Supporting Information

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

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Physical Measurements and Instrumentation.

Materials and Methods. All chemicals including solvents and silica gel for TLC and column chromatography were obtained from well-known commercial sources and were used without further purification, as appropriate. Solvents were distilled and dried by standard procedure before use. Melting points was measured in open capillaries and were uncorrected. ¹H-NMR (400 MHz) and ¹³C-NMR (400 MHz) spectra were recorded in Bruker-400 Avance NMR spectrometer. Chemical shifts were reported in ppm downfield from the internal standard tetramethylsilane (TMS). Elemental analysis was recorded in Thermo Finnigan EA FLASH 1112 SERIES.

Gelation Studies. A weighed amount of a particular OPV was added into a sealed glass vial containing absolute EtOH and gently heated and sonicated to afford a clear solution. The solution was then cooled spontaneously to room temperature and left for ~0.5 h to check the stability of the gel using inverse flow method and each experiment was performed in duplicate. If a gel was formed, it was evaluated quantitatively by determining the critical gelator concentration (CGC) which is the minimum amount of gelator required to immobilize 1 mL of a particular solvent. In order to protonate 1 and 2, 30 µL concentrated HCl (12 N) was used in 1 mL of EtOH. Accordingly, [HCl] = 0.36 M, and [HCl] >> [1-2]. Under such conditions, complete protonation of 1-2 were achieved.

FT-IR Spectroscopy. As prepared EtOH solutions were drop-coated on the CaF_2 cell and the spectra were recorded in a Perkin Elmer BX FT-IR Spectrometer.

UV-Vis and Fluorescence Spectroscopy. The UV-Vis and fluorescence spectra of solutions and gels of various gelators were recorded on a Shimadzu model 2100 spectrophotometer and a Hitachi F-4500 spectrofluorimeter respectively, both equipped with a temperature-controller bath. Excitation wavelength of 450 nm has been used for the variable temperature fluorescence spectra of **P1** and **P2** in EtOH.

Scanning Electron Microscopy (SEM). The gels were carefully drop-coated onto the brass stubs and were allowed to freeze-dry. The samples were then coated with gold sputter and analyzed on a Quanta 200 SEM operated at 10-15 kV.

Dynamic Light Scattering (DLS). DLS measurements were performed at room temperature using a Malvern Zetasizer NanoZS particle sizer (Malvern Instruments Inc., MA) instrument. Diluted solutions of the gel of **P2** in EtOH were examined under dust-free conditions. Average hydrodynamic diameters (D_h) reported were obtained from Gaussian analysis of the intensity-weighted particle size distributions.

Atomic Force Microscopy (AFM). Solutions of each of these gelators were drop-coated on mica and then carefully air-dried. Each sample was analyzed using a Bruker diInnova SPM instrument: Tapping mode, 10 nm tip radius, silicon tip, 292 KHz resonant frequency, 0.7-1 Hz scan speed, 256x256 and 512x512 – pixels.

Polarized Optical Microscopy (POM). A diluted solution of the OPV derivatives in EtOH was drop-coated on a pre-cleaned glass slide and it was left overnight for drying in a dust free environment and finally evacuated. Optical birefringence was followed under a polarized optical microscope (Olympus BX51) equipped with a heating stage (Mettler FP82HT) and a central processor (Mettler FP90).

Fluorescence Microscopy. A diluted solution of the OPV derivatives in EtOH was drop-coated on a precleaned glass slide and it was left overnight for drying in a dust free environment and finally evacuated. The fluorescence microscopic image was taken on an Olympus IX-71 microscope with the excitation of 340-400 nm UV-light.

Powder X-ray Diffraction (PXRD). Gels were scooped onto a glass slide and dried under vacuum for the corresponding PXRD measurement. These samples were analyzed using a Bruker D8 Advance instrument (θ , 2 θ geometry with Scintillation Detectors). The X-ray beam generated with rotating Cu anode at the wavelength of KR beam at 1.5418 Å was directed toward the film edge and scanning was recorded up to a 2 θ value of 30°. Finally the data were analyzed and interpreted using the Bragg's equation.

