# Electronic Supporting Information

## A novel hydroxyl-containing polyimide as the colorimetric and ratiometric chemosensor for reversible detection of fluoride ion

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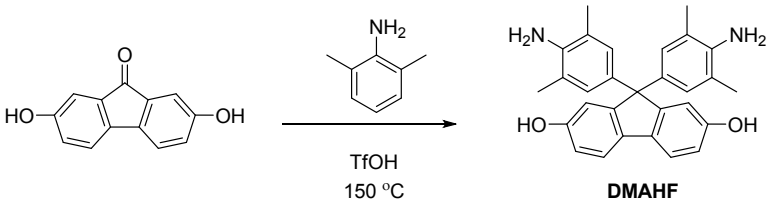
**Contents**

## 1. Synthesis and characterization of diamine monomer

***9,9-bis(4-amino-3,5-dimethylphenyl)-9H-fluorene-2,7-diol (DMAHF)***




**Scheme 1** Synthesis route of diamine monomer **DMAHF**

2,7-Dihydroxy-9-fluorenone (10.6 g, 0.05 mol), 2,6-dimethylaniline (74.6 g, 0.40 mol) and methylsulfonic acid (2.40 g, 0.025 mol) were added to a 500 mL round-bottomed flask equipped with a magnetic stirrer and reflux condenser. A stream of argon was introduced and the mixture was heated at 150 °C for 14 h. After that, the reaction mixture was cooled down to 110 °C, and then poured into triethylamine (200 mL) and stirred at 110 °C for 20 min. The precipitated product was isolated by suction filtration and washed thoroughly with ethanol and distilled water several times at room temperature before drying in a vacuum oven. Yield: 72.6%, $^{1}$H NMR (DMSO-$d_6$, 400 MHz, $\delta$, ppm): 9.20 (s, 2H), 7.42 (d, $J$ = 8.7 Hz, 2H), 6.68-6.60 (m, 4H), 6.52 (s, 4H), 4.40 (s, 4H), 1.95 (s, 12H); $^{13}$C NMR (DMSO-$d_6$, 151 MHz, $\delta$, ppm): 156.3, 154.1, 142.9, 134.2, 131.5, 127.8, 120.5, 112.0, 114.4, 113.4, 63.8, 18.6; ESI-HRMS, *m/z* (%): Calcd for $C_{29}H_{29}N_2O_2^+$ ([M+H]$^+$): 437.2224 (100), Found: 437.2226 (100).

