

## Supporting Information

### Dual luminescent covalent organic framework for nitro-explosives detection

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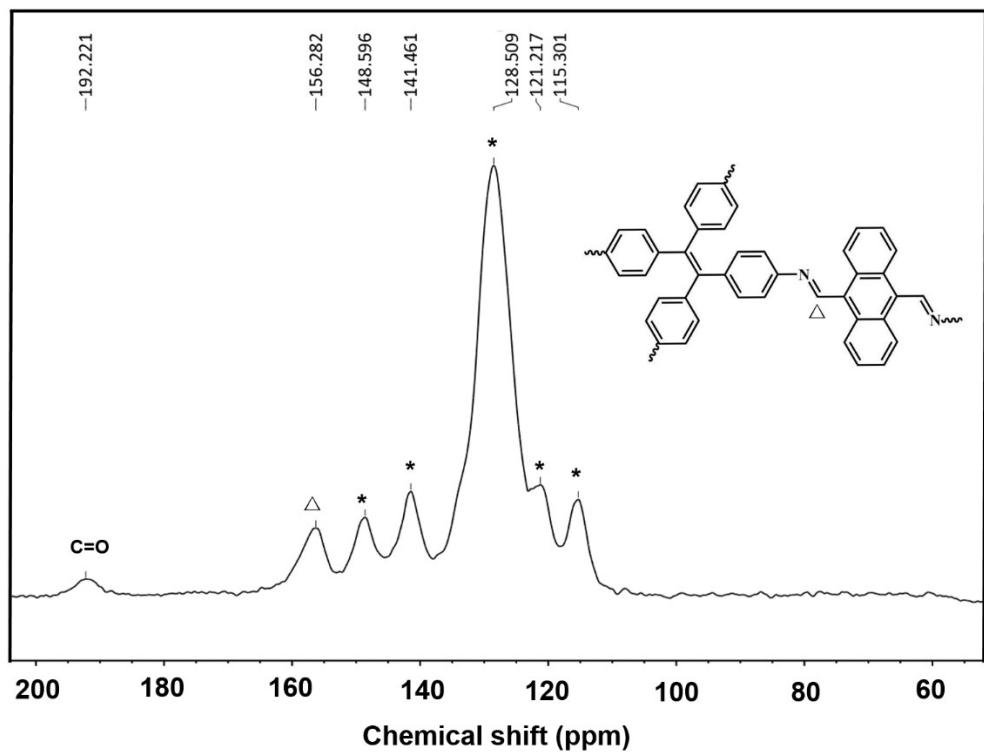
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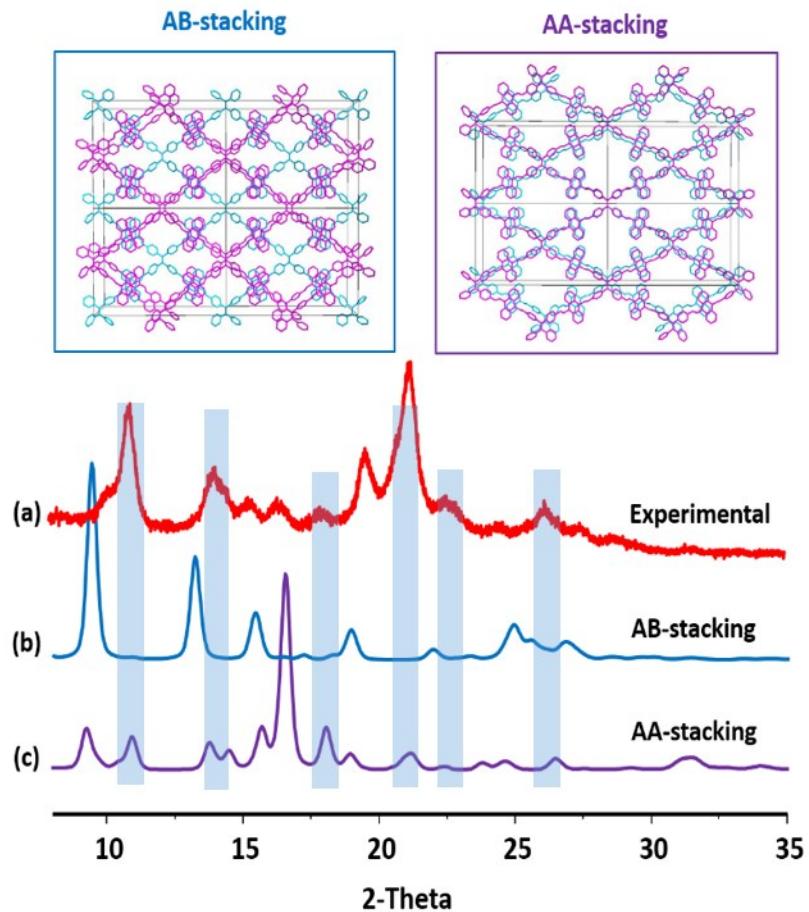
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(i)  **$^{13}\text{C}$  CP/MAS Solid-state NMR spectrum of DL-COF**



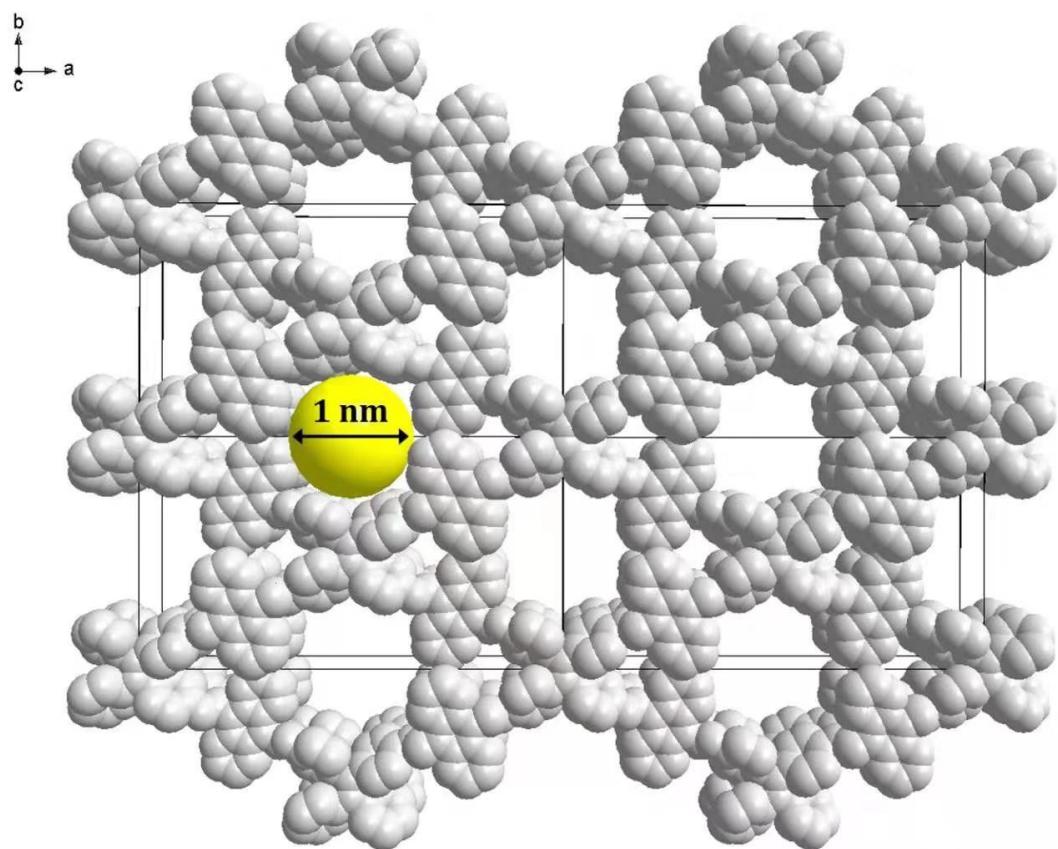
**Fig. S1**  $^{13}\text{C}$  CP/MAS Solid-state NMR spectrum of DL-COF: The triangle ( $\triangle$ ) represent chemical shift of imine carbon and the asterisks (\*) represent chemical shifts of aromatic carbons.

