A recyclable, fluorescent, and colorimetric sensor for fluoride anion in water using a crosslinked polymer functionalized with hydroxyl quinolinium

1. The optimization of the molar ratio of AHPEQB/TRIM



S. Fig. 1 The change in fluorescent intensity at 540 nm versus fluoride concentration for CpA1T1 (black curve), CpA1T3 (red curve), CpA1T5 (blue curve), and CpA1T7 (indigo blue).

2. Morphology studies for CpA1T5



S. Fig. 2 SEM images of CpA1T5.

3. Thermal stability of CpA1T5

The thermal stability of the polymer CpA1T5 was characterized by TGA (S. Fig. 3). The 5% weight loss temperature below 100 °C could be ascribed to the removal of adsorbed water. The weight loss of the organic skeleton occurred in the temperature range from 305 to 500°C, demonstrating CpA1T5 is thermal stable.



S. Fig. 3 Thermogravimetric curves of CpA1T5.

4. N₂ adsorption-desorption analysis of CpA1T5



S. Fig. 4 Isotherms and pore distribution of CpA1T5.

The Brunauer–Emmett–Teller (BET) equation was used to measure the surface area (m^2/g) of the sensor. The pore volume (cm^3/g) and pore diameter (Å) were analyzed by the Barrett–Joyer–Halendal (BJH) model. It was found that the CpA₁T₅ has

microporous and mesoporous structure (S. Fig. 4). The pore size distributes mainly in 1.0-4.5 nm and 4.5-10 nm. Surface area of 216.0m²/g, Pore diameter of 5.938Å, pore volume 0.2783cc/g.

5. Anion response of AHPEQB

S. Fig. 5 Color of AHPEQB in DI water $(1.0 \times 10^{-5} \text{ mol/L})$ in the presence of various anions $(1.0 \times 10^{-4} \text{ mol/L})$ (a). Absorbance (b) and fluorescence (c) spectra of AHPEQB in DI water $(1.0 \times 10^{-5} \text{ mol/L})$ in the presence of various anions $(1.0 \times 10^{-4} \text{ mol/L})$.

6. UV-Vis spectra of CpA1T5 in DI water in the presence of various anions



S. Fig. 6 UV-Vis spectra of CpA1T5 (0.6 mg/mL) in DI water in the presence of various anions $(1.0 \times 10^{-4} \text{ mol/L})$.

7. Fluorescence spectra of CpA1T5 in HEPES buffer in the presence of various anions

The anionic response of CpA1T5 in 2-[4-(2-hydroxyethyl)-1-piperazinyl]ethane sulfonic acid (HEPES) buffer at pH 7.0 (S. Fig. 7) was also investigated, similar phenomena as that in DI was was observed.



S.Fig. 7 Fluorescence spectra of CpA1T5 in HEPES buffer ($1.0 \times 10^{-5} \text{ mol/L}$) in the presence of various anions ($1.0 \times 10^{-4} \text{ mol/L}$).

8. Influence of CpA1T5 concentration

We investigated fluoride sensing at a lower CpA1T5 concentration (0.12 mg/mL) (S. Fig. 8), similar result was observed, but the fluorescence enhancement upon the addition of F^- was not as great as that at 0.6 mg/mL.



S. Fig. 8 Fluorescence spectra of CpA1T5 in DI water (0.12 mg/mL) in the presence of F^- (1.0×10⁻⁴ mol/L).

9. Investigation of anti-jamming ability of CpA1T5



S. Fig. 9 Selectivity of CpA1T5 for F⁻ in the presence of other anions in DI water at pH 7. Black bars represent the addition of an excess of the appropriate anion $(1.0 \times 10^{-4} \text{ mol/L})$ to a suspension of CpA1T5 (0.6 mg/mL) in DI water and red bars represent the subsequent addition of F⁻ (1.0 × 10⁻⁴ mol/L) to the suspension (λ_{ex} = 420 nm, λ_{em} = 540nm).

10. Determination of fluoride anion concentration in mouthwash samples



S. Fig. 10 The fluorescence emission spectra (ex = 420nm) of CpA1T5 (0.6 mg/mL) toward different volumes of mouthwash sample $1^{\#}(a)$ and $2^{\#}$ (b).