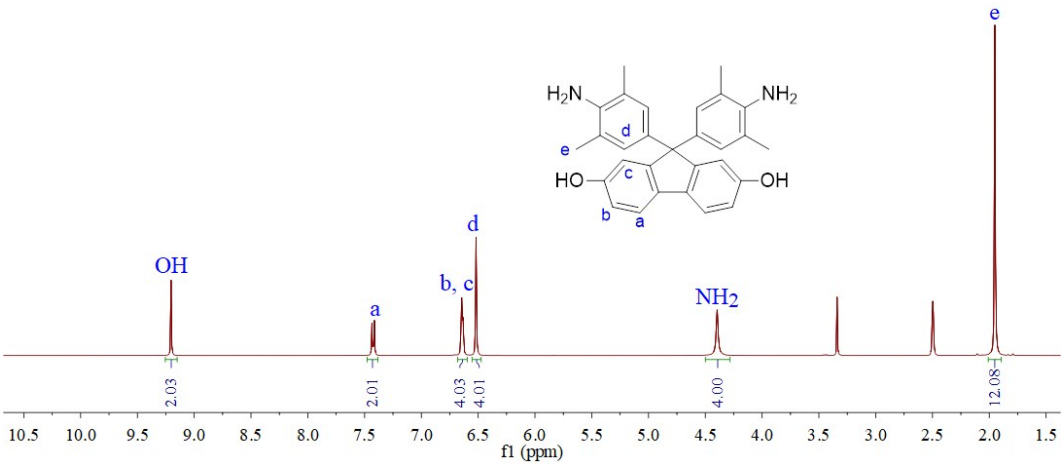



**Fig. S1** $^{1}$H NMR spectrum of diamine monomer **DMAHF**

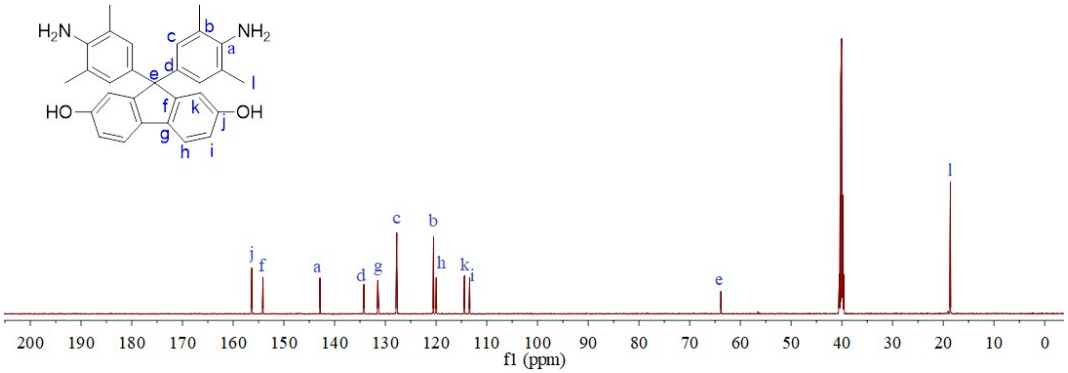



**Fig. S2** $^{13}$C NMR spectrum of diamine monomer **DMAHF**

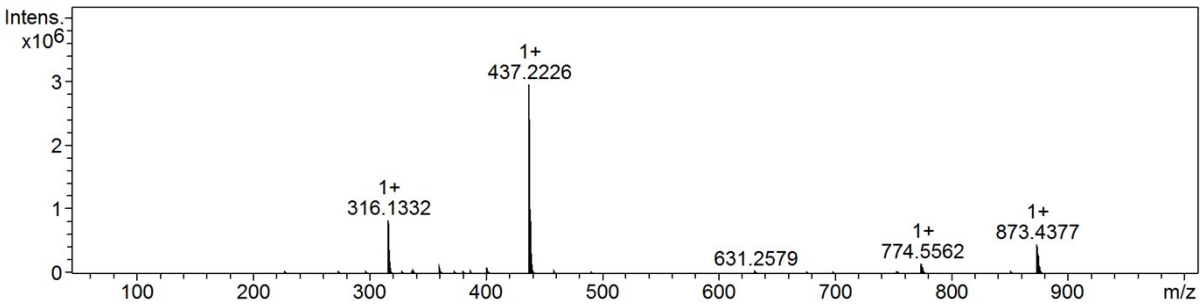



**Fig. S3** HRMS spectrum of diamine monomer **DMAHF**

## 2. Characterization spectra of PI-1 film

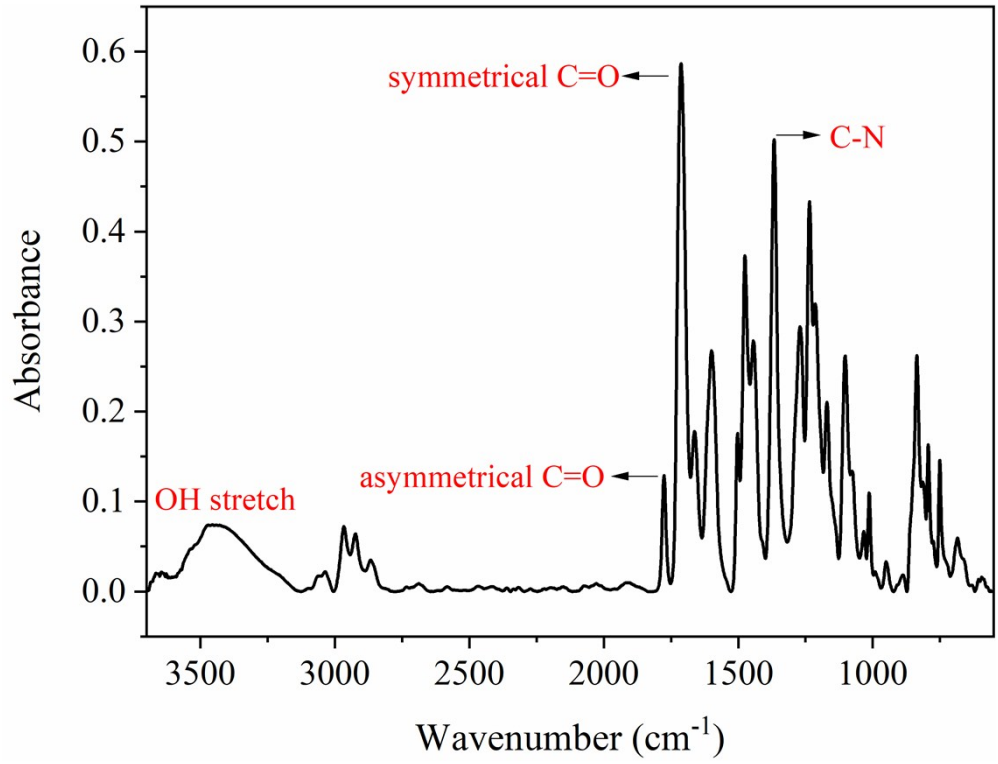