**(ii) PXRD pattern of DL-COF with simulated AA and AB-stacking structures**



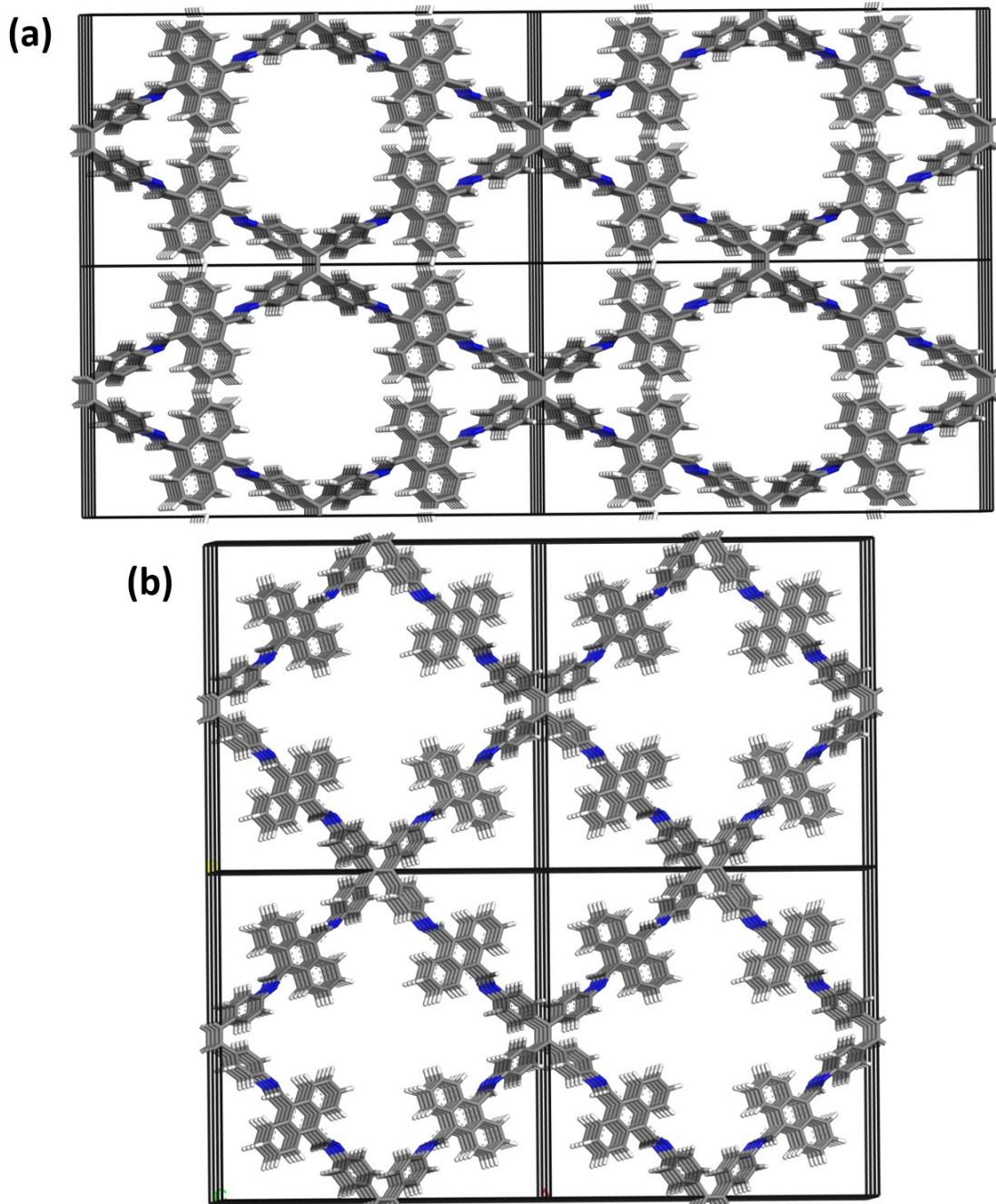
**Fig. S2** (a) Experimentally observed PXRD pattern of DL-COF, (b) Simulated PXRD pattern for AB-stacking structure and (c) Simulated PXRD pattern for AA-stacking structure.

**(iii) Pore size of simulated AA-stacking structure**



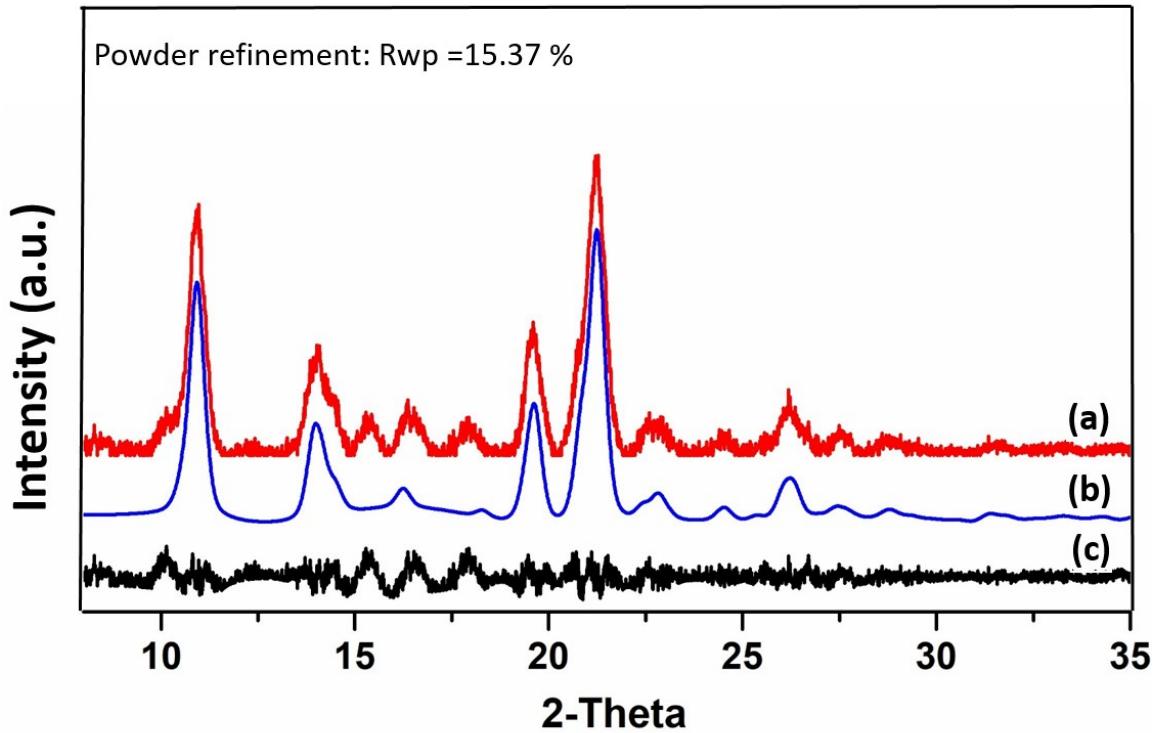
**Fig. S3** Pore size of simulated AA-stacking structure

