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Supporting Information

Hydrazone connected stable luminescent Covalent Organic Polymer for ultrafast detection of nitro-explosives

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i. PXRD spectra of H-COP

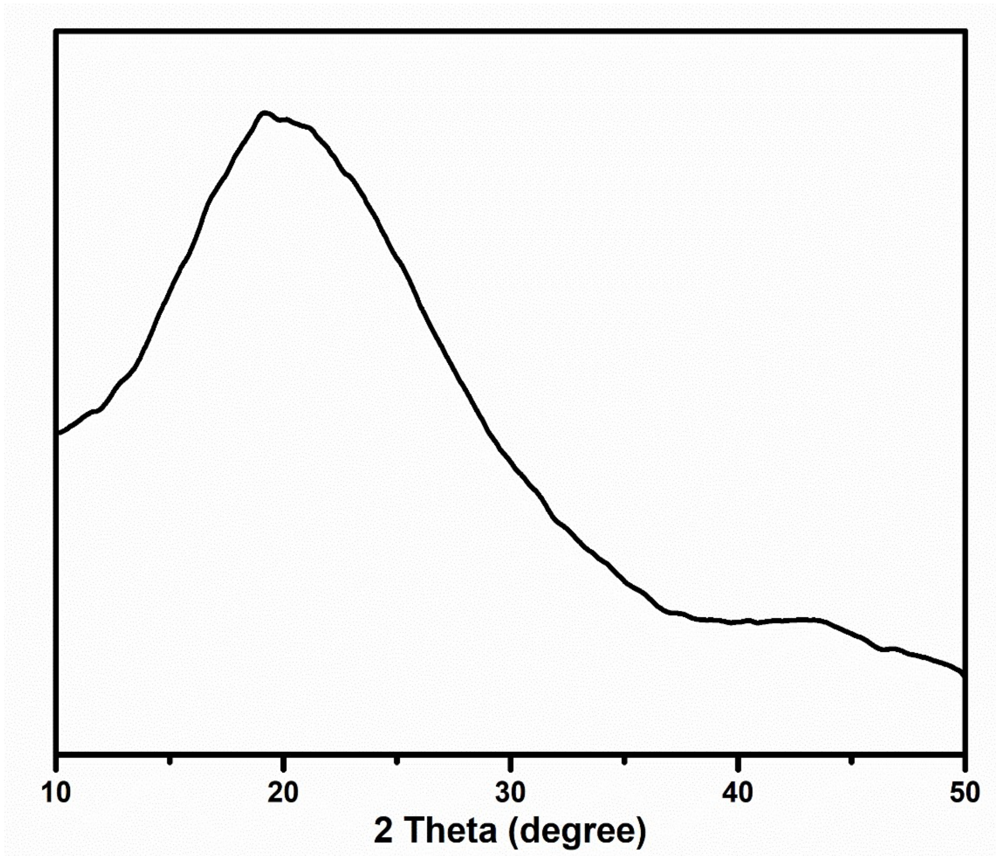

Fig. S1 PXRD spectra for **H-COP**

