Supplementary Information

A hydrazide organogelator for the fluoride sensing with hyperchromicity and gel-to-sol transition

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1. Scheme of DPH synthesis

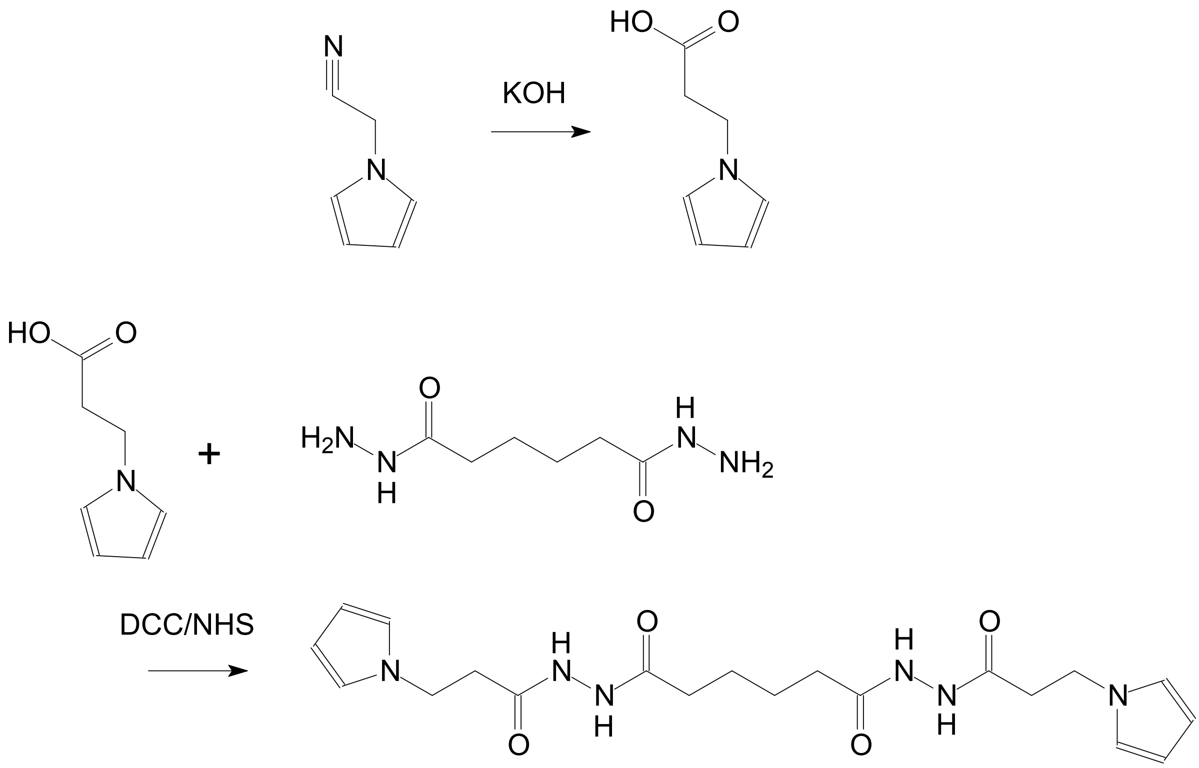

Figure S1. Scheme of DPH synthesis. 1-(2-Cyanoethyl)-pyrrole was hydrolyzed to Py-COOH with KOH. DPH was synthesized by conjugation of Py-COOH with adipic acid through DCC/NHS chemistry.

