Electronic Supplementary Information

A Diketopyrrolopyrrole-Based Fluorescecnt Porous Organic Polymer as Fluoride Sensing Device

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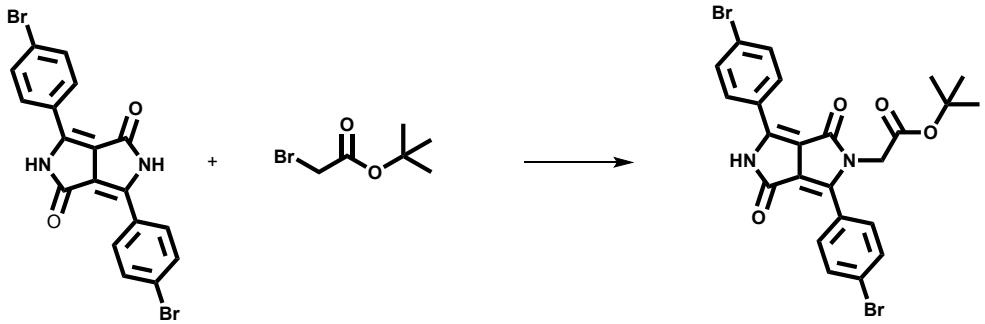
Materials and Methods

Commercial chemicals and dry solvents were used as received. 3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione[1], tetrakis(4-ethynylphenyl)methane[2] were synthesized according to literature procedures.

Synthesis of Uni-DPP



To a stirred suspension of 3,6-bis(4-bromophenyl)pyrrolo-[3,4-c]pyrrole-1,4(2H,5H)-dione (1.14 g, 2.6 mmol) in DMF (30 mL) at room temperature, potassium tert-butoxide (0.81 g, 7.1 mmol) was added under N2. The mixture turned into purple and was stirred for 30 min. tert-butyl 2-bromoacetate (0.76 g, 3.9 mmol) was gradually added and the resultant reddish mixture was stirred for 6 h at room temperature. The mixture was poured into 400 mL of water and stirred for 1 h. The crude product was obtained by filtration and then further purified by flash column chromatography using DCM/ethyl acetate = 5/1 as the eluent. Yield: 0.65 g (51%).[1]HNMR(400MHz, DMSO): 11.46(s, 1H), 8.37-8.39(d, 2H), 7.80-7.84(m, 4H), 7.73-7.50 (d， 2H), 4.53 (s, 2H), 1.29 (s, 9H); 13C NMR (100 MHz, DMSO): δ = 167.4, 162.3, 161.0, 145.7, 144.3, 132.3, 132.0, 130.3, 129.7, 126.6, 126.4, 126.2, 124.8, 111.4, 108.1, 82.0, 43.8, 27.4;

Synthesis of Uni-DPP-PPN

The Uni-DPP-PPN was synthesized via Sonogashira coupling reaction using tetrakis(4ethynylphenyl)methane (1 equiv, 50 mg, 0.12 mmol) and tert-butyl 2-(3,6-bis(4-bromophenyl)-1,4-dioxo-4,5-dihydropyrrolo[3,4-c]pyrrol-2(1H)-yl)acetate (Uni-DPP; 2 equiv, 134.5 mg 0.24 mmol) in toluene/triethylamine (1:1, v/v) at 80 °C using palladium(0)tetrakis(triphenylphosphine) (0.14 mol %) and copper(I) iodide (0.26 mol %) as catalysis for 3 d. After cooling to room temperature, the precipitated polymers were isolated by filtration over a Buchner funnel and washed with 1 M hydrochloric acid (20 mL), followed with excess methanol, tetrahydrofuran, and dichloromethane. Then, the product was further extracted with dichloromethane by Soxhlet apparatus for 24 h. The solvent was removed under vacuum at room temperature to afford the DPP-PPN-m. Anal. Calcd. for Uni-DPP-PPN: C, 79.84; H, 4.94; N, 4.60. Found: C, 75.07; H, 4.30; N, 4.01;

COMPUTATIONAL METHODOLOGY

In this study, all the calculations were performed by utilizing the Gaussian 09 suite of programs[1]. The geometries of the isolated molecule and coordination complex were fully optimized at the method level of B3LYP/6-311G*[2-3]. No symmetry or geometry constraint was imposed during the optimizations. Frequency calculations were implemented at the same theoretical levels to corroborate that all the structures are genuine minima on the potential energy surface.