ii. ^{13}C CP/MAS Solid-state NMR spectrum of H-COP

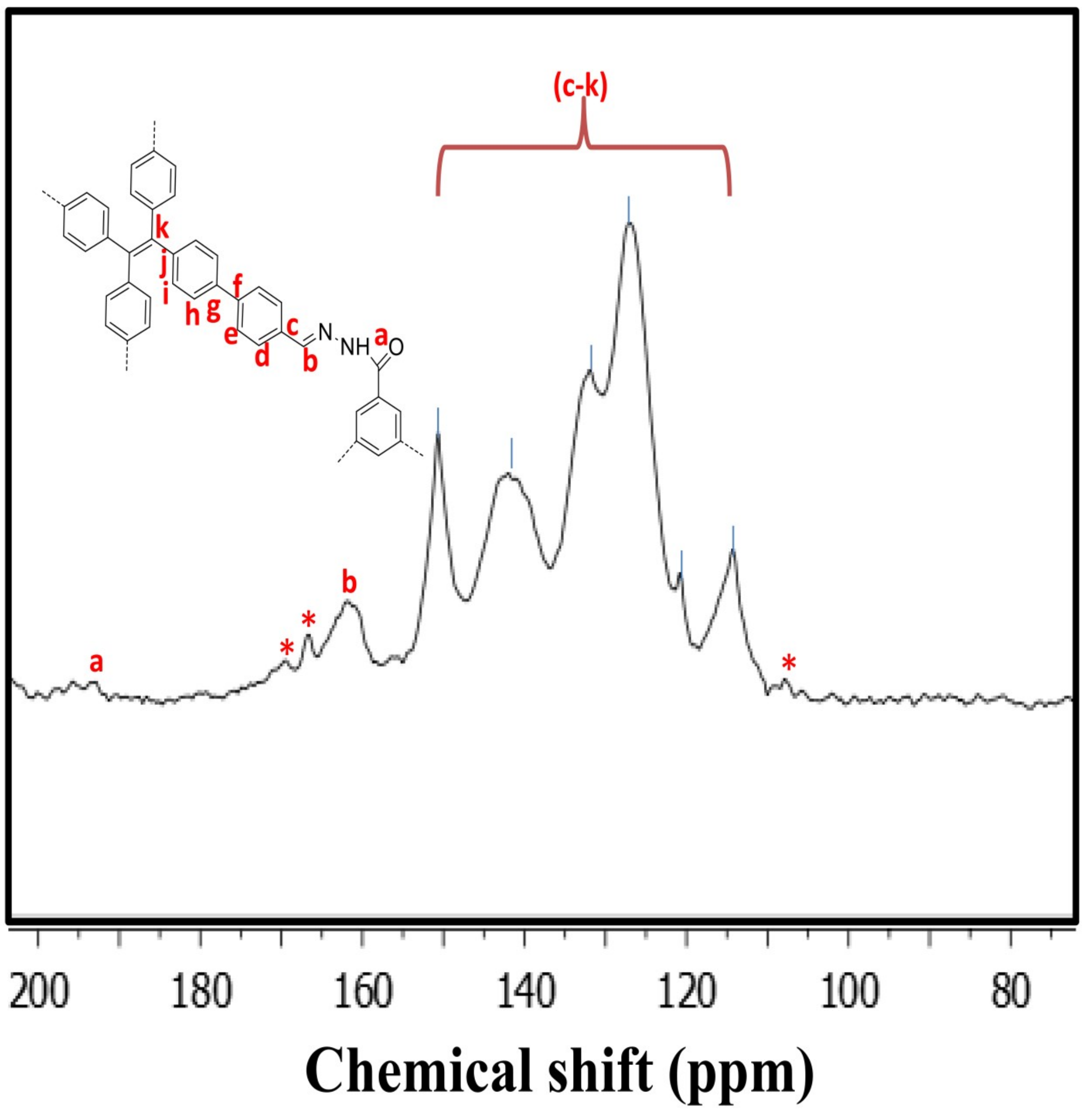

Fig. S2 ^{13}C CP/MAS Solid-state NMR spectrum of **H-COP**: The alphabets (a) represents chemical shift of C=O bond while (b) denotes chemical shift of imine carbon bond around 156 ppm, while Asterisks denote side bands.[1]

