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Supporting Information

Colorimetry and Phase Transition Characteristics in Sensing Fluoride Anion Based on Hydrazide Organogelators

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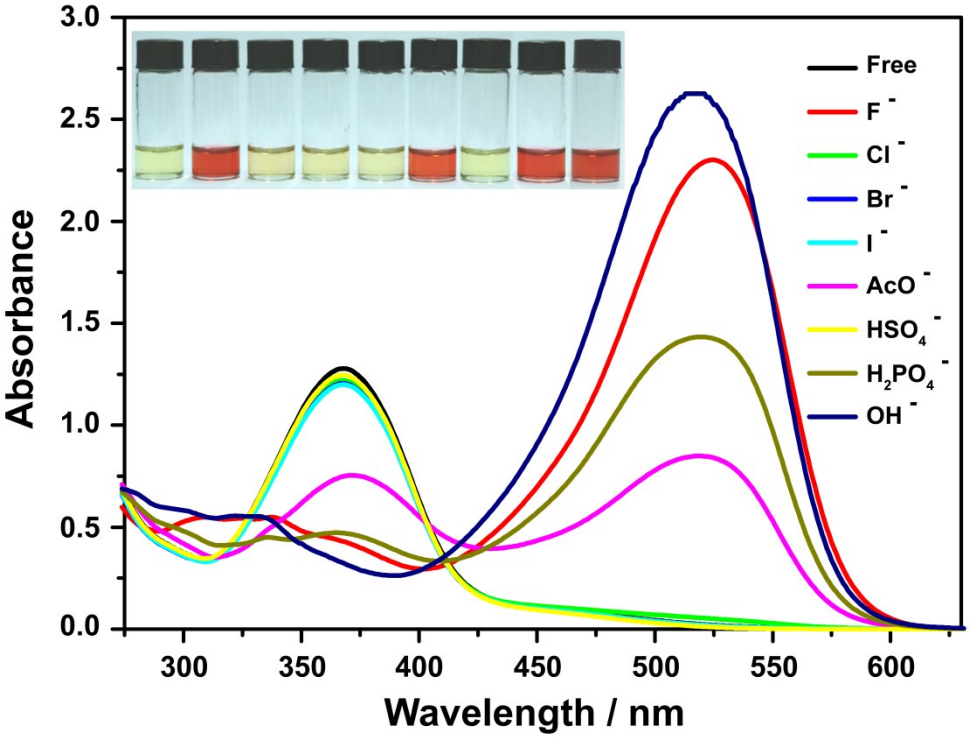

Figure S1 UV-vis spectra of BNB-t4 (1×10^{-4} mol L^{-1}) in DMSO upon addition of 30 equiv. of various anions (F^-, Cl^-, Br^-, I^-, AcO^-, HSO_4^-, $H_2PO_4^-$, and OH^-). Inset: the corresponding images of BNB-t4 in DMSO upon addition of 30 equiv. of various anions (from left to right: free, F^-, Cl^-, Br^-, I^-, AcO^-, HSO_4^-, $H_2PO_4^-$, and OH^-).

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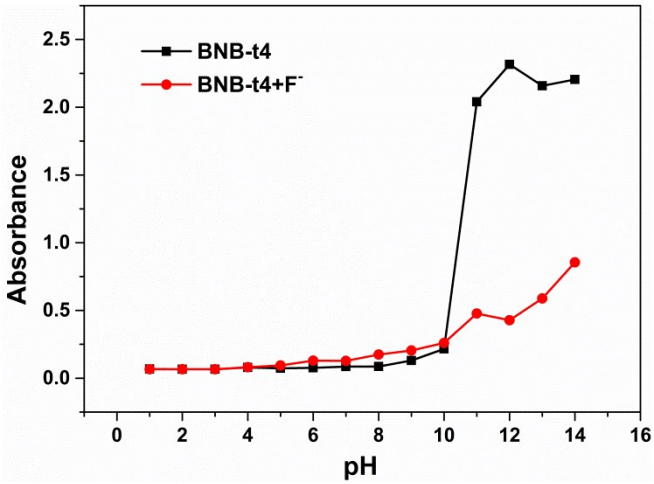


Figure S2. pH dependent absorbance of BNB-t4 at 485 nm with and without F^- (40 equiv.).