**Fig. S4** IR spectrum of **PI-OH** film

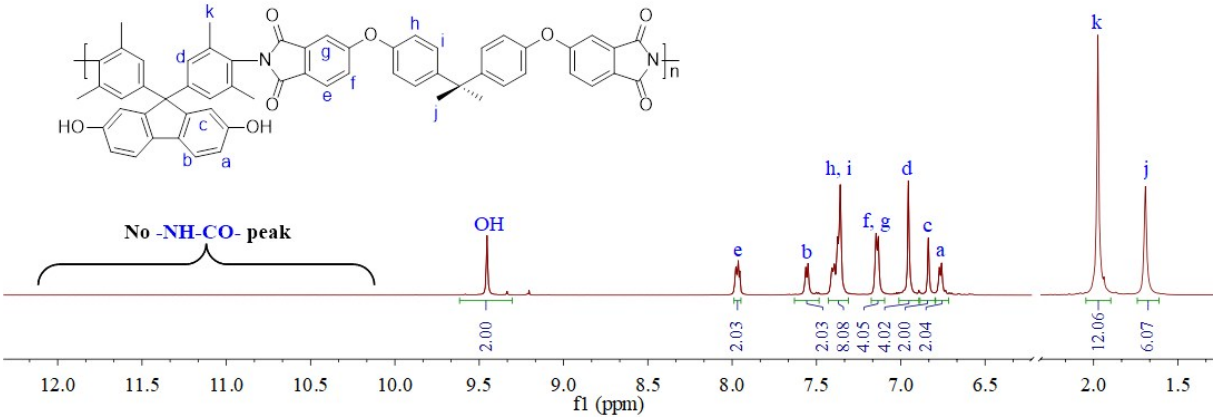



**Fig. S5** $^{1}$H NMR spectrum of **PI-OH**

## 3. TGA and DMA curves of PI-OH film

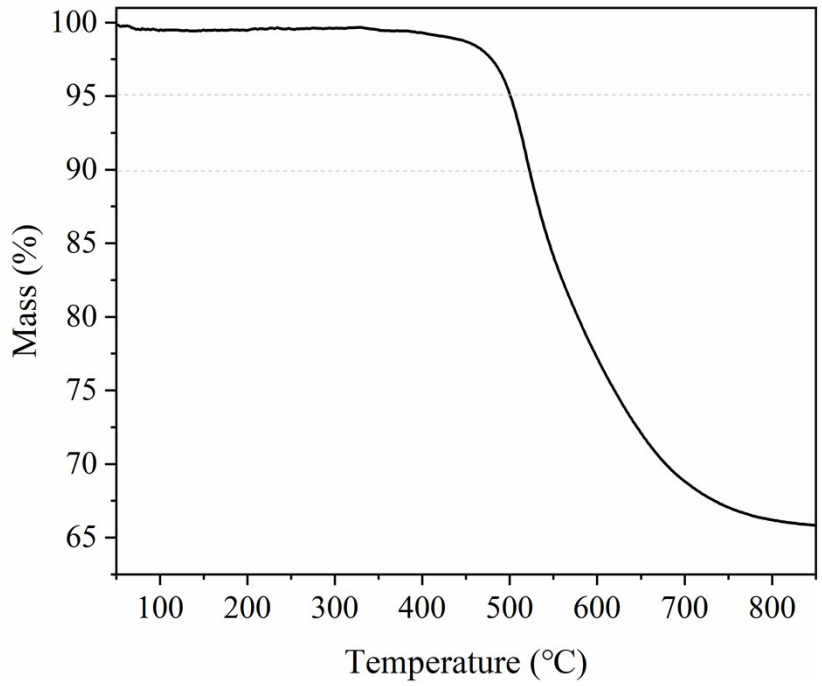



**Fig. S6** TGA curve of **PI-OH** film

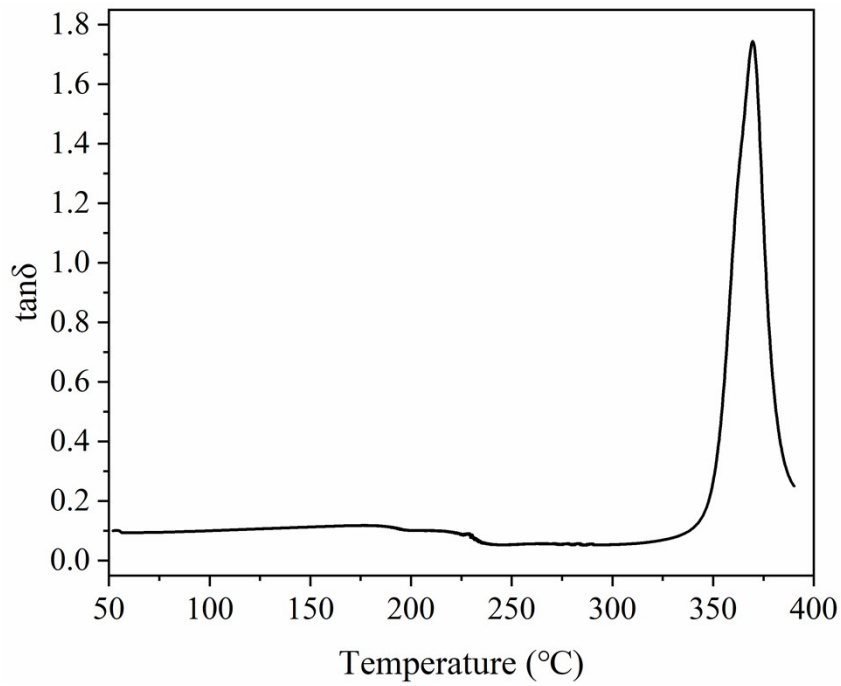



**Fig. S7** DMA curve of **PI-OH** film

## 4. Time-dependent experiments in the presence of $F^-$

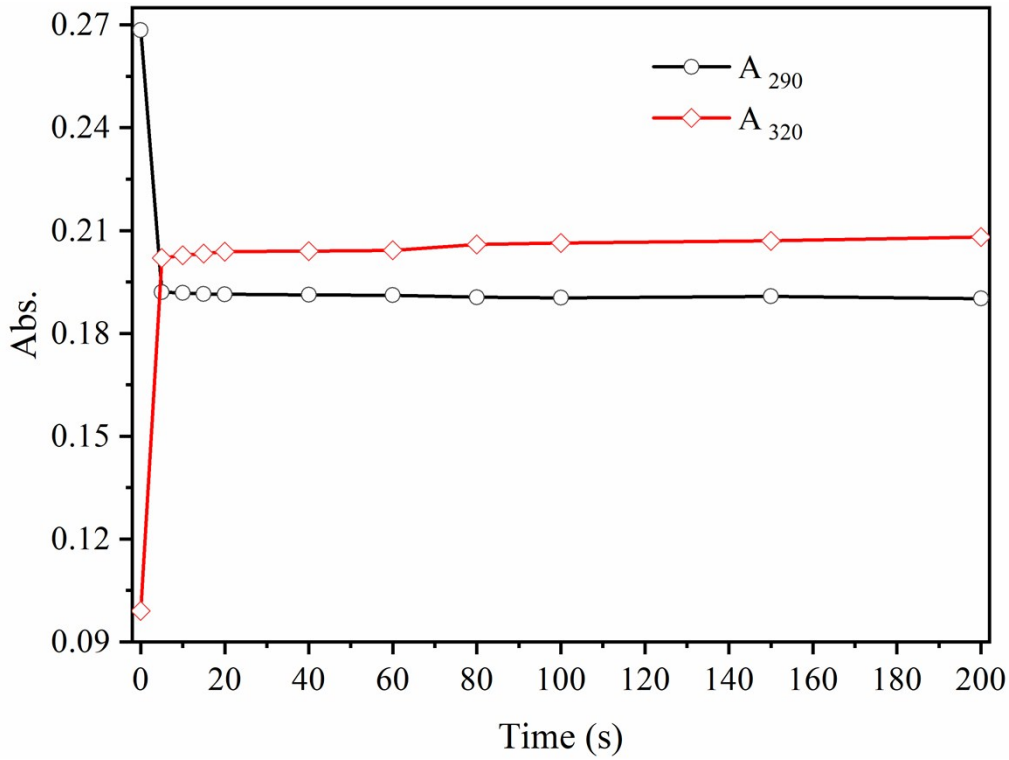
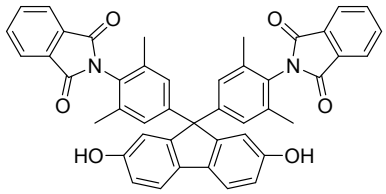



**Fig. S8** Time-dependent UV absorption (at 290 and 320 nm) of chemosensor **PI-OH** in DMSO

## 5. Cartesian coordinates and total energies of stationary points

All calculations were performed with the Gaussian 09 program. The Cartesian coordinates of all stationary points are listed. For each structure, absolute energies obtained at the B3LYP/6-31G (d) level are shown.




