

Electronic Supplementary Information

Rationally Designed Anion-Responsive-Organogels: Sensing F⁻ via Reversible Color Changes in Gel-Gel States with Specific Selectivity

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1. General experimental section

1.1 Materials and instruments

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. Fresh double distilled water was used throughout the experiment. All other reagents and solvents were commercially available at analytical grade and were used without further purification. ^1H NMR spectra were recorded on Mercury-400BB spectrometer (400MHz) and Bruker Digital RF spectrometer (300MHz). ^1H chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale with the solvent resonances as internal standards). Low-resolution mass spectra were recorded on a Bruker Esquire 6000 MS instrument. The X-ray diffraction analysis (XRD) was performed on a Rigaku D/Max-2400 X-Ray Diffractometer. The morphologies and sizes of the xerogels were characterized using field emission scanning electron microscopy (FE-SEM, JSM-6701F) at an accelerating voltage of 8 kV. The infrared spectra were performed on a Digilab FTS-3000 Fourier transform-infrared spectrophotometer. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). Ultraviolet-visible (UV-vis) spectra were recorded on a Shimadzu UV-2550 spectrometer.

1.2 General procedure for UV-vis experiments

UV-vis spectroscopy was carried out just after the addition of anions in DMSO solution, while keeping the host concentration constant (2.0×10^{-5} M) on a Shimadzu UV-2550 spectrometer. The solution of anions was prepared from their tetrabutylammonium salts.

1.3 General procedure for ^1H NMR titrations

For ^1H NMR titrations, two stock solutions were prepared in CDCl_3 : one of them contained the host only and the second one contained an appropriate concentration of guest. Aliquots of the two solutions were mixed directly in NMR tubes.

1.4 General procedure for concentration-dependent ^1H NMR measurements

The concentration-dependent ^1H NMR was carried out by gradually increasing the concentration of the CDCl_3 solution of **L1**. The initial concentration of the **L1** is 0.6 mM, the concentration was adjusted by directly adding right amount of powdery **L1** into the CDCl_3 solution.

2. Computational Methods

Geometries, energies, and first- and second-energy derivatives of all of the stationary points found here were fully optimized by hybrid density functional theory (DFT) using the GAUSSIAN 09 program suite.^[s1] For our DFT calculations, we used the hybrid gradient corrected exchange functional of Lee, Yang, and Parr ^[s2,s3]. A standardized 3-21G basis set was selected.

[s1] Frisch, M. J. et al., *Gaussian 09* (Revision A01), Gaussian, Inc., Pittsburgh PA. **2009**.

[s2] Lee, C.; Yang, W.; Parr, R.G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B.* **1988**, *37*, 785–789.

[s3] Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. Results Obtained with the Correlation Energy Density Functionals of Becke and Lee, Yang and Parr. *Chem. Phys. Lett.* **1989**, *157*, 200–206.

Complete List of Authors for References with more than 10 Authors

[s1] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Jr., Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision A.01; Gaussian, Inc., Wallingford CT, 2009.

