Electronic Supplementary Information

The construction of fluorescent heteropore covalent organic frameworks and their applications in spectroscopic and visual detection of trinitrophenol with high selectivity and sensitivity

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Section 1. Instruments and Methods

Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FT-IR) was carried out with a Nicolet 380 FT-IR spectrometer. The samples were prepared as KBr pellets.

Solid-state nuclear magnetic resonance spectroscopy (NMR)

The ^{13}C CP-MAS spectrum (NMR) was recorded on Agilent DD2 600 Solid NMR System with 4 mm zirconia rotors. The spinning rate is 9 KHz and the contact time is 3ms.

Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) was carried out on Waters TGA Q500 by heating the samples from 30 to 950 ^{o}C under nitrogen atmosphere at a heating rate of 10 ^{o}C/min.

Scanning electron microscopy (SEM)

Scanning electron microscopy was carried out using a XL30 FEG scanning electron microscope. The samples were dispersed over a slice of conductive adhesive adhered to a flat copper platform sample holder and then coated with gold using a sputter 9 coater (ambient temperature, 85 torr pressure in a nitrogen atmosphere, sputtered for 80 s from a solid gold target at a current of 20 mA) before being submitted to SEM characterization.

Powder X-ray diffraction (PXRD)

Powder X-ray diffraction (PXRD) patterns were recorded with a PANalytical X' Pert Powder system using monocromated Cu/K_{α} (λ = 0.1542 nm). The samples were spread on the square recess of XRD sample holder as a thin layer.

Nitrogen adsorption-desorption isotherm measurement

The Nitrogen adsorption-desorption isotherm measurements were carried out using a

Micromeritics ASAP 2020 system. Before gas adsorption measurements, the as-prepared samples (~ 40 mg) were activated by being immersed in anhydrous 1,4-dioxane and acetone for 12h for 3 times. The solvent was decanted and the sample was dried under dynamic vacuum at 120℃ for 4h. The resulting sample was then used for gas adsorption measurements from 0 to 1 atm at 77K. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface area. By using the non-local density functional theory model, the pore size distribution curve was derived from the sorption data.

Structural simulations and powder X-ray diffraction analysis

The Pawley refinement of the experimental PXRD was conducted by the Reflex module in the Material Studio 7.0. Before the simulations, the structures were firstly optimized in Gaussian 09 package by semi-empirical calculations at PM3 level. The simulations of different possible structures were carried out in Accelrys Material Studio 7.0 software package. The stimulated PXRD patterns were determined by the Reflex module. P1 space group was used for the simulations.

UV-vis (UV-vis) spectroscopy

UV-vis experiments were performed on a Unico 4802 UV-vis double beam spectrophotometer.

Fluorescence spectroscopy

The fluorescence spectra were collected at room temperature using the Hitachi F-700 spectrophotometer. The sampling voltage was 700V, the scanning speed was 1200 nm/min, and the width of excitation and launching slit were both 5.0 nm.

The fluorescence titration experiments of the COFs with various nitroaromatic compounds were carried out by gradual addition of the nitroaromatic analytes to acetonitrile suspensions of the COFs (2.0 mL) via micropipettes at room temperature. Stock solutions (1.0×10^{-4} M) of the nitroaromatic analytes were firstly prepared in acetonitrile. The acetonitrile suspensions of the COFs were prepared by dispersing the

COFs (5.0 mg) in acetonitrile (20 mL) and then being ultrasonicated to afford homogeneous dispersions. After standing for several minutes, the fluorescence emission spectra were recorded. All the measurements were excited at a wavelength of 370 nm.

For the naked-eye detection experiments, the stock solutions of the nitroaromatic compounds were injected into the acetonitrile suspensions of the COFs (2.0 mL), respectively, and their photographs were taken immediately.

Calculation of fluorescence quantum yields

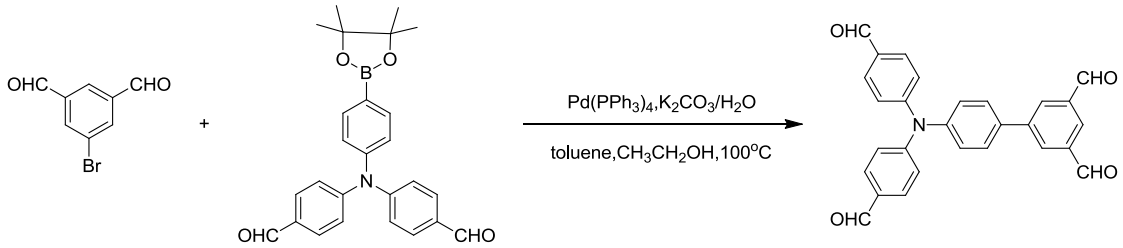
The quantify fluorescence quantum yield (Y) of the as-prepared COFs were calculated by reference method. By measuring the dilute solution of the COFs, model molecule and reference substance under the same excitation wavelength and recording integral fluorescence intensity and the absorbance of this specific wavelength, we get quantify fluorescence quantum of different determinands according to the formula (1).

$$Yu = Ys \cdot \frac{Fu}{Fs} \cdot \frac{As}{Au} \quad (1)$$

In the above formula, Yu and Ys respectively represents the fluorescence quantum yield of the measured and reference substance, Fu and Fs respectively represents the fluorescence intensity of the measured and reference substance, Au and As respectively represents the absorbance of the excited light at the specific wavelength of the measured and reference substance[1].

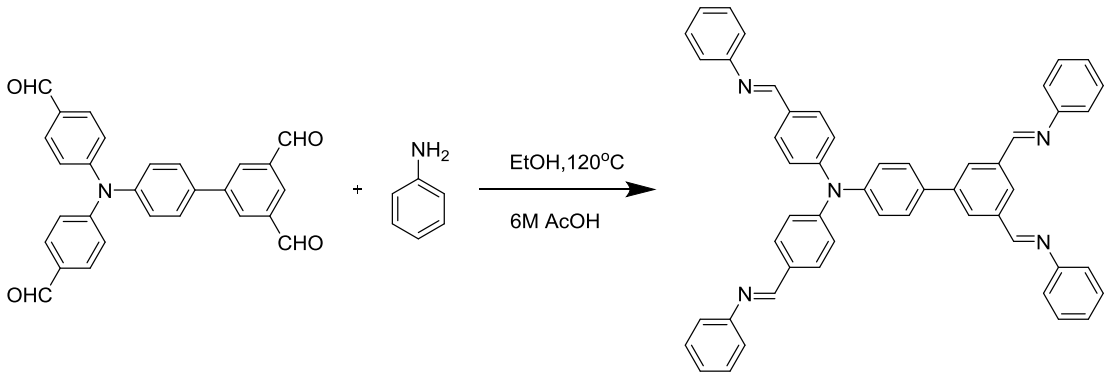
Quinine sulfate was selected as reference substance which gave standard fluorescence quantum yield of 0.5541 (Ys) at λex=370 nm. Acetonitrile suspensions of the COFs and quinine sulfate solution in proper concentration were recorded by absorption spectrum. Both COFs suspensions and reference solution were excited at a wavelength of 370 nm and calculated fluorescence integral intensity. The above test gave standard absorbance of 0.0382 (As) and standard fluorescence integral intensity of 228453 (Fs).

Section 2: Synthesis and Characterizations



4'-(Bis(4-formylphenyl)amino)-[1,1'-biphenyl]-3,5-dicarbaldehyde (BABD).

A mixture of 5-bromoisophthalaldehyde[2] (360 mg, 1.6 mmol), 4,4'-((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)azanediyl)dibenzaldehyde (768 mg, 1.8 mmol), K_2CO_3 (589 mg, 4.27 mmol) and $Pd(PPh_3)_4$ (116 mg, 0.1 mmol) in a mixed solvent of toluene/ethyl alcohol/water (15/5/2 mL) was heated at 100 ^oC for 12 h under argon atmosphere. After being cooled to room temperature, water (50 mL) was added. The mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was washed with water and brine, and then dried over $MgSO_4$. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (DCM/PE = 3:1 and then DCM) to give BABD as a yellow solid (302 mg, 43.3 %). ^1H NMR (500 MHz, DMSO-d_6) δ 10.19 (s, 2H), 9.90 (s, 2H), 8.52 (s, 2H), 8.38 (s, 1H), 7.93 (d, J = 8.3 Hz, 2H), 7.88 (d, J = 8.4 Hz, 4H), 7.35 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.4 Hz, 4H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 193.09, 191.71, 151.67, 146.08, 141.33, 137.93, 135.44, 133.22, 131.81, 129.24, 128.40, 127.52, 123.46.



The preparation of Model Molecule 3',5'-bis((E)-(phenylimino)methyl)-N,N-bis (4-((E)-(phenylimino)methyl)phenyl)-[1,1'-biphenyl]-4-amine

A mixture of **BABD** (10 mg, 0.0023 mmol), phenylamine (0.1 mL, 1.8 mmol), and 6 M AcOH (0.1 mL) were dissolved into EtOH (2 mL) in a sealed glass ampoule. The mixture was sonicated for 2 minutes and the ampoule was sealed after being degassed in a liquid nitrogen bath for 20 min. The ampoule was heated at 110 ^{o}C for 2 days. The solvent was evaporated and the mixture was washed with EtOH (2 × 20 mL). After dried under 80 ^{o}C for 12h, the model molecule was obtained as a yellow-green solid (7mg, 41.5%). ^{1}H NMR (500 MHz, dmso) δ 8.82 (s, 1H), 8.56 (s, 2H), 8.39 (s, 1H), 7.92 (d, J = 8.7 Hz, 2H), 7.86 (d, J = 8.6 Hz, 2H), 7.45 (t, J = 6.9 Hz, 3H), 7.43 – 7.38 (m, 4H), 7.34 (d, J = 8.4 Hz, 3H), 7.29 (dd, J = 14.3, 7.0 Hz, 4H), 7.26 – 7.17 (m, 8H).

Procedure for the preparation of COF-BABD-DB.

BABD (20.0 mg, 0.046 mmol) and 1,4-diaminobenzene (10.0 mg, 0.093 mmol) were dissolved in a mixture of o-dichlorobenzene/n-butyl alcohol/aqueous AcOH (6 M) (V/V/V, 5:5:1, 1.1 mL) in a sealed glass ampoule. The mixture was sonicated for 2 minutes and the ampoule was sealed after being degassed in a liquid nitrogen bath for 20 min. The ampoule was kept at 120 ^{o}C without disturbance for 3 days to yield a yellow solid. After being cooled to room temperature, the solvent was decanted and the solid was washed with anhydrous 1,4-dioxane and acetone each for 3 times and then dried under dynamic vacuum at 120 ^{o}C for 3 h to afford a yellow powder (23.21 mg, 82.1 %).

Procedure for the preparation of COF-BABD-BZ.

