

Electronic Supplementary Information for

A novel smart organogel which could allow two channels anion response by proton controlled reversible sol-gel transition and color changes

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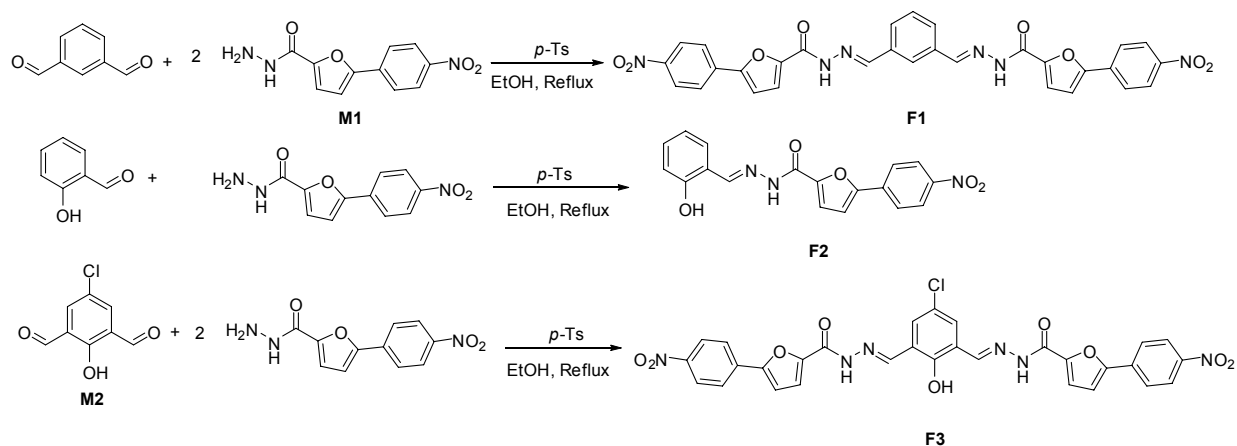
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Materials and methods

Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). ^1H and ^{13}C NMR spectra were recorded with a Mercury-400BB spectrometer at 400 and 100 MHz respectively. ^1H chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale) with the solvent resonances as internal standards. All NMR spectra were referenced to solvent. High-resolution mass spectra were recorded on a Bruker APEXII Fourier transform ion cyclotron resonance (FTICR) MS instrument. UV-visible spectra were recorded on a Shimadzu UV-2550 spectrometer. The infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer. The scanning electron microscope (SEM) observations were carried out by using a JSM-6701F field emission scanning electron microscope. The atomic force microscopy (AFM) observations were performed on a Seiko Model SPI3800 atomic force microscope. The X-ray diffraction analysis (XRD) was performed on a Rigaku D/Max-2400 X-Ray Diffractometer.

5-chloro-2-hydroxyisophthalaldehyde (**M1**)^{1,2} and 5-(4-nitrophenyl)furan-2-carbohydrazide (**M2**)³ were synthesized according to literature methods. The anions were used as the tetrabutylammonium salt, which were purchased from Alfa Aesar and used as received. Other reagents used in the study were analytical grade.

Synthesis



Scheme 1 Synthesis procedure for **F1-F3**

Compound F1

Isophthalaldehyde (268.2 mg, 2 mmol), 5-(4-nitrophenyl)furan-2-carbohydrazide (988.8 mg, 4 mmol) and catalytic amount of *p*-toluenesulfonic acid (*p*-TsOH) were combined in hot absolute ethanol (30 mL). The solution was stirred under reflux conditions for 6 hours, After cooling to room temperature, the yellow precipitate was filtrated, washed with hot absolute ethanol three times, then recrystallized with DMSO-EtOH to get yellow powdery product **F1** (1030.9 mg, 1.74 mmol) in 87% yield. The other compounds **F2** and **F3** were prepared by the similar procedure.

F1. m.p. > 300 °C, ¹H NMR (DMSO-d₆, 400 MHz) δ 12.06 (s, 2H, NH), 8.61(s, 2H, HC=N), 8.39-7.51 (m, 16H, ArH). IR (KBr, cm⁻¹) ν: 3438, 3334, 3237, 1676, 1599, 1551, 1507, 1335, 1274, 1105, 852. HRMS(ESI, *m/z*). calcd for C₃₀H₂₀N₆O₈(M+Na⁺) 615.1240, found 615.1235

F2. m.p. 259~261 °C, ¹H NMR (DMSO-d₆, 400 MHz) δ 12.16 (s, 1H, OH), 11.02 (s, 1H, NH), 8.75 (s, 1H, HC=N), 8.38-6.92 (m, 10H, ArH). ¹³C NMR (DMSO-d₆, 100 MHz) 157.46, 153.69, 153.15, 148.26, 147.22, 146.96, 135.04, 131.71, 129.04, 125.43, 124.50, 119.55, 119.02, 117.80, 116.52, 111.90. IR (KBr, cm⁻¹) ν: 3447, 3344, 3119, 1678, 1601, 1547, 1508, 1335, 1267, 1156, 852. HRMS(ESI, *m/z*). calcd for C₁₈H₁₃N₃O₅(M-H⁺) 350.0777, found 350.0782.