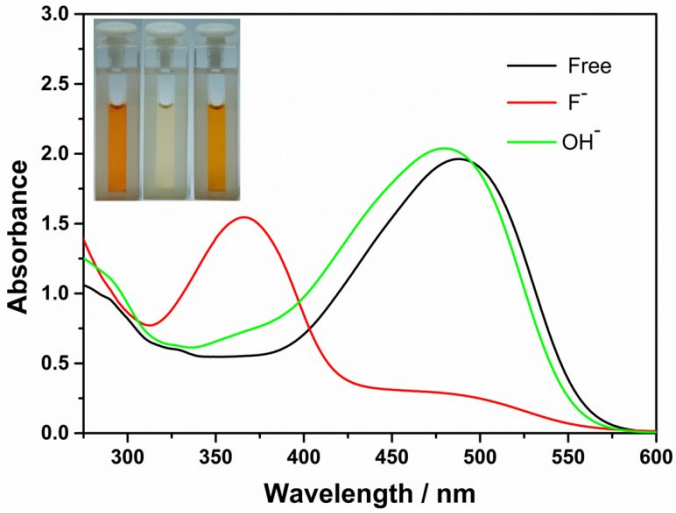


Figure S3. UV-vis spectra of BNB-t4 (1×10^{-4} mol L^{-1}) in HEPES buffer (pH=11) solution system upon addition of 40 equiv. of F^- and OH^-. Inset: the corresponding images of BNB-t4 (1×10^{-4} mol L^{-1}) in HEPES buffer (pH=11) upon addition of 40 equiv. of anions (from left to right: free, F^- and OH^-).

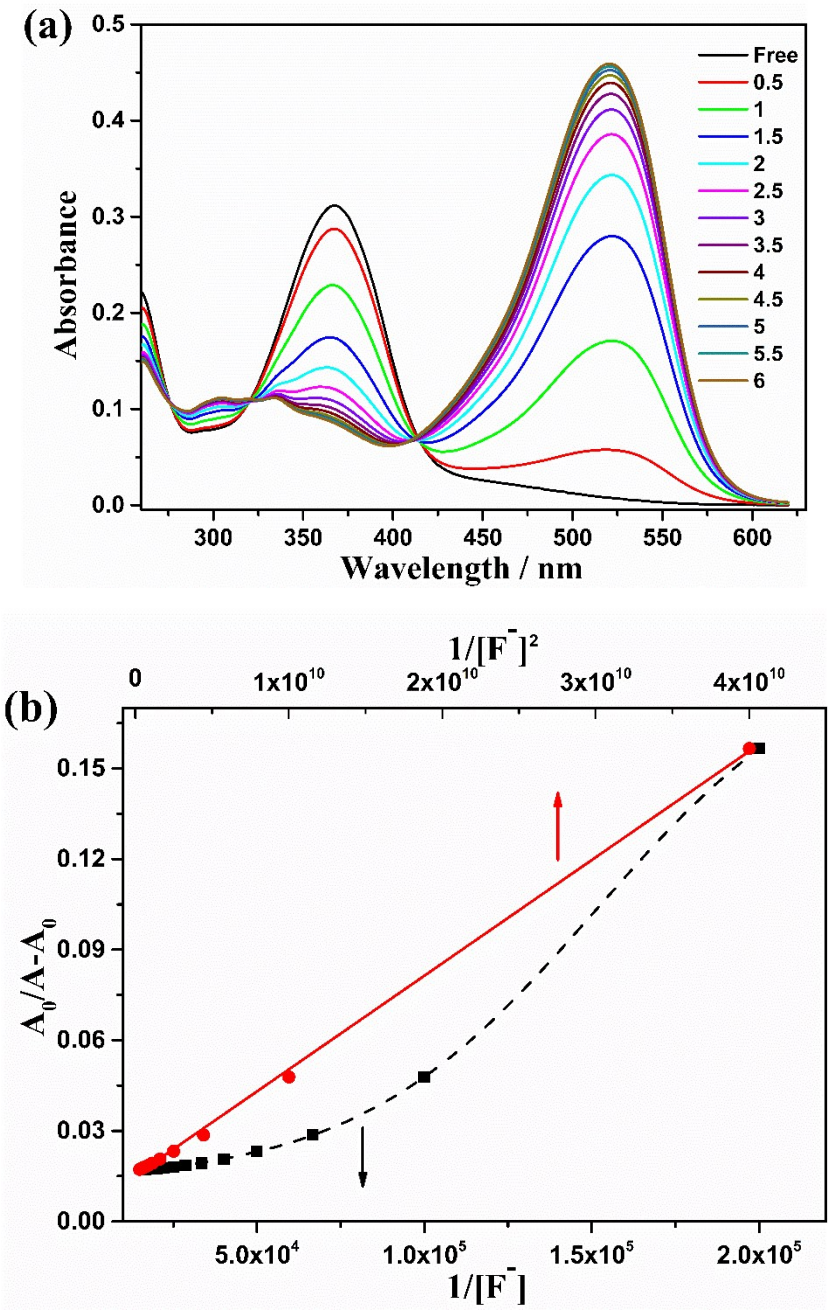


Figure S4 (a) UV-vis absorption spectra of BNB-t4 (1×10^{-5} M) in DMSO titrated with F^- (0-6 equiv.) (b) Benesi-Hildebrand plot for complexation of BNB-t4 with F^-. [F^-] is the concentration F^- added (M).