BABD (20.0 mg, 0.046 mmol) and benzidine (17.23 mg, 0.093 mmol) were dissolved in a mixture of o-dichlorobenzene/n-butyl alcohol/aqueous AcOH (6 M) (V/V/V, 5:5:1, 1.1 mL) in a sealed glass ampoule. The mixture was sonicated for 2 minutes and the ampoule was sealed after being degassed in a liquid nitrogen bath for 20 min. The ampoule was kept at 120 ^{o}C without disturbance for 3 days to yield a yellow solid. After being cooled to room temperature, the solvent was decanted and the solid was washed with anhydrous 1,4-dioxane and acetone each for 3 times and then dried under dynamic vacuum at 120 ^{o}C for 3 h to afford a yellow powder (29.34 mg, 83.0 %).

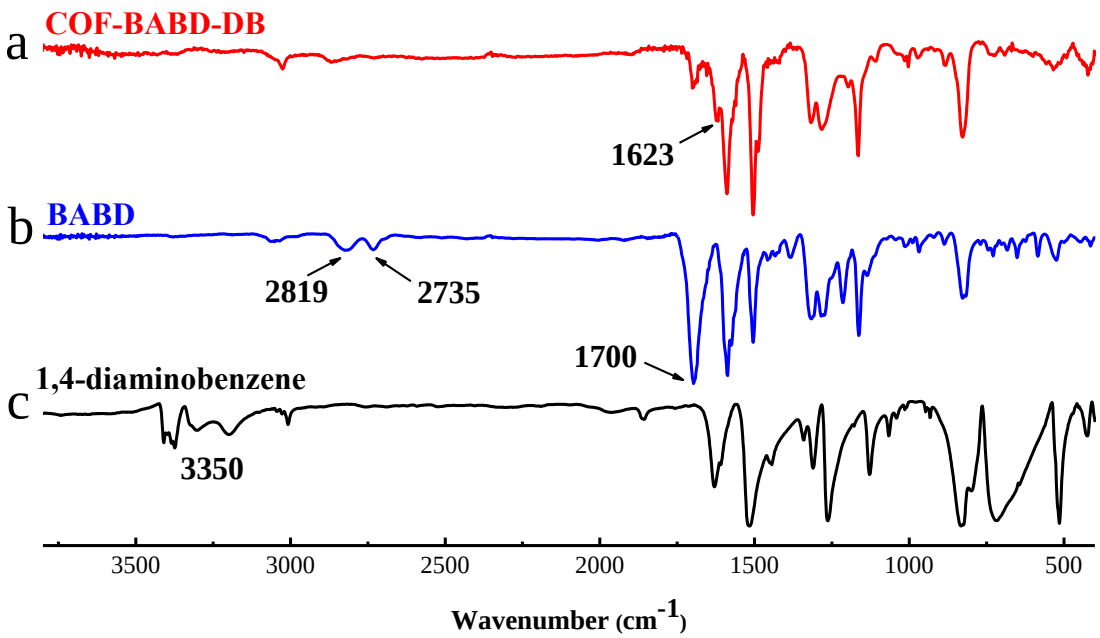


Fig. S1 FT-IR spectra of (a) **COF-BABD-DB**, (b) BABD, and (c) 1,4-diaminobenzene.

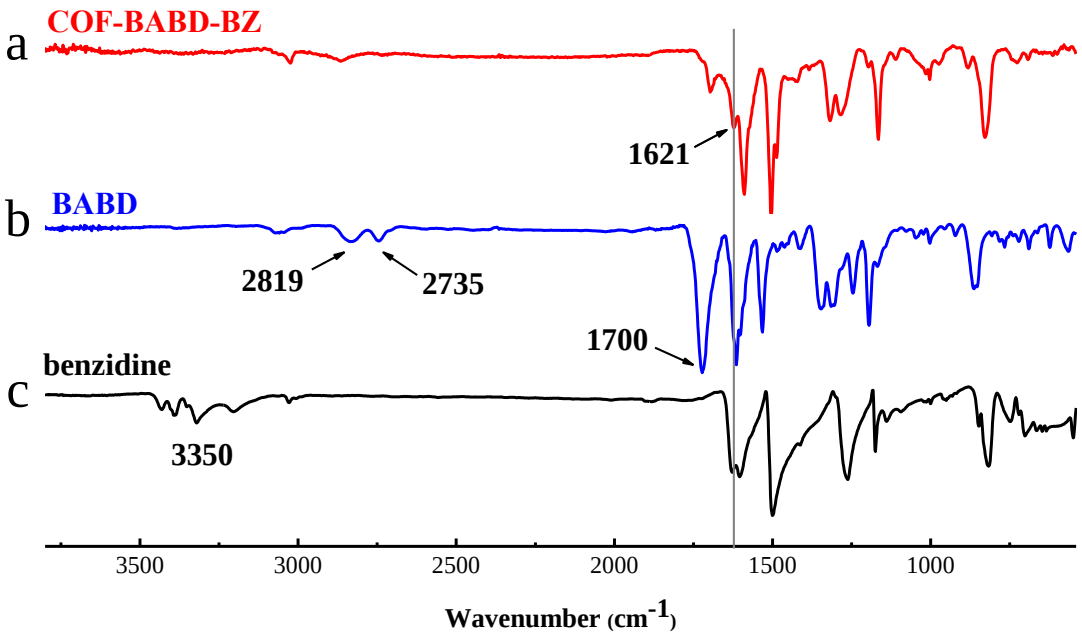


Fig. S2 FT-IR spectra of (a) **COF-BABD-BZ**, (b) BABD, and (c) benzidine.

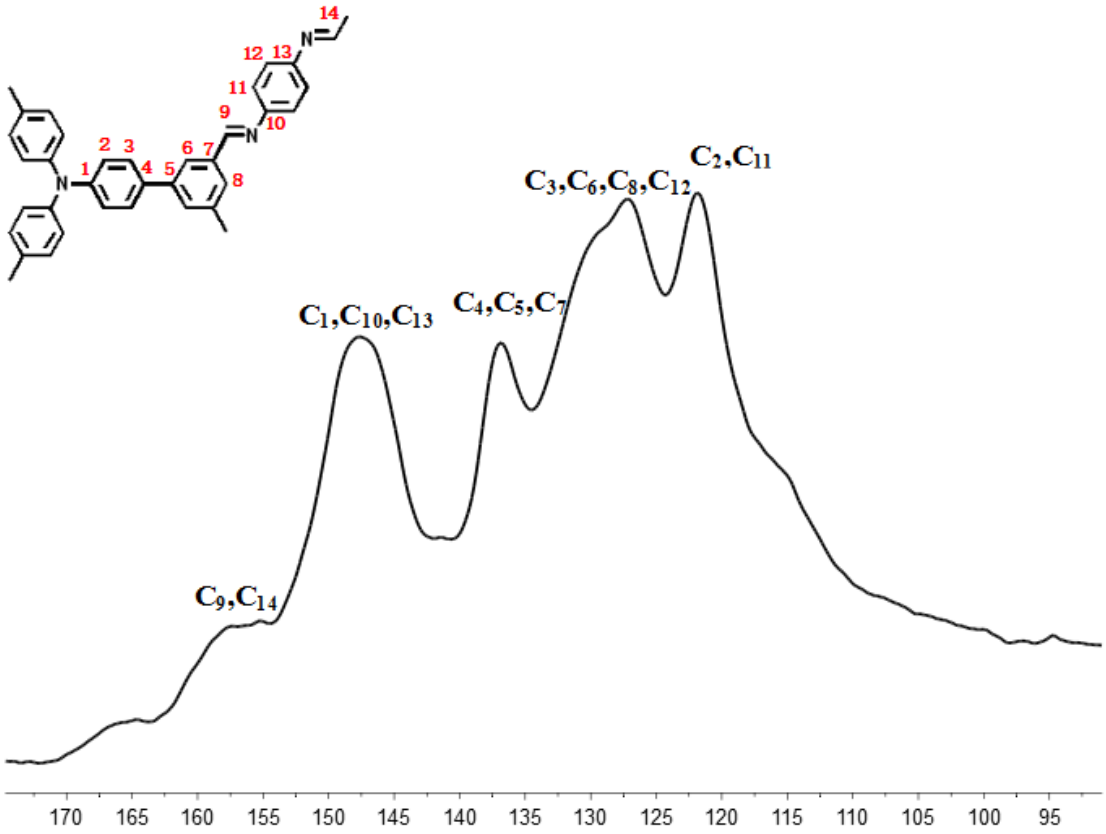


Fig. S3 Solid-state ^{13}C CP-MAS NMR spectrum of **COF-BABD-DB.**

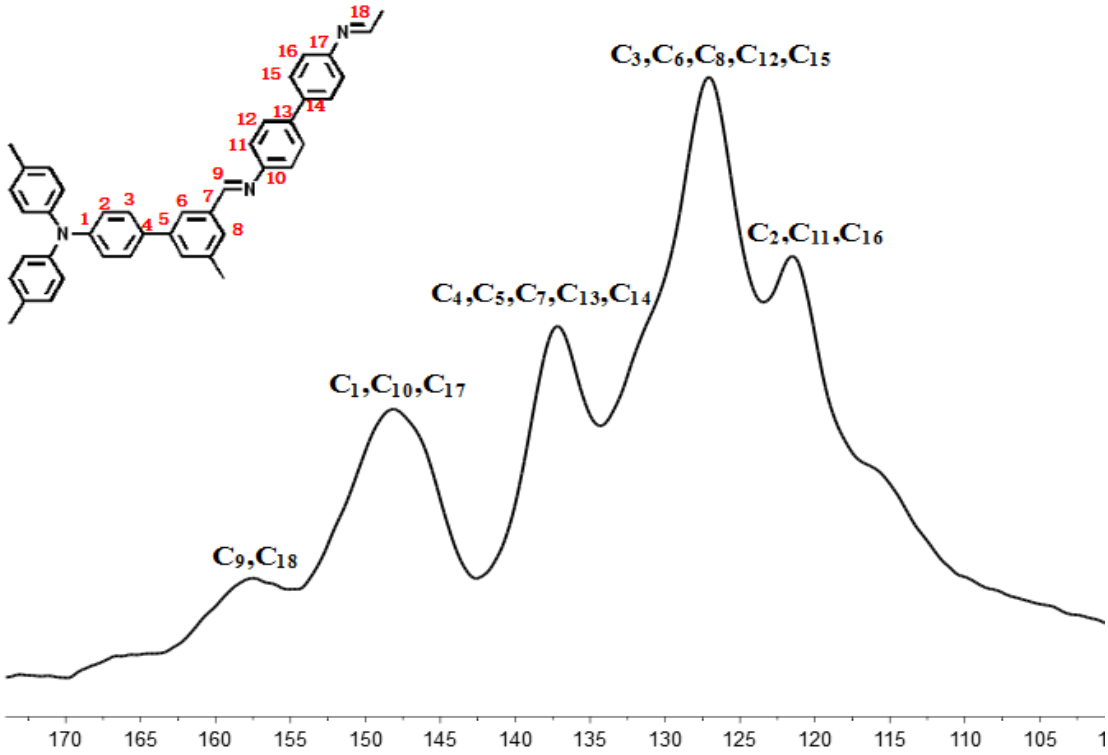


Fig. S4 Solid-state ^{13}C CP-MAS NMR spectrum of **COF-BABD-BZ.**

Table. S1 Elemental analysis of **COF-BABD-DB** and **COF-BABD-BZ**.

