Supporting Information for:

Self-Assembly of Pyrazine Containing Tetrachloroacenes

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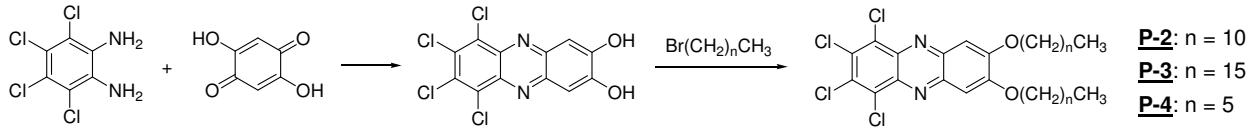
General Instrumentation: All ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were obtained with a Varian Gemini 400 MHz spectrometer at room temperature. Deuterated chloroform ($CDCl_3$) containing tetramethylsilane (TMS) as internal standard was used as the solvent for both ^{1}H NMR and ^{13}C NMR. The low resolution (LR)–ESI and LR-APCI mass spectra were recorded at the University of Illinois at Chicago. Optical properties of the molecules were obtained with Shimadzu UV-2450 UV-visible spectrophotometer. Fluorescence emission spectra were obtained on a Horiba fluorometer using a xenon lamp for excitation. Fluorescence quantum efficiency of **P-3** and **BP-3** was measured in $CHCl_3$ using a 10 × 10 mm cell with 9,10-diphenylanthracene as a standard.[1] For the fluorescence studies of the **P-3** and **BP-3** gels, a 1 × 10 mm cell under right angle and front face geometries were used. For the front face geometry, the cell was placed at a 45^{o} angle to the incident beam so that the incident beam does not pass through the cell. In the case of right angle geometry, the cell was placed at a 45^{o} angle opposite to the incident beam which is 90^{o} relative to the front face geometry. The fluorescence of diluted solutions of **P-3** and **BP-3** (10^{-5} M) in DCE and TCE (for Figures 5 and 7) were measured under right angle geometry, the same way as the gels.

Scanning electron microscopy images of each gel were obtained on JEOL JSM-5600 scanning electron microscope. Before imaging, all samples were sputter-coated (50 mA, 60 sec) with a thin layer of gold to prevent charging. Accelerating voltages and working distances are specified with each image. X-ray diffraction analyses were carried out on X'Pert PRO PANalytical diffractometer at 25 ^{o}C using Cu-Kα radiation (λ = 1.54 Å, 40 KV, 40 mA).

Synthesis and characterization of compounds: All chemicals and solvents were purchased from commercial sources and used as received without further purification. 2,7-Di-tert-butylpyrene-4,5,9,10-tetraone,[2] 1,2-bisalkoxy-4,5-diaminobenzene,[3,4] intermediate **A**,[5] 1,2-diamino-3,4,5,6-tetrachlorobenzene, and compounds **P-1** and **BP-3** were synthesized according to the previously reported procedures.[6]

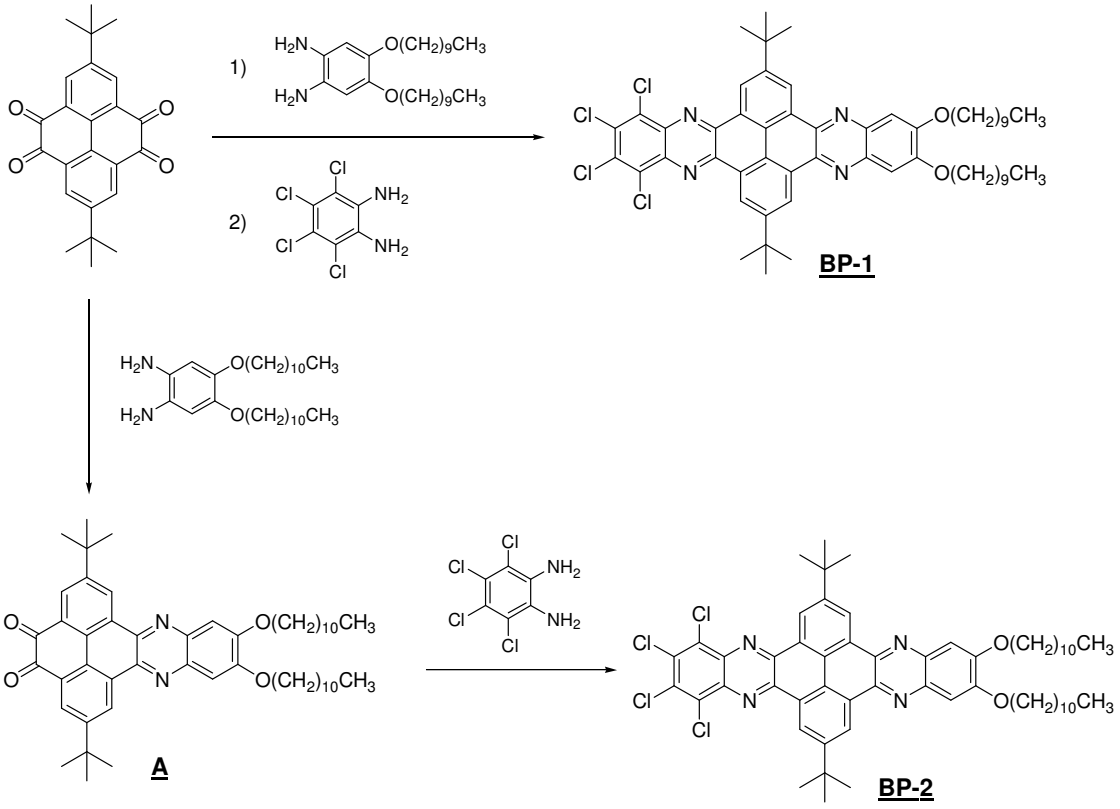


Compound P-2. 1,2-Diamino-3,4,5,6-tetrachlorobenzene (360 mg, 1.46 mmol) was dissolved in 30 mL of absolute ethanol. 2,5-Dihydroxy-1,4-benzoquinone (185 mg, 1.32 mmol) was added at once and the mixture was refluxed for 24 hours under a positive N_2 flow. After evaporating the solvent, without purification of the intermediate, the crude solid was dissolved in 10 mL *N*,*N*-dimethylformamide (DMF), followed by addition of potassium carbonate (K_2CO_3) (638 mg, 4.61 mmol). Then 1-bromoundecane (0.89 mL, 3.95 mmol) was added and the mixture was maintained at 60 ˚C for 36 hours. The mixture was cooled down to room temperature and poured into H_2O, filtered and washed thoroughly with H_2O. It was then dried over anhydrous sodium sulfate (Na_2SO_4). The product was purified by silica gel column chromatography (CH_2Cl_2/Hexane 1/4 v/v). The pure product was obtained as a yellow solid. (Two-step yield: 32%). ^{1}H NMR ($CDCl_3$) δ 7.45 (s, 2H), 4.25 (t, 4H, J = 6.6 Hz), 1.96 (m, 4H), 1.54 (m, 4H), 1.48-1.2 (m, 28H), 0.88 (t, 6H, J = 6.6 Hz). ^{13}C NMR ($CDCl_3$) δ 156.18, 142.61, 137.24, 132.07, 130.83, 105.50, 69.77, 31.94, 29.66, 29.62, 29.61, 29.38, 29.33, 28.71, 26.00, 22.70, 14.12. $[M+H]^+$: Calcd 657.25; Found 657.1.