**(iv) Simulated structures of AA-stacking on base of ETTA orientation**



**Fig. S4** Simulated AA-stacking structures on base of ETTA orientation

(iv) Pawley refined simulation patterns of DL-COF



**Fig. S5** XRD patterns of the DL-COF: (a) experimental, (b) Pawley refined and (c) difference between experimental and calculated data.

(vi) Thermal stability test of DL-COF

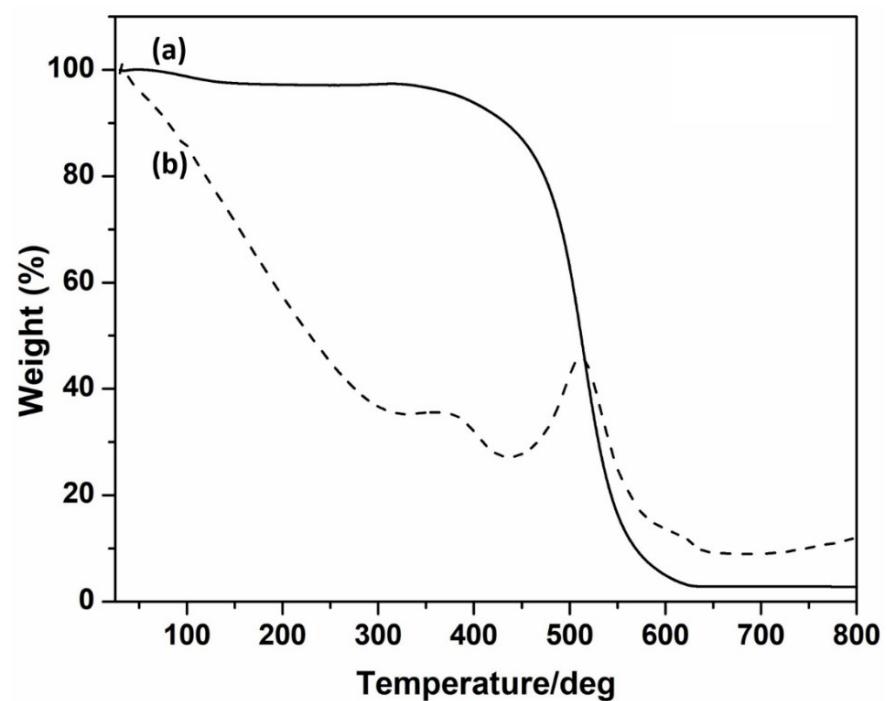
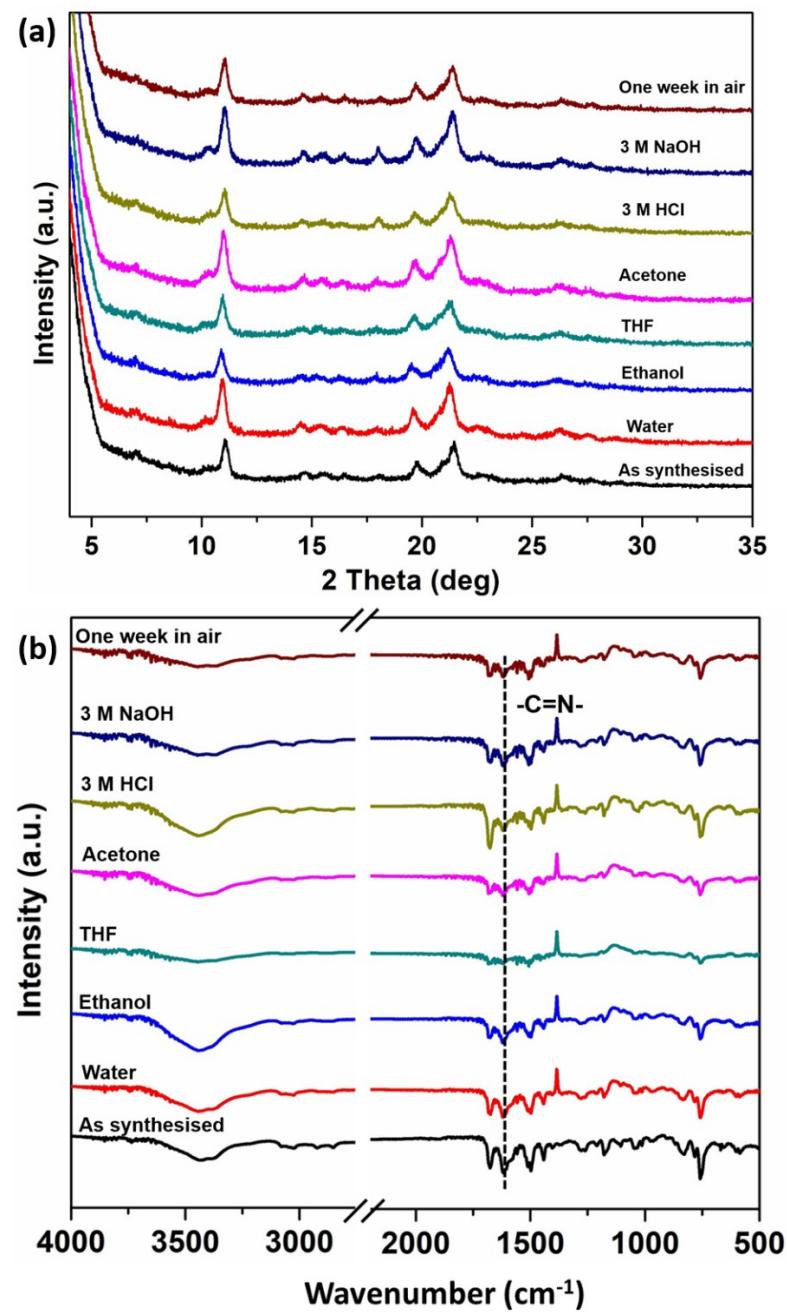