		C (%)	H (%)	N (%)
COF-BABD-DB	Theoretical	83.17	4.71	12.12
	Found	79.52	4.81	11.10
COF-BABD-BZ	Theoretical	85.57	4.83	9.60
	Found	82.28	4.92	8.96

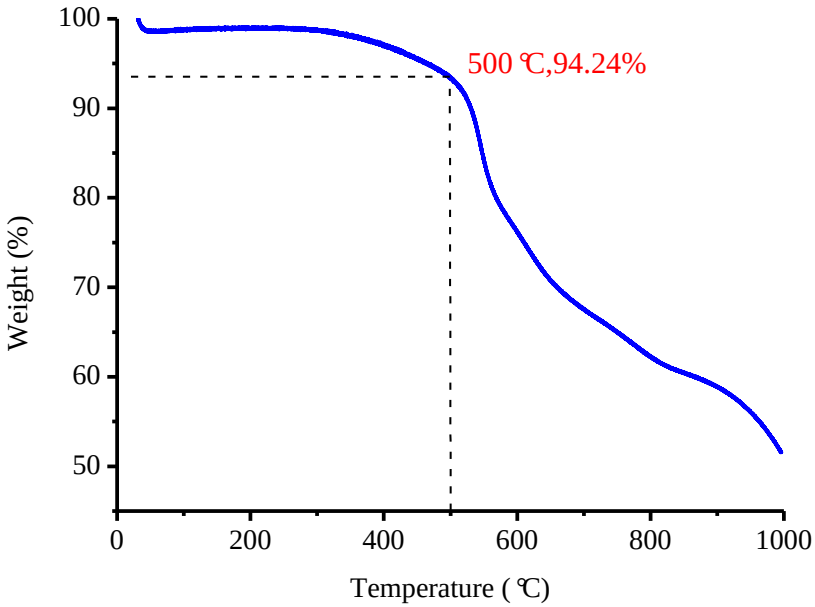


Fig. S5 TGA profile of **COF-BABD-DB**.

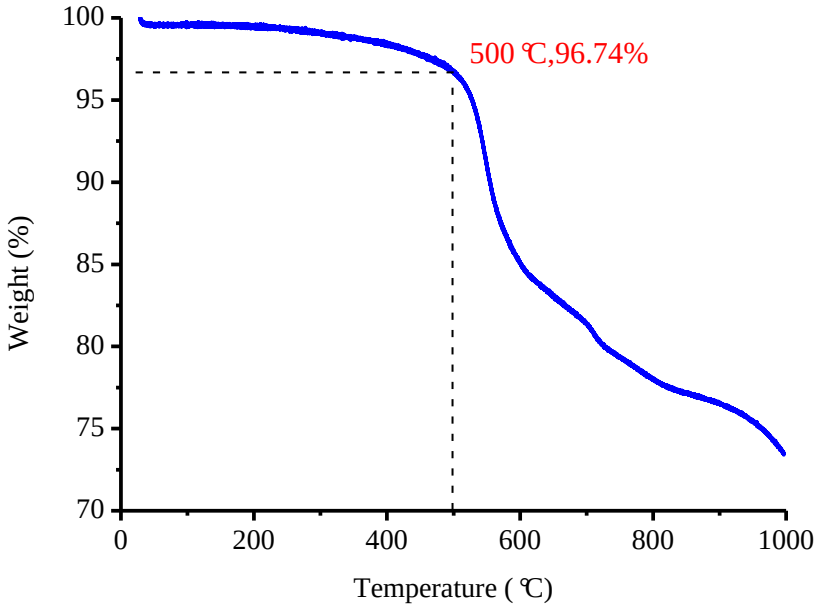


Fig. S6 TGA profile of **COF-BABD-BZ**.

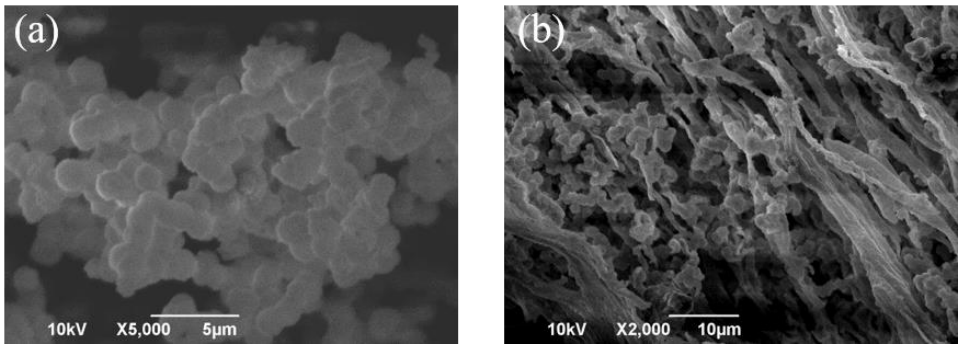


Fig. S7 SEM images of (a) **COF-BABD-DB**, and (b) **COF-BABD-BZ.**

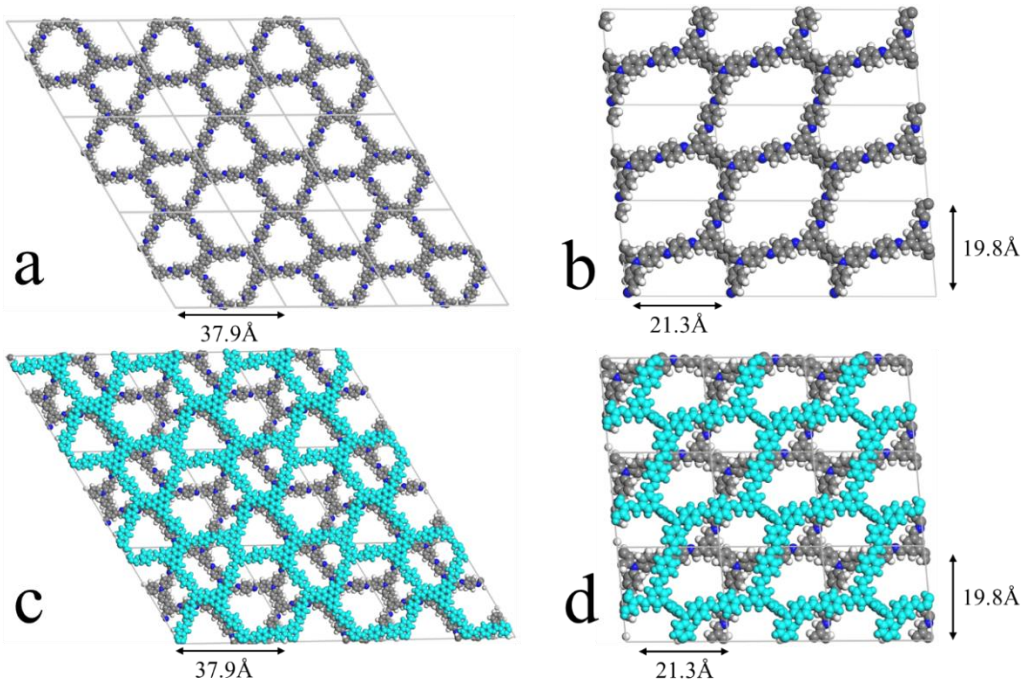


Fig. S8 The possible frameworks that theoretically could be generated from the condensation of BABD and 1,4-diaminobenzene: (a) DP-AA structure, (b) SP-AA structure, (c) DP-AB structure, and (d) SP-AB structure.

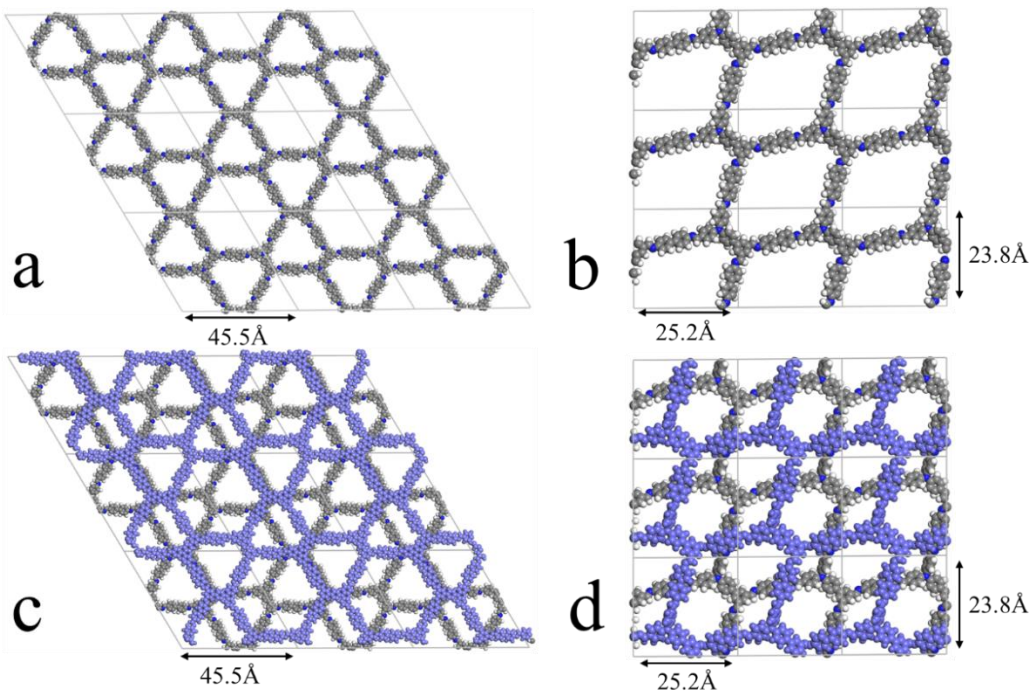


Fig. S9 The possible frameworks that theoretically could be generated from the condensation of BABD and benzidine: (a) DP-AA structure, (b) SP-AA structure, (c) DP-AB structure, and (d) SP-AB structure.

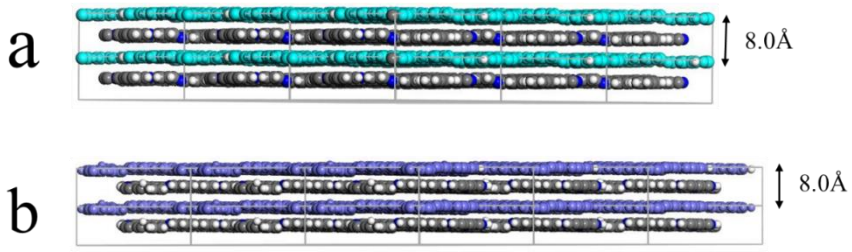


Fig. S10 Illustration of interlayer distances for (a) **COF-BABD-DB** and (a) **COF-BABD-BZ**.