2. ^{1}H NMR spectroscopy of Py-COOH

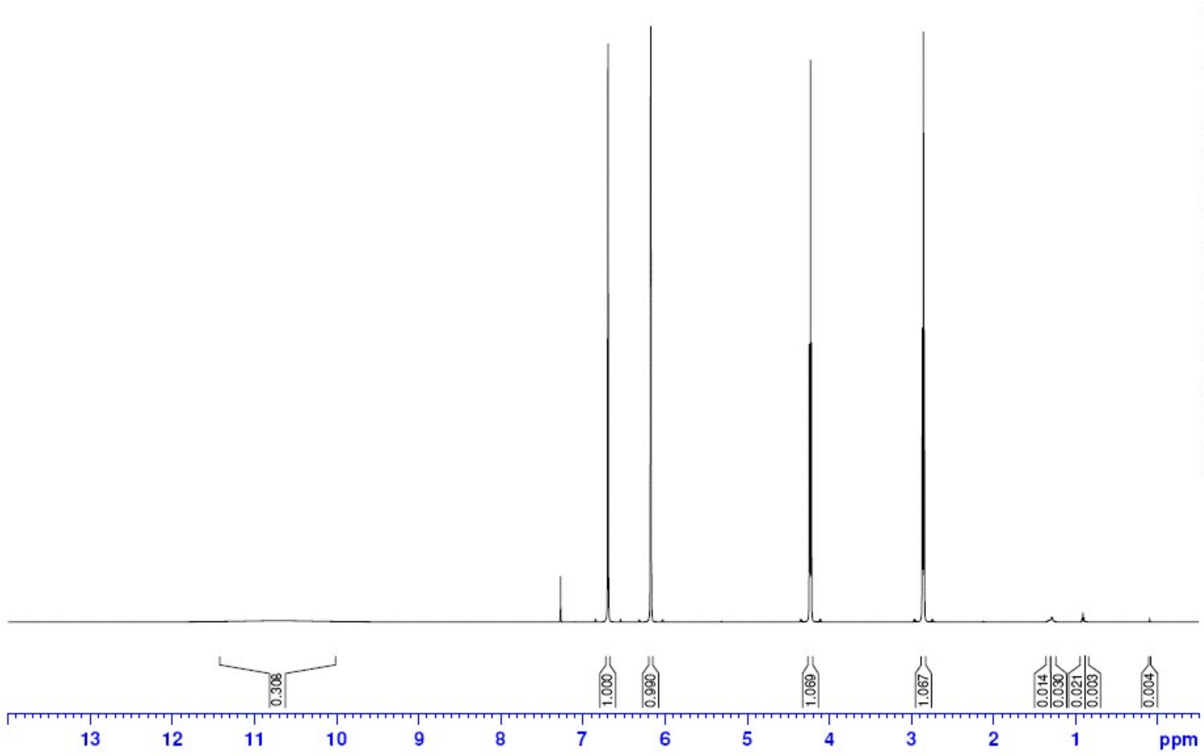

Figure S2. ^{1}H-NMR spectroscopy of the Py-COOH. Spectrum showed peaks at δ 2.85 (m, 2H); 4.24 (m, 2H); 6.03 (m, 2H-CH of pyrrole); 6.69 (m, 2H-CH of pyrrole); 10.69 (bs, H-OH of carboxyl).