Single-crystal X-ray Diffraction. Single crystal X-ray data for **1** and **P1** were collected on a Bruker SMART APEX CCD diffractometer using the SMART/SAINT software^{S1} at 293 K and on an Oxford Diffractometer^{S2} (CrysAlis CCD Xcalibur, Eos (Nova)) at 110 K respectively. Intensity data were collected using graphite-monochromatized Mo-Kradiation (0.71073 Å).

The structures were solved by direct methods using the SHELX-97^{S3} program incorporated into WinGX.^{S4} Empirical absorption corrections were applied with SADABS.^{S5} Refinement of coordinates and anisotropic thermal parameters of non-hydrogen atoms were performed with the full-matrix least-squares method.

(S1) SMART/SAINT; Bruker AXS, Inc.: Madison, WI, 2004.

(S2) CrystAlis CCD and CrystAlis RED, Version 1.171.33.31; Oxford Difraction Ltd: Abingdon, Oxfordshire,

England, 2009.

(S3) Sheldrick, G. M. Acta Crystallogr. 2008, A64, 112.

(S4) Farrugia, L. J. J. Appl. Crystallogr. 1999, 32, 837.

(S5) Sheldrick, G. M. SADABS; University of Göttingen, Göttingen, Germany, 1999.

1. Synthesis: Synthesis of the compound 1 and 2 has been achieved as given below.^{S6}

1a. General Synthetic Scheme:

(iii) ÓR 4a: $\mathbf{R} = n \cdot \mathbf{C}_4 \mathbf{H}_9$ 3a: $R = n - C_4 H_9$ 3b: $R = n - C_8 H_{17}$ 4b: $R = n - C_8 H_{17}$ OR OR PO(OEt)₂ (iv) (EtO)₂OI II N. ÓR ÓR 1: $R = n - C_4 H_9$, 5a: $\mathbf{R} = n \cdot \mathbf{C}_4 \mathbf{H}_9$ 2: $R = n - C_8 H_{17}$ 5b: $R = n - C_8 H_{17}$

Reagents, conditions and yields: (i) *n*-alkyl bromide, K_2CO_3 , CH_3CN , reflux, 48 h, yield = 85% (R = *n*-C₄H₉) and 80% (R = *n*-C₈H₁₇); (ii) Paraformaldehyde, HBr, HOAc, 80 °C, 2 h, yield = 60% (R = *n*-C₄H₉) and 55% (R = *n*-C₈H₁₇); (iii) P(OEt)₃, 140-150 °C, 4 h, yield = 99% (R = *n*-C₄H₉) and 98% (R = *n*-C₈H₁₇); (iv) K^tBuO, pyridine carboxaldehyde, dry THF, 5-6 min, yield= 75% (R = *n*-C₄H₉) and 77% (R = *n*-C₈H₁₇).

1b. Synthesis and Characterization: 1,4-di-*n*-alkoxy-2,5-biphosphonates (**5a** and **5b**) were synthesized according to a reported procedure.^{S7} To a mixture of biphosphonate (1 mmol) and different isomeric pyridine carboxaldehyde (2 mmol) in dry THF, K^tBuO (4 mmol) was added under Ar atmosphere and the mixture has been stirred at room temperature for 5-6 min. The completion of the reaction was confirmed by monitoring TLC. Excess ^tBuOK was quenched by adding a few drops of water and the solvent was removed under high vacuum pump. The mixture was partitioned between CHCl₃ and water. Rotary evaporation of the organic part gave a crude product which was purified by repetitive precipitation of the solid residue in *n*-hexane.

4-(2,5-Bis(butoxy)-4-((E)-2-(pyridin-4-yl)vinyl)styryl)pyridine (1): yield = 75%; Yellow-orange crystal; m.p. 202-203 °C; IR (Neat, cm⁻¹): 3368, 3053, 2953, 2933, 2872, 1630, 1593, 1492, 1422, 1265, 1207, 1066, 975, 860, 808, 740; ¹H-NMR (400 MHz, CDCl₃): δ 1.04 (t, *J* = 7.6 Hz, 6H), 1.541 (m, 4H), 1.85 (m, 4H), 4.09 (t, *J* = 6.4 Hz, 4H), 7.06 (d, *J* = 16.8 Hz, 2H), 7.13 (s, 2H), 7.37 (d, *J* = 6 Hz, 4H), 7.64 (d, *J* = 16.4 Hz, 2H), 8.58 (d, *J* = 5.6 Hz, 4H); ¹³C-NMR (100 MHz, CDCl₃) δ 13.85, 19.36, 31.38, 68.99, 110.77, 120.80, 126.53, 127.72, 144.97, 150.06, 151.29; HRMS: *m*/*z* calcd. for C₂₈H₃₂N₂O₂ (M+H)⁺: 429.25, found: 429.2544; Elemental analysis: calcd. for C₂₈H₃₂N₂O₂ : C, 78.47; H, 7.53; N, 6.54; found: C, 78.72; H, 7.77; N, 6.92.

