n*-butyl chains may also serve as a medium for the crystallization of the gelator itself.

Further the gelation was accompanied with aggregation induced <sup>50</sup> enhancement in emission (AIEE) and the gel also showed multistimuli responsiveness. Moreover, the formation of nano-spheres from the rigid bola-amphiphilic OPV comprising *n*-octyl chains and their transformation into superstructured organogels upon increasing concentration of the gelator was observed. A <sup>55</sup> remarkable selectivity towards the Cl<sup>-</sup> counterion on the gelation of the protonated OPVs is also noteworthy.



**Figure 1.** (a) Chemical structures of the OPV derivatives 1 and 2 and their protonated forms P1 and P2. (b,c) SEM images of the aggregates of 1 (45 mM) and 2 (10 mM) from EtOH respectively. (d) Part of the unit cell of the crystal of 1 showing C—H··· $\pi$  and C—H···N H-bonding interactions (viewed along c-axis). (e) A comparison of the simulated XRD pattern of single crystal with 65 the PXRD pattern of the micro-rods of 1.

A hot solution of **1** (45 mM; Fig. 1a) in EtOH upon spontaneous cooling to ~25 °C results in the formation of multiple single crystals that belong to a centrosymmetric 70 tetragonal space group (I4<sub>1</sub>/a) (Fig. S1e). The C—H··· $\pi$  and C—H···N H-bonding interactions are mainly responsible for the self-assembly of **1** into crystals (Fig. 1d and S1b-d). In contrast, when a hot solution of **1** (45 mM) in EtOH was bath sonicated at 2-5 °C, it afforded a colloidal solution. Investigation of the rolloidal aggregates showed the presence of well-defined 1-D molecular rods with uniform size and shape (Fig. 1b and S2a-e). Moreover, the rods displayed smooth outside surface and sharp edges. The lengths of these rods of high aspect ratio vary in the range of 10-300 µm. Further, scanning electron microscopic (SEM) images reveal the hollow feature of these rods having an open rectangular end. However, sonication of a less concentrated solution of **1** (10 mM) in EtOH under the same condition yielded molecular rods with rugged rectangular ends (Fig. S2f). The etching of the molecules of **1** by EtOH in the central part of the solid rods during sonication was probably responsible for such s hollow structure formation.<sup>8</sup>

The simulated XRD pattern from the single-crystal was then compared with the powder X-ray diffraction (PXRD) pattern obtained from these hollow rods, which showed remarkable similarity between the two (Fig. 1e). Thus the molecular <sup>10</sup> arrangements of **1** in the micro rods may be essentially the same with that of the single-crystal structure.<sup>7</sup>

The compound **2**, on the other hand, induced gel formation albeit at a higher critical gelator concentration (CGC ~46 mM) when a hot solution of the same in EtOH was sonicated briefly at 15 ~5 °C (Fig. S3 and table S1). The gel of **2** revealed the presence of solid rectangular rod-like aggregates under SEM (Fig. 1c and S4a-c). The morphology of **2** was further verified by atomic force microscopy (AFM), polarized optical microscopy (POM) and fluorescence microscopic investigations (Fig. S4d-g).

We have further achieved complete protonation of these pyridyl ended OPVs by either adding HCl (12 M) solution or by passing HCl gas into a solution in EtOH. The protonation was also evident from an obvious yellow-to-red color change of the solution of **1** (Fig. 2a,b) as well as by large downfield shifts of the <sup>25</sup> pyridyl H<sub>a</sub> and H<sub>b</sub> protons, from 8.55 to 8.8 and 7.65 to 8.15 ppm respectively in <sup>1</sup>H NMR spectroscopy (Fig. S5).