3. [1]H NMR spectroscopy of DPH

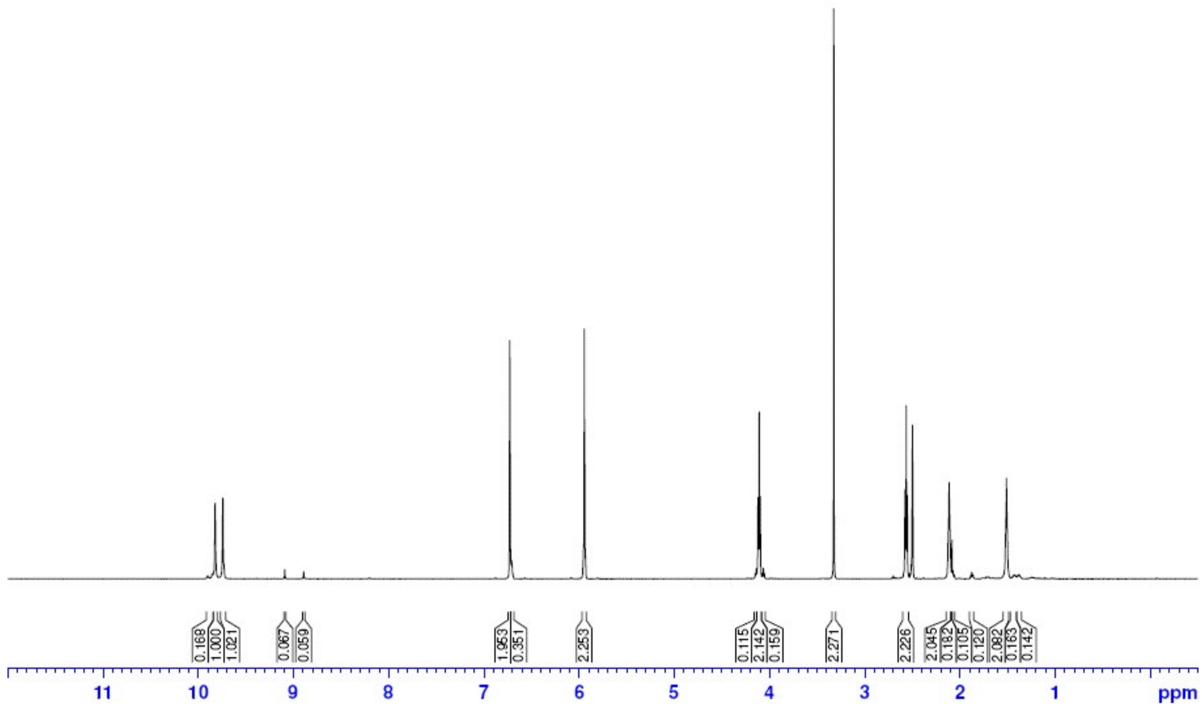

Figure S3. ^{1}H-NMR spectroscopy of the DPH. Spectrum showed peaks at δ 1.51 (m, 4H); 2.11 (m, 4H); 2.59 (m, 4H); 4.14 (s, 4H); 5.95 (m, 4H-CH of pyrrole); 6.71 (m, 4H-CH of pyrrole).

4. ^{13}C-NMR spectroscopy of Py-COOH

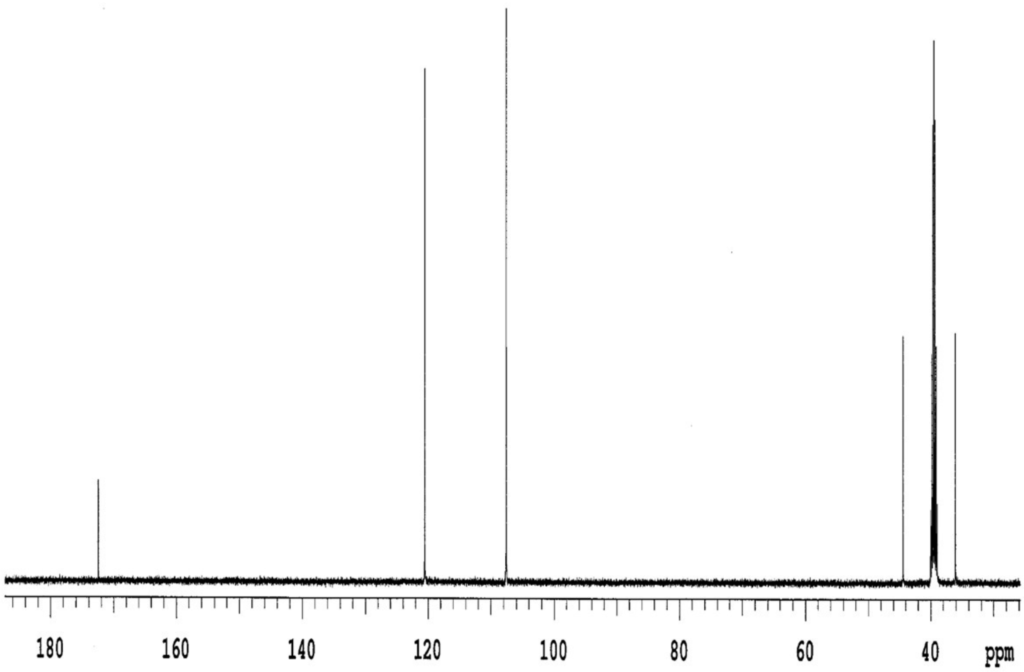

Figure S4. ^{13}C-NMR spectroscopy of Py-COOH. Spectrum of Py-COOH is as follows: δ 172.53, 120.54, 107.61, 44.46, 36.12.