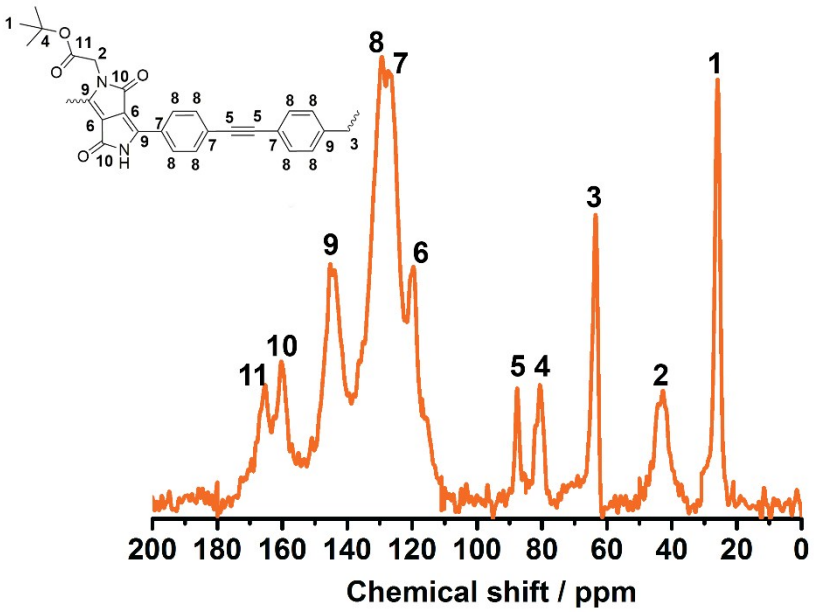


Fig. S1 Solid state ^{13}C NMR spectrum of Uni-DPP-PPN

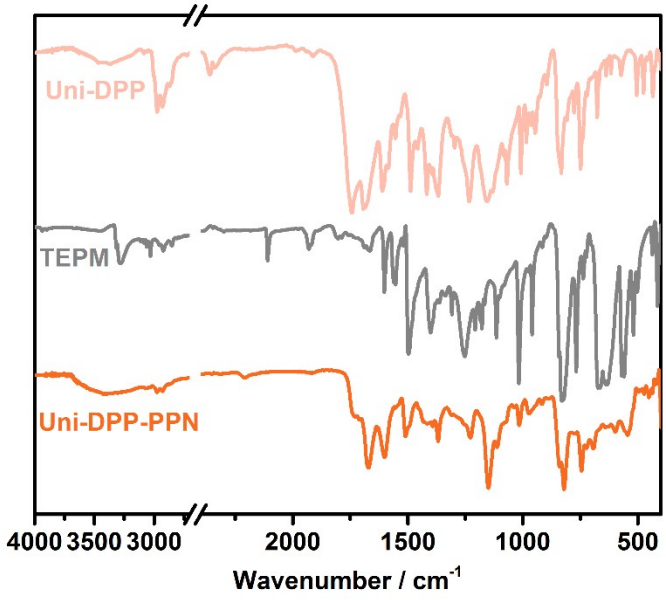


Fig. S2 FTIR spectra of Uni-DPP, TEPE and Uni-DPP-PPN