Compound P-3. 1,2-Diamino-3,4,5,6-tetrachlorobenzene (385 mg, 1.57 mmol) was dissolved in 20 mL of absolute ethanol. 2,5-Dihydroxy-1,4-benzoquinone (220 mg, 1.57 mmol) was added at once and

the mixture was refluxed for 24 hours under a positive N_2 flow. After evaporating the solvent, without purification of the intermediate, the crude solid was dissolved in 10 mL DMF, followed by addition of K_2CO_3 (760 mg, 5.50 mmol). Then bromohexadecane (1.44 mL, 4.71 mmol) was added and the mixture was maintained at 60 ˚C for 2 days. The mixture was cooled down to room temperature and poured into H_2O, filtered and washed thoroughly with H_2O. It was then dried over anhydrous Na_2SO_4. The product was purified by silica gel column chromatography (CH_2Cl_2/Hexane 1/4 v/v). The pure product was obtained as a yellow solid. (Two-step yield: 15%). ^{1}H NMR ($CDCl_3$) δ 7.45 (s, 2H), 4.25 (t, 4H, J = 6.6 Hz), 1.96 (m, 4H), 1.54 (m, 4H), 1.48-1.2 (m, 48H), 0.88 (t, 6H, J = 6.6 Hz). ^{13}C NMR ($CDCl_3$) δ 156.19, 142.62, 137.25, 132.07, 130.84, 105.50, 69.77, 31.94, 29.73, 29.71, 29.68, 29.62, 29.61, 29.38, 29.32, 28.71, 26.00, 22.70, 14.12 (3 aliphatic peaks not seen due to overlapping signals). $[M+H]^+$: Calcd 797.40; Found 797.3.

Compound P-4. 1,2-Diamino-3,4,5,6-tetrachlorobenzene (678 mg, 2.76 mmol) was dissolved in 20 mL of absolute ethanol. 2,5-Dihydroxy-1,4-benzoquinone (386 mg, 2.76 mmol) was added at once and the mixture was refluxed for 24 hours under a positive N_2 flow. After evaporating the solvent, without purification of the intermediate, the crude solid was dissolved in 20 mL DMF, followed by addition of K_2CO_3 (1.33 g, 9.65 mmol). Then 1-bromohexane (1.17 mL, 8.27 mmol) was added and the mixture was maintained at 60 ˚C for 24 hours. The mixture was cooled down to room temperature and poured into H_2O, filtered and washed thoroughly with H_2O. It was then dried over anhydrous Na_2SO_4. The product was purified by silica gel column chromatography (CH_2Cl_2/Hexane 1/3 v/v). The pure product was obtained as a yellow solid. (Two-step yield: 28%). ^{1}H NMR ($CDCl_3$) δ 7.45 (s, 2H), 4.25 (t, 4H, J = 6.6 Hz), 1.97 (m, 4H), 1.55 (m, 4H), 1.46-1.3 (m, 8H), 0.93 (t, 6H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$) δ 156.18, 142.60, 137.23, 132.06, 130.83, 105.49, 69.77, 31.48, 28.67, 25.66, 22.58, 14.00. $[M+H]^+$: Calcd 517.09; Found 517.1.



Compound BP-1. 2,7-Di-*tert*-butylpyrene-4,5,9,10-tetraone (200 mg, 0.53 mmol) was suspended in 40 mL chloroform ($CHCl_3$) and 10 mL acetic acid (AcOH). To that mixture 1,2-bisdecyloxy-4,5-diaminobenzene (202 mg, 0.48 mmol) was added at once. The reaction mixture was refluxed under a positive N_2 flow. After 3 hours, without any purification, 1,2-diamino-3,4,5,6-tetrachlorobenzene (156 mg, 0.59 mmol) was added to the intermediate **A** solution in $CHCl_3$/AcOH. The mixture was refluxed for additional 12 hours under a positive N_2 flow. After cooling it to room temperature, the reaction mixture was extracted with H_2O and 10% aqueous sodium hydroxide (NaOH) solution. The organic layer was dried over anhydrous Na_2SO_4, and filtered with hot $CHCl_3$. The remaining solvent was removed under vacuum. The crude product was purified by silica gel column chromatography (CH_2Cl_2/Hexane 1/2 v/v) to give the pure product as a yellow solid (Two-step yield: 40%). ^{1}H NMR ($CDCl_3$) δ 9.76 (d, 2H, *J* = 2.0 Hz), 9.72 (d, 2H, *J* = 2.0 Hz), 7.56 (s, 2H), 4.31 (t, 4H, *J* = 6.8 Hz), 2.02 (m, 4H), 1.76 (s, 18H), 1.61 (m, 4H), 1.52-1.2 (m, 24H), 0.90 (t, 6H, *J* = 6.8 Hz). ^{13}C NMR ($CDCl_3$) δ 153.47, 150.87, 144.08, 140.04, 139.94, 137.60, 133.20, 131.65, 129.84, 127.92, 125.41, 125.07,

124.42, 106.84, 69.26, 35.84, 31.97, 31.82, 29.69, 29.64, 29.48, 29.41, 28.98, 26.13, 22.72, 14.15. $[M+H]^+$: Calcd 995.43; Found 995.3.