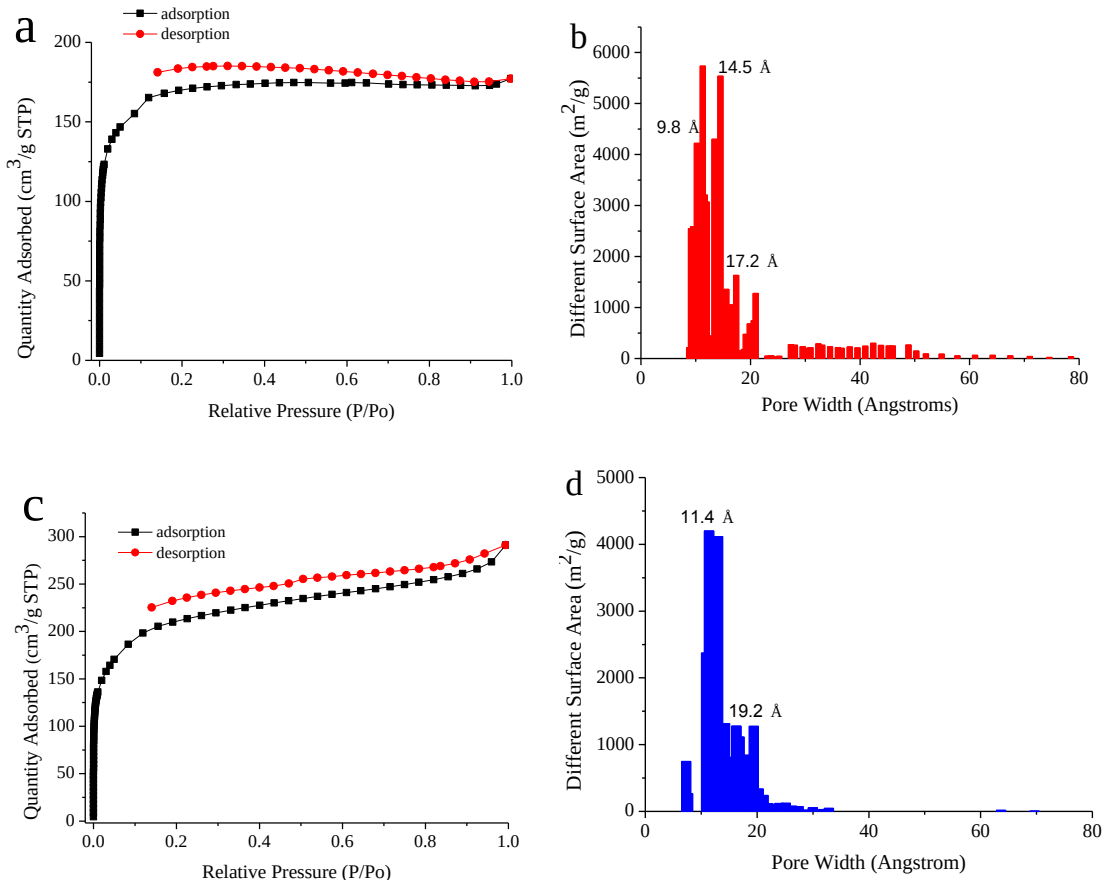


Fig. S11 N_2 adsorption-desorption isotherms (77 K) of (a) **COF-BABD-DB** and (c) **COF-BABD-BZ**, and pore size distribution profiles of (b) **COF-BABD-DB** and (d) **COF-BABD-BZ**.

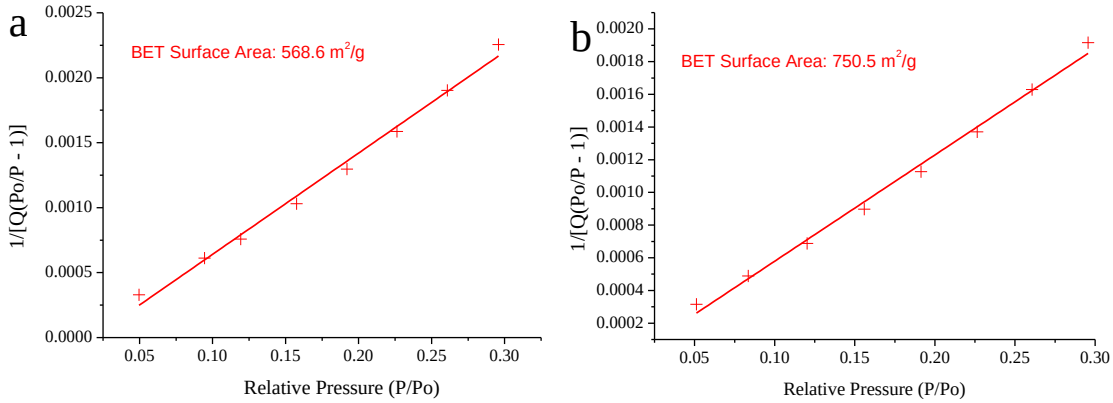


Fig. S12 BET surface area plots for (a) **COF-BABD-DB** and (b) **COF-BABD-BZ** calculated from their N_2 adsorption isotherms.

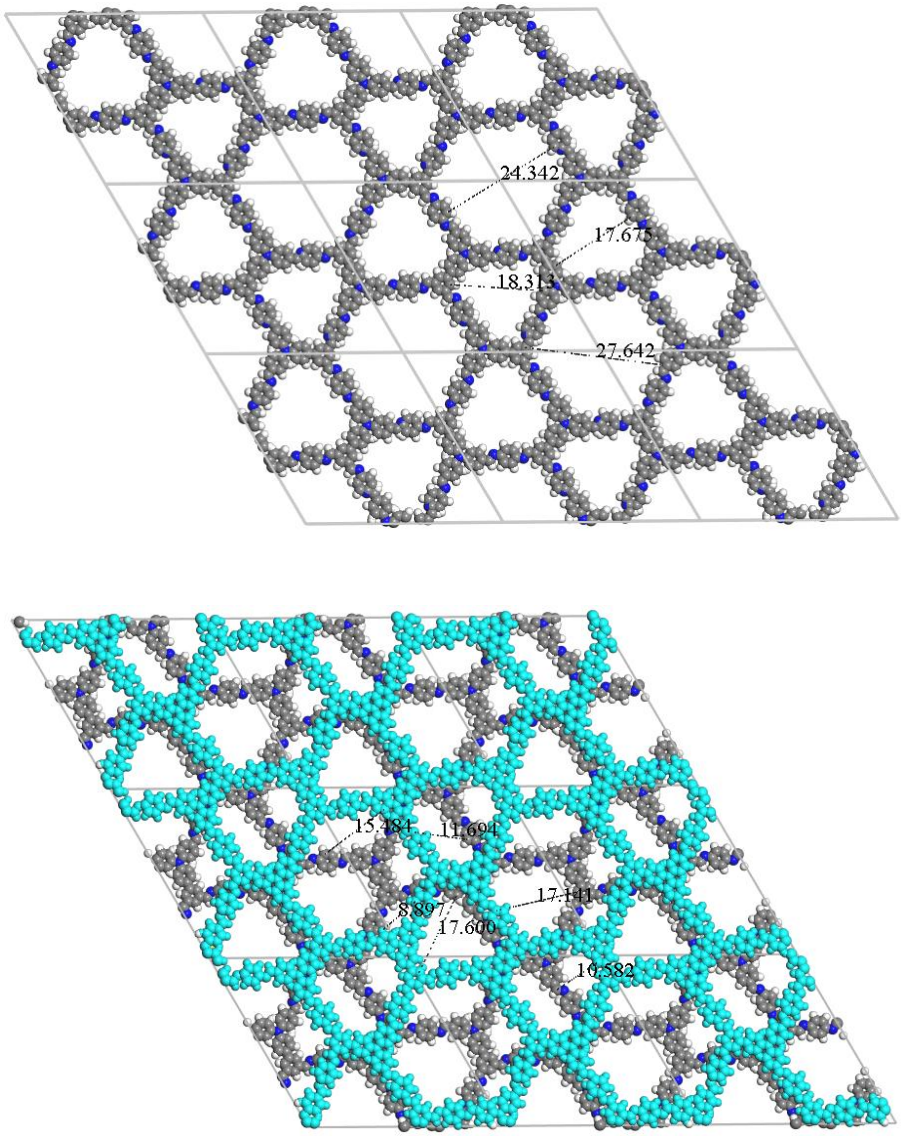


Fig. S13 Illustration of pore size distributions for **COF-BABD-DB** with eclipsed (AA) stacking (top) and staggered (AB) stacking (bottom).

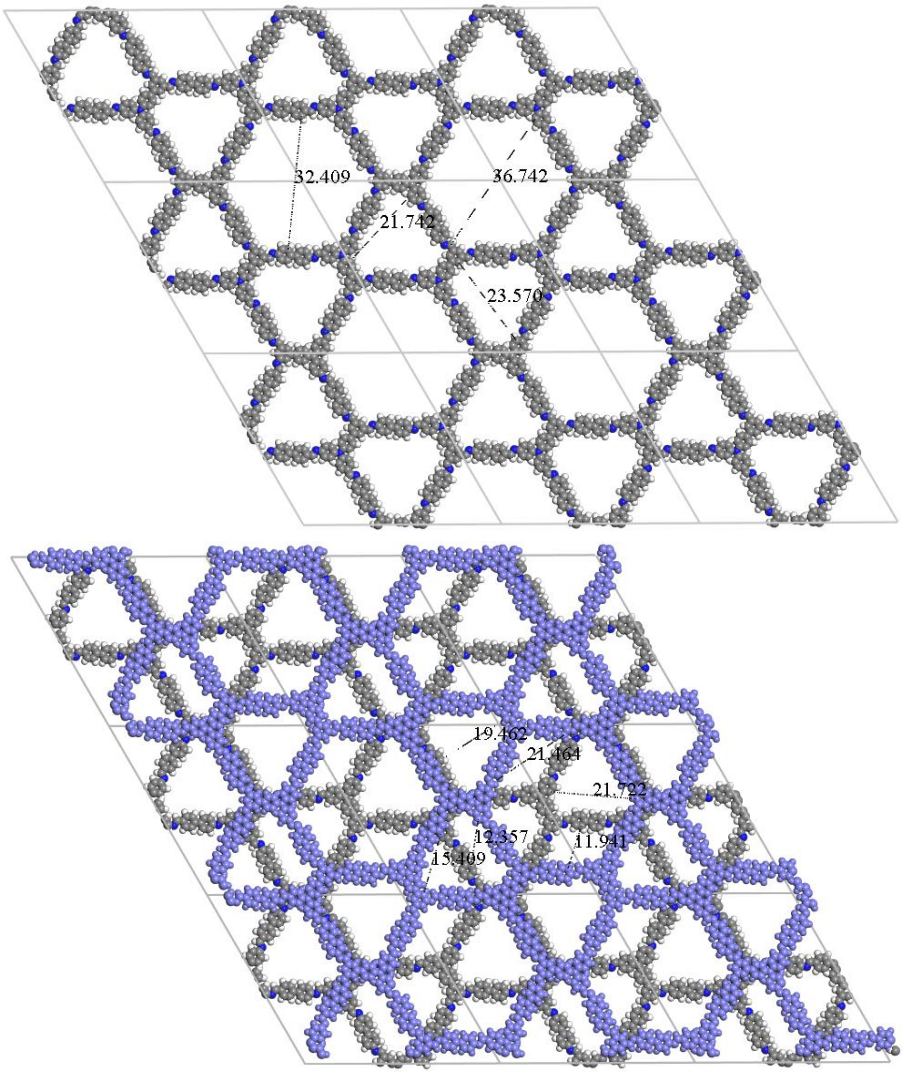


Fig. S14 Illustration of pore size distributions for **COF-BABD-BZ** with eclipsed (AA) stacking (top), and staggered (AB) stacking (bottom).