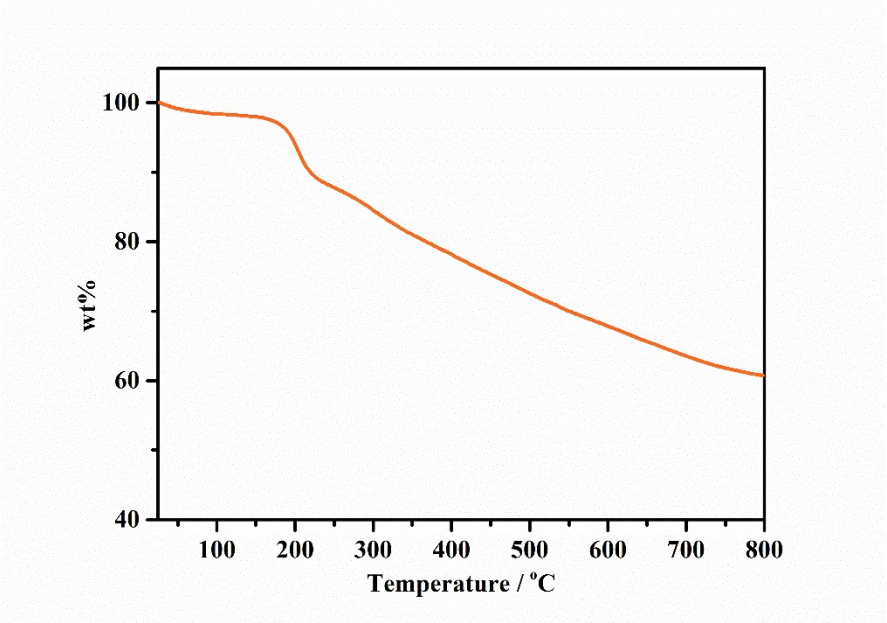


Fig. S3 TGA profile of Uni-DPP-PPN

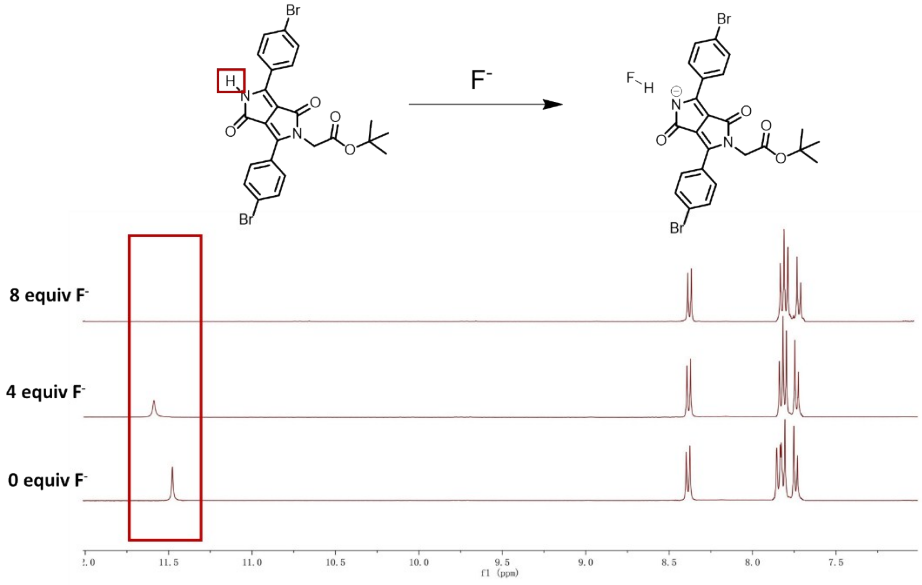


Fig. S4 ^{1}H NMR spectra of Uni-DPP in the presence of 0 equiv., 4 equiv. and 8 equiv. of F^-