Compound BP-2. The intermediate **A** (340 mg, 0.432 mmol) was dissolved in 16 mL $CHCl_3$ and 4 mL AcOH. To that solution, 1,2-diamino-3,4,5,6-tetrachlorobenzene (128 mg, 0.52 mmol) was added at once. The reaction mixture was refluxed for 12 hours under a positive N_2 flow. After cooling it to room temperature, the reaction mixture was extracted with H_2O and 10% aqueous NaOH solution. The organic layer was dried over anhydrous Na_2SO_4, and filtered with hot $CHCl_3$. The remaining solvent was removed under vacuum. The crude product was purified by silica gel column chromatography (CH_2Cl_2/Hexane 1/2 v/v) to give the pure product as a yellow solid (yield: 87%). ^{1}H NMR ($CDCl_3$) δ 9.77 (d, 2H, *J* = 2.4 Hz), 9.74 (d, 2H, *J* = 2.0 Hz), 7.58 (s, 2H), 4.32 (t, 4H, *J* = 6.8 Hz), 2.02 (m, 4H), 1.76 (s, 18H), 1.61 (m, 4H), 1.52-1.2 (m, 28H), 0.90 (t, 6H, *J* = 7.0 Hz). ^{13}C NMR ($CDCl_3$) δ 153.39, 150.79, 143.99, 139.97, 139.85, 137.53, 133.12, 131.60, 129.78, 127.86, 125.32, 125.05, 124.36, 106.78, 69.23, 35.84, 31.97, 31.83, 29.72, 29.70, 29.50, 29.42, 28.98, 26.14, 22.73, 14.15 (1 aliphatic peak not seen due to overlapping signals). $[M+H]^+$: Calcd 995.43; Found 995.3.

Organogelation: The suspension of a weighed amount of each compound in an organic solvent was heated in a screw-cap vial until the solid dissolved. The vial was then left undisturbed to cool it down. After cooling to room temperature, gelation was considered successful if no flow was observed upon inverting the vial.

Drop-Casting Film Preparation: Each compound was dissolved in CH_2Cl_2, and the solution was drop-cast onto a clean cover glass surface. Then, it was left undisturbed for several minutes, until the solvents evaporated.

Single Crystal Growth: The suspension of compound **P-4** in hexane was heated in a screw-cap vial until the solid dissolved. After cooling, it formed aggregates. Then, CH_2Cl_2 was added into the vial until the aggregates redissolved. The vial was left undisturbed with a vent for slow solvent evaporation. After a few days, straight needles were observed at the bottom.

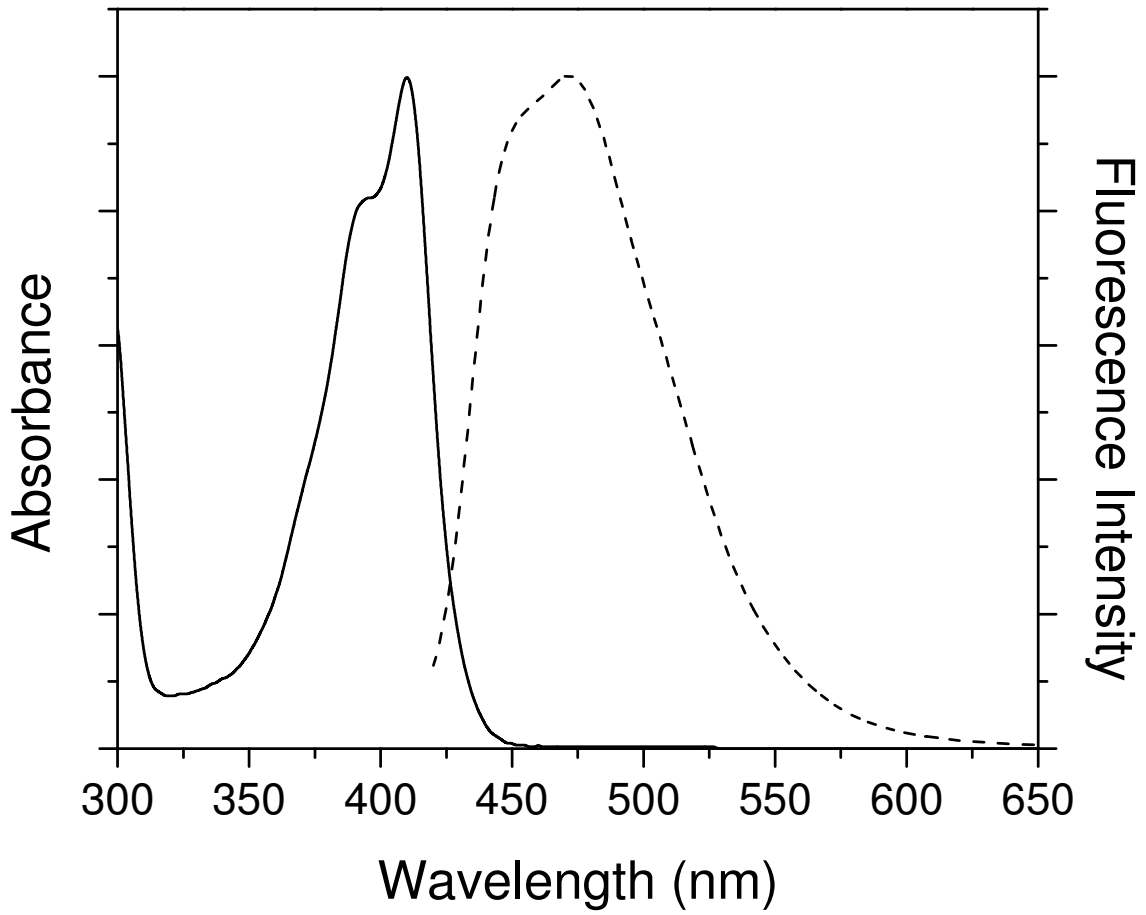


Figure S1. UV-vis absorption (solid line) and fluorescence (dashed line, excited at 410 nm) spectra of **P-1** in $CHCl_3$.