F3. m.p. > 300 °C, ¹H NMR (DMSO-d₆, 400 MHz) δ 12.66 (s, 1H, OH), 12.39 (s, 2H, NH), 8.75 (s, 2H, HC=N), 8.39-7.52 (m, 14H, ArH). IR (KBr, cm⁻¹) ν: 3433, 3333, 3110, 1683, 1598, 1510, 1338, 1271, 1158, 852. Anal. calcd for C₃₀H₁₉ClN₆O₉: C 56.04, H 2.98, N 13.07; found C 56.15, H 2.76, N 13.11.

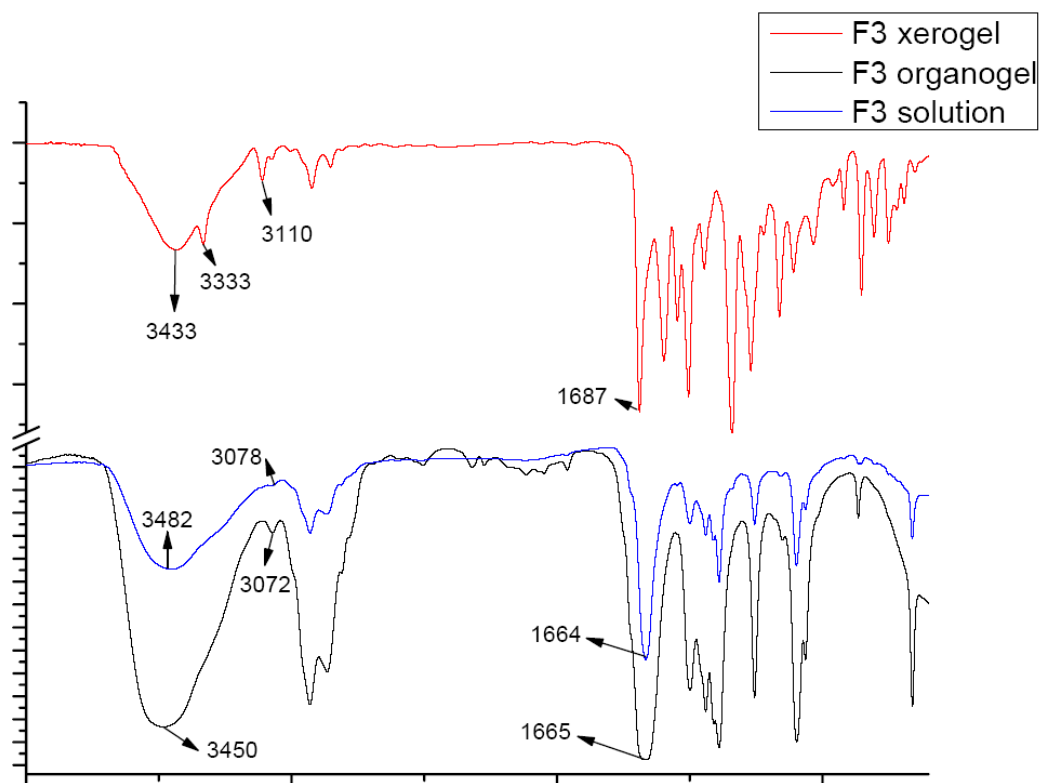


Fig. S1 FT-IR of F3 in the solid state (xerogel), the gel phase and the sol phase (fresh solution in DMF)

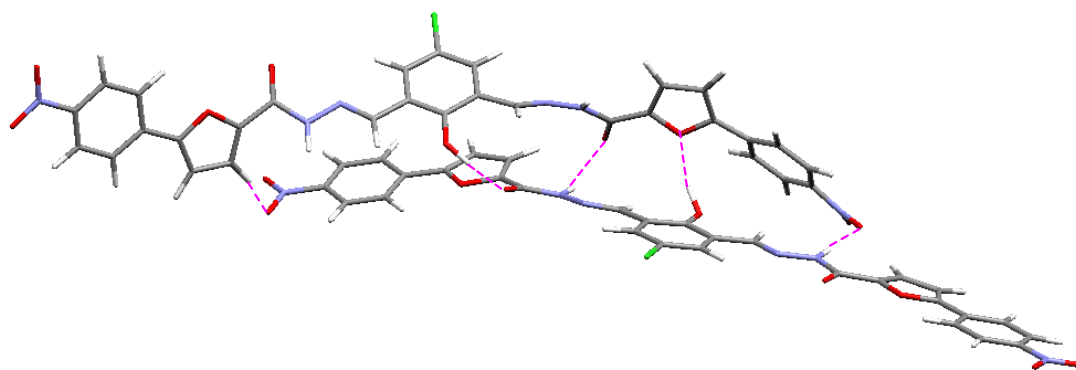


Fig. S2 The optimized hydrogen bonding self-assemble model of F3 in the gel obtained by DFT studies

Computational Methods

Geometries and energies of the stationary points found here were fully optimized by hybrid density functional theory (DFT) using the GAUSSIAN 03 program suite.⁴ Exchange and correlation were treated by the BHandHLYP method, which is based on Becke's half-and-half method⁵ and the gradient-corrected correlation functional of Lee and coworkers.⁶ This hybrid DFT method has been shown to be quite reliable for finding both the geometries and energies.⁷ The 3-21G basis set with polarization (d) were selected for all the atoms.