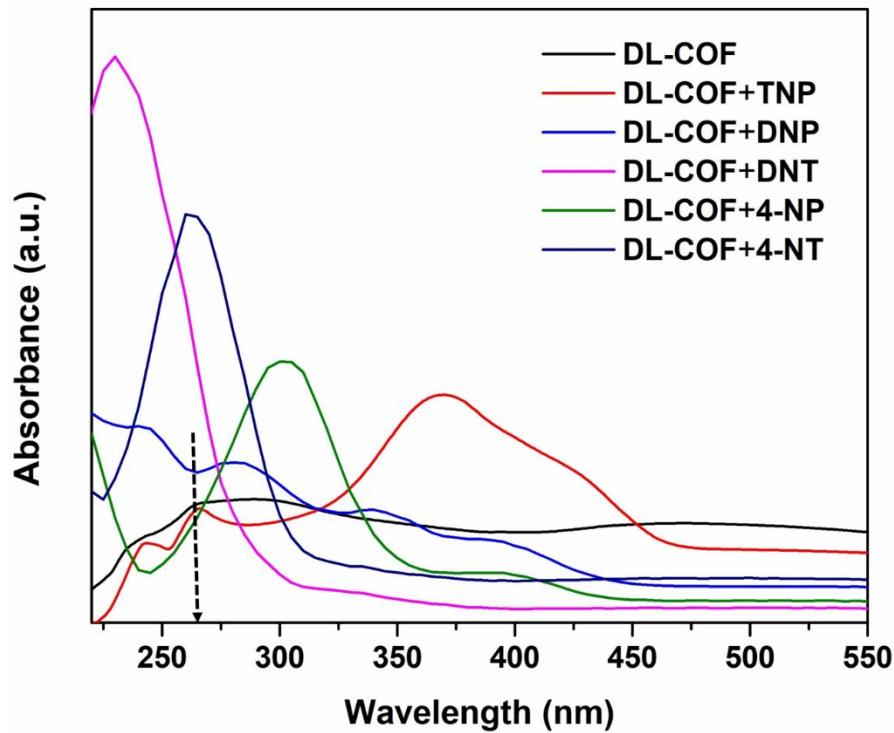
Fig. S6 (a) TGA and (b) DSC curves of the DL-COF

(vii) Chemical stability tests of DL-COF



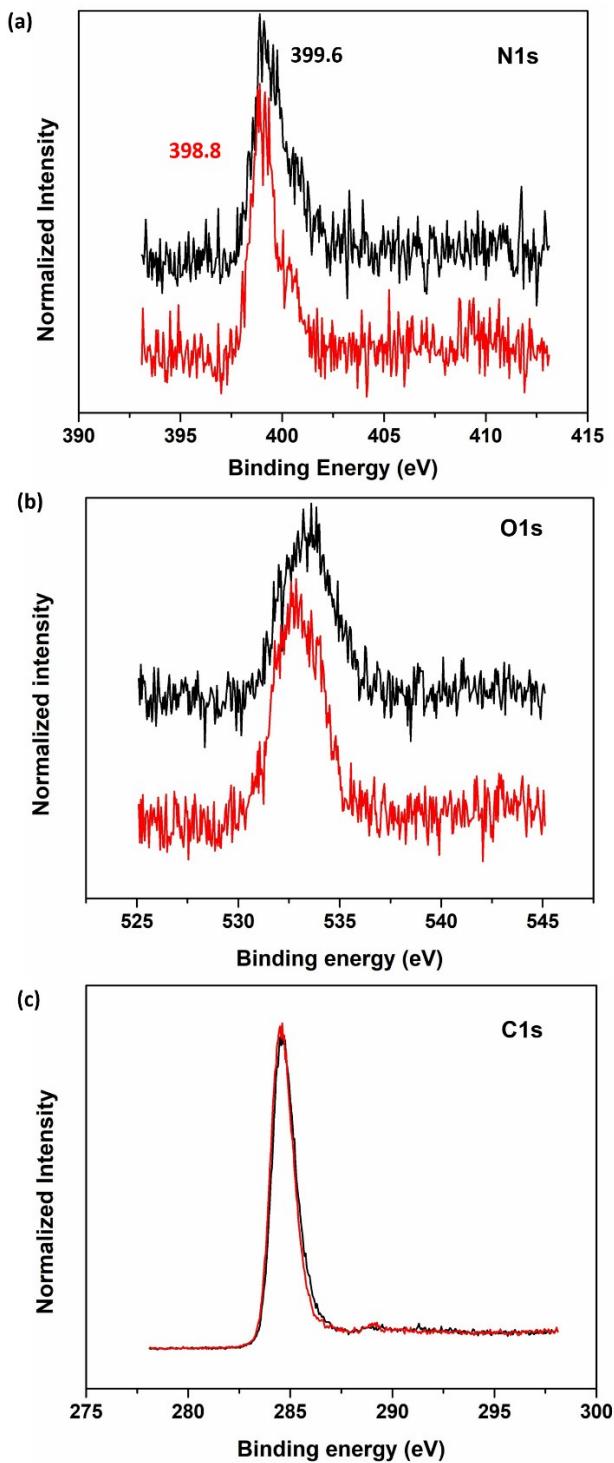
**Fig. S7** (a) PXRD patterns of the DL-COF after treatment in different chemical environments (b) FTIR spectra of the DL-COF after treatment in different chemical environments.

(viii) UV-Visible absorbance of DL-COF and tested nitro explosive analytes



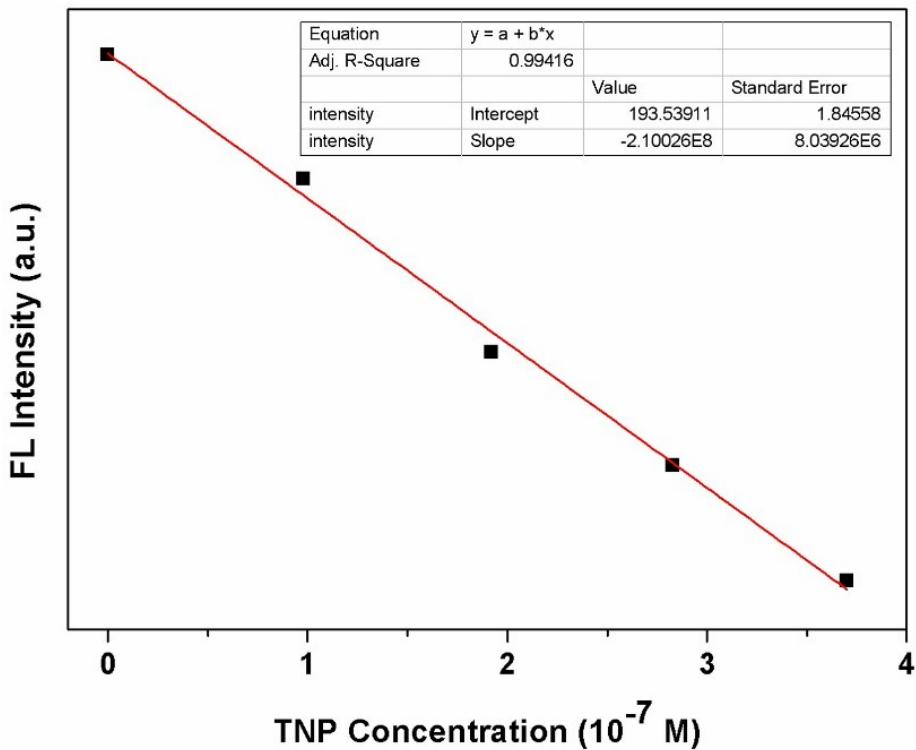
**Fig. S8** UV-visible absorbance of DL-COF and DL-COF with nitro explosive analytes.