**1**

**Fig. S9** Model compound **1** for theoretical calculation

**Table S1**. Compound **1**, Total energy and atomic coordinates.

**1** $E_{tot}$ = -2295.00259486 a.u.

| Atom | X | Y | Z | | | | |
|---|---|---|---|---|---|---|---|
| C | 8.615085 | -3.99174 | -0.72389 | H | -0.694618 | 4.020295 | -5.271149 |
| C | 8.887912 | -3.57157 | 0.584798 | N | -4.869993 | -1.327699 | 0.047895 |
| C | 8.014284 | -2.71383 | 1.265576 | C | -5.769516 | -1.401773 | -1.041058 |
| C | 6.873486 | -2.30002 | 0.592871 | C | -6.873485 | -2.300159 | -0.592858 |
| C | 6.602462 | -2.71737 | -0.70984 | C | -6.602479 | -2.717181 | 0.709965 |
| C | 7.460236 | -3.56719 | -1.3935 | C | -5.313896 | -2.102823 | 1.144248 |
| C | 5.769381 | -1.40175 | 1.040965 | C | -8.014163 | -2.71432 | -1.26555 |
| N | 4.869744 | -1.3281 | -0.04796 | C | -8.887687 | -3.572059 | -0.584646 |
| C | 5.313744 | -2.10333 | -1.14417 | C | -8.614879 | -3.991895 | 0.724151 |
| O | 4.74219 | -2.2205 | -2.20787 | C | -7.460152 | -3.566992 | 1.393754 |
| O | 5.638849 | -0.84067 | 2.108385 | O | -4.742366 | -2.219684 | 2.20799 |
| C | 3.658503 | -0.5588 | -0.04523 | O | -5.638973 | -0.840964 | -2.108629 |
| C | 2.576206 | -0.98413 | 0.743534 | H | 9.311826 | -4.657445 | -1.225516 |
| C | 1.40372 | -0.2252 | 0.718345 | H | 9.792076 | -3.917848 | 1.077549 |
| C | 1.281907 | 0.928134 | -0.06674 | H | 8.214582 | -2.381486 | 2.279506 |
| C | 2.382666 | 1.32237 | -0.83155 | H | 7.237845 | -3.88584 | -2.407226 |
| C | 3.578897 | 0.597705 | -0.8362 | H | 0.560957 | -0.560198 | 1.315263 |
| C | 0.000004 | 1.785572 | -2.9E-05 | H | 2.320025 | 2.217337 | -1.441197 |
| C | -1.28198 | 0.928239 | 0.066588 | H | -0.187986 | 6.186286 | -1.306547 |
| C | 0.139835 | 2.769562 | 1.179567 | H | -0.491931 | 5.676372 | -3.712358 |
| C | 0.092478 | 4.103269 | 0.726544 | H | -0.363563 | 1.458751 | -2.893967 |
| C | -0.09203 | 4.103365 | -0.72635 | H | 0.363207 | 1.458384 | 2.893932 |
| C | -0.13971 | 2.769715 | -1.1795 | H | 0.492514 | 5.675889 | 3.71274 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.21942 | 5.151482 | -1.63779 | H | 0.188859 | 6.186111 | 1.306959 |
| C | -0.39121 | 4.865338 | -2.99304 | H | -2.320106 | 2.217708 | 1.440784 |
| C | -0.43807 | 3.536376 | -3.43414 | H | -0.561054 | -0.560248 | -1.315256 |
| C | -0.31435 | 2.477336 | -2.52353 | H | 4.887166 | 0.397682 | -2.544105 |
| C | 0.314287 | 2.477013 | 2.523584 | H | 5.675873 | 1.073514 | -1.114417 |
| C | 0.438168 | 3.535932 | 3.434309 | H | 4.561002 | 2.071186 | -2.061935 |
| C | 0.391659 | 4.86495 | 2.993336 | H | 1.672272 | -2.492382 | 1.987933 |
| C | 0.220043 | 5.151266 | 1.638103 | H | 3.044722 | -3.080975 | 1.03569 |
| C | -2.38277 | 1.322672 | 0.831243 | H | 3.32825 | -2.066934 | 2.454279 |
| C | -3.57905 | 0.598088 | 0.835872 | H | -1.672423 | -2.492723 | -1.987449 |
| C | -3.65868 | -0.55851 | 0.045044 | H | -3.327981 | -2.066522 | -2.454683 |
| C | -2.57637 | -0.984 | -0.74361 | H | -3.045672 | -3.080662 | -1.035948 |
| C | -1.40383 | -0.22515 | -0.71842 | H | -4.561183 | 2.071844 | 2.061253 |
| O | -0.60303 | 3.206252 | -4.75234 | H | -5.676011 | 1.074101 | 1.113752 |
| O | 0.60293 | 3.205642 | 4.752483 | H | -4.887552 | 0.398479 | 2.543687 |
| C | 4.739272 | 1.060553 | -1.68374 | H | -8.214449 | -2.38223 | -2.279567 |
| C | 2.659228 | -2.22408 | 1.600505 | H | -9.791757 | -3.918606 | -1.077384 |
| C | -2.65946 | -2.22397 | -1.60056 | H | -9.311538 | -4.657617 | 1.225878 |
| C | -4.73949 | 1.06116 | 1.683207 | H | -7.237775 | -3.885391 | 2.40756 |
| H | 0.694591 | 4.019615 | 5.271393 | | | | |