4-(2,5-Bis(octyloxy)-4-((E)-2-(pyridin-4-yl)vinyl)styryl)pyridine (2): yield = 77%; Yellow orange solid; m.p. 138-139 °C; IR (Neat, cm⁻¹): 3356, 2956, 2918, 2855, 1627, 1594, 1324, 1211, 1038, 965, 844, 800; ¹H-NMR (400 MHz, CDCl₃): δ 0.88 (t, *J* = 6.4 Hz, 6H), 1.30-1.65 (m, 20H), 1.86-1.92 (m, 4H), 4.07 (t, *J* = 6.4 Hz, 4H), 7.06 (d, *J* = 16.4 Hz, 2H), 7.13 (s, 2H), 7.37 (d, *J* = 6 Hz, 4H), 7.65 (d, *J* = 16.4 Hz, 2H), 8.57 (d, *J* = 6 Hz, 4H); ¹³C-NMR (100 MHz, CDCl₃): δ 14.02, 22.59, 26.21, 29.23, 29.31, 29.33, 31.73, 69.39, 110.84, 120.78, 126.49,

126.58, 127.85, 145.11, 149.96, 151.34; HRMS: m/z calcd. for C₃₆H₄₈N₂O₂ (M+H)⁺: 541.37, found: 541.3794; Elemental analysis: calcd. for C₃₆H₄₈N₂O₂ : C, 79.96; H, 8.95; N, 5.18; found: C, 78.78; H, 8.84; N, 5.29.

References.

(S6) Bhattacharjee, S.; Datta, S.; Bhattacharya, S. Chem. Eur. J. 2013, 19, 16672.

(S7) (a) Shao, H.; Chen, X.; Wang, Z.; Lu, P. J. Phys. Chem. B 2007, 111, 10386. (b) Jin, J. -Y.; Zin, Z. -Z.;

Xia, Y.; Zhou, Z. -Y.; Wu, X.; Zhu, D. -X.; Su, Z. -M. Polymer 2007, 48, 4028.

2. Characterization of 1 and 2:









3. Supporting Tables and Figures:

Table S1. Summary of gelation of **2**, **P1** and **P2** in different solvents and/or solvent mixtures. The value given in the parentheses is the CGC value expressed in mM. G = Gel, T.G = Transparent gel, S = Soluble, O.G = Opaque gel, P.G = Partial gel, I = Insoluble.

Medium	2	P1	P2	
Methanol	O.G (37)	S	Ι	
Ethanol	O.G (46.2)	T.G (2.1)	O.G (13.5)	
Propan-1-ol	O.G (55.5)	T.G (3.7)	O.G (10.2)	
Butan-1-ol	S	O.G (5.8)	S	
Pentan-1-ol	S	S	S	
Ethanol/5% H ₂ O (v/v)	P.G	S	S	
Tetrahydrofuran	S	S	O.G (13.1)	
Dimethyl sufoxide	S	O.G (23.3)	S	

Table S2. Intramolecular and intermolecular interactions in the single-crystal of P1.