(ix) XPS measurements of DL-COF and 4-NP+DL-COF



**Fig. S9** XPS spectra of DL-COF (black curves) and 4-NP+DL-COF (red curves). The C 1s signal at 284.5 eV, which is attributed to aromatic carbons. The O 1s at a binding energy of 533 eV and 532 eV are due to air contamination, water and hydroxyl groups in the sample. [21]

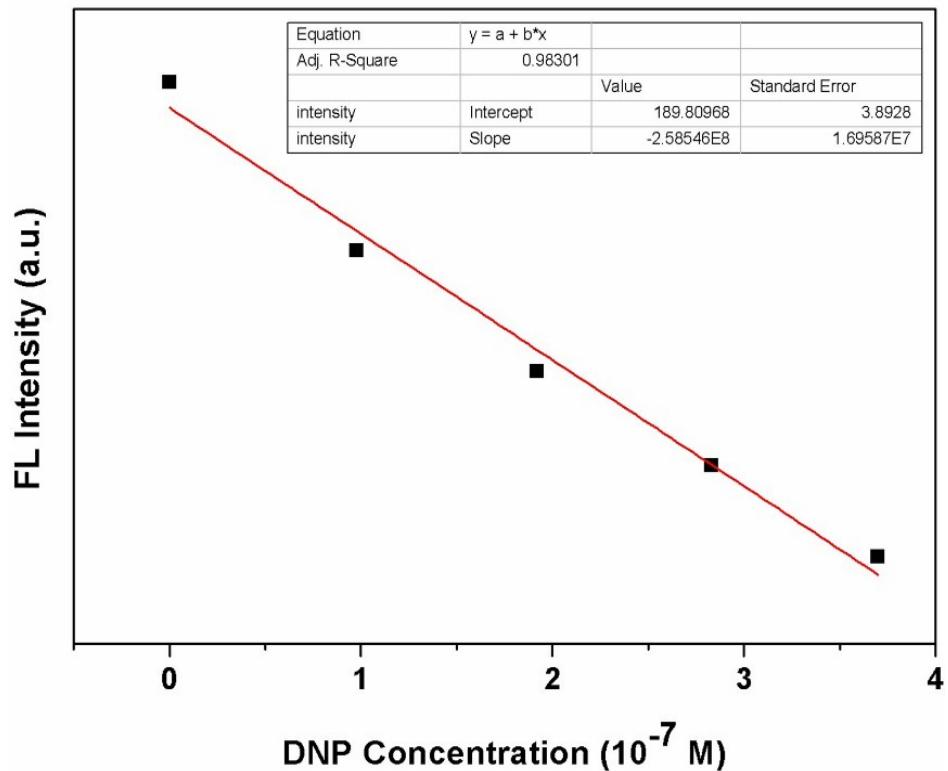
**(x) Limit of detection (LOD) calculations of nitro explosive analytes**



**Fig. S10** Linear region of fluorescence intensity of DL-COF upon incremental addition of TNP at  $\lambda_{em} = 311$  nm (upon  $\lambda_{ex} = 264$  nm) at room temperature.

**Calculation of Detection limit (LOD) for TNP:**

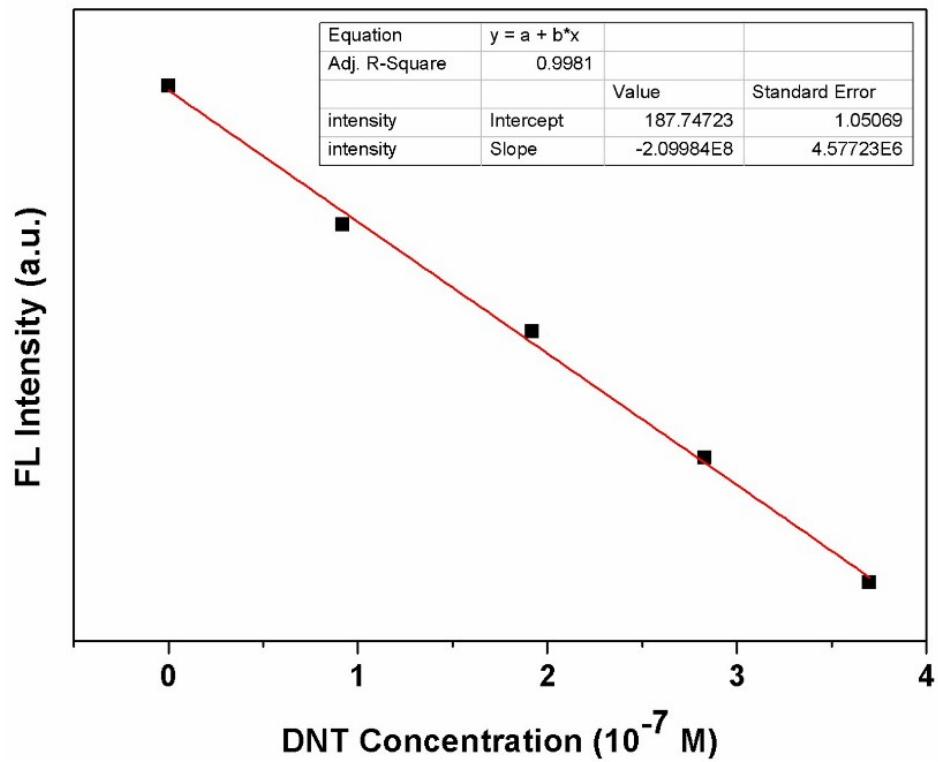
Slope from graph (m)	2.10026E+8 M <sup>-1</sup>
Standard deviation ( $\sigma$ )	4.0124
Limit of detection ( $3\sigma/m$ )	57.31 nM ( <b>13.10 ppb</b> )



**Fig. S11** Linear region of fluorescence intensity of DL-COF upon incremental addition of DNP at  $\lambda_{em} = 311$  nm (upon  $\lambda_{ex} = 264$  nm) at room temperature.