Table. S2 Fluorescence quantum yields of the COFs and the model molecule.

	Fu	**Au**	**Yu**
Model Molecule	2132	0.0355	0.0055
COF-BABD-DB	65691	0.0271	0.223
COF-BABD-BZ	152164	0.0259	0.541

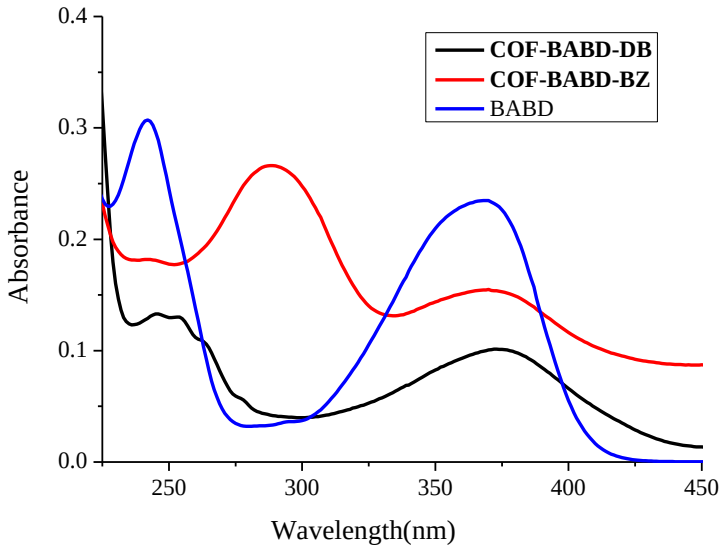


Fig. S15 UV-Vis absorption spectra of **COF-BABD-DB** and **COF-BABD-BZ** and BABD (0.002mg/ml) in acetonitrile. The samples of the COFs suspensions were prepared by dispersing the COFs (1.0 mg) in acetonitrile (2 mL) and then the suspensions were sonicated for 5 min.

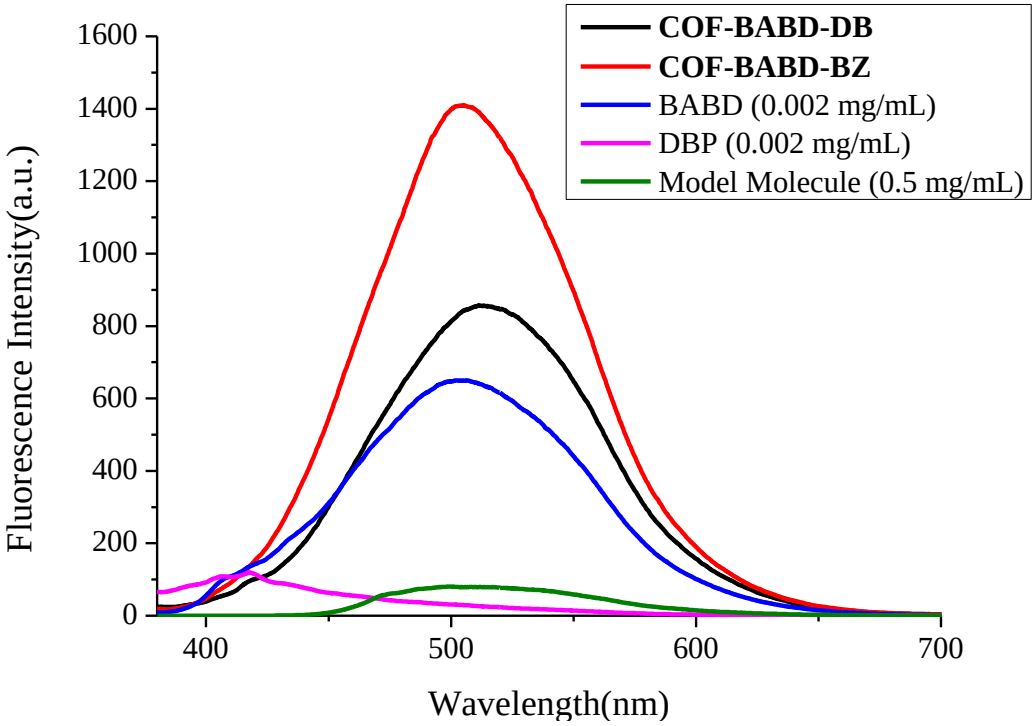


Fig. S16 Fluorescence emission spectra of the COFs, monomers and model molecule in acetonitrile.

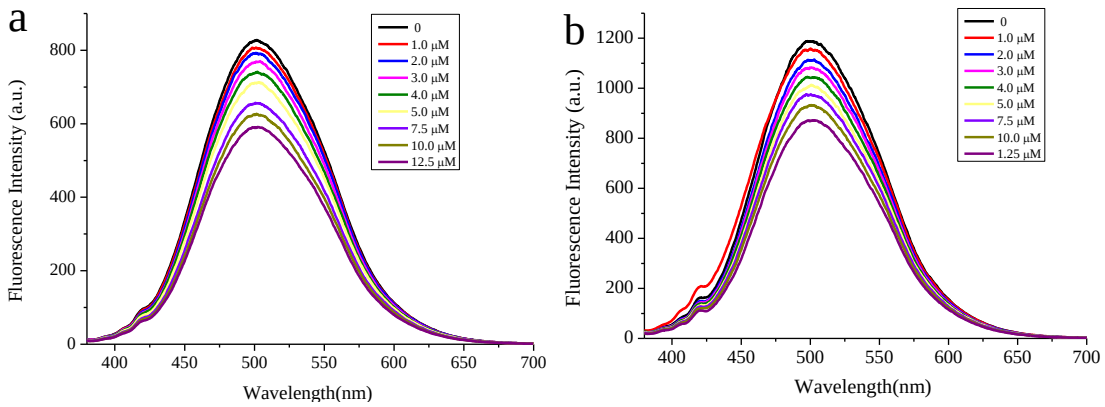


Fig. S17 Fluorescence spectra of acetonitrile suspension of (a) **COF-BABD-DB** and (b) **COF-BABD-BZ** upon increasing addition of DNP.

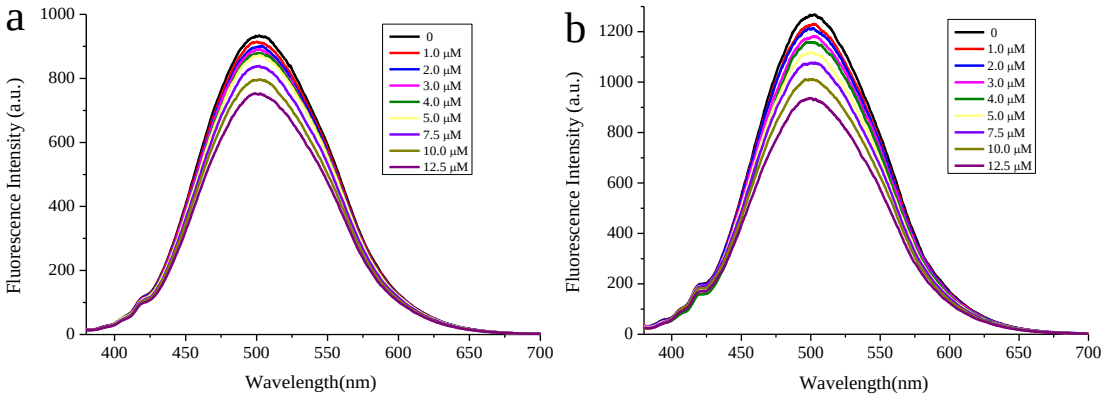


Fig. S18 Fluorescence spectra of acetonitrile suspension of (a) **COF-BABD-DB** and (b) **COF-BABD-BZ** upon increasing addition of DNB.

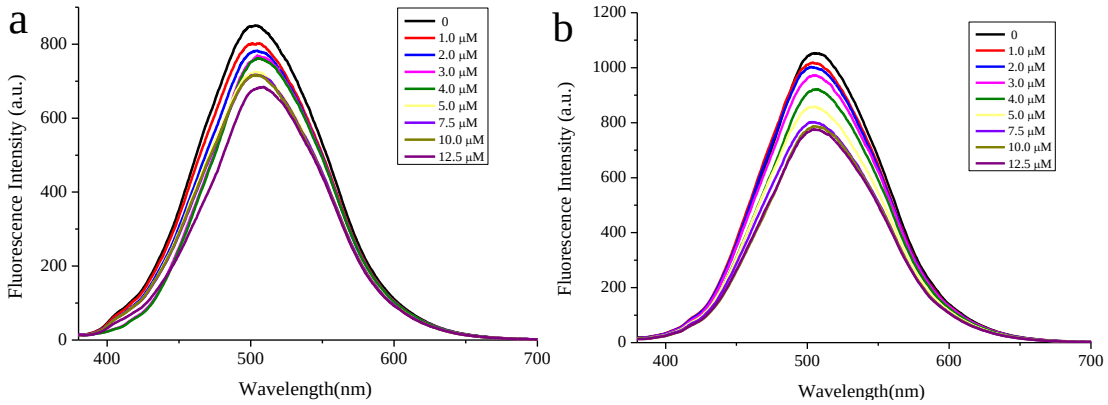


Fig. S19 Fluorescence spectra of acetonitrile suspension of (a) **COF-BABD-DB** and (b) **COF-BABD-BZ** upon increasing addition of NP.

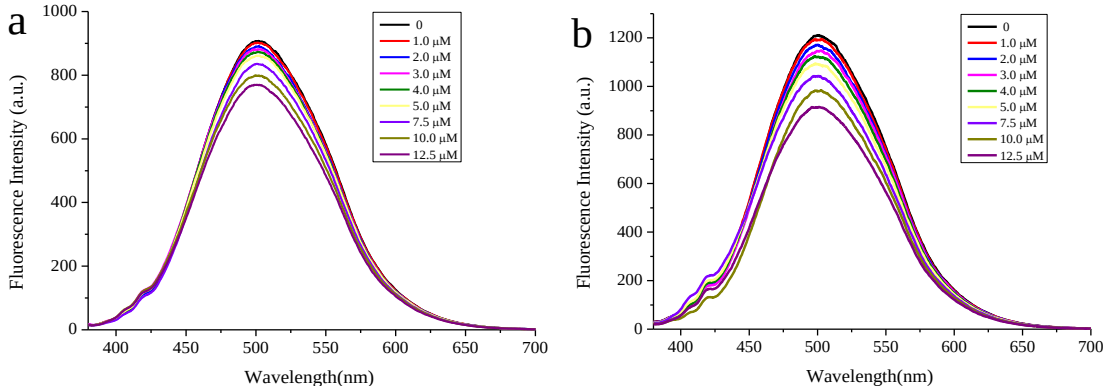


Fig. S20 Fluorescence spectra of acetonitrile suspension of (a) **COF-BABD-DB** and (b) **COF-BABD-BZ** upon increasing addition of NB.