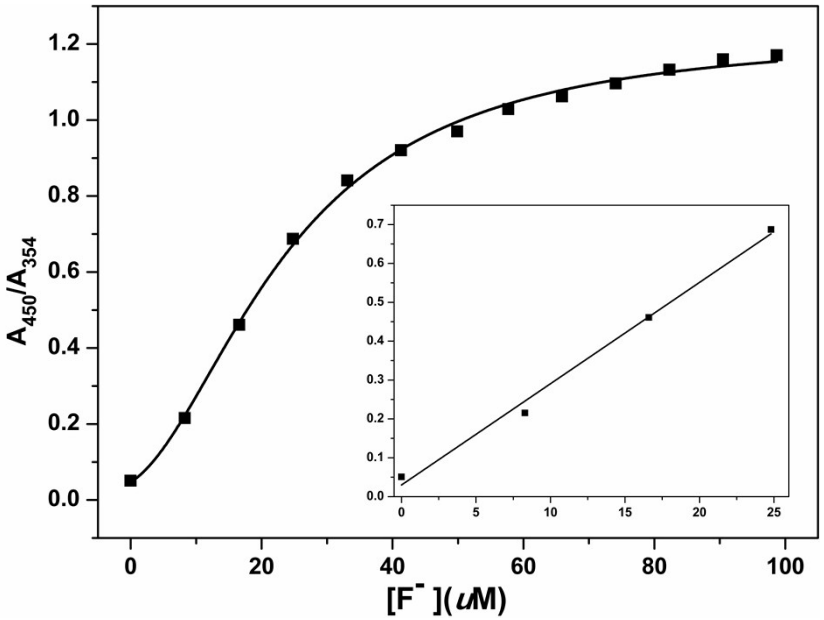


Figure S5 Calibration curve of BNB-t4 (1×10^{-5} M) in chloroform titrated with F^-. The curve was plotted with the absorbance ratio (A_{450}/A_{354}) vs F^- concentration. Inset shows the linear responses at low F^- concentrations.

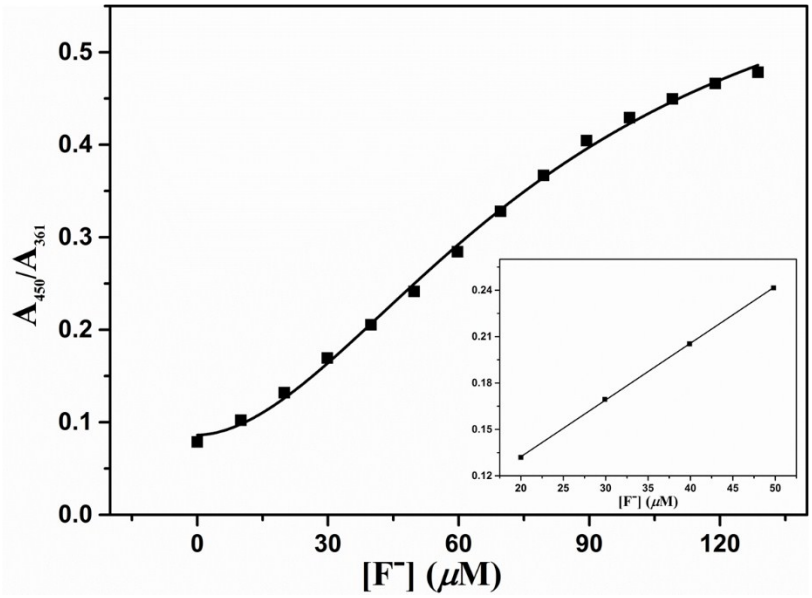


Figure S6 Calibration curve of BNBC-t8 (1×10^{-5} M) in chloroform titrated with F^-. The curve was plotted with the absorbance ratio (A_{450}/A_{361}) vs F^- concentration. Inset shows the linear responses at low F^- concentrations.