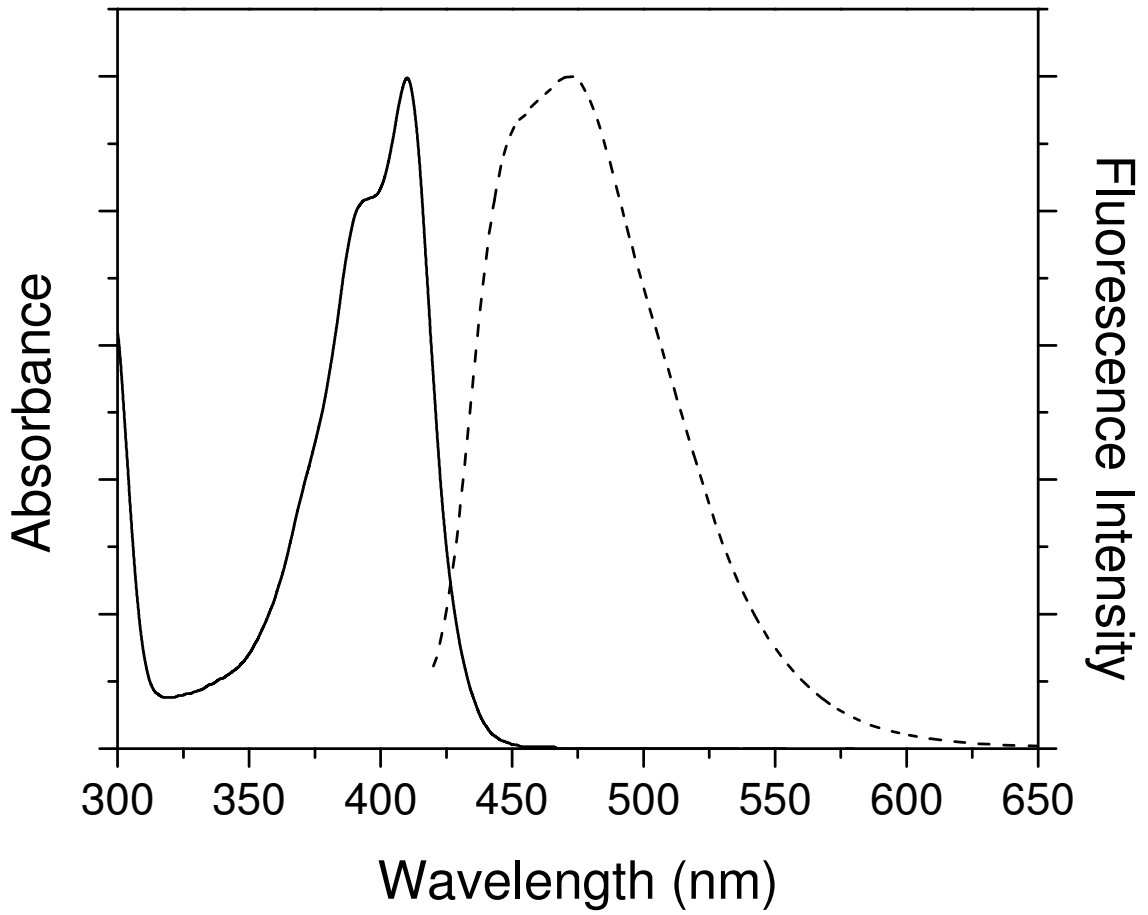


Figure S2. UV-vis absorption (solid line) and fluorescence (dashed line, excited at 410 nm) spectra of **P-2** in $CHCl_3$.

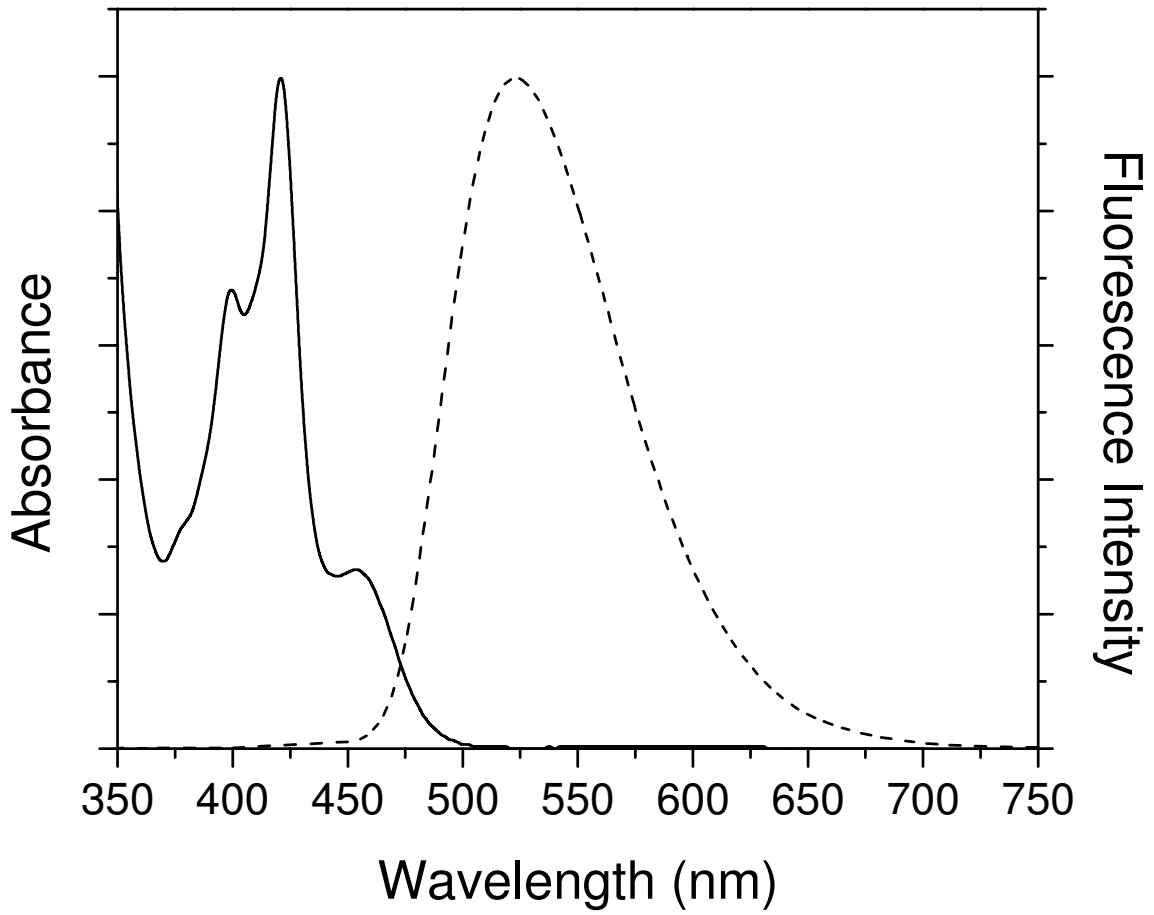


Figure S3. UV-vis absorption (solid line) and fluorescence (dashed line, excited at 421 nm) spectra of **BP-1** in $CHCl_3$.