$\mathbf{D}-\mathbf{H}\odot\odot\mathbf{A}^{\#}$	r(D–H)/Å	r(D–A)/Å	r(H···A)/Å	∠ D–H⊙⊙⊙A/º	Symmetry
N2-H2N····Cl1	0.86	3.016(4)	2.195(1)	159.4(2)	x,y,z
N1–H1N····Cl2A	0.86	3.075(4)	2.295(1)	150.9(2)	-x+2,-y,-z+2
N1–H1N····Cl2B	0.86	2.676(7)	1.856(6)	158.8(3)	-x+2,-y,-z+2
O1E-H1E····Cl1	0.82	3.107(5)	2.314(1)	163.0(3)	x,+y+1,+z
C14–H14C…O2	0.96	3.638(6)	2.987(3)	126.2(3)	-x+2,-y+1,-z+1
С9–Н9…О1Е	0.93	3.410(6)	2.871(4)	118.2(3)	x,+y-1,+z
C28–H28A…O1E	0.96	3.655(8)	2.720(6)	164.9(3)	x,+y,+z-1
C10–H10…O1E	0.93	3.265(6)	2.571(5)	131.7(3)	x,+y-1,+z
C7–H7····Cl1	0.93	3.502(5)	2.874(1)	125.9(2)	x+1,+y,+z
C8–H8…Cl1	0.93	3.501(5)	2.866(1)	126.5(3)	x+1,+y,+z
C22–H22····Cl1	0.93	3.583(4)	2.706(1)	157.5(2)	-x+1,-y,-z+2
C23–H23…Cl2A	0.93	3.483(5)	2.804(1)	130.7(3)	x-1,+y,+z
C19–H19····Cl2A	0.93	3.670(5)	2.887(1)	142.7(2)	x,y,z
C2E–H2C···Cl2B	0.96	2.986(9)	2.293(6)	128.4(8)	x-1,+y,+z
C25–H25B····Cl2B	0.97	3.362(7)	2.698(6)	126.0(3)	-x+2,-y+1,-z+1
C19–H19…Cl2B	0.93	3.504(8)	2.599(6)	164.4(3)	x,y,z
C15–H15…Cl2B	0.93	3.673(7)	2.751(6)	170.9(2)	x,y,z
C12–H12B····Cl2C	0.97	3.112(7)	2.463(9)	124.0(4)	-x+2,-y,-z+1
C23–H23…Cl2C	0.93	3.186(9)	2.404(9)	141.6(5)	x-1,+y,+z
C5–H5…Cl2C	0.93	3.298(5)	2.426(9)	156.1(5)	x,y,z
C13–H13B····Cl2C	0.97	3.342(7)	2.770(6)	118.4(4)	-x+2,-y,-z+1
С7–Н7…С12С	0.93	3.395(5)	2.559(9)	149.7(4)	x,y,z
C11–H11A····Cl2C	0.97	3.443(8)	2.931(9)	114.1(4)	-x+2,-y,-z+1
C1–H1···Cl2C	0.93	3.895(5)	2.978(5)	168.9(4)	x,y,z
С12–H12A…π [Cg(4)]	0.97	3.593(5)	2.74	147	x,y,z
С28–H28С…π [Cg(1)]	0.96	3.790(6)	2.91	153	x,y,z
$\pi[\mathrm{Cg}(2)]\cdots\pi[\mathrm{Cg}(3)]$		3.892(2)			x,y,z



(e) Crystal data of 1: CCDC No. 1021892; Molecular formula: $C_{28}H_{32}N_2O_2$; Tetragonal; a = 27.745(9) Å; b = 27.745(9) Å; c = 6.4943(14) Å; $\alpha = \beta = \gamma = 90^{\circ}$; V = 4999.21(3) Å³; T = 293 K; space group: I 4₁/a, Z = 8; $\rho_{calcd} = 1.139 \text{ g/cm}^{-3}$; $\mu(MoK\alpha) = 0.071 \text{ mm}^{-1}$; reflns measured, 37796; unique reflns, 2201; no. of parameters = 153; $R_{obs} = 0.067$; w $R_{2obs} = 0.199$; $\Delta \rho_{min,max} = -0.248$, 0.211 eÅ⁻³; gof = 0.95.

Figure S1. (a) Unit cell of the crystal of **1** along the c-axis (30% probability ellipsoids). (b) Unit cell of the crystal of **1** along the c-axis showing the pyridine ring C—H protons of **1** interacts with the aromatic core of the pyridine ring that belongs to a different unit of **1** through C—H… π interactions. (c) Unit cell of the crystal of **1** along the c-axis showing the —OCH₂ protons of the *n*-butyl chain of **1** interacts with the aromatic core of the pyridine ring that belongs to a different unit of **1** through C—H… π interactions. (d) Unit cell of the crystal of **1** along the c-axis showing the C—H protons of the central benzene ring as well as that of the vinylic bond of **1** interacts with the pyridyl N-atom that belongs to a different unit of **1** through C—H…N interactions. (e) Crystal data of **1**.