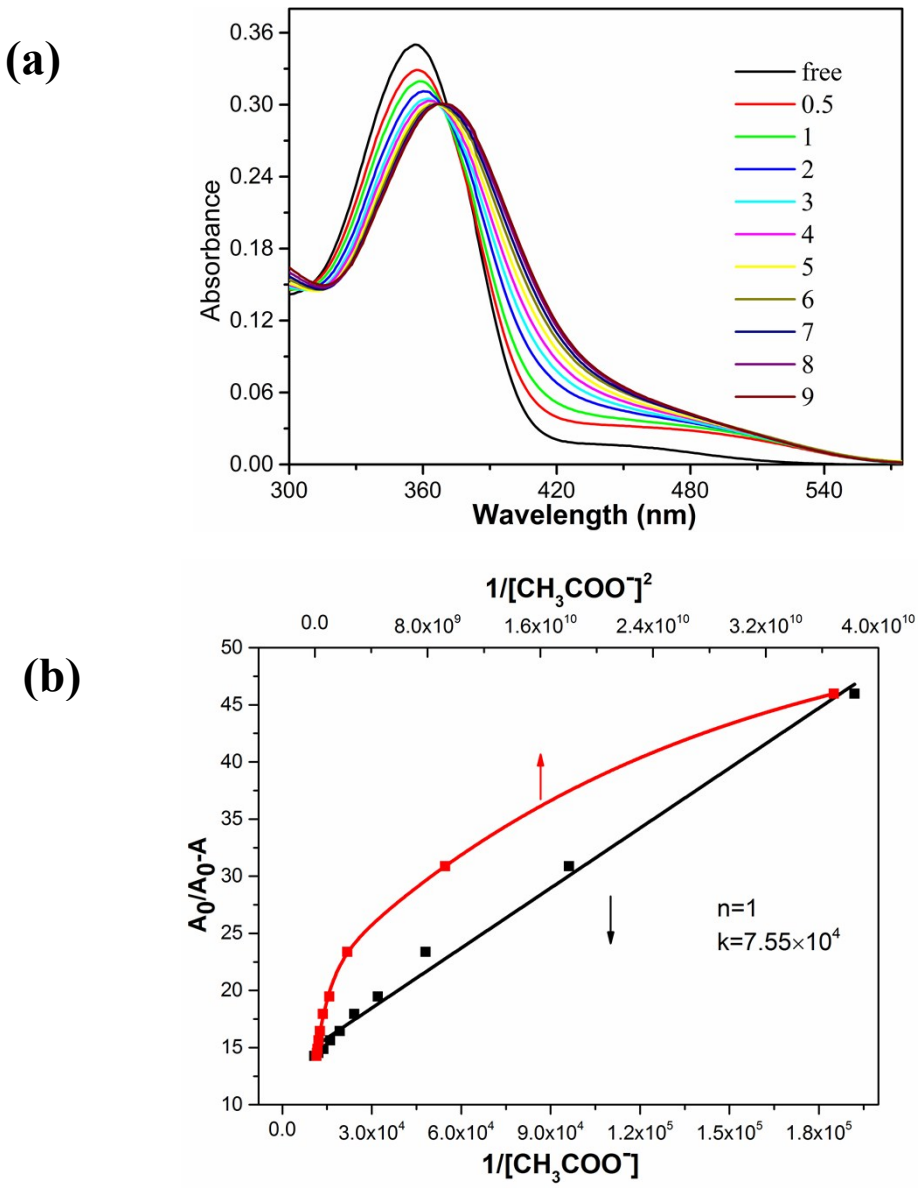


Figure S7 (a) UV-vis absorption spectra of BNB-t4 (1×10^{-5} M) in chloroform titrated with CH_3COO^- (0-9 equiv.) (b) Benesi-Hildebrand plot for complexation of BNB-t4 with CH_3COO^-.