5. ^{13}C-NMR spectroscopy of DPH

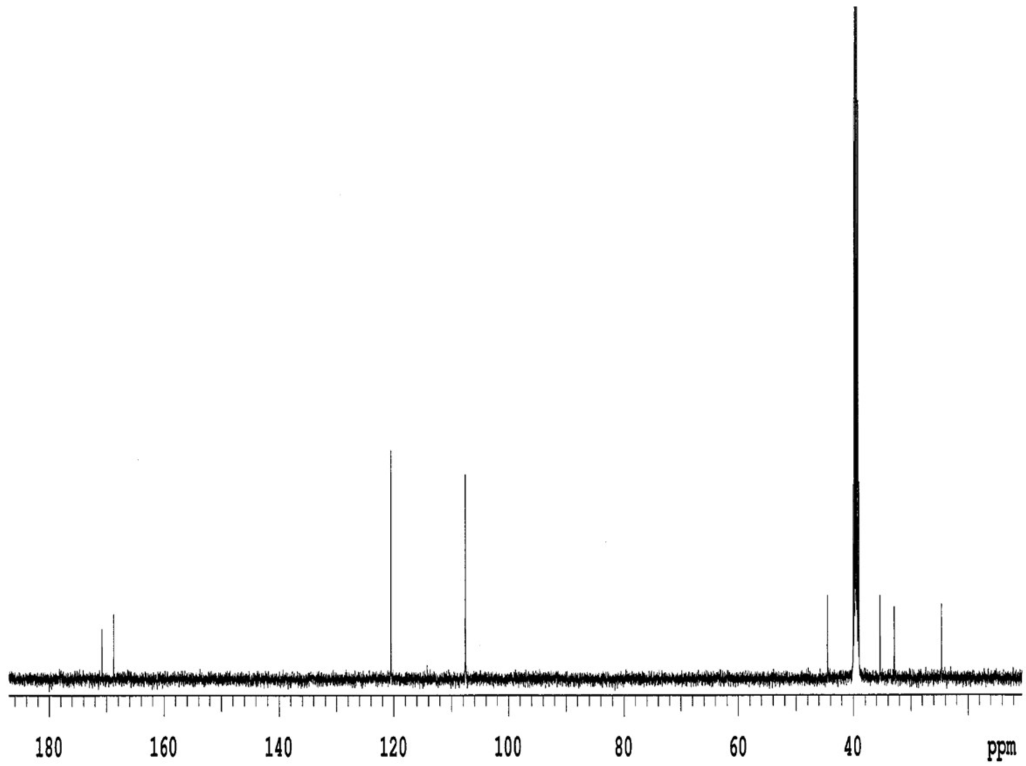

Figure S5. ^{13}C-NMR spectroscopy of DPH. Spectrum of DPH is as follows: δ 170.83, 168.72, 120.53, 107.60, 44.50, 35.38, 32.91, 24.66.

6. High-resolution mass spectroscopy of Py-COOH

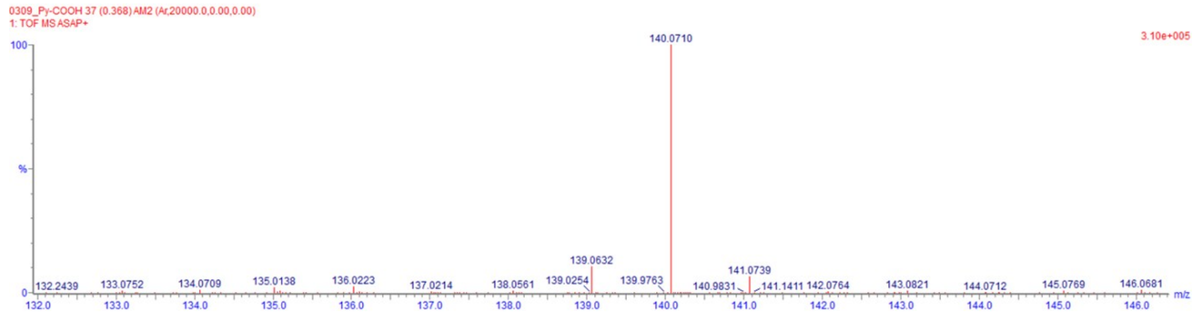

Figure S6. High-resolution mass spectroscopy of Py-COOH. HRMS of Py-COOH calculated for C7H10NO2: 140.07. Found: 140.07.