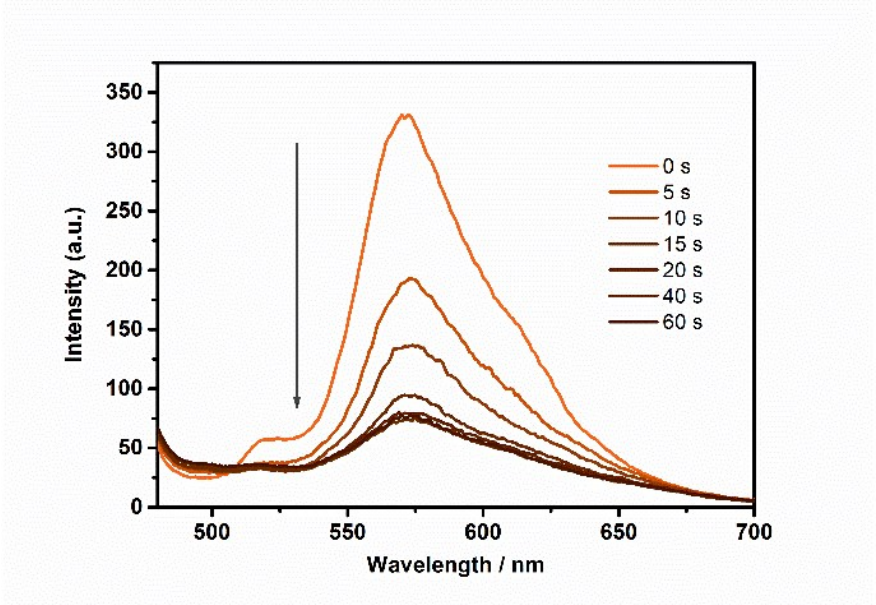


Fig. S5 Emission spectra of Uni-DPP-PPM upon incubation into F^- solution (0.015 mM in THF) at various time intervals

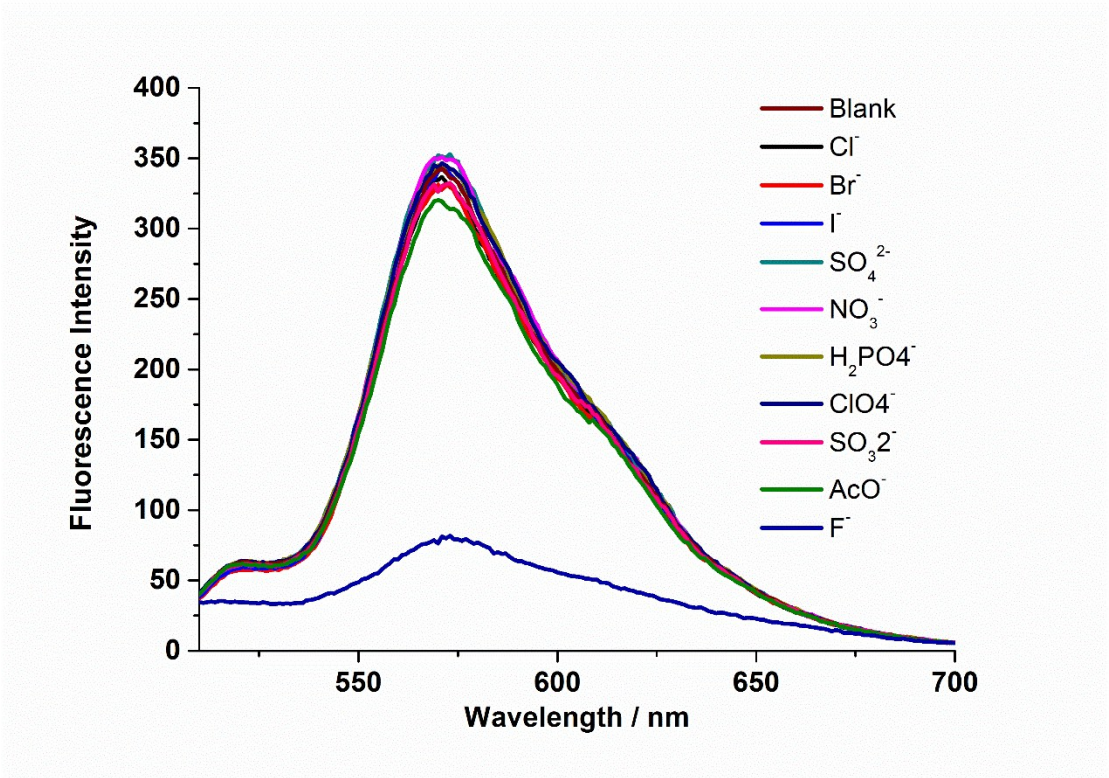


Fig. S6 Fluorescence spectra of Uni-DPP-PPN suspension in THF (0.1 mg/mL in THF) before (Blank) and after the addition of F^- (0.015 mM) and other anions (1.5mM)