**Calculation of Detection limit (LOD) for DNP:**

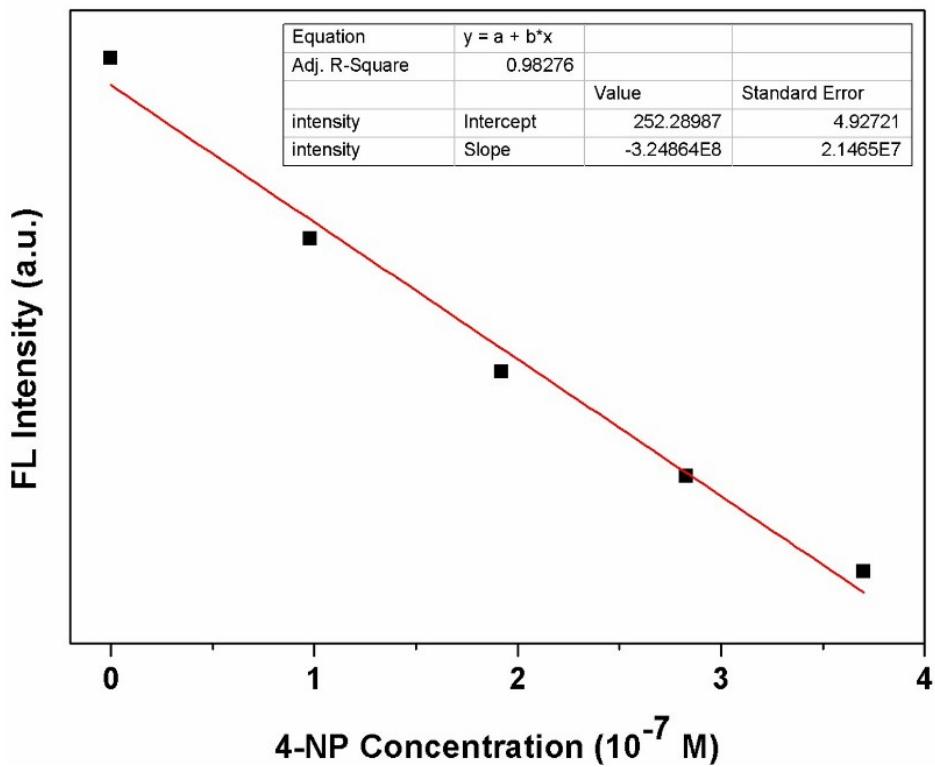
Slope from graph (m)	$2.58546E+8 \text{ M}^{-1}$
Standard deviation ( $\sigma$ )	4.0124
Limit of detection ( $3\sigma/m$ )	46.50 nM ( <b>8.56 ppb</b> )



**Fig. S12** Linear region of fluorescence intensity of DL-COF upon incremental addition of DNT at  $\lambda_{em} = 311$  nm (upon  $\lambda_{ex} = 264$  nm) at room temperature.

**Calculation of Detection limit (LOD) for DNT:**

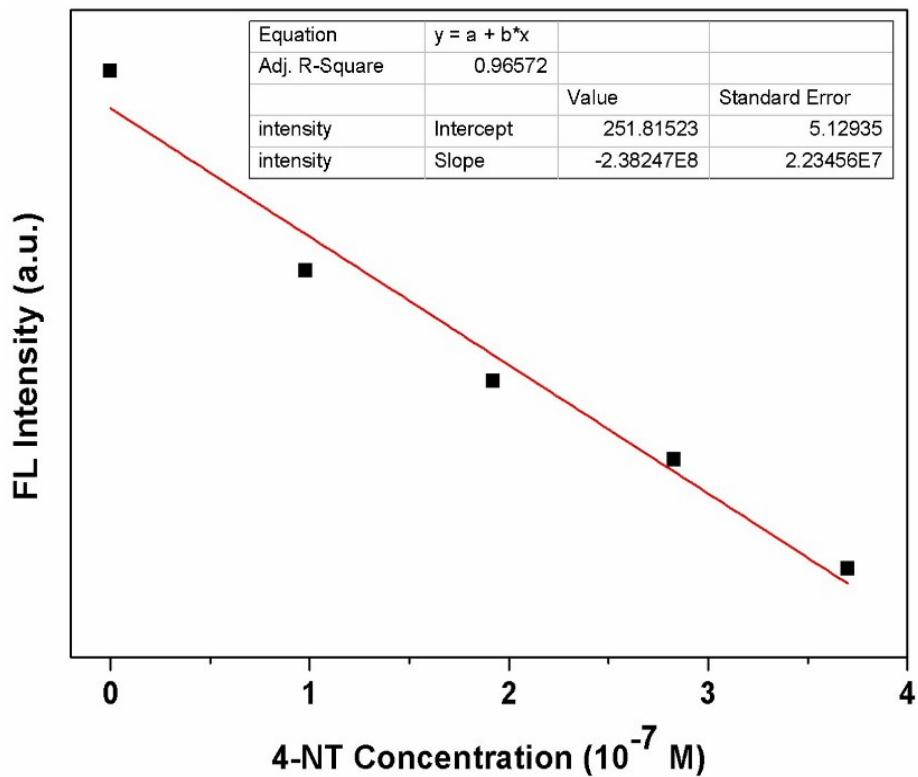
Slope from graph (m)	2.09984E+8 M <sup>-1</sup>
Standard deviation ( $\sigma$ )	4.0124
Limit of detection ( $3\sigma/m$ )	57.32 nM ( <b>10.40 ppb</b> )



**Fig. S13** Linear region of fluorescence intensity of DL-COF upon incremental addition of 4-NP at  $\lambda_{em} = 311$  nm (upon  $\lambda_{ex} = 264$  nm) at room temperature.

**Calculation of Detection limit (LOD) for 4-NP:**

Slope from graph (m)	3.24864E+8 M <sup>-1</sup>
Standard deviation ( $\sigma$ )	4.0124
Limit of detection ( $3\sigma/m$ )	37.05 nM ( <b>5.15 ppb</b> )