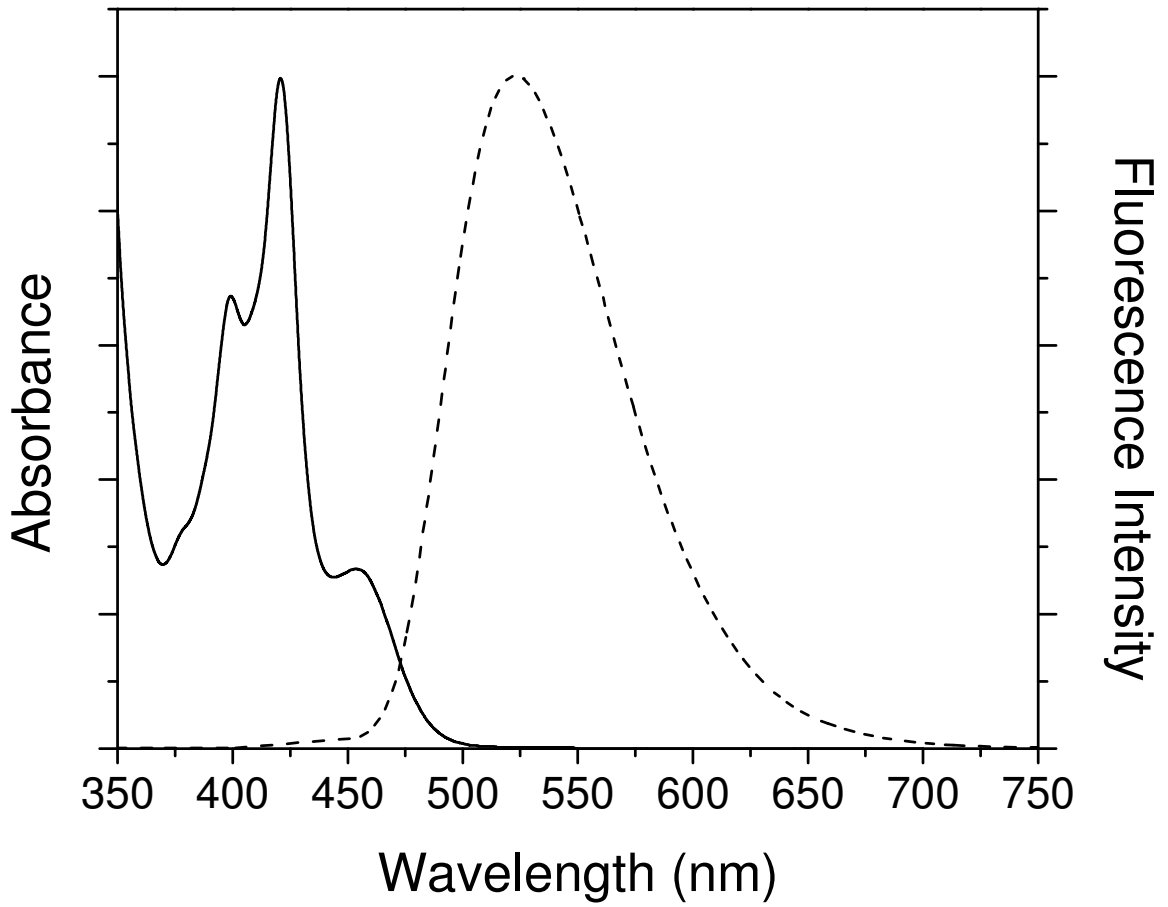


Figure S4. UV-vis absorption (solid line) and fluorescence (dashed line, excited at 421 nm) spectra of **BP-2** in $CHCl_3$.

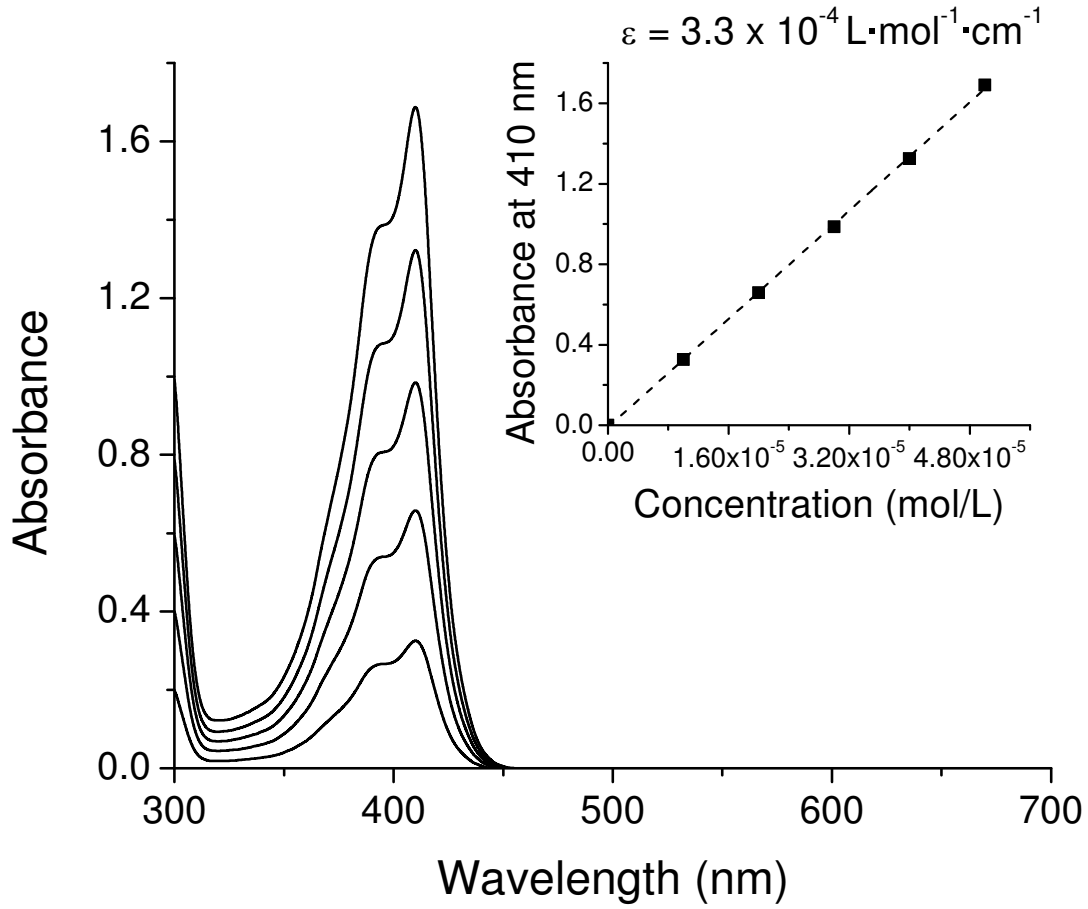


Figure S5. Beer's law plot of **P-3** in $CHCl_3$.