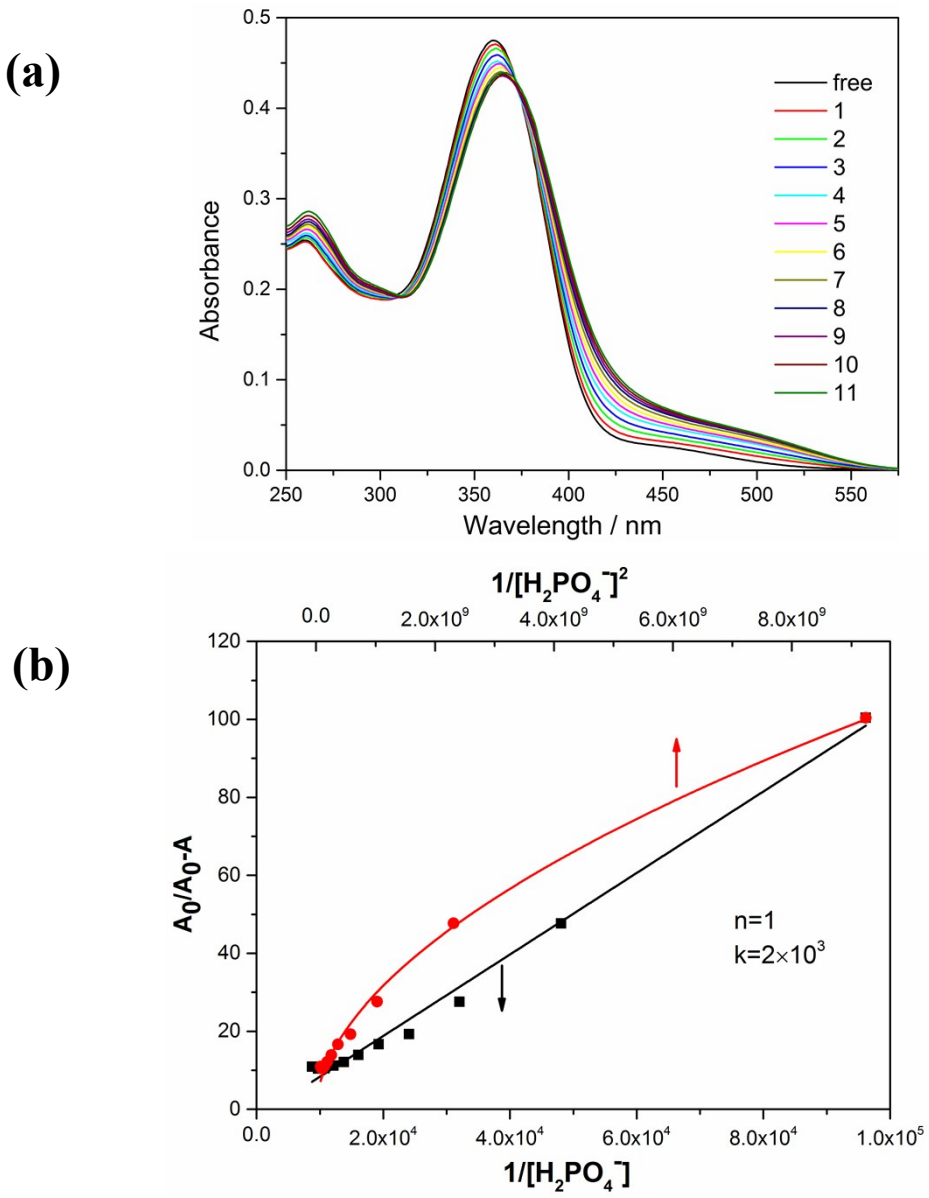


Figure S8 (a) UV-vis absorption spectra of BNB-t4 (1×10^{-5} M) in chloroform titrated with $H_2PO_4^-$ (b) Benesi-Hildebrand plot for complexation of BNB-t4 with $H_2PO_4^-$.

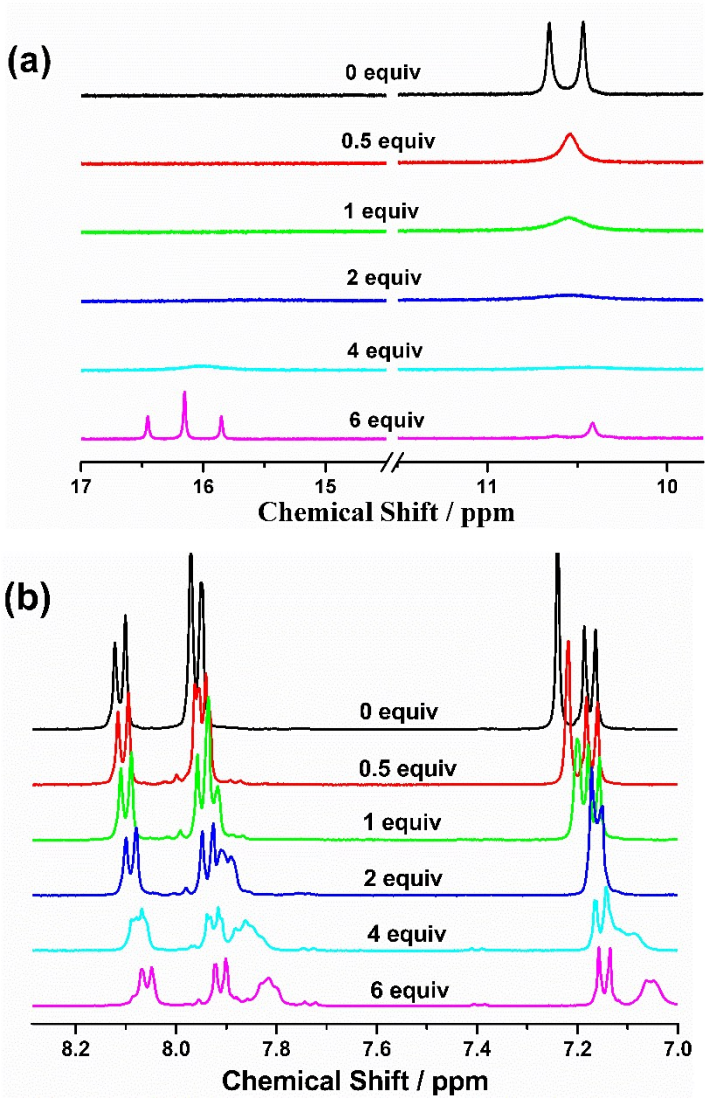


Figure S9 The partial ^{1}H NMR spectra of BNBC-t8 (1×10^{-2} mol L^{-1}) in DMSO-*d*6 upon the addition of F^{-}.