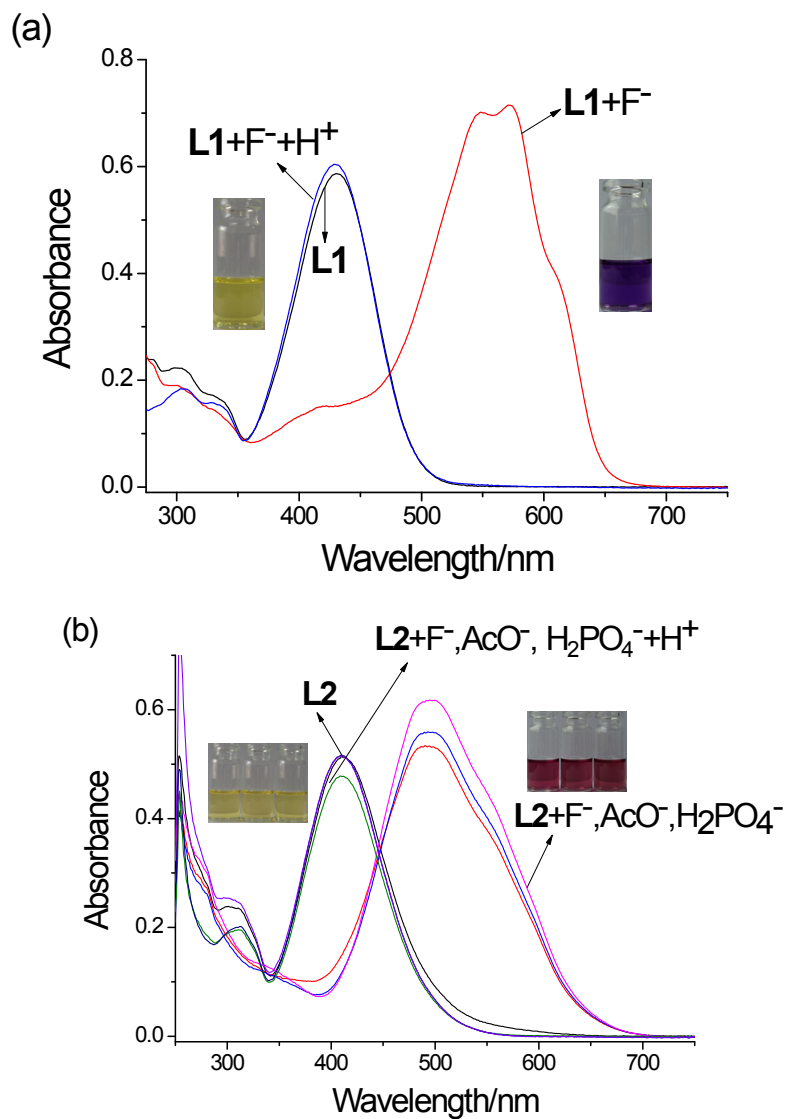


Figure S1. UV-vis spectra response and photograph of a) L1 (2.0×10^{-5} M) in DMSO upon the addition of 50 equiv. of F^- and subsequent addition of H^+ . b) L2 (2.0×10^{-5} M) in DMSO upon the addition of 50 equiv. of F^- , AcO^- and $H_2PO_4^-$ and subsequent addition of H^+ .

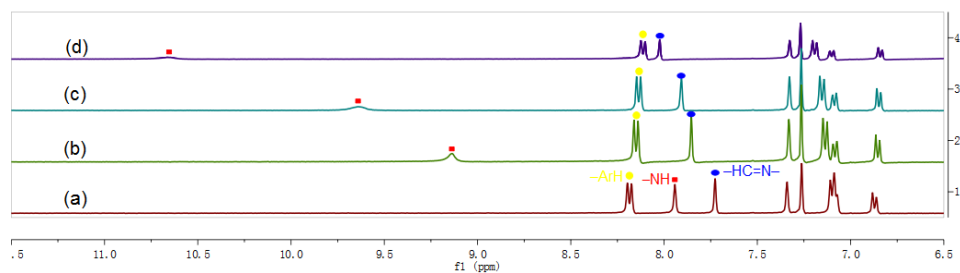


Figure S2. Partial ^1H NMR spectra of **L1** (0.01 M) in CDCl_3 upon the addition of AcO^- : a) Free; b) 0.5 equiv. of AcO^- ; c) 1.0 equiv. of AcO^- ; d) 2.0 equiv. of AcO^- .

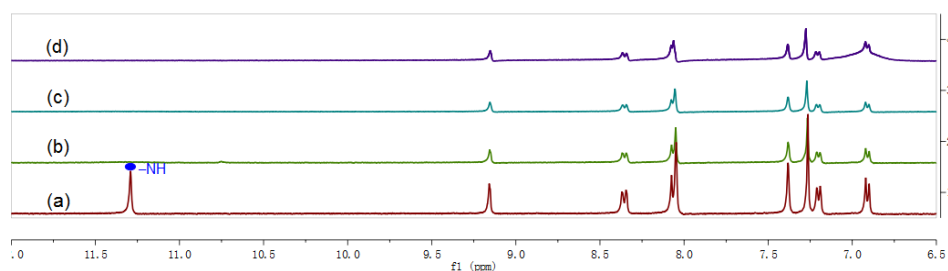


Figure S3. Partial ^1H NMR spectra of **L3** (0.01 M) in CDCl_3 upon the addition of AcO^- : a) Free; b) 0.5 equiv. of AcO^- ; c) 1.0 equiv. of AcO^- ; d) 2.0 equiv. of AcO^- .