iii. Photo-physical study

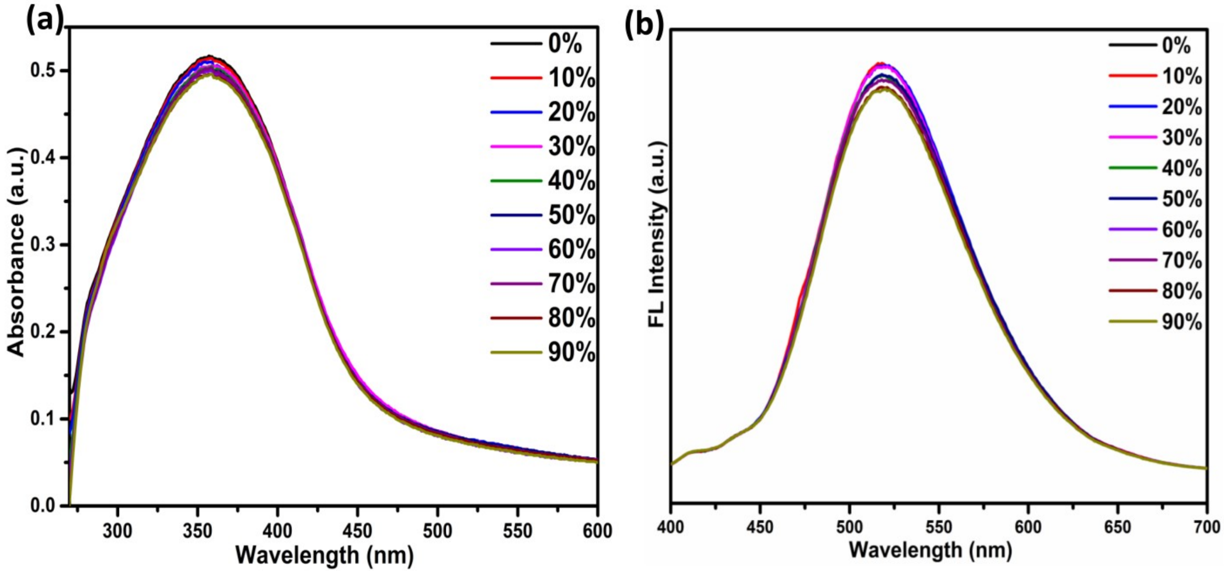

Fig. S3 UV-vis absorption spectra and emission spectra of **H-COP** dissolving in DMF with a different fraction (0% – 90%) of H_2O

iv. Luminogenic status

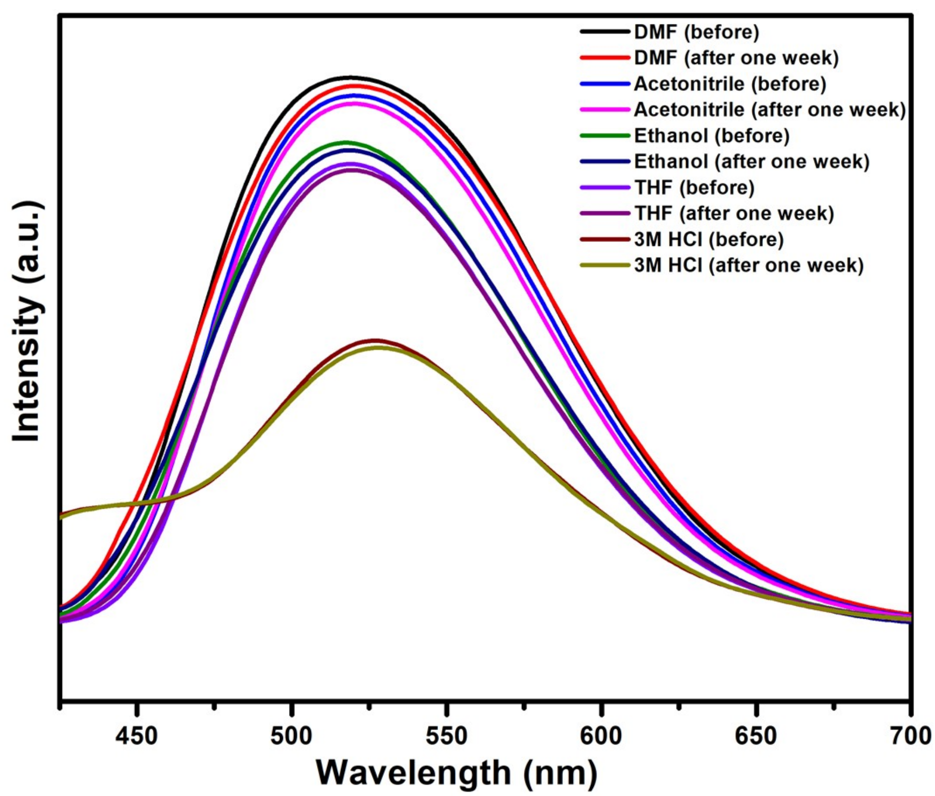

Fig. S4 Luminogenic status of **H-COP** in different chemical environments after one week