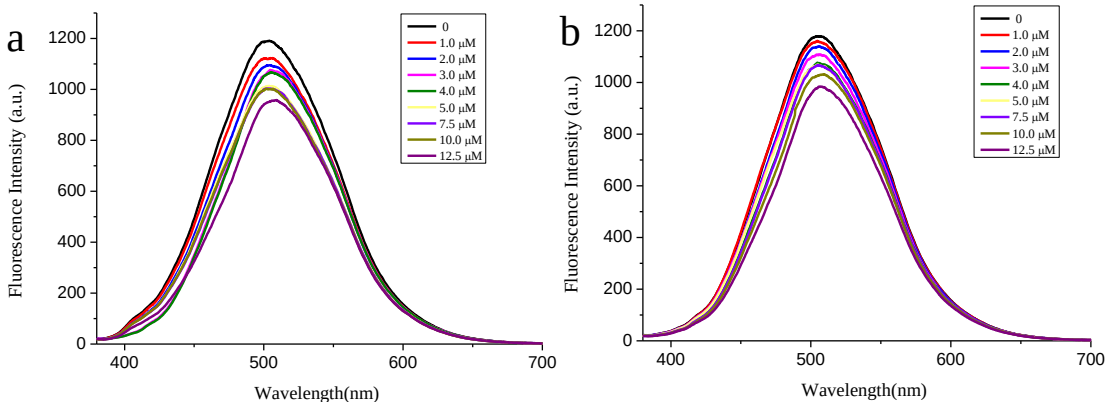


Fig. S21 Fluorescence spectra of acetonitrile suspension of (a) **COF-BABD-DB** and (b) **COF-BABD-BZ** upon increasing addition of NT.

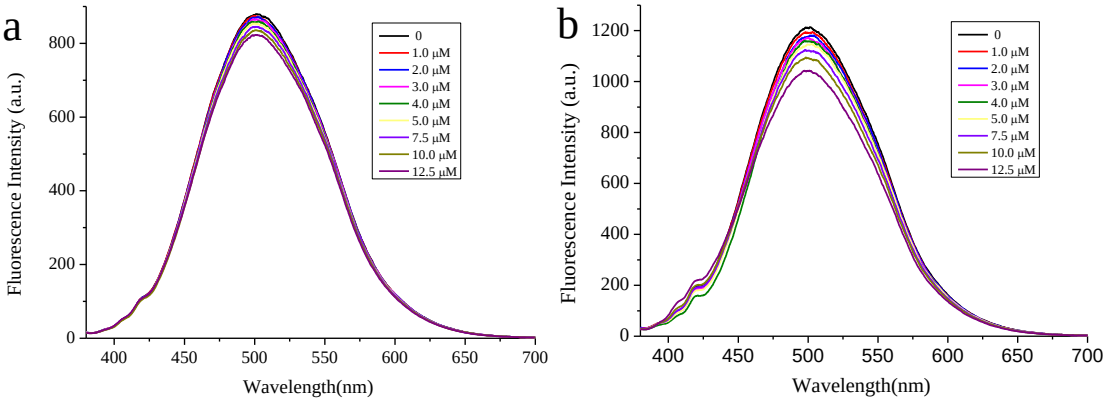


Fig. S22 Fluorescence spectra of acetonitrile suspension of (a) **COF-BABD-DB** and (b) **COF-BABD-BZ** upon increasing addition of DNT.

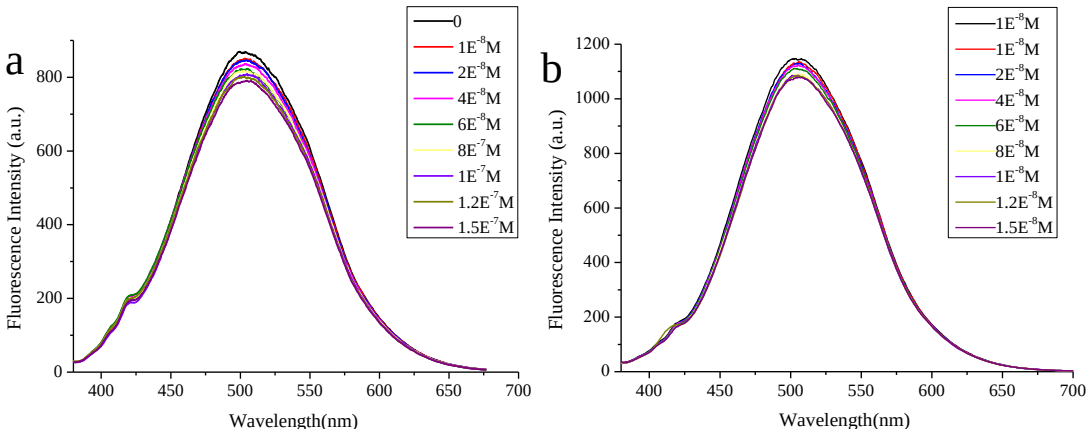


Fig. S23 Fluorescence spectra of acetonitrile suspension of (a) **COF-BABD-DB** and (b) **COF-BABD-BZ** upon increasing addition of TNP. The data were used to generated the Stern–Volmer plots of TNP.

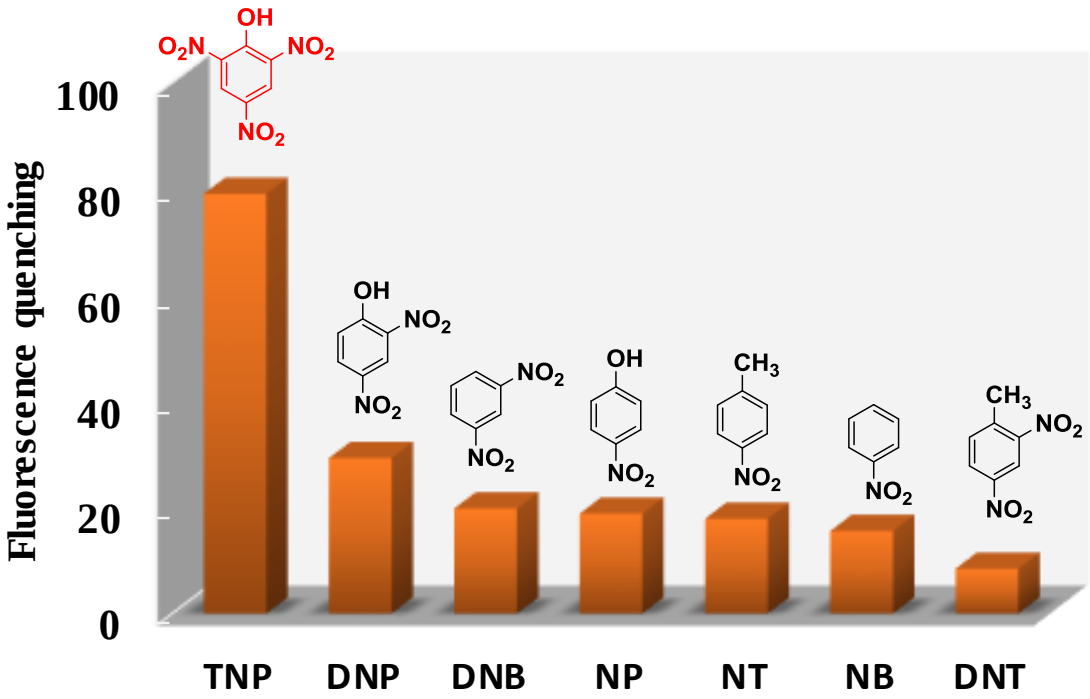


Fig. S24 Fluorescence quenching (%) of **COF-BABD-DB** with various nitroaromatic analytes at a concentration of 12.5 μM. TNP quenched 79.0% of the fluorescence emission of **COF-BABD-DB**. For the other nitroaromatics, their quenching efficiencies are less than 29%.

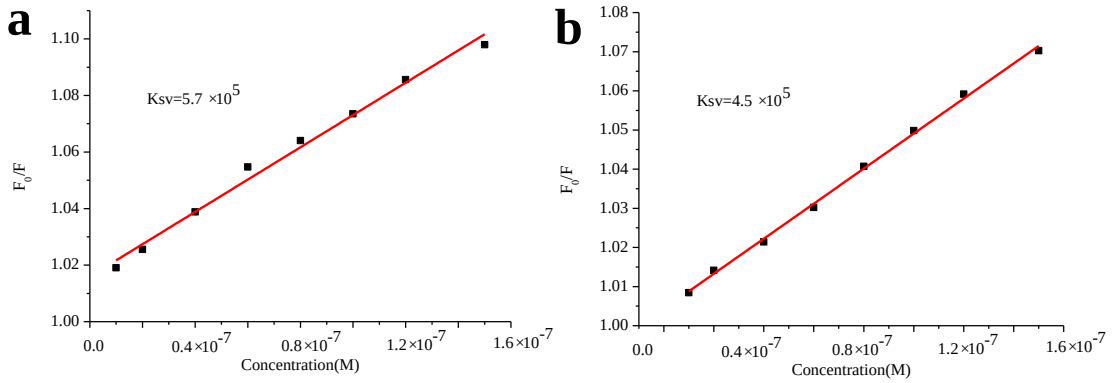


Fig. S25 Stern–Volmer plots for the quenching of (a) **COF-BABD-DB** and (b) **COF-BABD-BZ** dispersions in acetonitrile by TNP.

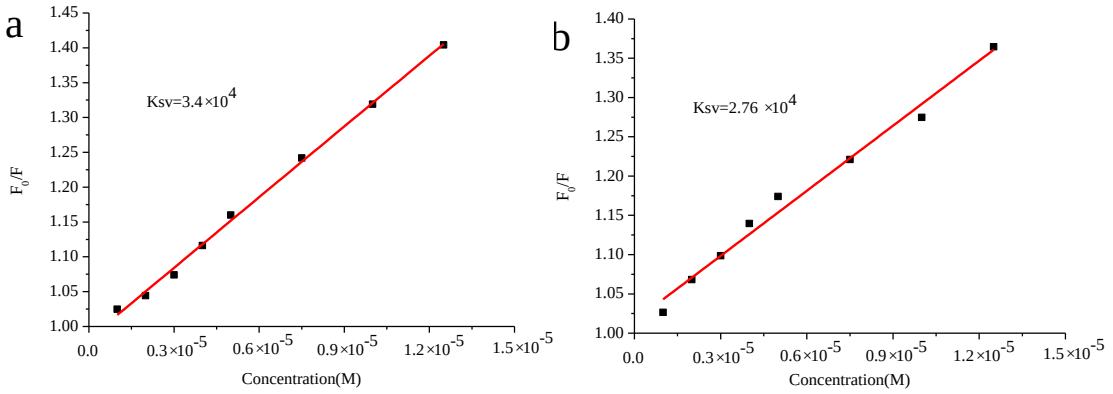


Fig. S26 Stern–Volmer plots for the quenching of (a) **COF-BABD-DB** and (b) **COF-BABD-BZ** dispersions in acetonitrile by DNP.