**Table S2**. Complex **1**-2F$^-$, Total energy and atomic coordinates.

**1**-2F$^-$ $E_{tot}$ = -2494.74162783 a.u.

| Atom | X | Y | Z | | | | |
|---|---|---|---|---|---|---|---|
| C | -8.495979 | -4.317203 | 0.040289 | C | 8.233069 | -4.5081 | -1.176854 |
| C | -8.790139 | -3.665779 | -1.173208 | C | 8.979965 | -3.535738 | -0.48401 |
| C | -7.939921 | -2.681435 | -1.684331 | C | 8.371506 | -2.374729 | 0.001242 |
| C | -6.796811 | -2.367255 | -0.956531 | O | 6.369804 | -0.082437 | 0.768059 |
| C | -6.504582 | -3.015107 | 0.252152 | O | 3.90684 | -3.289959 | -1.508025 |
| C | -7.345889 | -3.995694 | 0.766674 | F | -0.634941 | 6.237931 | -5.032854 |
| C | -5.722891 | -1.383285 | -1.235092 | F | 0.590559 | -0.070412 | 5.293307 |
| N | -4.81712 | -1.491406 | -0.153094 | H | -9.17471 | -5.079981 | 0.414577 |
| C | -5.232445 | -2.467661 | 0.783261 | H | -9.691987 | -3.935127 | -1.717987 |
| O | -4.649344 | -2.774532 | 1.809983 | H | -8.154123 | -2.171073 | -2.619247 |
| O | -5.615597 | -0.633395 | -2.191589 | H | -7.105917 | -4.489463 | 1.704273 |
| C | -3.61581 | -0.710561 | -0.023931 | H | -0.529402 | -0.408562 | -1.379366 |
| C | -2.531209 | -0.967189 | -0.87912 | H | -2.297642 | 1.792535 | 1.840924 |
| C | -1.372258 | -0.202943 | -0.726569 | H | 0.1687 | 5.80901 | 2.331733 |
| C | -1.260496 | 0.801708 | 0.244098 | H | 0.433496 | 4.915557 | 4.641567 |
| C | -2.362167 | 1.027634 | 1.074708 | H | 0.330207 | 0.882194 | 3.157894 |
| C | -3.543811 | 0.288568 | 0.959145 | H | -0.357143 | 1.845437 | -2.588574 |
| C | 0.007028 | 1.677091 | 0.326602 | H | -0.413912 | 6.144374 | -2.705033 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 1.283693 | 0.835629 | 0.114709 | H | -0.139137 | 6.239135 | -0.22307 |
| C | -0.133755 | 2.844433 | -0.683006 | H | 2.21738 | 2.1868 | -1.267833 |
| C | -0.075498 | 4.084909 | 0.004032 | H | 0.66398 | -0.723993 | 1.464344 |
| C | 0.090328 | 3.846376 | 1.41813 | H | 0.572721 | 0.931371 | 5.334859 |
| C | 0.136157 | 2.448336 | 1.665993 | H | -0.600875 | 5.285682 | -4.702465 |
| C | 0.199804 | 4.733451 | 2.50495 | H | 6.274634 | -5.080371 | -1.929583 |
| C | 0.346941 | 4.242634 | 3.790958 | H | 8.731814 | -5.402016 | -1.54401 |
| C | 0.395749 | 2.83294 | 4.071539 | H | 10.044319 | -3.693209 | -0.326096 |
| C | 0.285561 | 1.944742 | 2.940686 | H | 8.934903 | -1.61591 | 0.537138 |
| C | -0.298136 | 2.788746 | -2.051749 | C | 4.588473 | 1.016209 | -1.792776 |
| C | -0.397325 | 3.994613 | -2.832392 | H | 5.460345 | 1.358623 | -1.222649 |
| C | -0.334256 | 5.239427 | -2.110205 | H | 4.934013 | 0.230931 | -2.476892 |
| C | -0.180486 | 5.278362 | -0.736277 | H | 4.223885 | 1.853073 | -2.395656 |
| C | 2.325723 | 1.26111 | -0.713691 | C | 2.747403 | -2.422531 | 1.480322 |
| C | 3.50021 | 0.51671 | -0.871831 | H | 2.654362 | -3.29817 | 0.826332 |
| C | 3.6311 | -0.686159 | -0.161943 | H | 3.721144 | -2.488735 | 1.98051 |
| C | 2.613494 | -1.139001 | 0.69588 | H | 1.971842 | -2.480985 | 2.249242 |
| C | 1.4541 | -0.369932 | 0.80962 | C | -2.600363 | -2.036765 | -1.943194 |
| O | 0.529738 | 2.403816 | 5.278577 | H | -2.947126 | -2.994209 | -1.534376 |
| O | -0.532595 | 3.949389 | -4.113027 | H | -3.294103 | -1.751112 | -2.742715 |
| N | 4.821736 | -1.477183 | -0.322516 | H | -1.61432 | -2.197924 | -2.389254 |
| C | 4.85594 | -2.725086 | -0.987754 | C | -4.699565 | 0.5638 | 1.891693 |
| C | 6.264196 | -3.182015 | -0.909272 | H | -5.645033 | 0.671548 | 1.345515 |
| C | 7.008187 | -2.213194 | -0.220861 | H | -4.827303 | -0.253759 | 2.611248 |
| C | 6.097827 | -1.107581 | 0.165296 | H | -4.524729 | 1.485788 | 2.453876 |
| C | 6.86335 | -4.33883 | -1.396695 | | | | |