v. Chemical stability

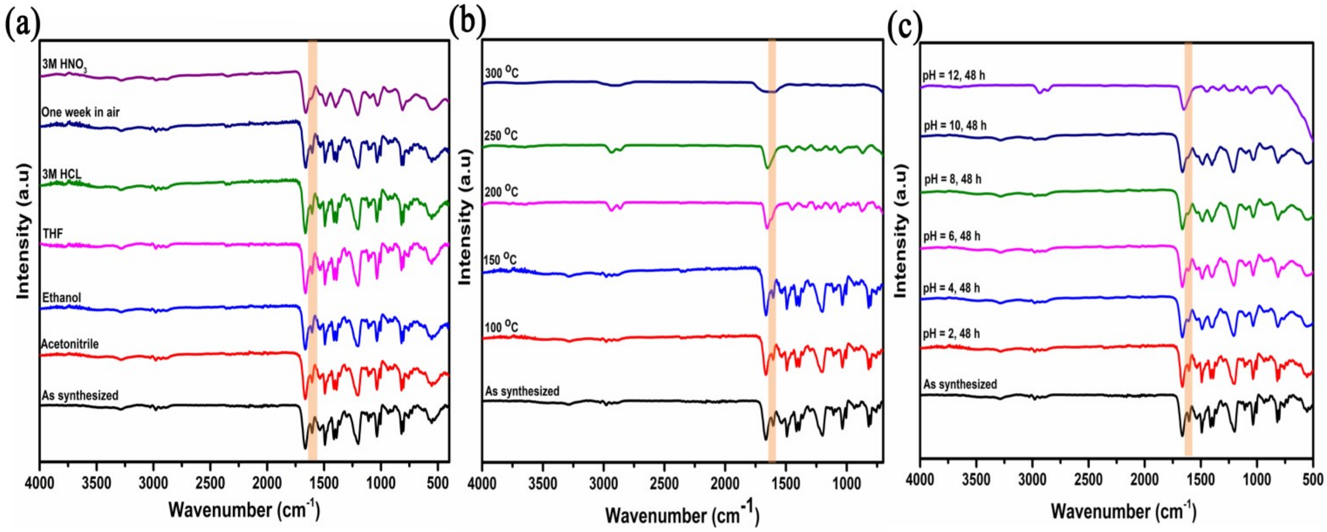

Fig. S5 The **H-COP** FTIR spectra after (a) treatment with different chemical environments and (b) heating at different temperatures (c) soaked in different pH

vi. The thermal stability test of H-COP

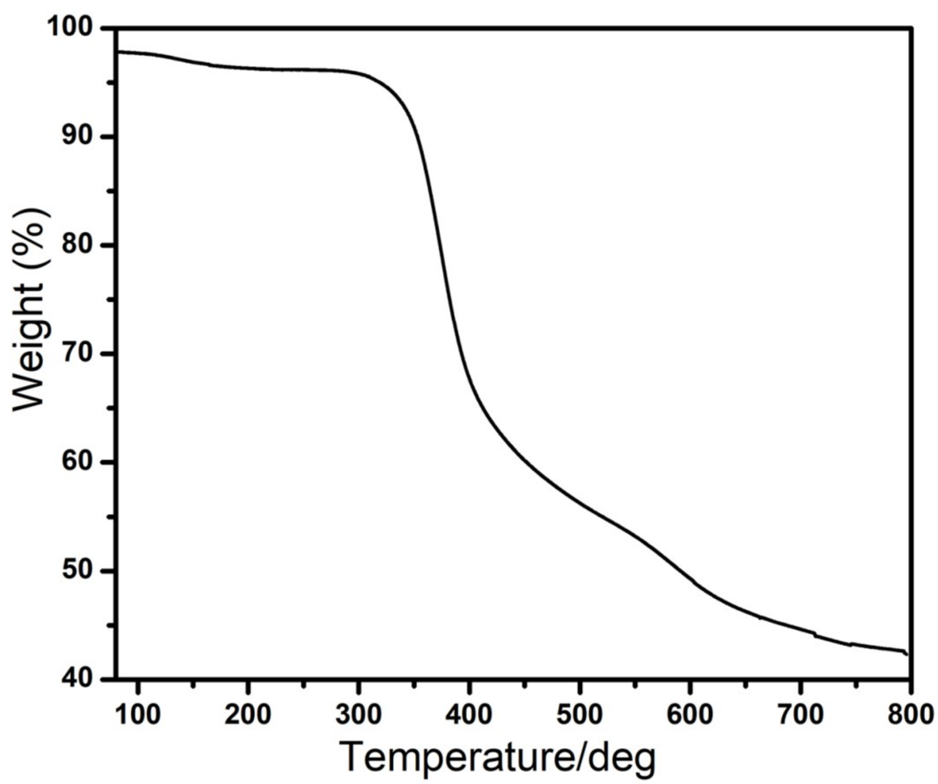

Fig. S6 The **H-COP** TGA curve.