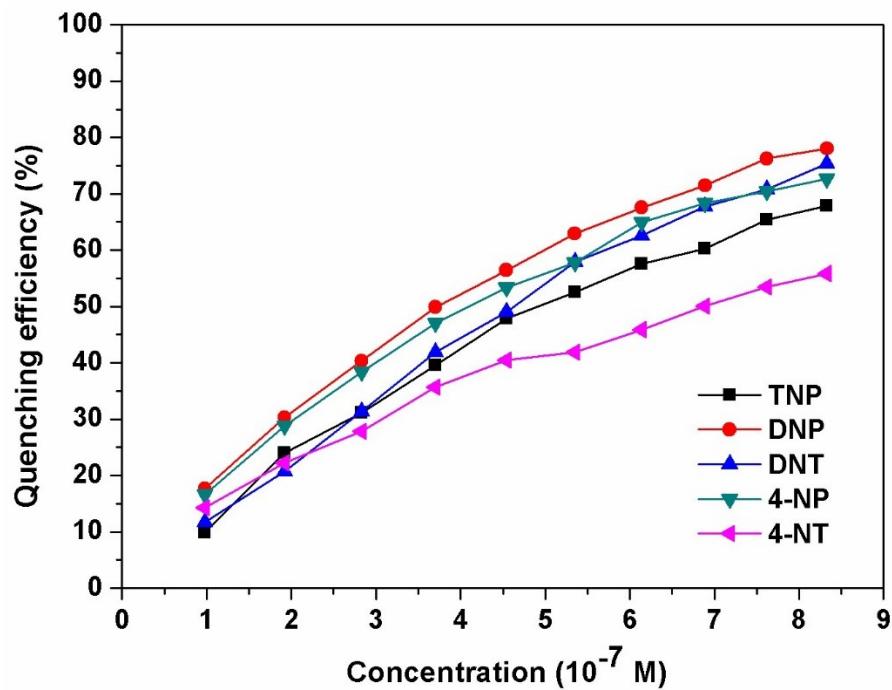


**Fig. S14** Linear region of fluorescence intensity of DL-COF upon incremental addition of 4-NT at  $\lambda_{em} = 311$  nm (upon  $\lambda_{ex} = 264$  nm) at room temperature.

**Calculation of Detection limit (LOD) for 4-NT:**

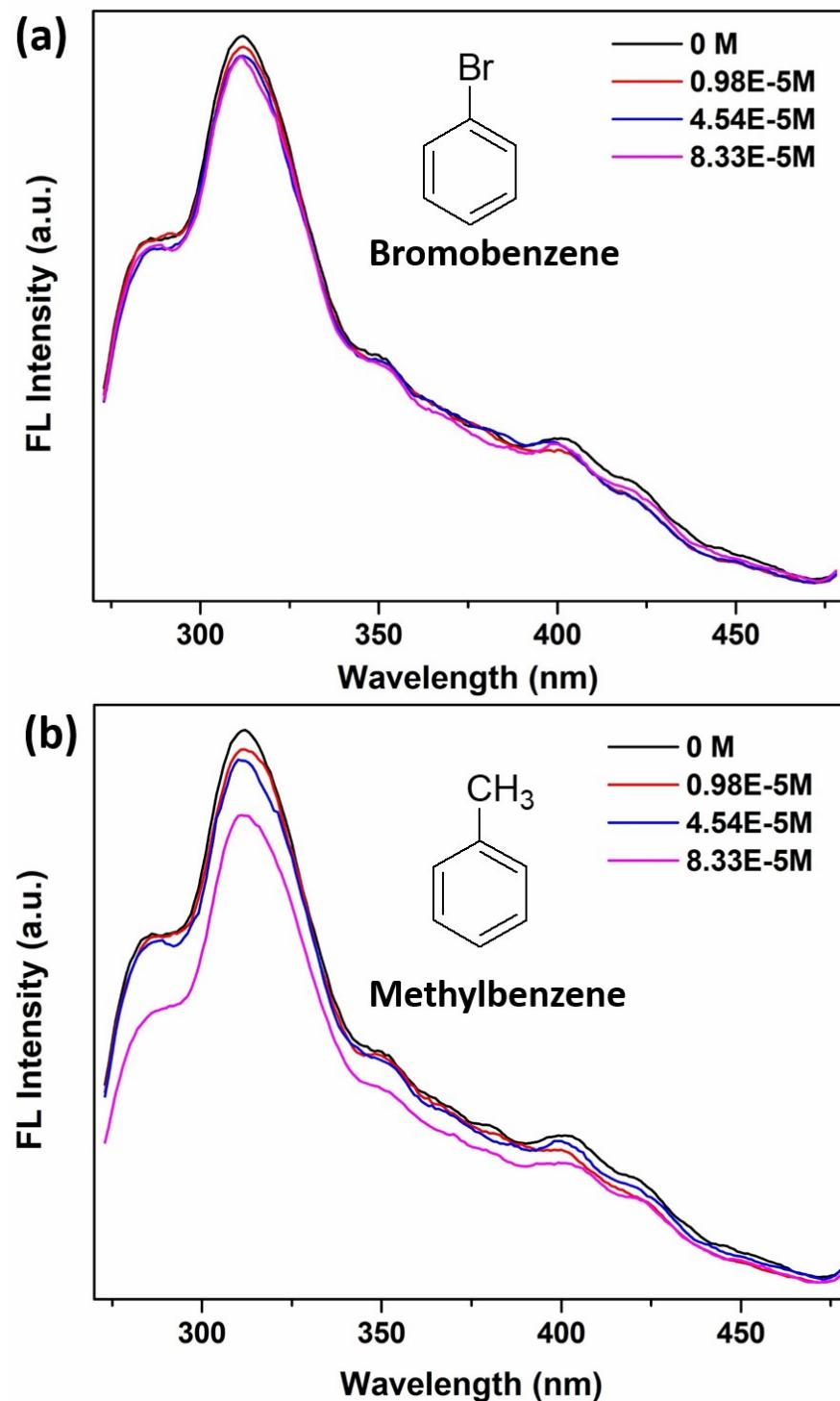
Slope from graph (m)	2.38247E+8 M <sup>-1</sup>
Standard deviation ( $\sigma$ )	4.0124
Limit of detection ( $3\sigma/m$ )	50.52 nM ( <b>6.92 ppb</b> )

(xi) Quenching efficiency (%) against concentrations of nitro explosive analytes



**Fig. S15** Quenching efficiency (%) against various concentrations of nitro explosive analytes.

(xii) Fluorescence quenching pattern of non-explosives analytes



**Fig. S16** Fluorescence quenching pattern of non-explosives analytes at  $\lambda_{em} = 311$  nm (upon  $\lambda_{ex} = 264$  nm) at room temperature.

**(xiii) Comparison study of tested nitro explosive analytes with reported COFs and MOFs**

**Table S1.** Comparison study of TNP with other COFs and MOFs.

Materials	Ksv ( $M^{-1}$ )	LOD	Medium	Ref.
DL-COF	$2.42 \times 10^6$	$57.31 \times 10^{-9} M$ (13.10 ppb)	EtOH	This work
Covalent organic frameworks (COFs)				
TAPB-TFP-COF	$3.20 \times 10^4$	NA	MeCN	[1]
iPrTAPB-TFPB-COF	$3.0 \times 10^4$	NA	MeCN	[1]
iPrTAPB-TFP-COF	$1.8 \times 10^4$	NA	MeCN	[1]
Metal organic frameworks (MOFs)				
$[(CH_3)_2NH_2].2[Eu_6(OH)_8(ADBA)_6(H_2O)_6]$ (DMF) <sub>15</sub>	$1.282 \times 10^5$	NA	D. Water	[2]
$\{[Zn(C_{34}H_{18}O_8)_{0.5}(C_{20}N_2H_{16})_{0.5}].[0.5(C_{20}N_2H_{16})]\}_n$	$8.10 \times 10^4$	NA	DMF	[3]
$\{[0.2Me_2NH_2][Zn_8(ad)_4(BPDC)_6] \cdot G\}_n$	$6.40 \times 10^4$	$12.90 \times 10^{-6} M$	Water	[4]
$[Cd(NDC)_{0.5}(PCA)]_n$	$3.50 \times 10^4$	NA	MeCN	[5]
$[Zn_2(NDC)_2(bpy)].Gx$	$0.40 \times 10^4$	NA	EtOH	[6]