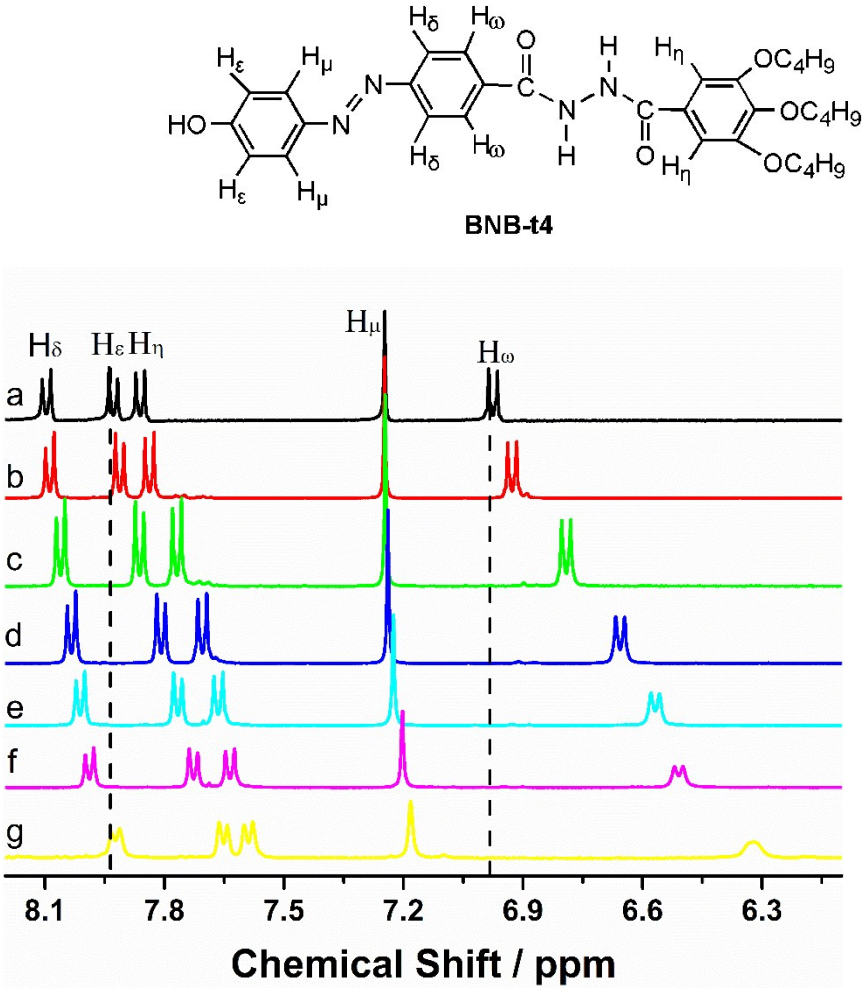
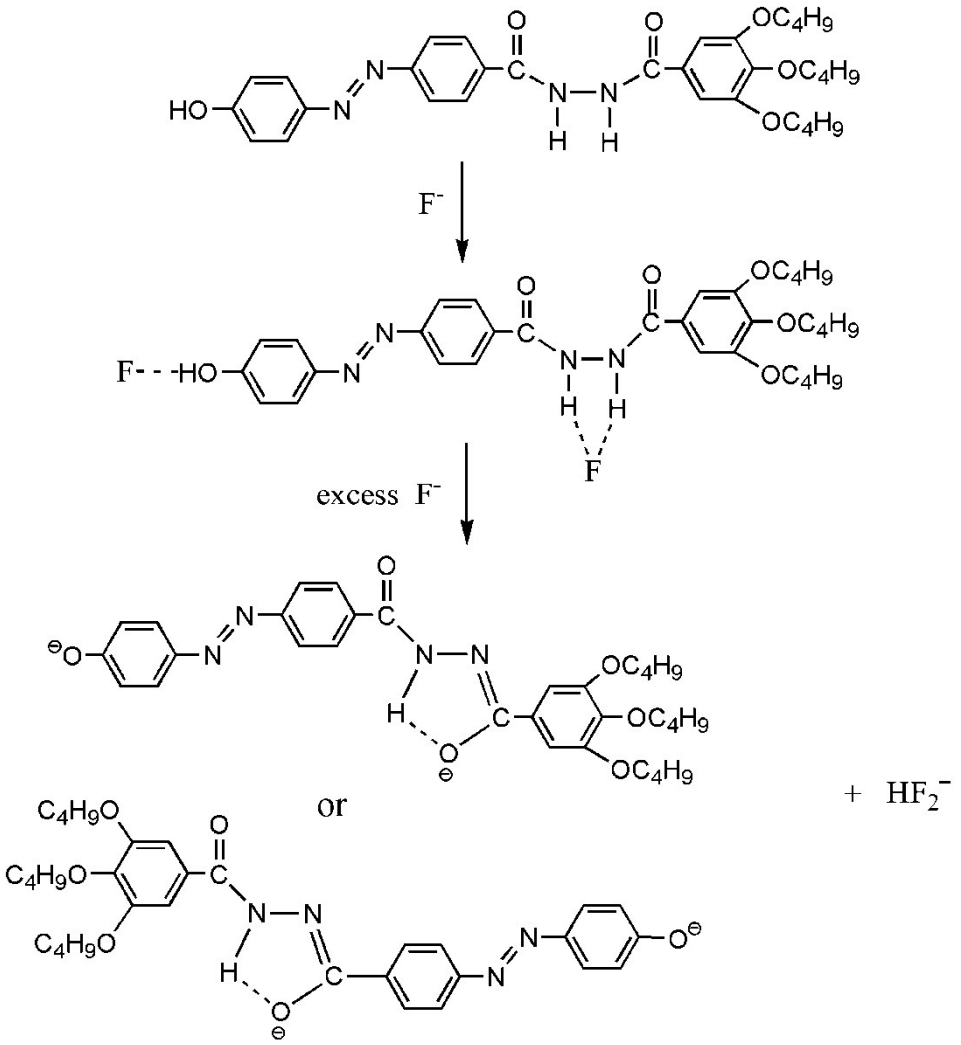