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Interestingly, the protonated form of 1, i.e, P1 formed upon addition of HCl (12 M, 30  $\mu$ L) to a 6 mM solution of 1 in EtOH (1 mL), displayed excellent thermoreversible gelation when sonicated for ~25 s at ~5 °C (Fig. 2c). The gel obtained initially was transparent, which on further sonication for ~1 min turned into a translucent gel and finally yielded an opaque gel when sonicated for a longer time (~2 min) (Fig. S6). Moreover, P1 could gelate EtOH at a concentration as low as 2.1 mM and the 35 gel formation even did not require a sonication at a higher concentration (10 mM) of the gelator (Table S1). These gels showed strong luminescence (inset in Fig. 2c).

In order to check the effect of counterions towards the gelation of **P1**, various other concentrated acids such as HBr, HI, 40 HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and CH<sub>3</sub>COOH were used instead of HCl. In contrast, none of these triggered gelation of **1** and instead only a gelatinous precipitate was formed in EtOH. Thus the present system could selectively trap toxic HCl gas via gel formation.<sup>2c</sup>

In addition, the gel of **P1** exhibited multi-stimuli responsive <sup>45</sup> property.<sup>9</sup> For example, addition of only ~5% water abolished the gel of **P1** (Table S1). Further, addition of an equiv. of NaOH as a source of OH<sup>-</sup> neutralized **P1** to **1**, resulting in the formation of a sol instantaneously. The representative SEM and AFM of the gel of **P1** showed presence of well-defined fibers of high aspect <sup>50</sup> ratios (Fig. 2e,f). Moreover, the fibers of **P1** exhibited strong birefringence when viewed under POM, demonstrating an anisotropic packing of **P1** during aggregation (Fig. 2g and S7b).

Interestingly, the gel of **P1** at moderate concentration (~10 mM) on aging for ~2 days at ambient conditions spontaneously 55 furnished few transparent, deep red colored crystals inside the 3-D gel matrix (Fig. 2d). When the gelator concentration was increased to ~65 mM, majority of the gelator molecules slowly

transformed into multiple single-crystals through phase

separation within  $\sim 2$  days (Fig. S8). This suggests that the <sup>60</sup> molecular packing in the crystal is presumably maintained in the gel matrix as well. However, the gel of **P1** remained stable over several months without formation of crystals in the gel phase when the concentration was maintained near the CGC.



Figure 2. Photographs of (a,b) solution of 1 and P1 and (c) gel of <sup>65</sup> P1 in EtOH (6 mM) under normal and UV light (> 365 nm; inset) respectively. (d) Crystal formation inside the gel of P1 within ~48 h. (e-g) SEM, AFM and POM images of P1 (0.5 mM) from EtOH respectively. (h) Unit cell of the crystal of P1 (H-atoms were removed for clarity). (i) Packing arrangement of P1 in the crystal <sup>70</sup> shows how OPV-units are held together by C—H…Cl H-bonding interactions (rest of the H-atoms were removed for clarity). (j) Comparison of a simulated XRD pattern of a single-crystal with the PXRD pattern of the xerogel of P1.

To address the above issue more quantitatively, the crystal 75 structure of P1, which was obtained from its parent gel, was analyzed by single crystal X-ray diffraction. The crystal of P1 is refined in the centrosymmetric triclinic space group (P -1) with an asymmetric unit that contains half of the two molecules of P1 <sup>80</sup> in the protonated form, two Cl<sup>-</sup> ions and one EtOH molecule (Fig. S9a). One of the associated Cl<sup>-</sup> ion showed positional disorder (Fig. S9). The OPV-units are stacked via parallel-displaced  $\pi$ - $\pi$ stacking interactions (Fig. 2h and S10a).<sup>10</sup> This parallel arrangement is supported by few N-H. Cl and multiple 85 C—H···Cl H-bonding interactions (Fig. 2i, S10b and table S2). Multiple C—H··· $\pi$  interactions between the *n*-butyl chain of one molecule and the pyridine ring of the other molecules also helps in inducing further growth of the crystal (Fig. S10c). The EtOH molecule in the unit cell also participates in C-H···Cl, 90 O-H…Cl and C-H…O H-bonding interactions, suggesting the crucial role of the alcoholic solvents in gelation (Fig. S10d). These observations clearly indicate that multiple  $X - H \cdots Cl$  (X = C, N, O) interactions among the slipped  $\pi$ - $\pi$  stacked OPV-units account for the rapid crystallization and also provide the most 95 acceptable reason for HCl-selective gelation phenomenon.