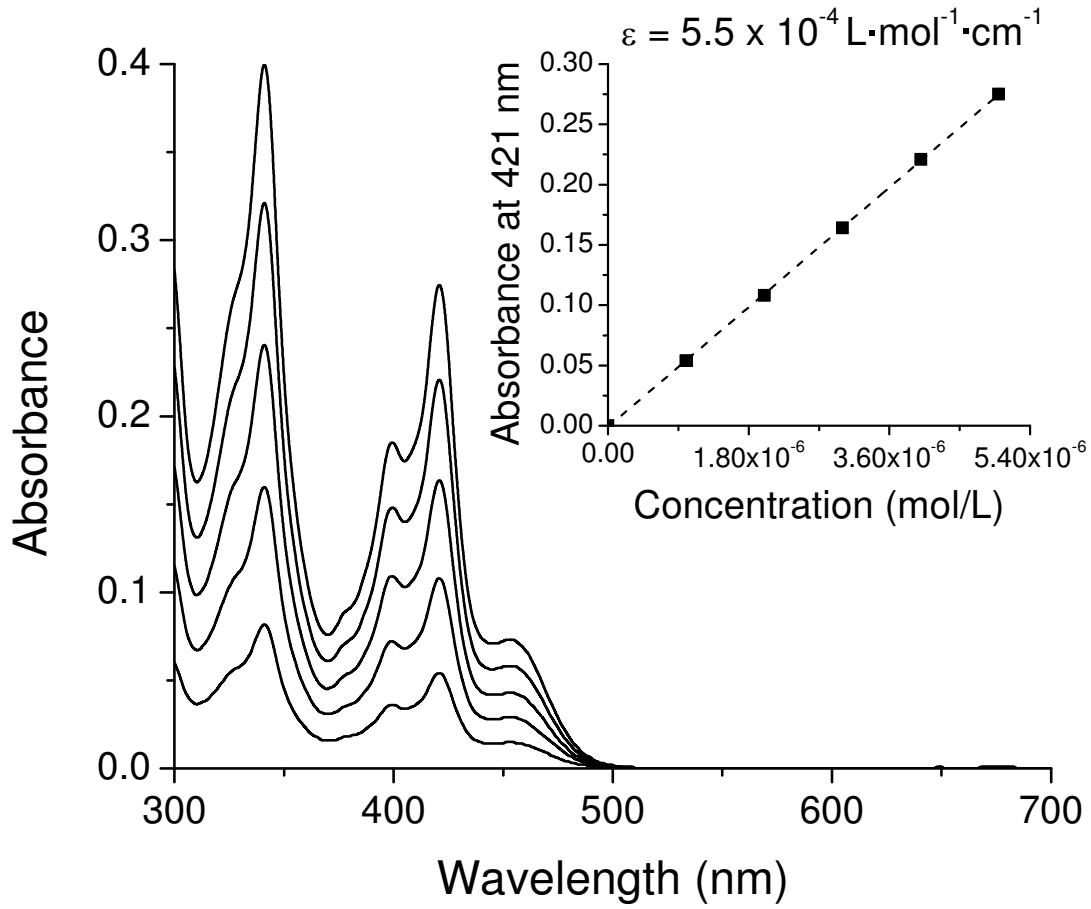


Figure S6. Beer's law plot of **BP-3** in $CHCl_3$.

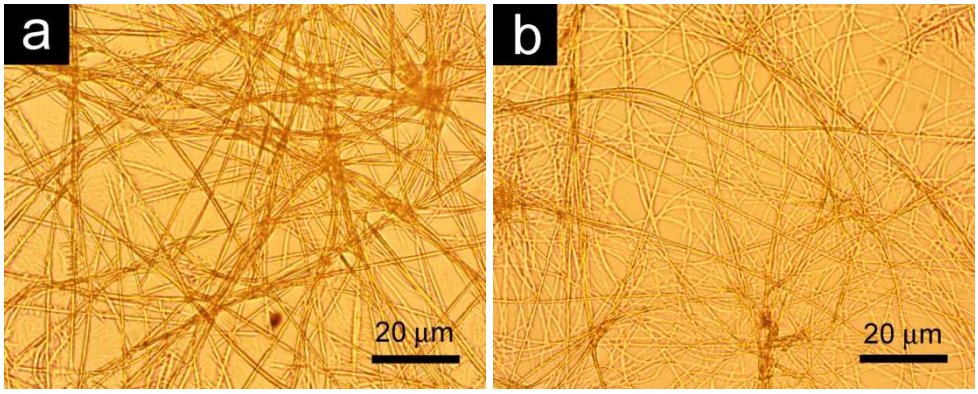


Figure S7. POM images of the cast films of **P-1** (a) and **P-2** (b).

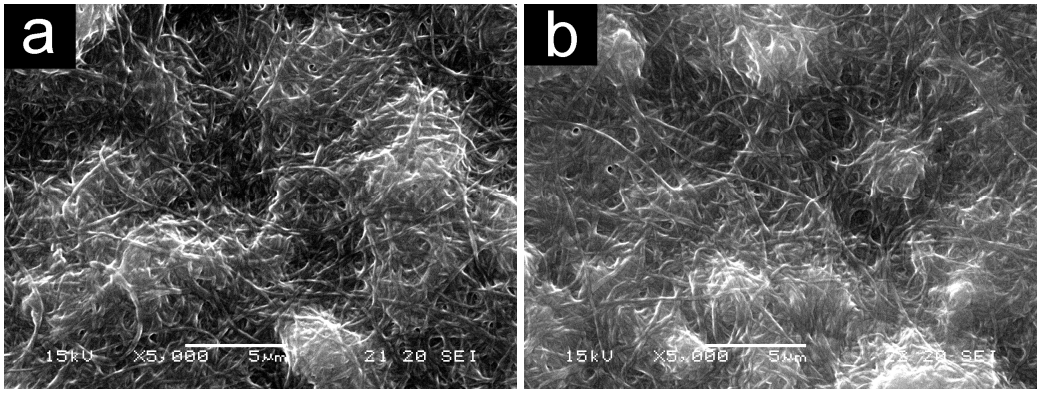


Figure S8. SEM images of the xerogels of **BP-1** (a) and **BP-2** (b).