vii. LOD calculations for tested nitro explosive analytes:

Standard Deviation (σ) calculation:

Blank Readings	FL Intensity
Reading 1	7.86E+06
Reading 2	7.83E+06
Reading 3	7.72E+06
Reading 4	7.28E+06
Reading 5	7.01E+06
Standard Deviation (σ)	3.76616E+05

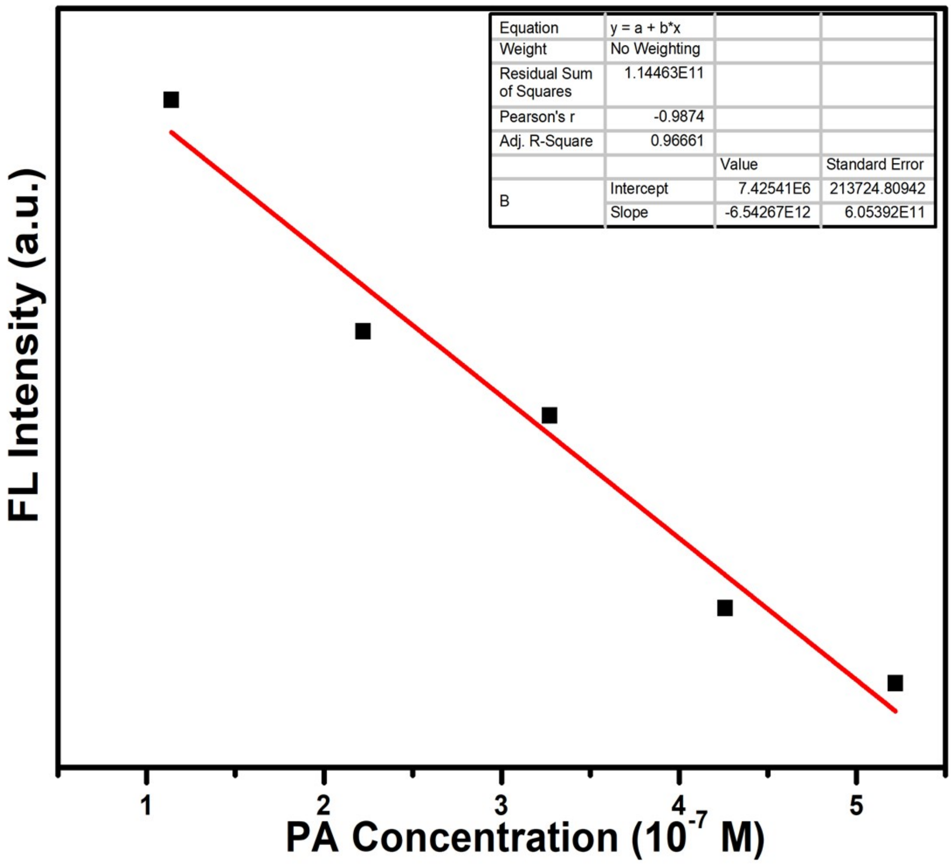

Fig. S7 Linear region of fluorescence intensity of **H-COP** upon incremental addition of PA at λ_{em} = 500 nm (upon λ_{ex} = 378 nm) at room temperature.

Calculation of Detection limit (LOD) for PA:

Slope (m)	6.5426E+12
Standard deviation (σ)	3.76616E+05
Limit of detection (3σ/m)	0.17 µM