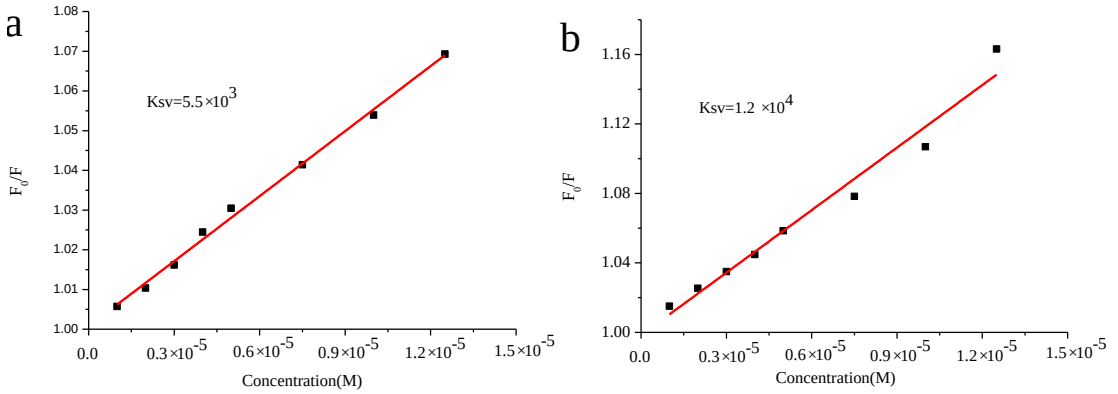


Fig. S27 Stern–Volmer plots for the quenching of (a) **COF-BABD-DB** and (b) **COF-BABD-BZ** dispersions in acetonitrile by DNT.

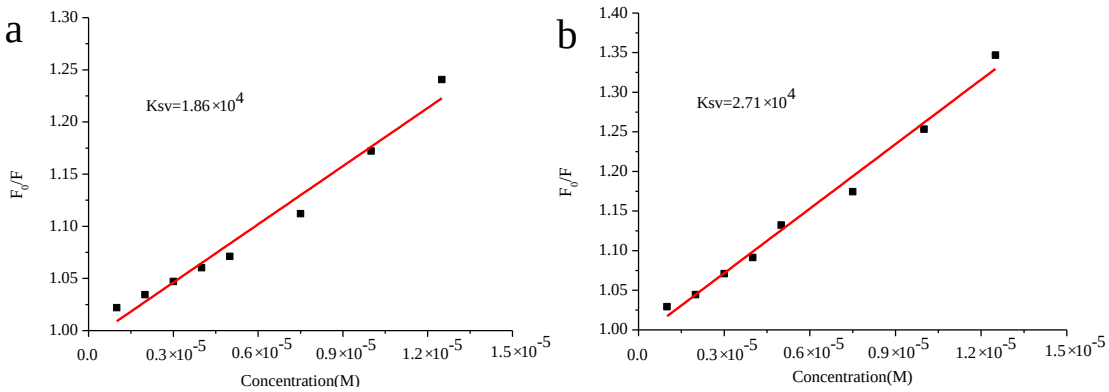


Fig. S28 Stern–Volmer plots for the quenching of (a) **COF-BABD-DB** and (b) **COF-BABD-BZ** dispersions in acetonitrile by DNB.

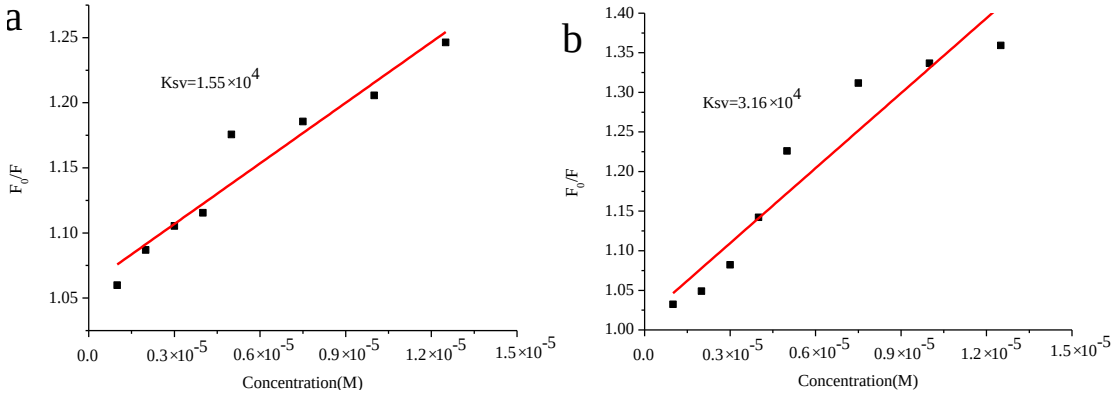


Fig. S29 Stern–Volmer plots for the quenching of (a) **COF-BABD-DB** and (b) **COF-BABD-BZ** dispersions in acetonitrile by NP.

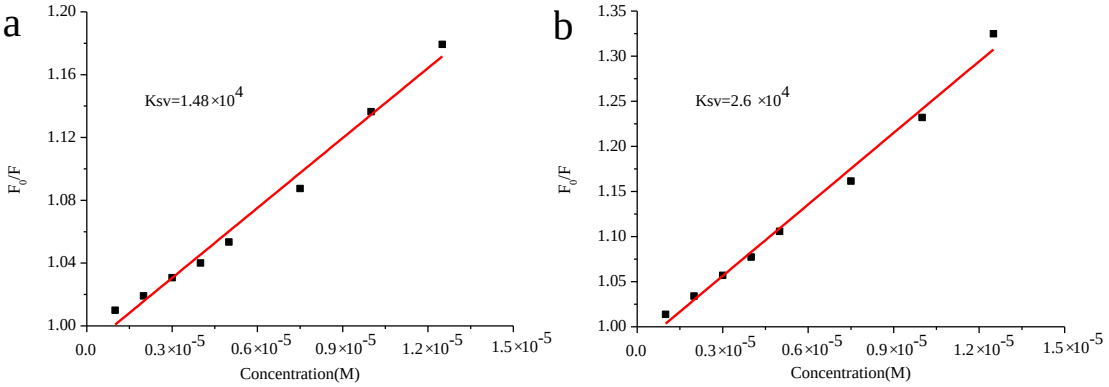


Fig. S30 Stern–Volmer plots for the quenching of (a) **COF-BABD-DB** and (b) **COF-BABD-BZ** dispersions in acetonitrile by NB.

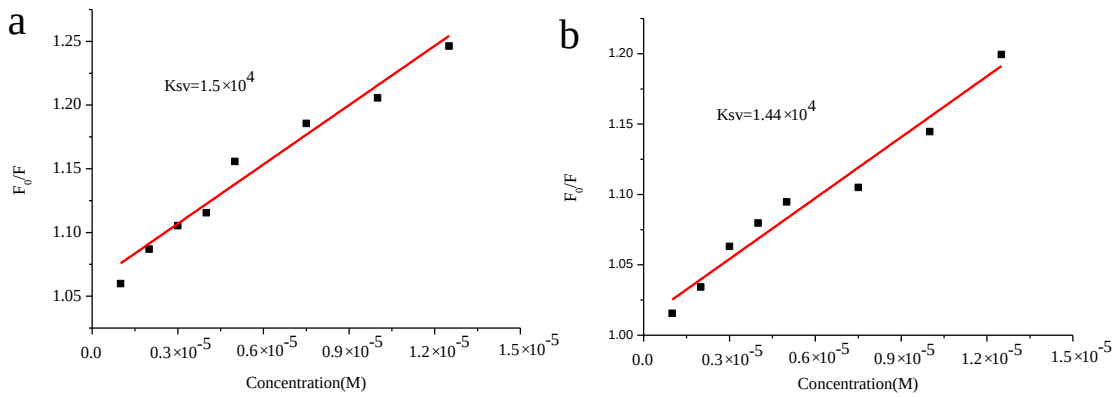


Fig. S31 Stern–Volmer plots for the quenching of (a) **COF-BABD-DB** and (b) **COF-BABD-BZ** dispersions in acetonitrile by NT.

Table. S3 Stern–Volmer quenching constants (Ksv) towards TNP of different POP-based chemosenors.

	Chemosenors	Excitation wavelength (nm)	FL emission @maximum intensity (nm)	Fluorescence quenching (%)	K_{SV} (M^{-1})	References
1	**COF-BABD-DB**	370	510	79	5.7×10^5	This work
2	**COF-BABD-BZ**	370	505	92	4.5×10^5	This work
3	**Py-Azine COF**	470	522	69	7.8×10^4	S3
4	**PCTF-8**	395	562	71	1.3×10^5	S4
5	**TRIPTA**	365	513	62	2.7×10^6	S5
6	**TAPB-TFPB**	285	425	80	5.9×10^4	S6
7	**TAPB-TFP**	300	425	67	3.2×10^4	S6
8	***i*PrTAPB-TFP**	290	334	68	1.8×10^4	S6
9	***i*PrTAPB-TFPB**	285	425	64	3.0×10^4	S6
10	**TPECz**	331	524	76	4.0×10^5	S7
11	**TfpBDH-CONs**	365	541	63	2.6×10^4	S8
12	**COP-61**	365	533	-	2.4×10^5	S9
13	**COP-64**	365	533	-	9.8×10^4	S9
14	**COP-301**	372	412	99	2.6×10^5	S10
15	**COP-401**	396	456	94	8.3×10^4	S10
16	**DTF**	500	570	-	2.1×10^3	S11

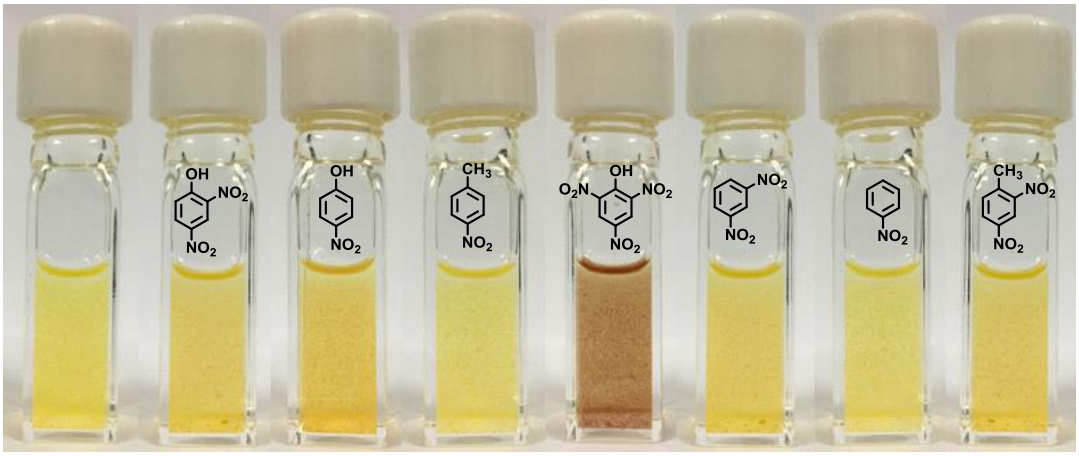


Fig. S32 Photographs of **COF-BABD-DB** dispersions in acetonitrile in the presence of various nitroaromatic analytes (4.0 μM).