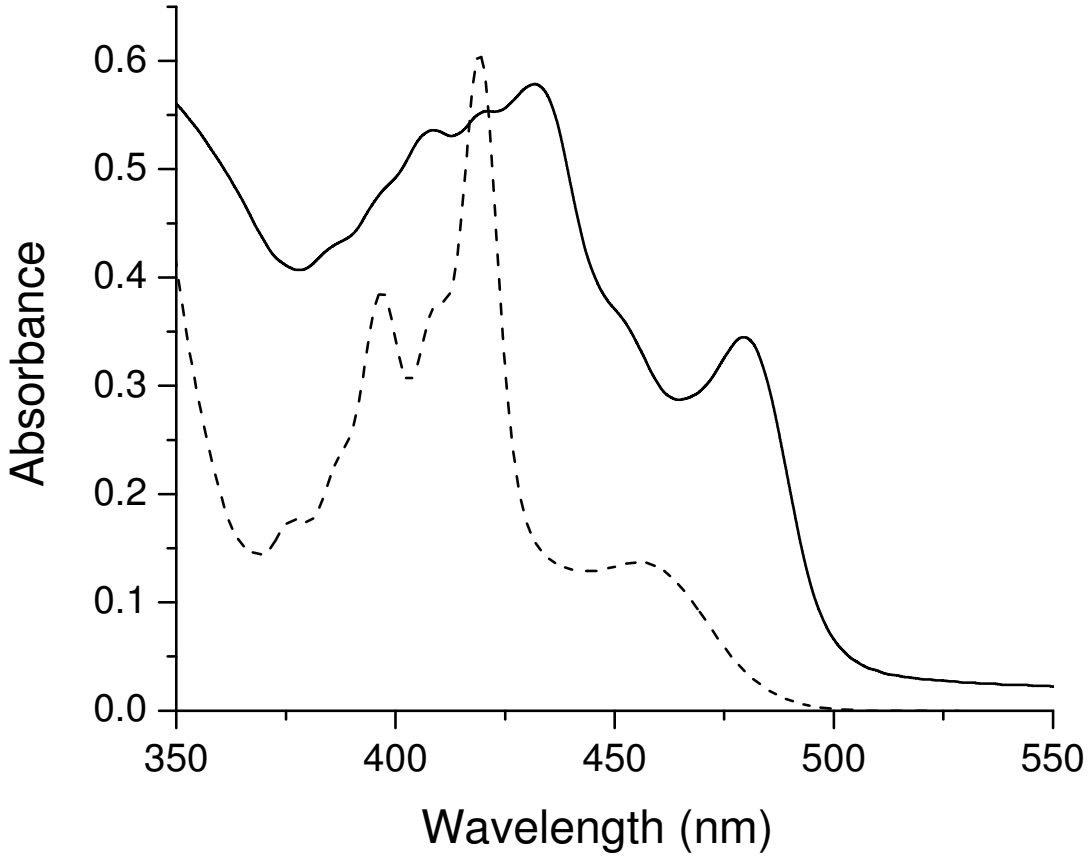


Figure S9. UV-vis absorption spectra of **BP-3** in solution (5×10^{-6} M, dashed line) and in the gel state (5 mM, solid line). In both cases, TCE was used as a solvent.

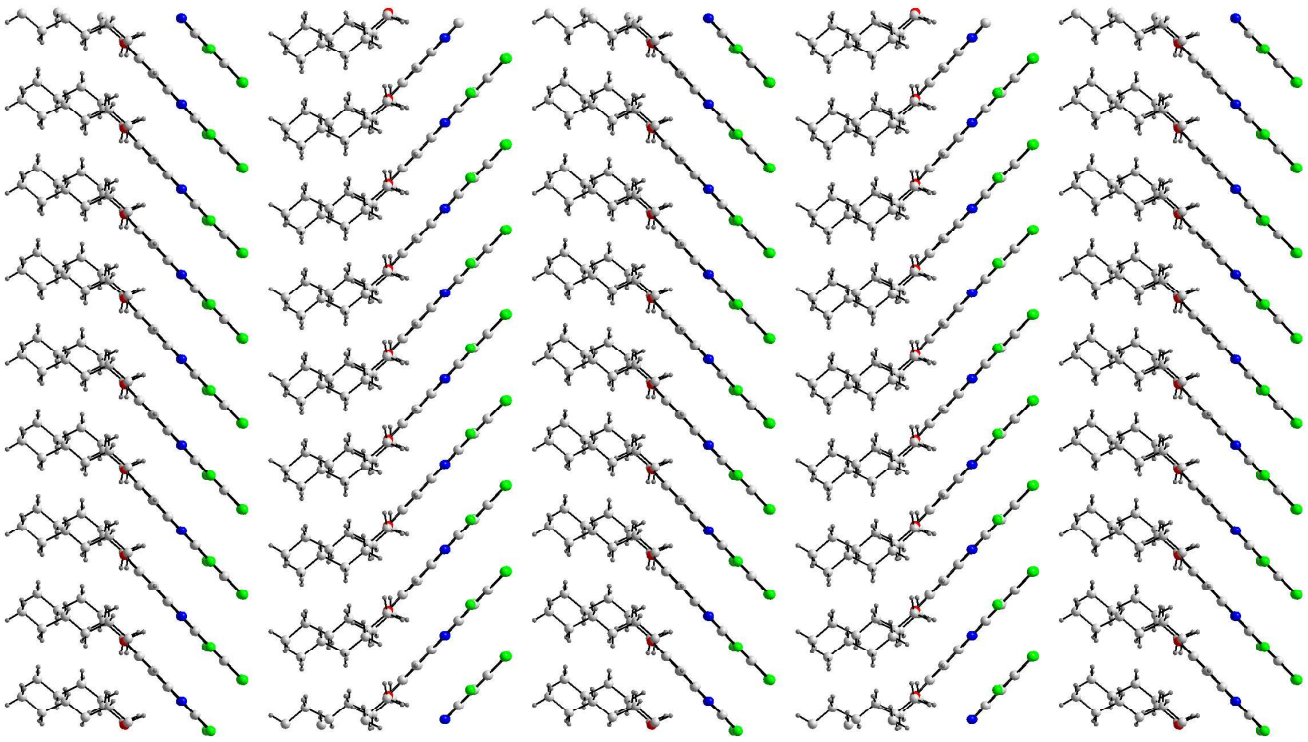


Figure S10. Herringbone structure of the crystal of compound **P-4**.