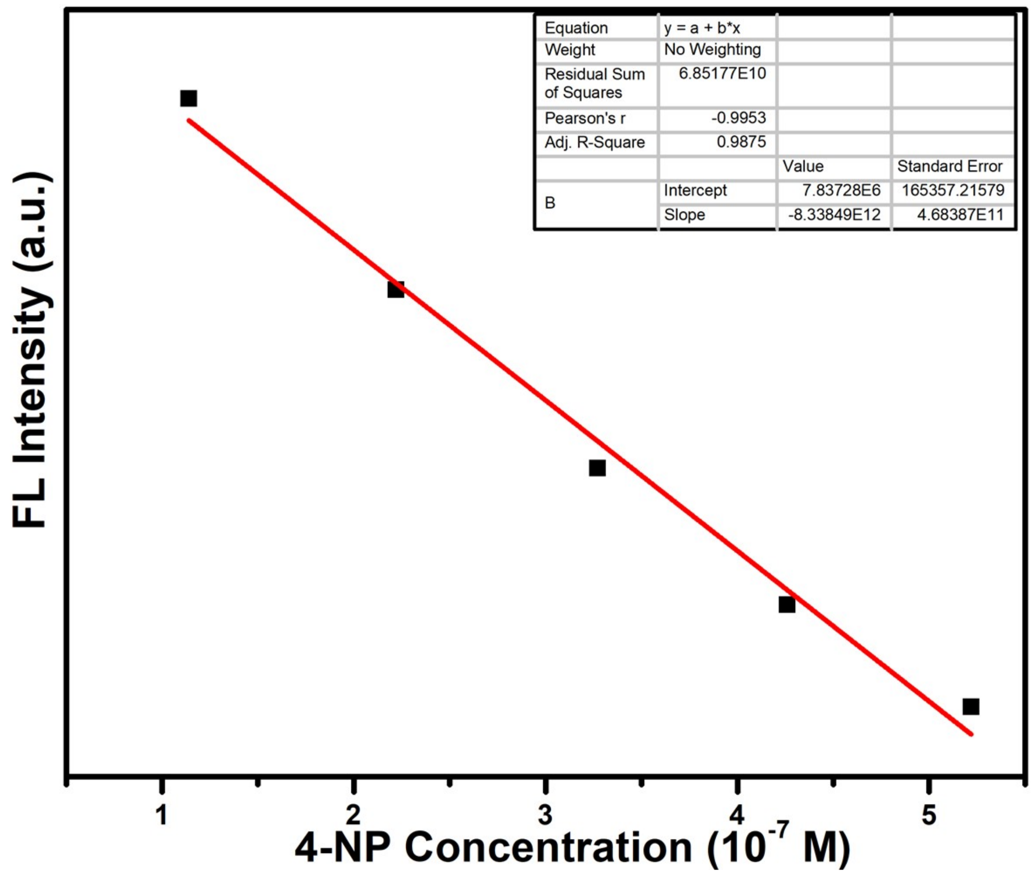

Fig. S8 Linear region of fluorescence intensity of **H-COP** upon incremental addition of 4-NP at λem = 500 nm (upon λex = 378 nm) at room temperature.

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

Slope (m)	8.33849E+12
Standard deviation (σ)	3.76616E+05
Limit of detection (3σ/m)	0.13 μM

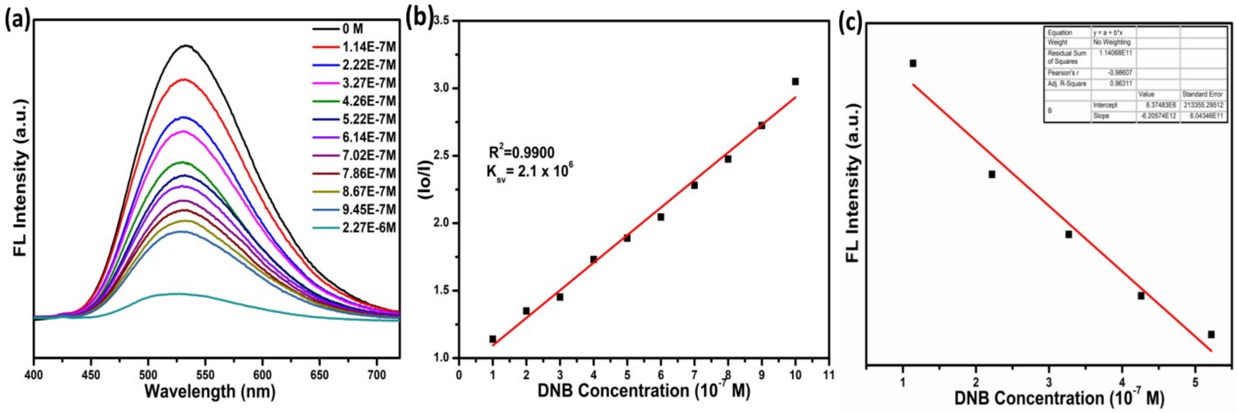

Fig. S9 Quenching titration graph and LoD calculation for DNB.