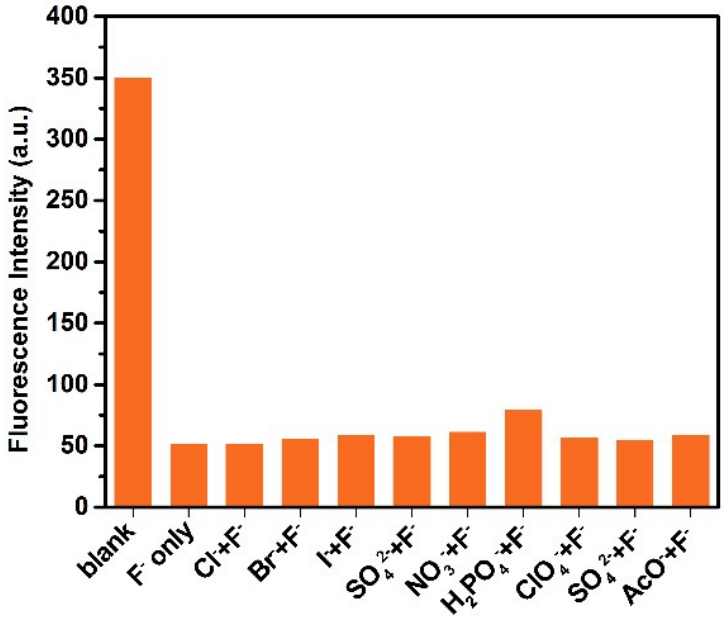


Fig. S7 The effect of co-existent ions to sensitivity of Uni-DPP-PPN to F- (0.015 mM for F- and 1.5mM for other anions)

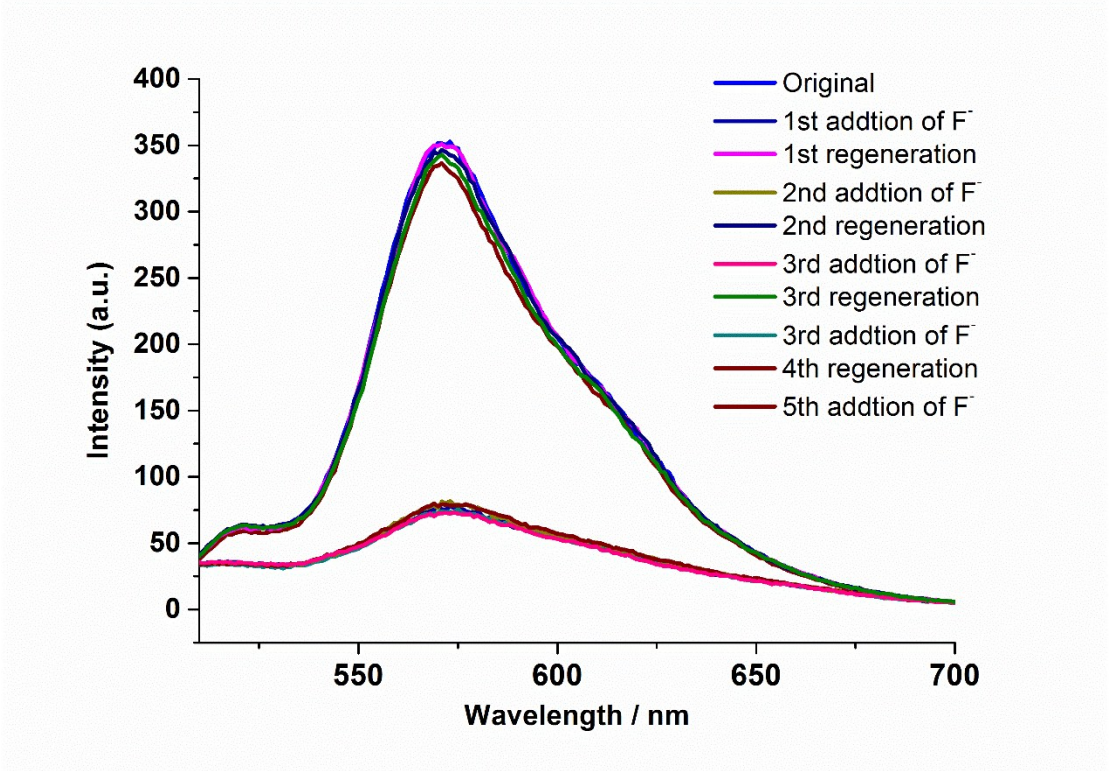


Fig. S8 Fluorescence spectra of Uni-DPP-PPN in each regeneration cycle

Table S1 Electron density maps of HOMO and LUMO of Uni-DPP-PPN segment and its deprotonated counterpart