7. High-resolution mass spectroscopy of DPH

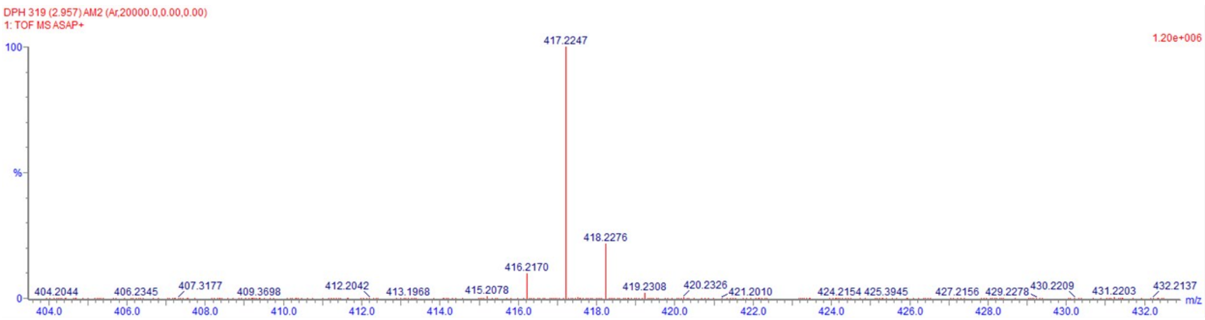

Figure S7. High-resolution mass spectroscopy of DPH. HRMS of DPH calculated for C20H28N6O4: 416.21. Found: 417.22.

8. Selective detection of F^{-} ion without interference by other anions

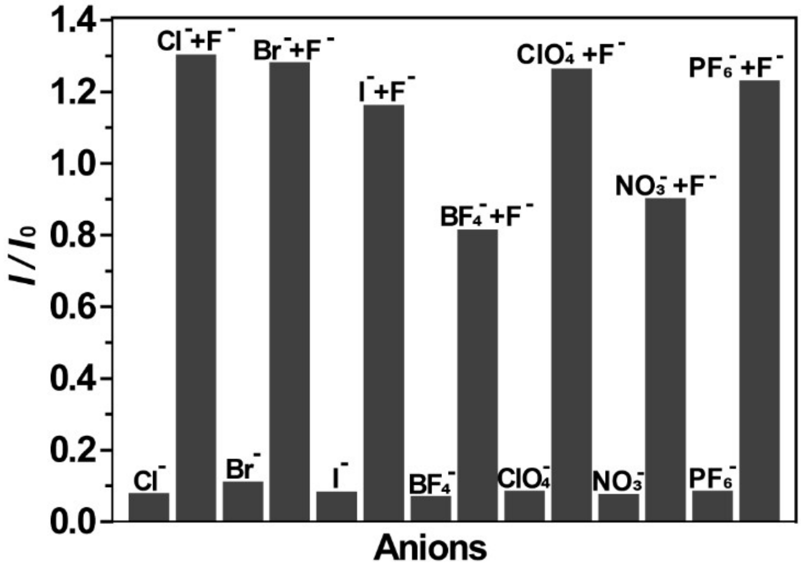

Figure S8. Selective detection of fluoride ion using DPH solution in DMF (DPH conc. = 0.1 mM). 5 equiv. anions were added to DPH solution for test. Presence of other anions did not interfere the selective interaction of DPH with fluoride ion (I_0: absorbance intensity of DPH).