Calculation of Detection limit (LOD) for DNB:

Slope (m)	6.20574E+12
Standard deviation (σ)	3.76616E+05
Limit of detection (3σ/m)	0.18 µM

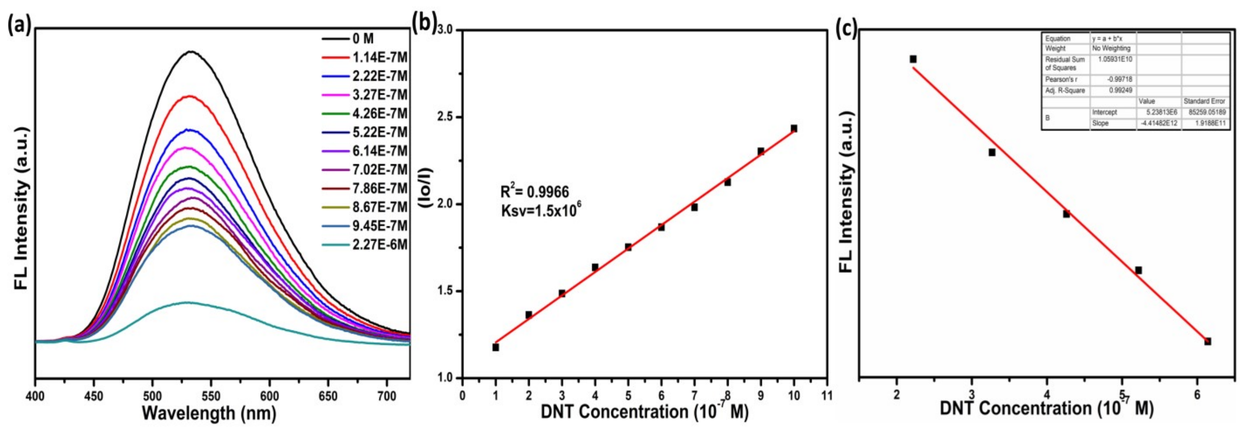

Fig. S10 Quenching titration graph and LoD calculation for DNT.

Calculation of Detection limit (LOD) for DNB:

Slope (m)	4.41482E+12
Standard deviation (σ)	3.76616E+05
Limit of detection (3σ/m)	0.25 μM