NA= Not available

**Table S2.** Comparison study of DNP with other COFs and MOFs.

Materials	K <sub>sv</sub> (M <sup>-1</sup> )	LOD	Medium	Ref.
DL-COF	4.28 ×10 <sup>6</sup>	46.50×10 <sup>-9</sup> M (8.56 ppb)	EtOH	This work
Covalent organic frameworks (COFs)				
TRIPTA-COF	2.13×10 <sup>6</sup>	NA	MeCN	[7]
TfpBDH-COF	3.5×10 <sup>3</sup>	NA	Isopropylalcohol	[8]
Py-Azine COF	2.10×10 <sup>3</sup>	NA	MeCN	[9]
Metal organic frameworks (MOFs)				
In-ADBA	8.99×10 <sup>4</sup>	NA	Water	[2]
FJI-H15	2.54×10 <sup>4</sup>	NA	Dimethylacetamide	[10]
UiO-68-mtpdc/etpdc	2.30×10 <sup>4</sup>	NA	Methanol	[11]

NA= Not available

**Table S3.** Comparison study of DNT with other COFs and MOFs.

Materials	K <sub>sv</sub> (M <sup>-1</sup> )	LOD	Medium	Ref.
DL-COF	3.71 ×10 <sup>6</sup>	57.32×10 <sup>-9</sup> M (10.40 ppb)	EtOH	This work
Covalent organic frameworks (COFs)				
TRIPTA-COF	1.19×10 <sup>6</sup>	NA	MeCN	[7]
Py-Azine COF	9.10×10 <sup>3</sup>	NA	MeCN	[9]
iPrTAPB-TFP-COF	8.80×10 <sup>3</sup>	NA	MeCN	[1]
TAPB-TFP-COF	8.70×10 <sup>3</sup>	NA	MeCN	[1]
iPrTAPB-TFPB-COF	1.20×10 <sup>3</sup>	NA	MeCN	[1]
Metal organic frameworks (MOFs)				
[Y <sub>1.8</sub> Eu <sub>0.2</sub> (PDA) <sub>3</sub> (H <sub>2</sub> O)1]·2H <sub>2</sub>	5.01×10 <sup>4</sup>	NA	MeCN	[12]
[Zn <sub>2</sub> (NDC) <sub>2</sub> (bpy)]·Gx	5.1×10 <sup>3</sup>	NA	EtOH	[13]
Eu <sub>3</sub> (MFDA) <sub>4</sub> (NO <sub>3</sub> ) <sub>3</sub> (DMF) <sub>3</sub>	1.30×10 <sup>3</sup>	NA	DMF	[14]

NA= Not available

**Table S4.** Comparison study of 4-NP with other COFs and MOFs.

Materials	K <sub>sv</sub> (M <sup>-1</sup> )	LOD	Medium	Ref.
DL-COF	3.18 ×10 <sup>6</sup>	37.05×10 <sup>-9</sup> M (5.15 ppb)	EtOH	This work
Covalent organic frameworks (COFs)				
TRIPTA-COF	5.80×10 <sup>5</sup>	NA	MeCN	[7]
Py-Azine COF	5.90×10 <sup>2</sup>	NA	MeCN	[9]
Metal organic frameworks (MOFs)				
UPC-21	3.09 ×10 <sup>6</sup>	0.0896 ppm	DMSO	[15]
In-ADBA	5.11 ×10 <sup>4</sup>	NA	Water	[2]
BUT-13	4.70 ×10 <sup>4</sup>	NA	Water	[16]
BUT-12	4.20 ×10 <sup>4</sup>	NA	Water	[16]
[Zn <sub>2</sub> (TPOM)(NH <sub>2</sub> -BDC) <sub>2</sub> ]·4H <sub>2</sub> O	2.17 ×10 <sup>4</sup>	NA	DMF	[17]
UPC-17	1.26 ×10 <sup>4</sup>	NA	THF	[18]
[Zn(L)(H <sub>2</sub> O)]·H <sub>2</sub> O	1.25 ×10 <sup>4</sup>	3.34 μM	Water	[19]
UiO-68-mtpdc/etpdc	7.20 ×10 <sup>3</sup>	NA	Methanol	[11]

NA= Not available

**Table S5.** Comparison study of 4-NT with other COFs and MOFs.

Materials	K <sub>sv</sub> (M <sup>-1</sup> )	LOD	Medium	Ref.
DL-COF	1.56 ×10 <sup>6</sup>	50.52×10 <sup>-9</sup> M (6.92 ppb)	EtOH	This work
Covalent organic frameworks (COFs)				
Py-Azine COF	4.5 ×10 <sup>2</sup>	NA	MeCN	[9]
Metal organic frameworks (MOFs)				
[Y <sub>1.8</sub> Eu <sub>0.2</sub> (PDA) <sub>3</sub> (H <sub>2</sub> O)1]·2H <sub>2</sub> O	1.1×10 <sup>4</sup>	NA	MeCN	[12]
[Zn <sub>2</sub> (NDC) <sub>2</sub> (bpy)]·Gx	1.16×10 <sup>4</sup>	NA	EtOH	[13]
[Tb0.2Y0.18(PDA)3(H <sub>2</sub> O)1]·2H <sub>2</sub> O	0.39×10 <sup>4</sup>	NA	MeCN	[20]

**(xiv) TCSPC calculation for average fluorescence lifetime measurement**

**Table S6.** TCSPC calculation of DL-COF and nitro explosives analytes

Sample	T1	T2	B1	B2	A1=[B1/SumB]	A2=[B2/SumB]	$\langle I \rangle$ (ns)	$\chi^2$
DL-COF	1.3413	12.1924	0.106	0.015	0.8760	0.1239	2.68	1.18
DL-COF+TNP	1.4514	6.5424	0.077	0.020	0.7938	0.2061	2.50	1.47
DL-COF+DNP	1.0415	7.9345	0.120	0.012	0.9090	0.0909	1.66	0.94
DL-COF+DNT	0.9924	7.0937	0.111	0.015	0.8809	0.1190	1.71	0.93
DL-COF+4-NP	1.4020	6.3395	0.084	0.013	0.8659	0.1340	2.06	0.92
DL-COF+4-NT	1.2320	7.5945	0.090	0.015	0.8571	0.1428	2.14	1.07

Where,  $\langle I \rangle = A1T1+A2T2$  and  $\chi^2$  is the accuracy factor. [7]

## (xv) References

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**Graphical Abstract.**