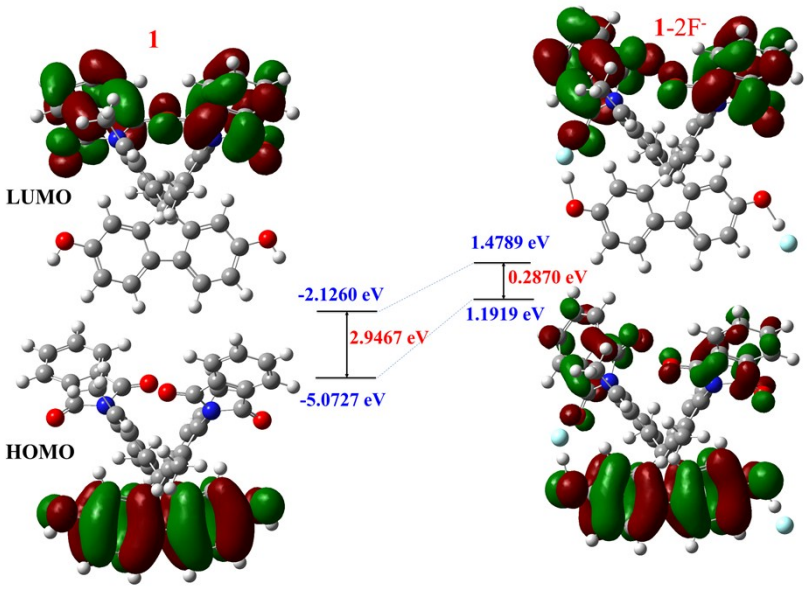



**Fig. S10** Calculated (DFT B3LYP/6-31G (d) level) HOMO-LUMO energy levels

## 6. UV-*vis* absorption and IR spectra change of PI-OH film upon immersing in the solution of $F^-$

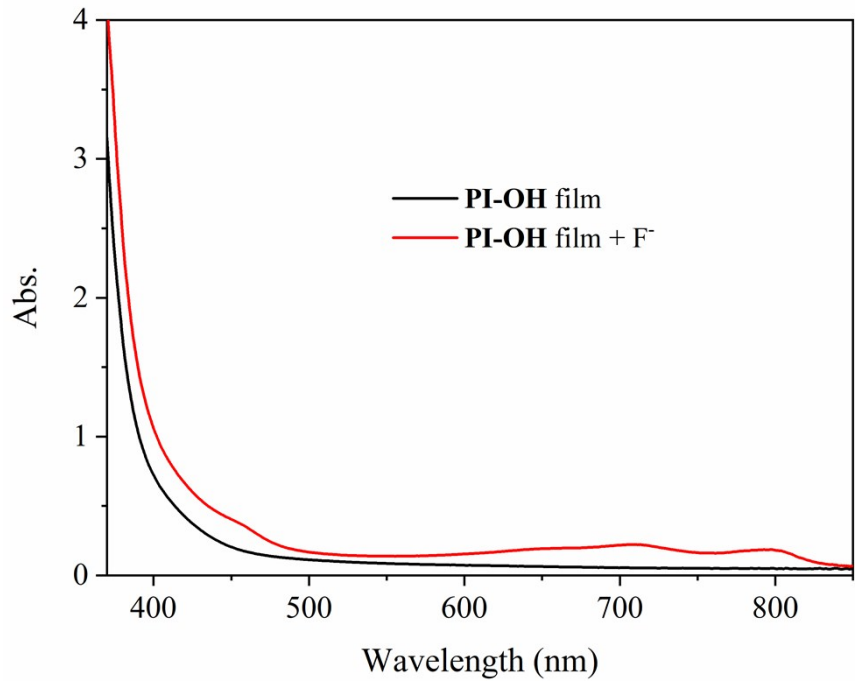



**Fig. S11** UV-*vis* absorption spectral change of **PI-OH** film upon immersing in the solution of $F^-$ ($10^{-1}$ M).

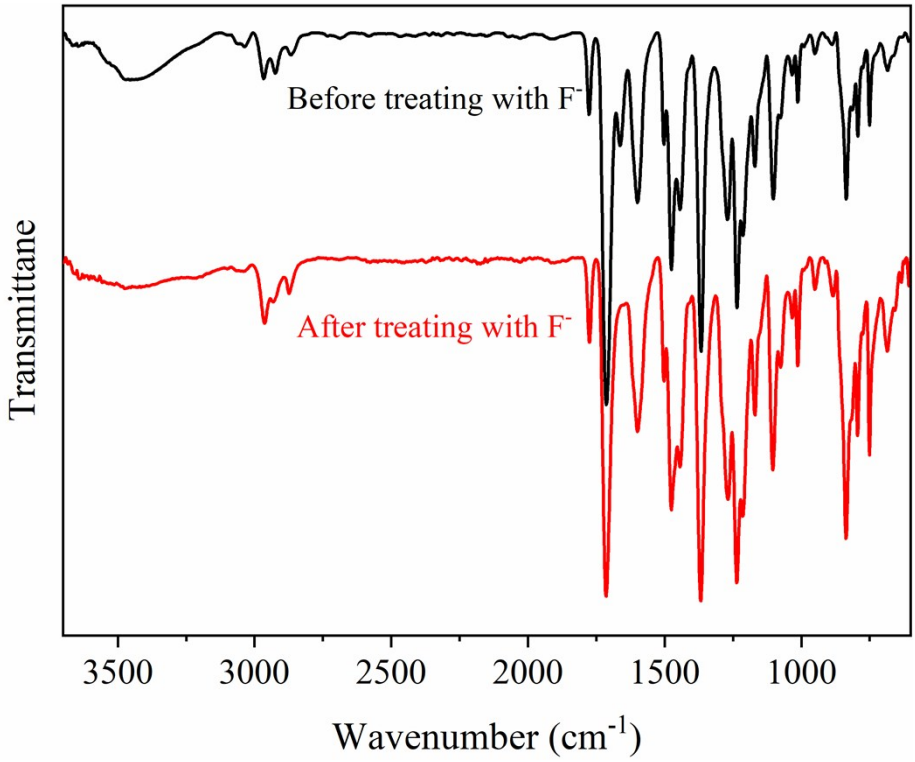



**Fig. S12** FTIR spectra of **PI-OH** film before and after $F^-$ treating.

## 7. Detection of fluoride ion in DMSO/water media

On the basis of the successful titration tests in DMSO, we further evaluated the water effect on the binding affinity of chemosensor **PI-OH** for $F^-$ by carrying out the UV-*vis* spectroscopic titration experiments. The results are shown as **Fig. S13**.