However, a comparison of the simulated XRD pattern from the single-crystal with the PXRD pattern obtained from the xerogel, reveals the presence of identical first order reflection peak (Fig. 2j). However, significant differences exist between the 100 two, indicating the molecular arrangement in the gel is probably Published on 13 March 2015. Downloaded by Mahidol University on 21/03/2015 04:40:33.

not exactly same with that of the crystals.7c,d

Additional experiments were performed to further prove the role of C-H...Cl H-bonding in the gelation process. A precipitate of 1.2HClO<sub>4</sub> obtained upon addition of HClO<sub>4</sub> (11.7 5 M) to a solution of 1 in EtOH, was washed with excess of EtOH to remove the excess acid. Interestingly, the DMSO solution of the dried residue of 1.2HClO<sub>4</sub> (25 mM) transformed into an opaque gel instantaneously when HCl (12 M, 30 µL) was added to it (Fig. S11a). Since ClO<sub>4</sub> anions are generally non-interactive <sup>10</sup> with the C-H protons,<sup>11</sup> the above result further indicates that the C—H···Cl H-bonding plays a crucial role in the gelation process. Addition of tetrabutylammonium chloride (TBACl), a source of Cl<sup>-</sup> ion, to the above DMSO solution also resulted in aggregation. Titration of the solution of 1.2HClO<sub>4</sub> in DMSO-d<sub>6</sub> with 15 increasing proportion of TBACl, resulted in progressive upfield shift of the pyridyl H<sub>a</sub> and H<sub>b</sub> protons of the OPV-backbone (Fig. S11b), indicating the Cl ion induced aggregation of the protonated OPV. However, the evidence of the involvement of C-H···Cl H-bonding in the aggregation process of the former 20 could not be clearly observed from the NMR studies. This is because the upfield shift of the protons might be caused due to the aggregation of the OPV derivatives or due to the combination

of C—H···Cl H-bonding and aggregation in the solution state. In contrast, **P2** formed an opaque gel only at a relatively

<sup>25</sup> higher CGC of 13.5 mM (inset in Fig. 3a,c and Table S1). This is presumably due to the higher solubility of **P2** in EtOH.



<sup>40</sup> Figure 3. (a-c) AFM, SEM and fluorescence microscopic images of P2 at high concentration (15 mM) from EtOH respectively. Insets in (a) and (c) show the photograph of gel of P2 in EtOH (20 mM) under normal light and UV light (> 365 nm) respectively. (d,f) AFM (0.2 mM) and SEM (2 mM) images of P2 <sup>45</sup> from EtOH respectively. (e) height image of a spherical aggregate in fig. (d).

Morphological investigation of the gel of **P2** also showed the presence of fibers at a concentration larger than the CGC (15 mM). The fibers show high aspect ratios with several hundreds of micrometers in length and the diameters in the range of ~0.5 to 3  $\mu$ m (Fig. 3a-c and S12a). Whereas, at a concentration much lower than CGC (< 1 mM), it revealed the formation of well-defined nano-spheres with diameters in the range of 150-300 nm and an <sup>55</sup> average height of ~20 nm (Fig. 3d,e). Similar spherical aggregates were also observed under SEM, POM and fluorescence microscopic studies (Fig. S12c-e). Performing SEM at a moderate concentration reveals that these extended fibers

probably originate from the nano-spheres as a result of their <sup>60</sup> fusion at higher concentrations (Fig. 3f).<sup>2b</sup> Dynamic light scattering studies also confirmed the presence of aggregates with an average hydrodynamic diameter of  $188 \pm 20$  nm in the EtOH solution of **P2** (0.9 mM) (Fig. S13).