9. Determination of F^- ion content in toothpaste

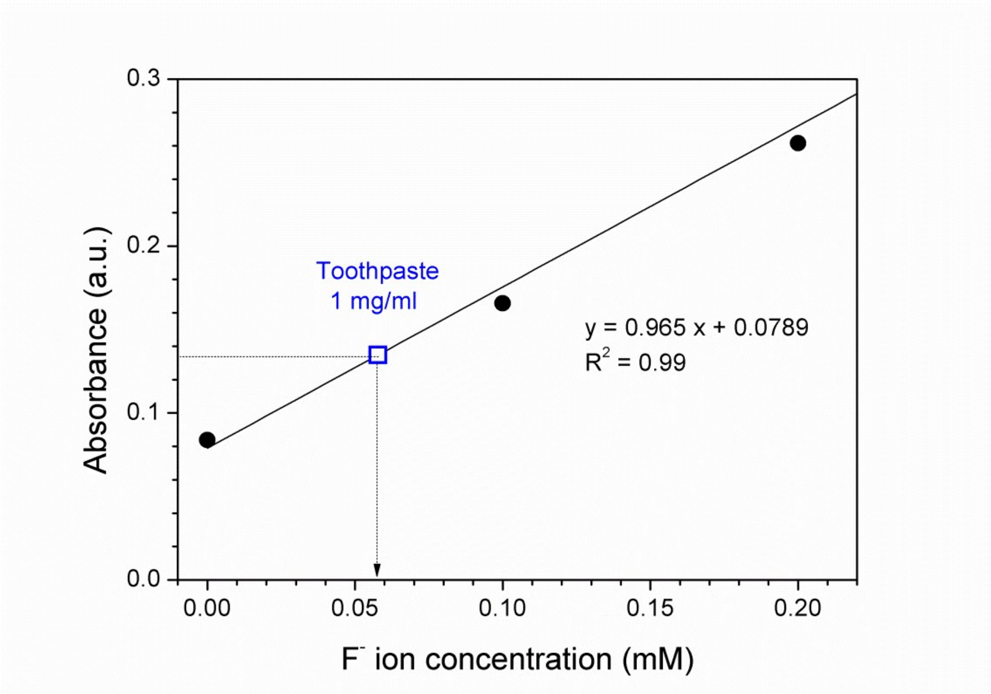

Figure S9. Determination of F- ion content in 1 mg/ml solution of toothpaste. The calibration curve was drawn using the tetrabutylammonium fluoride solutions at various concentrations.