Upon addition of $F^-$ to **PI-OH** in 10% aqueous DMSO solution (DMSO/$H_2O$; 90/10, v/v), the results are similar with the result of the UV-*vis* absorption titrations in pure DMSO solvent, but the addition of the more $F^-$ is required (1000 equiv. *vs*. 50 equiv.). In aqueous solution, fluoride ion can format the hydrogen bond with water. Therefore, the binding affinity of chemosensor **PI-OH** for $F^-$ becomes very weak in aqueous media. This conclusion is insistent with the reported by others.[1-3]

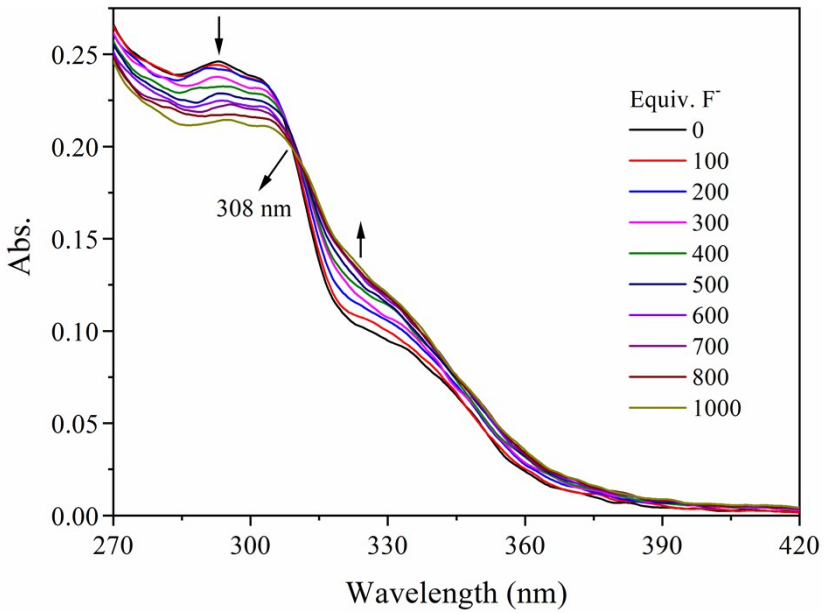



**Fig. S13** UV-*vis* absorption spectra of **PI-OH** (10 $\mu$M in DMSO/$H_2O$, v/v, 90/10) with the addition of different equivalents of fluoride ion (0-1000 equiv.).

**Table S3**. The comparison of chemosensor **PI-OH** with polymeric $F^-$ chemosensors available in the literature

| **Polymeric chemosensors type** | **Solvent** | **LOD** | **Reversibility & reusability** | **Detection in the film state** | **Ref.** |
|---|---|---|---|---|---|
| Nitrobenzofurazan-containing Polymers | THF | 0.8 $\mu$M | Yes | -- | [S1] |
| (S)-binaphthalene-based polymer | THF | -- | -- | -- | [S2] |
| Fluorinated Poly(arylene ether-1,3,4-oxadiazole)s | DMAc | 5.31 $\mu$M | -- | -- | [S4] |
| Polymer containing naphthalimide and imide moieties | $CH_2Cl_2$/DMSO (9/1, v/v) | -- | -- | Yes | [S5] |
| P(MMA-*co*-NBDAE)-*b*-PF-*b*-P-(MMA-*co*-NBDAE) triblock copolymer | THF | 4.78 $\mu$M | Yes | -- | [S6] |
| PEO-*b*-P($MEO_2$MA-*co*-OEGMA-*co*-SiCouMA) block copolymer | THF | 3.45 $\mu$M | -- | -- | [S7] |
| Polyethylene with side-chain triarylboranes | TCE | 0.56 $\mu$M | -- | Yes | [S8] |
| PEG containing fluorescein moiety | HEPES buffered water | 1.01 $\mu$M | -- | -- | [S9] |
| Urea-based polyacetylenes | DMF | 1 mM | -- | -- | [S10] |
| Poly(phenylene ethynylene) containing 2-thiohydantoin | DMSO | 113 $\mu$M | -- | -- | [S11] |
| Polymers incorporating benzo[d][1,2,3]triazole moieties | MeCN | 2 $\mu$M | -- | -- | [S12] |
| Conjugated polymer thin film-$Fe^{3+}$ complex | -- | 6.78 $\mu$M | -- | Yes | [S13] |
| Polyacrylate functionalized gold nanoparticles-$Al^{3+}$ complex | $H_2O$ | 18 $\mu$M | Yes | -- | [S14] |
| Polyamine derivative | $H_2O$/THF (9/1, v/v) | 2.12 $\mu$M | -- | -- | [S15] |
| 1,4-Diketo-pyrrolo[3,4-c]pyrroles (DPPs) based polymer films | -- | 1 $\mu$M | Yes | Yes | [S16] |
| 9,10-Azaboraphenanthrene-containing conjugated polymers | THF | -- | -- | Yes | [S17] |
| **Our chemosensor PI-OH** | DMSO | 1.79 $\mu$M | Yes | Yes | -- |

**Supplementary material references**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[2] F. Li, G. Wei, Y. Sheng, Y. W. Quan, Y. X. Cheng and C. J. Zhu, *Polymer*, 2014, **55**, 5689.

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[7] Y. Y. Jiang, X. L. Hu, J. M. Hu, H. Liu, H. Zhong and S. Y. Liu, *Macromolecules*, 2011, **44**, 8780.

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