Figure S10 Partial ^{1}H NMR spectra of BNB-t4 (5 mM) in DMSO-*d*6 upon the addition of F^- (a) free, (b) 0.5 equiv., (c) 2 equiv., (d) 4 equiv., (e) 6 equiv., (f) 8 equiv. and (g) 10 equiv.



Scheme S1 The probable mechanism for BNB-t4 to F^-.

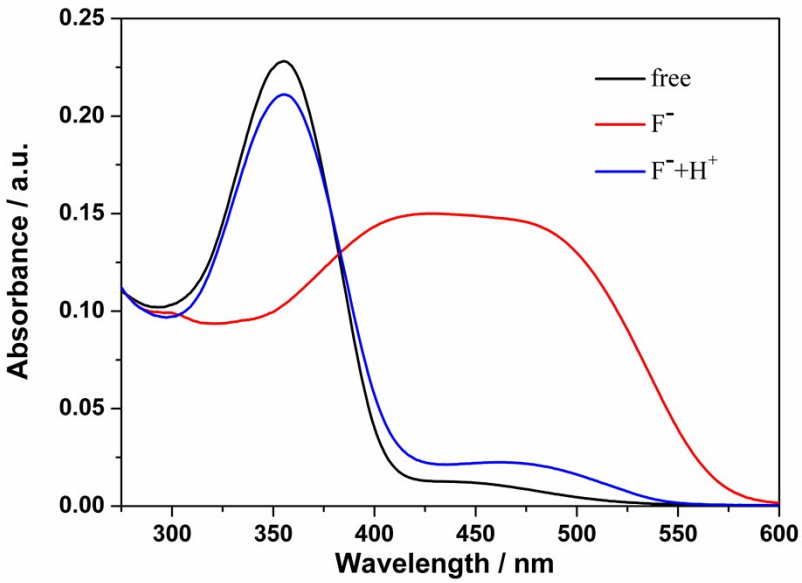
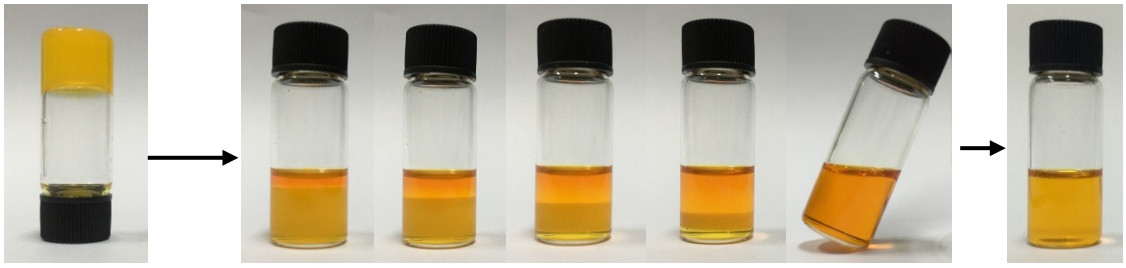
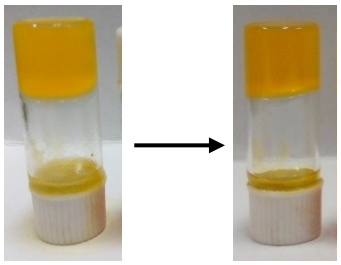