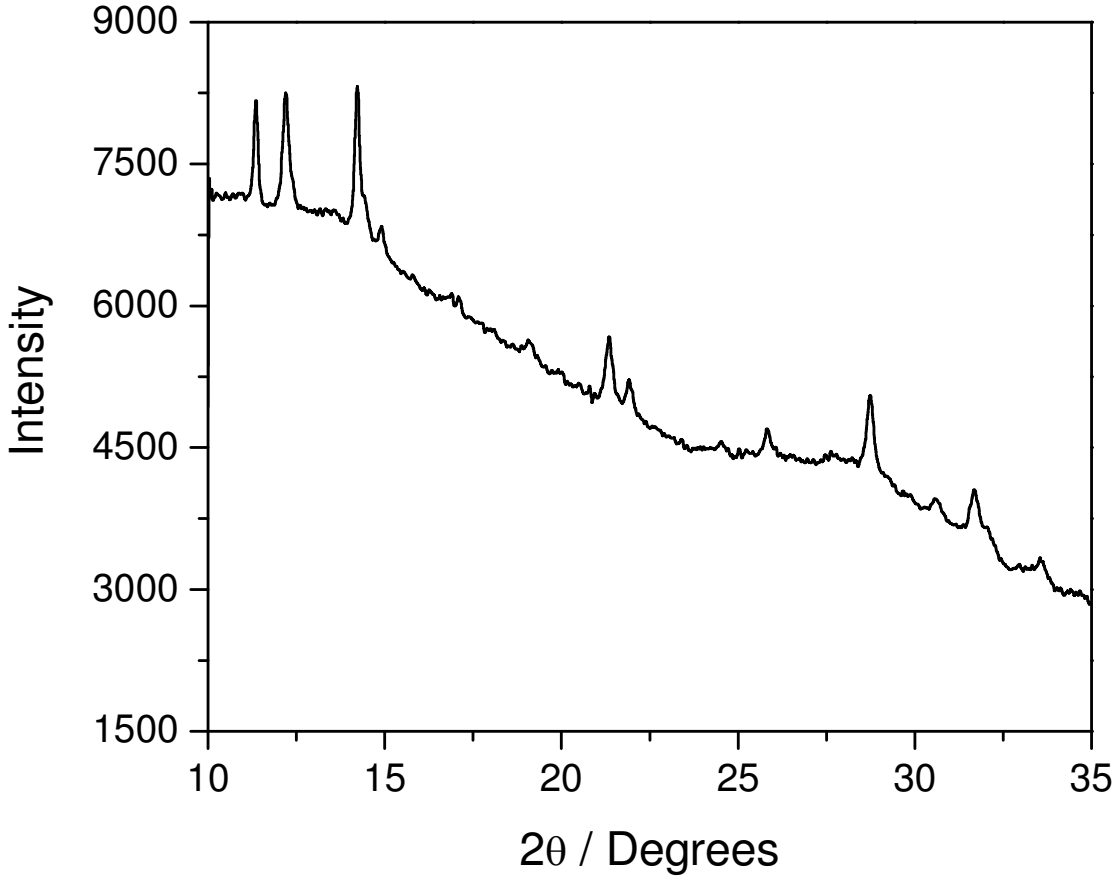


Figure S11. XRD powder pattern of the **P-3** xerogel.

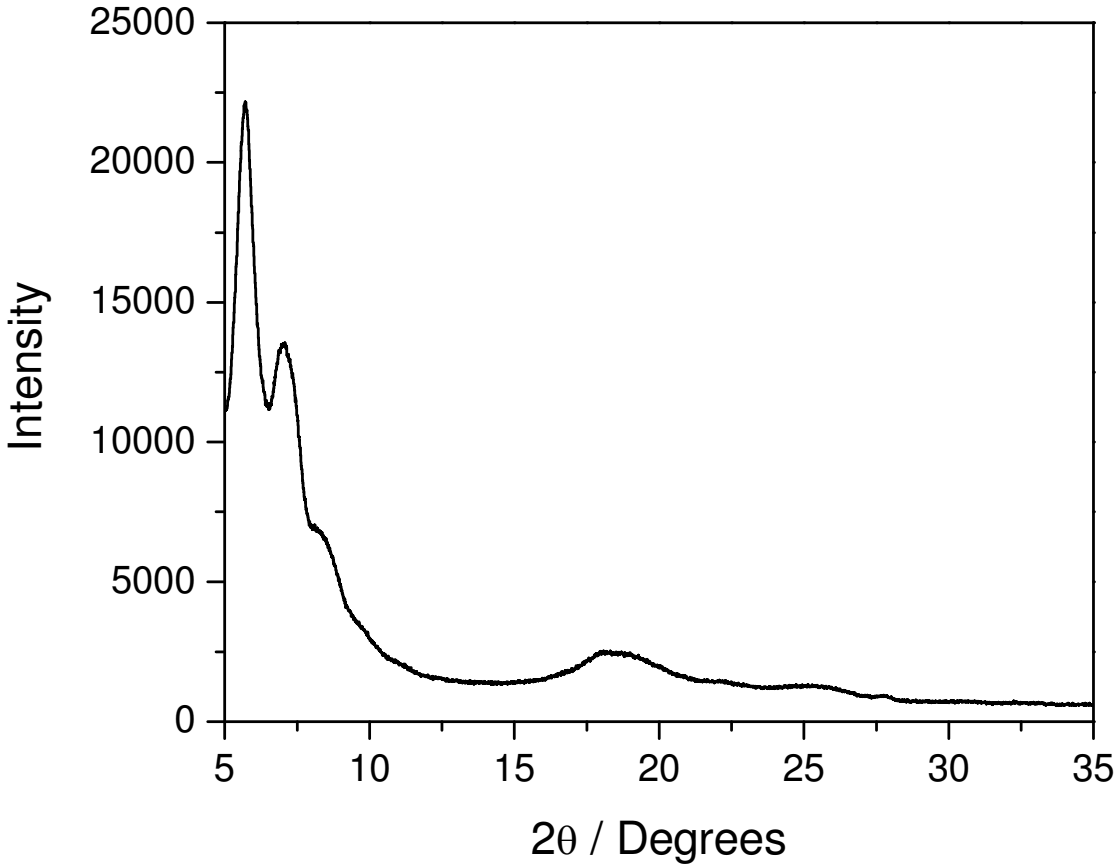


Figure S12. XRD powder pattern of the **BP-3** xerogel.

Table S1. Crystal data for compound **P-4**.

Chemical formula	$C_{24}H_{28}Cl_4N_2O_2$
Formula weight/g mol^{-1}	518.28
T/K	100(2)
λ/Å	0.71073
Crystal system	Orthorhombic
Space group	$P2_12_12$
Unit cell dimensions/Å	a = 15.8452(10)
	b = 30.3764(19)
	c = 4.9176(3)
Unit cell angles/^{o}	α = 90
	β = 90
	γ = 90
Volume/Å^3	2366.9(3)
Z	4
ρ(calculated)/Mg cm^{-3}	1.454
Absorption coefficient/mm^{-1}	0.526
F(000)	1080
θ range for data collection/^{o}	1.86 to 29.57
Index ranges	-21<=h<=22, -42<=k<=41,
	-6<=l<=6
Reflections collected	24821
Independent reflections	6631 [R(int) = 0.0355]
Completeness to θ = 26.77^o	99.8%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6631/0/290
Goodness-of-fit on F^2	1.027
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0306, wR_2 = 0.0682
R indices (all data)	R_1 = 0.0362, wR_2 = 0.0709
Largest diff. peak and hole/e Å^{-3}	0.347 and -0.253

References

1. Demas, J. N.; Crosby, G. A. *J. Phys. Chem*. **1971**, *75*, 991-1024.

2. Hu, J.; Zhang, D.; Harris, F. W. *J. Org. Chem.* **2005**, *70*, 707-708.

3. Wulfamn, D. S.; Cooper, C. F. *Synthesis* **1978**, 924-925.

4. Furst, A.; Berlo, R. C.; Hooton, S. *Chem. Rev.* **1965**, *65*, 51-68.

5. McGrath, K. K.; Jang, K.; Robins, K. A.; Lee, D.-C. *Chem. Eur. J.* **2009**, *15*, 4070-4077.

6. Robins, K. A.; Jang, K.; Cao B.; Lee, D.-C. *Phys. Chem. Chem. Phys.* **2010**, *12*, 12727-12733.