Spectroscopic experiments were performed in order to gain further information about the self-assemblies of both the protonated and non-protonated OPVs. The appearance of the N-H stretching peak at ~3378 cm<sup>-1</sup> for **P1** and **P2** confirms the protonation of the pyridyl N-atom (Fig. S14a). The distinct features in the UV-Vis absorption spectra include (i) the 70 protonated OPVs (**P1** and **P2**) showing well-resolved vibronic fine-structures for the electronic transition  $S_0 \rightarrow S_1$  and (ii) the absorption maxima of **1** and **2** showing large bathochromic shifts of ~55 nm on protonation (Fig. 4a). This result suggests that the protonated OPVs remain in the more planarized state in EtOH 75 solution compared to their non-protonated forms. Similar features were also in agreement with the crystal structures of **1** and **P1**.



Figure 4. (a) UV-Vis absorption spectra of 1, 2, P1 and P2 (10  $_{80} \mu$ M) in EtOH at 25 °C. (b) Temperature-dependent fluorescence spectra of P1 at 1.75 mM in EtOH.

Further, protonation of the pyridyl group caused a significant quenching of the fluorescence emission with concomitant redss shift of the emission maximum of ~112 nm (Fig. S14b). This again suggests that protonation promotes the planarization of the OPVs. Temperature-dependent emission spectra of the gelator P1 were also recorded in EtOH ([P1] = 1.75 mM). The emission intensity at 586 nm gradually increases as the hot solution at 45 <sup>90</sup> °C was cooled gradually to 15 °C, suggesting an AIEE phenomenon (Fig. 4b). Decreasing temperature causes an increase in viscosity of the solution through strong  $\pi$ - $\pi$ interactions among the OPV-backbone of P1 as observed in the crystal structure of P1. This, in turn, restricts the intermolecular <sup>95</sup> rotation (RIR) and accounts for the AIEE.<sup>12</sup> Similar observations were also recorded for the gel of P2 (Fig. S14c).

In conclusion, we have demonstrated the fabrication of microscopic hollow-rods with rectangular cross-section from the self-assembly of **1** in EtOH. Interestingly, the molecular <sup>100</sup> arrangements in the micro-rods were found to be same with that in the single-crystals of **1**. In contrast, the gels of **2** induced formation of solid molecular rods. However, protonation of **1**, i.e, **P1** resulted in the formation of a transparent gel in EtOH comprising fibrous networks. Interestingly, the crystallization of <sup>105</sup> the gelator in the 3-D gel of **P1** occurred within ~2 days of aging. HCl was the only acid that could induce the gel formation of **1**. The single-crystal structure of the crystals obtained in the gel showed the critical role of the Cl<sup>-</sup> ion in the formation of the gel and also the single-crystal via multiple, unconventional

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X—H···Cl (X = C, N, O) H-bonding interactions in the slipped  $\pi$ - $\pi$  stacked units of **P1**. Quantitative evidence of trapping of HCl by **1** was also reflected in the crystal structure of **P1**. On the other hand, the protonated form of **2**, i.e, **P2** formed only an opaque s organogel. Morphological studies of **P2** revealed the presence of

- s organogel. Morphological studies of P2 revealed the presence of spherical aggregates at a relatively low concentration which fused to form fibrous aggregates with increasing concentration of the gelator. Finally, AIEE exhibited by the gels of P1 and P2 holds promise in possible optoelectronic and imaging applications. To
- <sup>10</sup> the best of our knowledge, this is the first report of an OPV-based gel where crystallization of the gelator could be achieved from the gel itself along with various other noteworthy features.

#### Notes and references

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† Electronic supplementary information (ESI) available: Complete 20 experimental procedures, compound characterization, crystallographic

details and fig. S1-S14. See DOI: 10.1039/b000000x/

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Gel phase crystallization in a transparent gel via synergistic non-covalent interactions has been reported along with various remarkable features (see figure).