Figure S2. (a-e) SEM images of the aggregates of **1** (45 mM) at different magnifications from EtOH. (f) SEM image of **1** from EtOH at a concentration of 10 mM.



Figure S3. Photograph of a gel of 2 in EtOH (50 mM) under normal light.



Figure S4. (a-c) SEM images of **2** (45 mM) at different magnifications from EtOH. (d) AFM, (e) fluorescence microscopic and (f) POM images of **2** (20 mM) from EtOH respectively. (g) AFM height image of (d).



Figure S5. ¹H-NMR spectra of **1** and **P1** in DMSO-d₆ showing the chemical shifts (downfield) of different protons of **P1** compared to **1**; inset shows the partial ¹H-NMR spectra of **1** and **P1** (only aromatic region).



Figure S6. Photograph of gel of P1 (6 mM) after (a) ~25, (b) ~1 min and (c) ~2 min sonication in EtOH.



Figure S7. (a) Fluorescence microscopic and (b) POM images of P1 (0.5 mM) from EtOH respectively.



Figure S8. Photographs of the glass vials displaying crystallization of most of the gelator **P1** molecules into multiple single crystals through phase separation within two days when the gelator concentration has been kept at \sim 2.8 wt% (65 mM).



Figure S9. (a,b) Asymmetric unit and the unit cell of the crystal of P1 respectively (30% probability ellipsoids).



(e) Crystal data of P1: CCDC No. 1021893; Molecular formula: $C_{28}H_{32}O_2N_2$. 2HCl. C_2H_5OH ; triclinic; a = 9.7572(5) Å; b = 11.9316(6) Å; c = 13.8051(7) Å; α = 89.961(4)°; β = 102.504(4)°; γ = 110.060(5)°; V = 1469.12(14) Å³; T = 110 K; space group, *P*-1, Z = 2; ρ_{calcd} = 1.24 g/cm⁻³; μ (MoK α) = 0.260 mm⁻¹; reflns measured, 10862; unique reflns, 5731; no. of parameters = 359; R_{obs} = 0.086; w R_{2obs} = 0.226; $\Delta \rho_{min,max}$ = -0.762, 0.748 eÅ⁻³; gof = 1.03.

Figure S10. (a) Unit cell of the crystal of **P1** showing parallel-displaced π - π stacking among the OPV-units (Hatoms were not shown for clarity). (b) Unit cell of the crystal of **P1** showing C—H···Cl and N—H···Cl Hbonding interactions (rest of the H-atoms were not shown for clarity). (c) Unit cell of the crystal of **P1** showing C—H··· π H-bonding interactions (rest of the H-atoms were not shown for clarity). (d) Unit cell of the crystal of **P1** showing the involvement of the EtOH molecules in C—H···Cl, O—H···Cl and C—H···O H-bonding interactions (rest of the H-atoms were not shown for clarity). (e) Crystal data of **P1**.



Figure S11. (a) Sol to gel transition of the solution of 1.2HClO₄ in DMSO after addition of HCl (12M, 30 μ L). (b) Upfield shift of the various protons during the NMR titration of the solution of 1.2HClO₄ (7 mM) in DMSO-d₆ with increasing proportion of TBACl.



Figure S12. (a) POM image of **P2** (15 mM) from EtOH. (b-e) AFM (0.2 mM), SEM (0.5 mM), POM (0.2 mM) and fluorescence microscopic (0.2 mM) images of **P2** from EtOH respectively.



Figure S13. DLS studies of a solution of P2 (0.9 mM) in EtOH.



Figure S14. (a) FT-IR spectra of 1, 2, P1 and P2 drop-coated on the CaF_2 cell. (b) Fluorescence spectra of 1, 2, P1 and P2 at 1 μ M concentration in EtOH at 25 °C. (c) Temperature-dependent fluorescence spectra of P2 at 1.75 mM in EtOH.