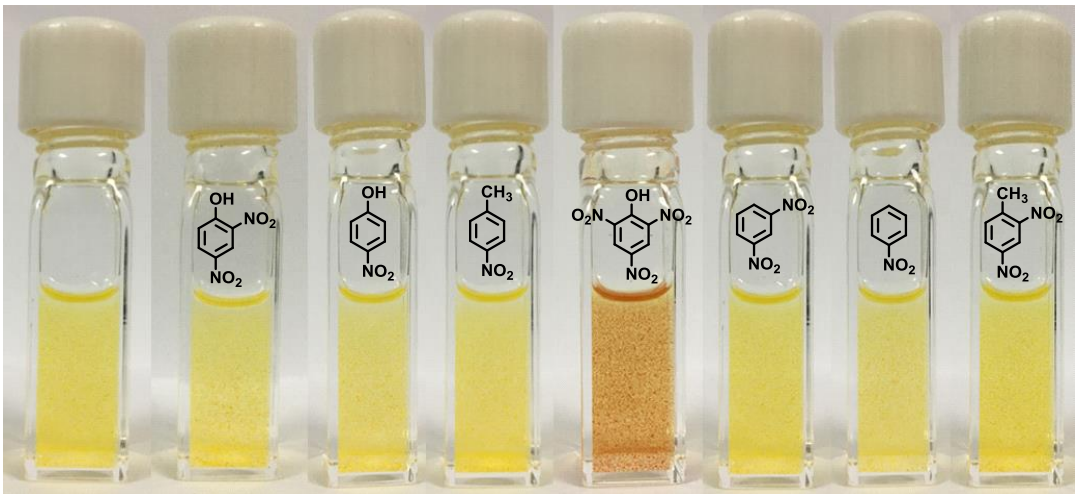


Fig. S33 Photographs of **COF-BABD-BZ** dispersions in acetonitrile in the presence of various nitroaromatic analytes (4.0 μM).

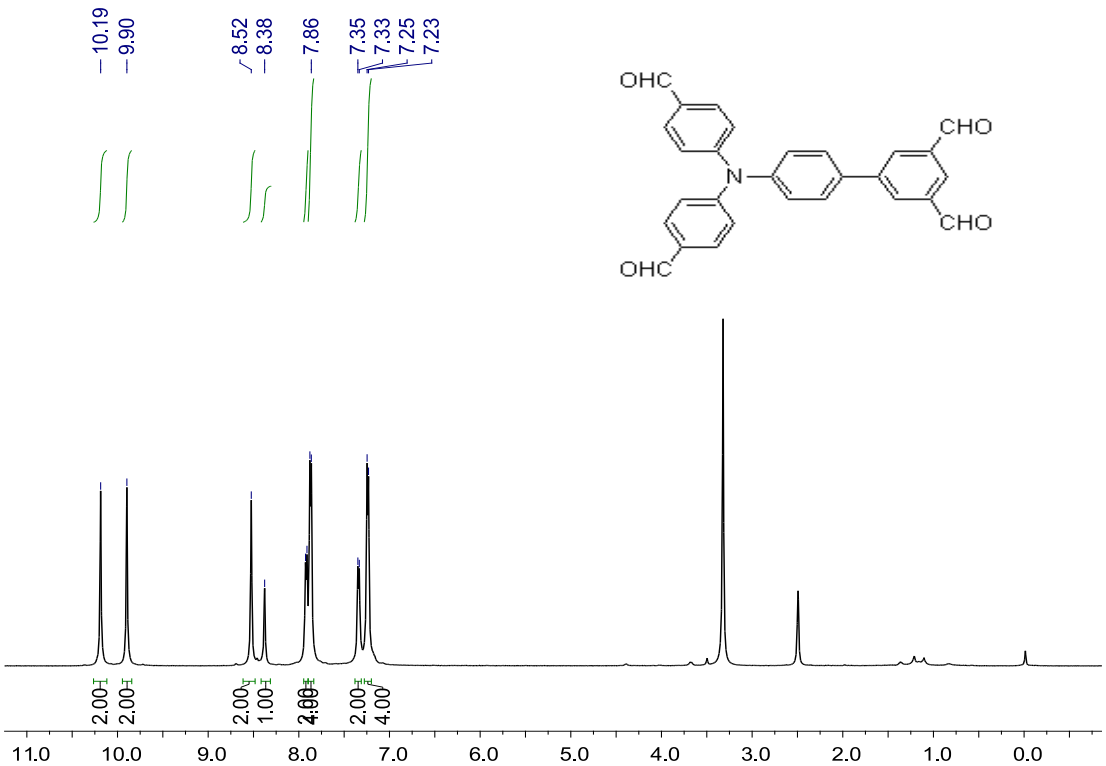


Fig. S34 The ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of BABD.

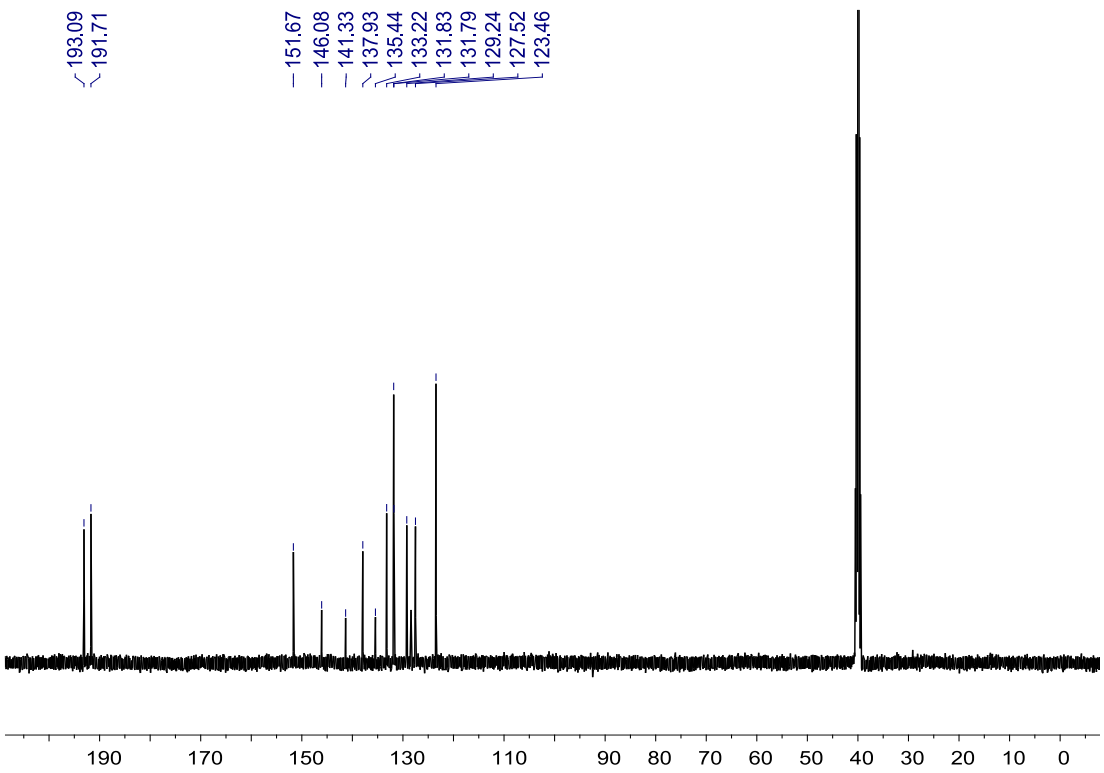


Figure. S35 ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of compound BABD.

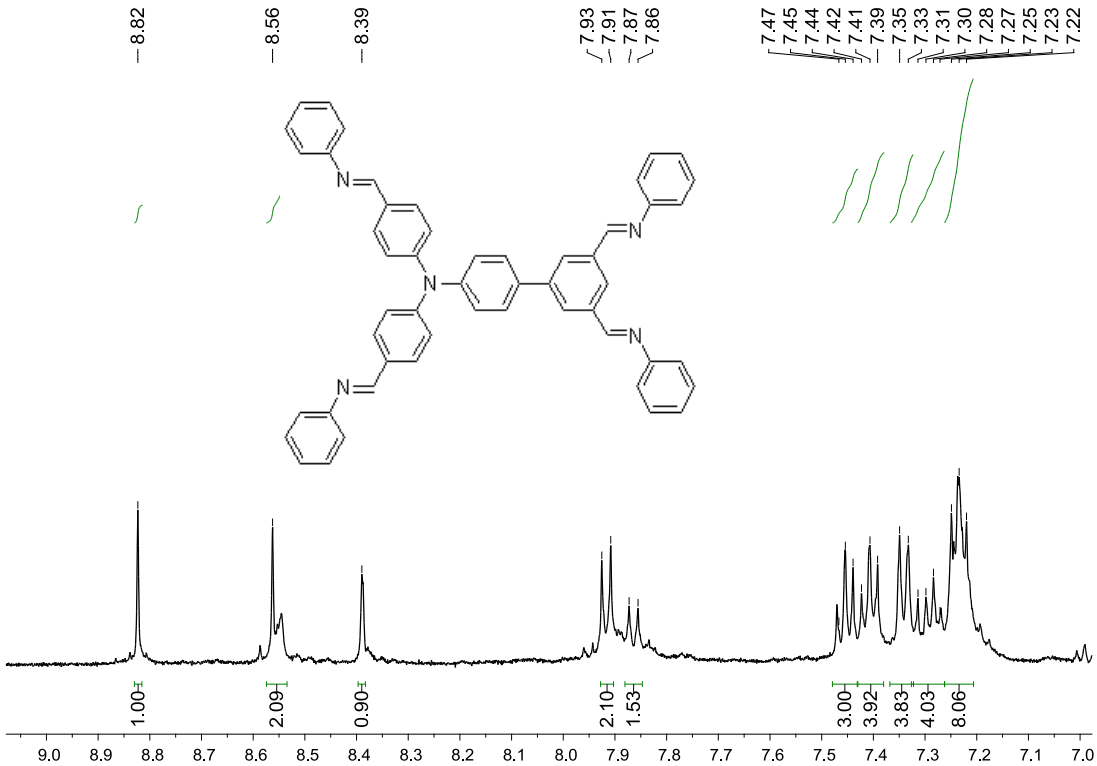


Fig. S36 ^{1}H NMR (500 MHz, DMSO-d_6) of the model molecule.

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