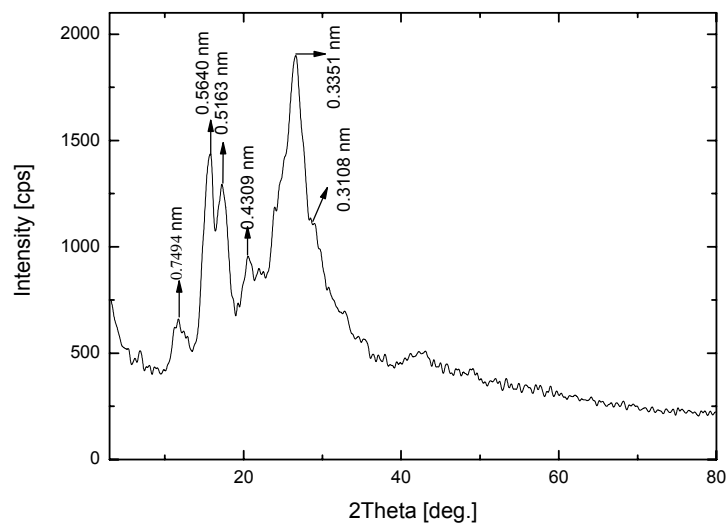


Fig. S3 XRD patterns of xerogel of **F3**



Fig. S4 Color changes observed upon the addition of various anions (10 mM) to DMF gel of **F3** (15.6 mM, 1.0 wt %). From left to right: free **F3**, **F3**+F⁻, **F3**+AcO⁻, **F3**+H₂PO₄⁻, **F3**+Cl⁻, **F3**+Br⁻, **F3**+I⁻, **F3**+ClO₄⁻, **F3**+HSO₄⁻.

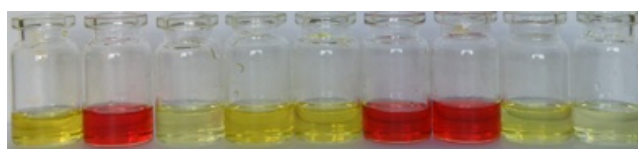


Fig. S5 Color changes observed upon the addition of various anions (50 equiv) to DMSO solutions of **F3** (2×10^{-5} M). From left to right: free **F3**, **F3**+F⁻, **F3**+Cl⁻, **F3**+Br⁻, **F3**+I⁻, **F3**+AcO⁻, **F3**+H₂PO₄⁻, **F3**+ClO₄⁻, **F3**+HSO₄⁻.

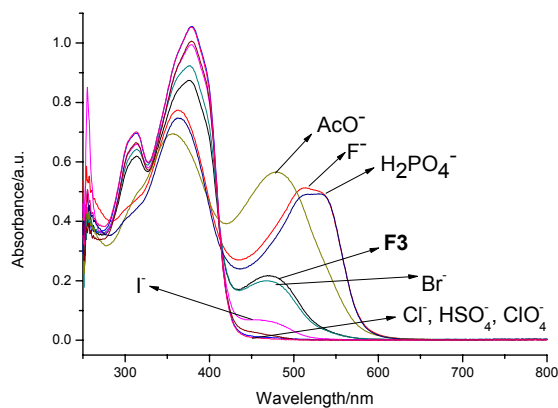


Fig. S6 UV-Vis absorption of **F3** (2×10^{-5} M) in the presence of 50 equiv of various anions in DMSO at room temperature.

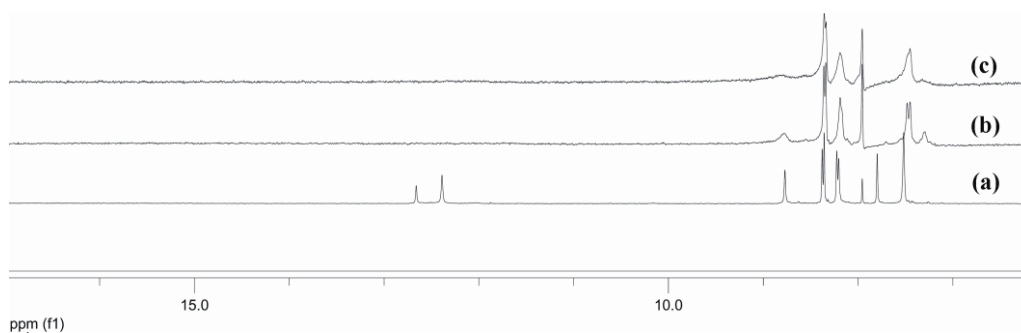


Fig. S7 Partial ^1H NMR spectra of compound **F3** (2.5 mM) in $\text{DMSO}-d_6$ upon the addition of AcO^- . (a) Free, (b) 1 equiv of AcO^- , (c) 5 equiv of AcO^- .

Reference

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