Figure S11 UV-vis spectra of BNB-t4 (1×10^{-5} mol L^{-1}) in chloroform, upon addition of 10 equiv. of F^- (10 equiv.), and then added H^+ (such as $HClO_4$ or methanol) (10 equiv.).



(a) (b) (c) (d) (e) (f) (g)

Figure S12 Photographs of (a) the chloroform gel of BNB-t4 (8.0 mg/mL), (b) immediately after addition of solid tetrabutylammonium acetate (TBAA) (10 equiv.), (c) after 20 min, (d) after 40 min, (e) after 60 min, (f) after 88 min, (g) addition of 0.05 mL MeOH.

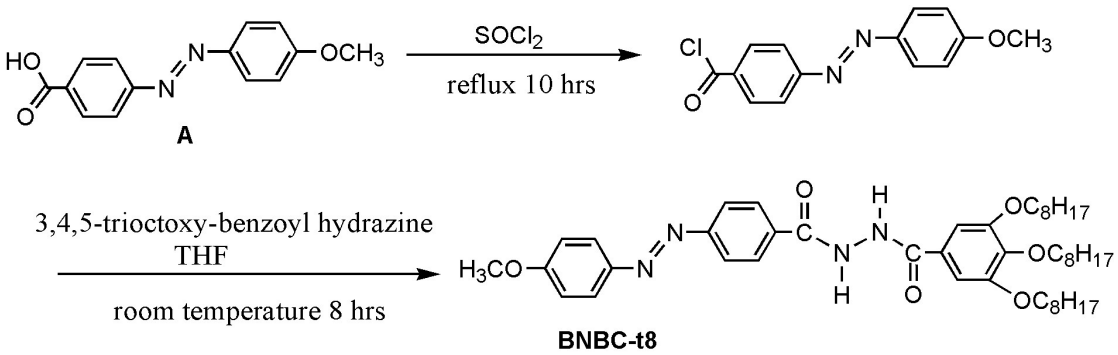


(a) (b)

Figure S13 Photographs of (a) the chloroform gel of BNB-t4 (8.0 mg/mL) (b) immediately after addition of solid tetrabutylammonium iodide (TBAI) (10 equiv.).

Experimental Section

Synthesis



Scheme S2. Synthetic route for BNBC-t8.

The compound, N-(3,4,5-octanoxyphenyl)-N'-4-[(4-methoxyphenyl)azophenyl] benzohydrazide (BNBC-t8), was synthesized following the mechanism shown in Scheme S2.

4- (4'-methoxyphenyl)azobenzoic acid (A, 2.63 g, 0.01 mol) and thionyl chloride (50 mL) were refluxed for 10 *h*. 4-(4'- methoxyphenyl)azobenzoic acid chloride was collected after removing unreacted thionyl chloride. 4-(4'- methoxyphenyl)azobenzoic acid chloride was dissolved in tetrahydrofuran, 3,4,5-trioctoxy-benzoyl hydrazine was added slowly, and the resulting mixture was stirred for 8 *h*. The resulted reaction mixture was poured into an excess

of ice water, and the precipitate was recrystallized from acetone.

^{1}H NMR (400 MHz, DMSO-*d6*), (ppm, from TMS): 10.65 (s, 1H), 10.46 (s, 1H),8.17–8.07 (d, 2H, J=8.08), 8.03–7.87 (m, 4H), 7.24 (s, 2H), 7.21–7.13 (d, 2H, J =8.60), 4.08–3.97 (m, 6H), 3.96–3.85 (m, 3H), 1.82–1.59 (m, 6H), 1.52–1.18 (m, 30H), 0.94–0.78 (m, 9H).

FT-IR (KBr, pellet, cm^{-1}): 3334, 3237, 2927, 2856, 1666, 1638, 1586, 1550, 1498, 1465, 1427, 1390, 1328, 1253, 1180, 1122, 1029, 902, 841, 749, 723, 592, 555.

Elemental analysis: calculated for $C_{45}H_{66}N_4O_6$ (%): C, 71.21; H, 8.76; N, 7.38. Found: C, 71.35; H, 8.87; N, 7.21.