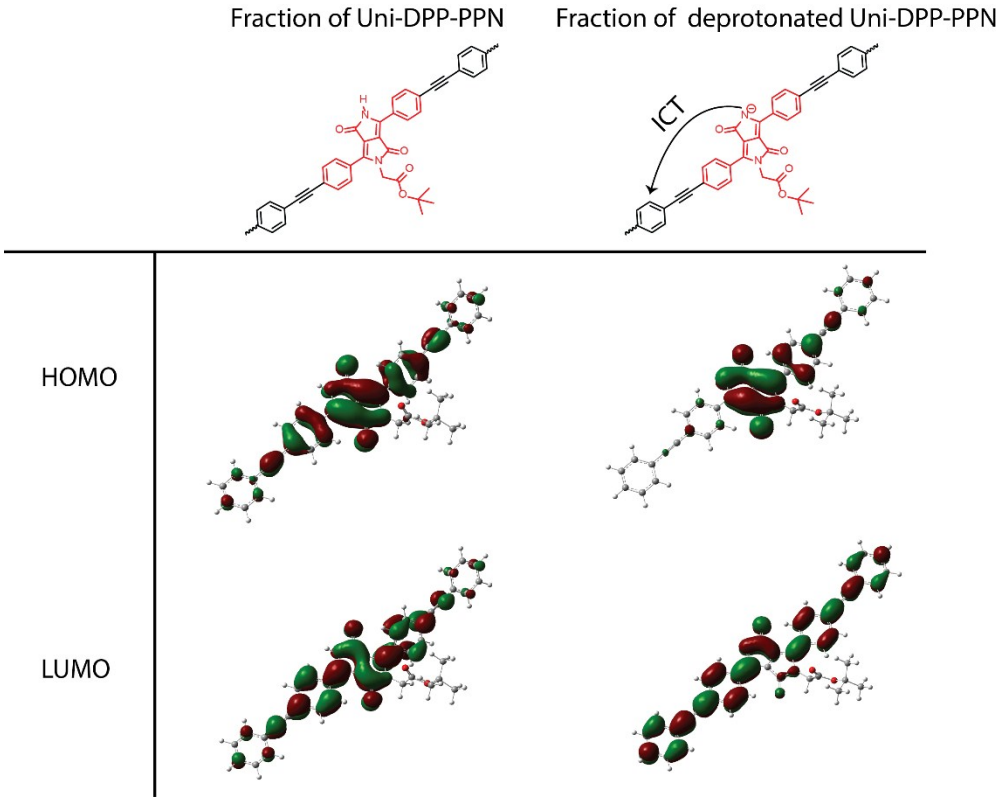


Table S2 Comparison of Uni-DPP-PPN with other reported analogue as fluoride sensors

Sensor	Stern-Volmer Constant	Detection of Limits	Reference
Uni-DPP-PPN	2.34×10^5 M^{-1}	18 ppb (0.95 μM)	This work
PPS [N-((pyridin-4-yl)methylene)pyridin-4-amine]		3 μM	[4]
FS@UiO-66		4.4 μM	[5]
pyrene-tagged UiO-66-NH_2		0.82 μM	[6]
Eu-MOF 1		2 μM	[7]
Eu^{3+}@MIL-121	2.07×10^3 M^{-1}	0.063 μM	[8]
MOTIPS-TPE		90 nM	[9]
$Eu(NTA\text{-}S15)_3L$		180 μM	[10]
Borane–aza-BODIPY		0.1 ppm	[11]
4-bromo-2,6-bis-(hydroxymethyl)phenol		1.5 μM	[12]
Boron-based microporous organic		2.6 μM	[13]

polymer			

Reference

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