10. Benesi-Hildebrand plot

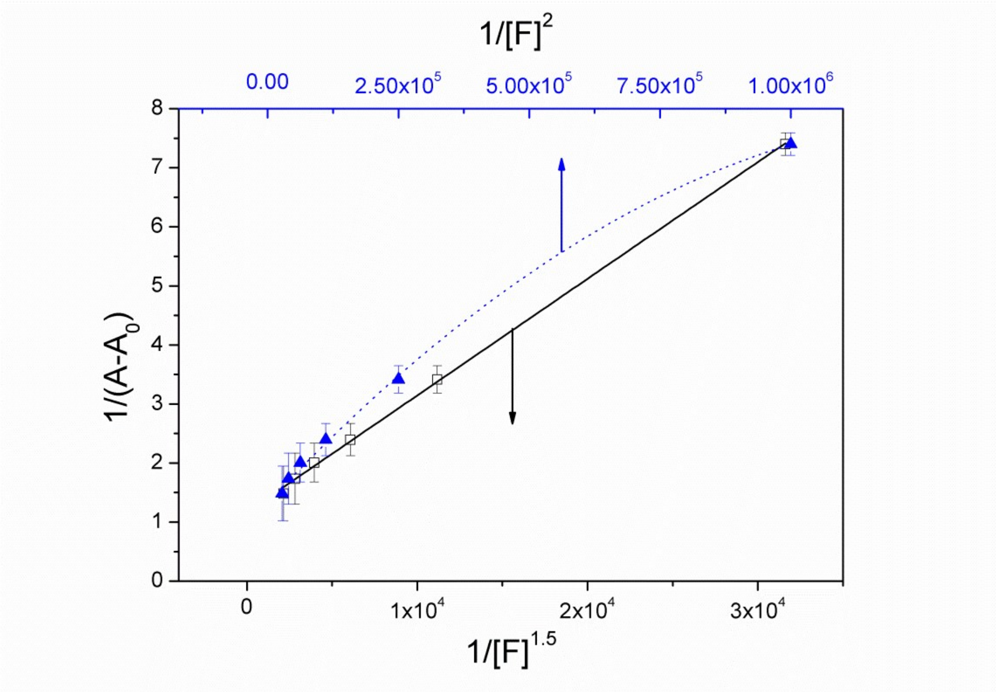

Figure S10. Benesi-Hildebrand plots were drawn with reciprocals of $[F\text{-}]^{1.5}$ and $[F\text{-}]^{2}$.

11. Proposed binding mechanism of F$^-$ ion to DPH

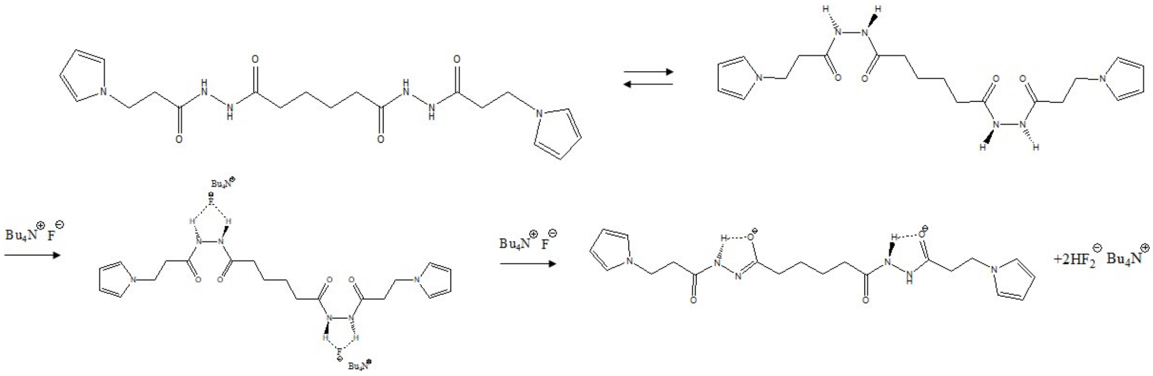

Figure S11. The potential mechanism of F- binding to the hydrazide group of DPH resulting in isomeric transformation.

12. Comparison of limit of detection (LOD) for F^- ion

No.	Chemosensor	LOD (μM)	Medium	Recognition motif	Ref.
1	N-(3,4,5-tributoxyphenyl)-N0-4-[(4-hydroxyphenyl) azophenyl] benzohydrazide	0.043	$CHCl_3$	hydrazide	1
2	bis(4-(2,4-dimethyl-phenylazo)-phenol)diethylene triimine	1.0	DMSO, DMF	azophenol	2
3	Copilar[5]arene PF5	0.026	water	Pillar[5]arene	3
4	1,8-naphthalimide,4-(2,2-dichiloroacetamide)-N-n-butyl-naphthalimide	0.52	CH_3CN	amino group	4
5	phenolphthalein-dialdehyde-(2-pyridyl) hydrazine-Al complex	0.13	Water/ DMSO mix	hydrazine-Al	5
6	Isophorone-boronate ester	0.033	THF	Picanol boronate	6
7	3-[[bis(pyridylmethyl)amino] methyl]-1,2-dihydroxy anthraquinone - $NiCl_2$ complex	1.3	CH_3CN	hydrazine-Ni	7
8	(2E)-2-(naphthylmethylene) hydrazinecarbothioamide	140	DMSO/ H_2O mix	Thiosemicarbazone-Fe complex	8
9	AM-PDIs	0.14	CH_2Cl_2	hydrazide	9
10	julolidine-functionalized N-(2-aminoethyl)-5-nitropyridin-2-amine	19.4	DMSO	hydrazine	10
11	DPH	0.49	DMF, DMSO	hydrazide	This work

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