viii. Fluorescence quenching pattern of non-explosives analytes

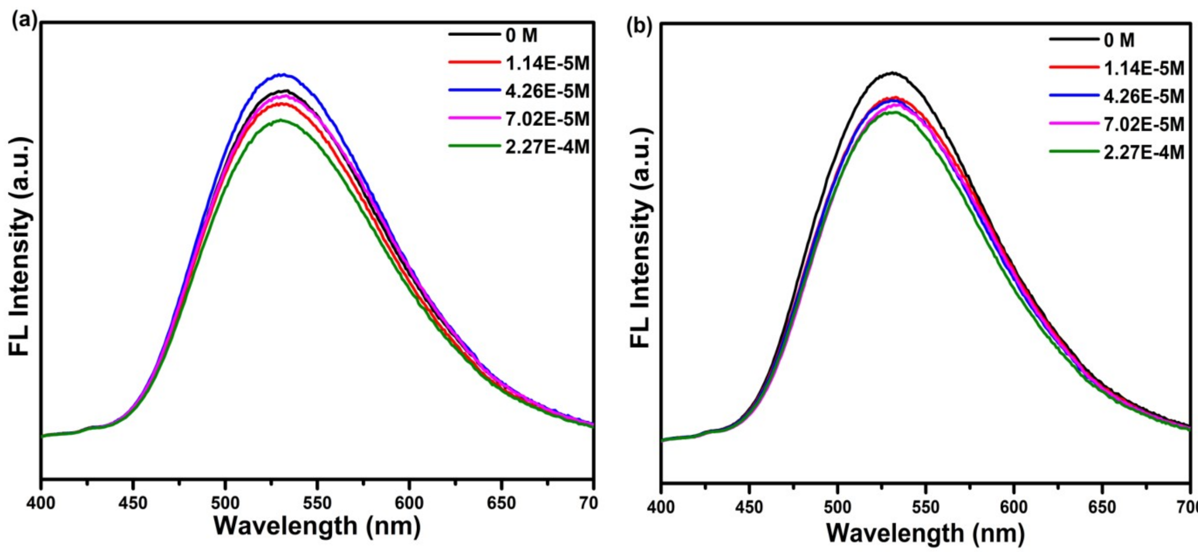

Fig. S11 Fluorescence quenching pattern for non-explosives analyte (a) Methyl benzene and (b) Dibromobenzene (λem = 500 nm & λex =378 nm) at room temperature.

ix. Comparison study of tested nitro explosive analytes with reported Polymers

Table S1 PA sensing comparison with reported Polymers

Materials	K_{sv}	LOD	Medium	Ref.
H-COP	2.5×10^6 M^{-1}	0.17 μM	DMF	This work
$[Tb_2(PBA)_3(H_2O)_3 \cdot DMF \cdot 3H_2O]_n$	4.5×10^4 L/mol	0–30 μmol/L	$DMF.H_2O$	2
FPP-3	6020 M^{-1}	13.20 ppb	DMF/K_2CO_3	3
$PS\text{-}OPV\text{-}NH_2$	NA	58 nM	H_2O	4
H-COP-612	2.51×10^5 M^{-1}	NA	DMF	5
$[Zn(\mu\text{-}HCIP)(\mu\text{-}pbix) \cdot 2H_2O]_n$	4.37×10^4 M^{-1}	56.46 ppb	DMF	6
Cd-based CPs	96907 M^{-1}	15 ppb	DCM	7
H-COP-301	2.6×10^5 M^{-1}	1 ppm	Methanol	8
H-COP-401	8.3×10^4 M^{-1}	1 ppm	Methanol	8
(Ln-CPs)($[Eu(L)_2(H_2O)]BrH_2O)_n$(EuBr)	17000 M^{-1}	10^{-5} M	H_2O	9
($[TbL_2(H_2O)_2]BrH_2O)_n$(TbBr)	20200 M^{-1}	10^{-5} M	H_2O	9
TBAFP1	5.3×10^5 M^{-1}	144 nM	THF	10
TBAPF2	2.4×10^5 M^{-1}	151 nM	THF	10
(Ln-CPs)	2.6×10^5 L/mol	0.28 $\mu molL^{-1}$	Ethanol	11
$[Zn_3(mtrb)_3(btc)_2 \cdot 3H_2O]_n$	3.26×10^4 M^{-1}	0.22 μM	Methanol	12

NA= Not available

Table S2. 4-NP sensing comparison with reported Polymers

Materials	K_{Sv} (M^{-1})	LOD	Medium	Ref.
H-COP	3.8×10^6	0.13 µM	DMF	This work
(Ln-CPs)	1.9×10^5	0.98 µM	Ethanol	11
$[Zn_3(mtrb)_3(btc)_2{\cdot}3H_2O]_n$	1.276×10^4	NA	Methanol	12
$[Cd_2(obtz)(Meip)_2{\cdot}H_2O]_n$	0.0879	≤20 ppm	Ethanol	13
$[Cd(obtz)(ndc){\cdot}0.5H_2O]_n$	0.0662	≤30 ppm	Ethanol	13
(BpaD)	NA	0.6 µM	(PBS:ethanol=9:1)	14
(BpaP)	NA	0.23 µM	(PBS:ethanol=9:1)	14
$[Tb(BTEC)_{0.5}(HCOO)(H_2O)_2]$	2.04×10^4	0.46ppm	THF	15
LCP	3.8×10^4	0.49×10^{-3} M	H_2O	16

NA= Not available

Note:

PA and 4-NP references are available for comparison with reported luminescent polymer materials. PA comparison table has been shown in original manuscript, while other explosives like DNT, DNB didn't contain enough data for comparison with luminescent polymers. Hence our polymer shows greater selectivity for these explosives among reported polymer materials.

x. TCSPC profile and calculation for average fluorescence lifetime

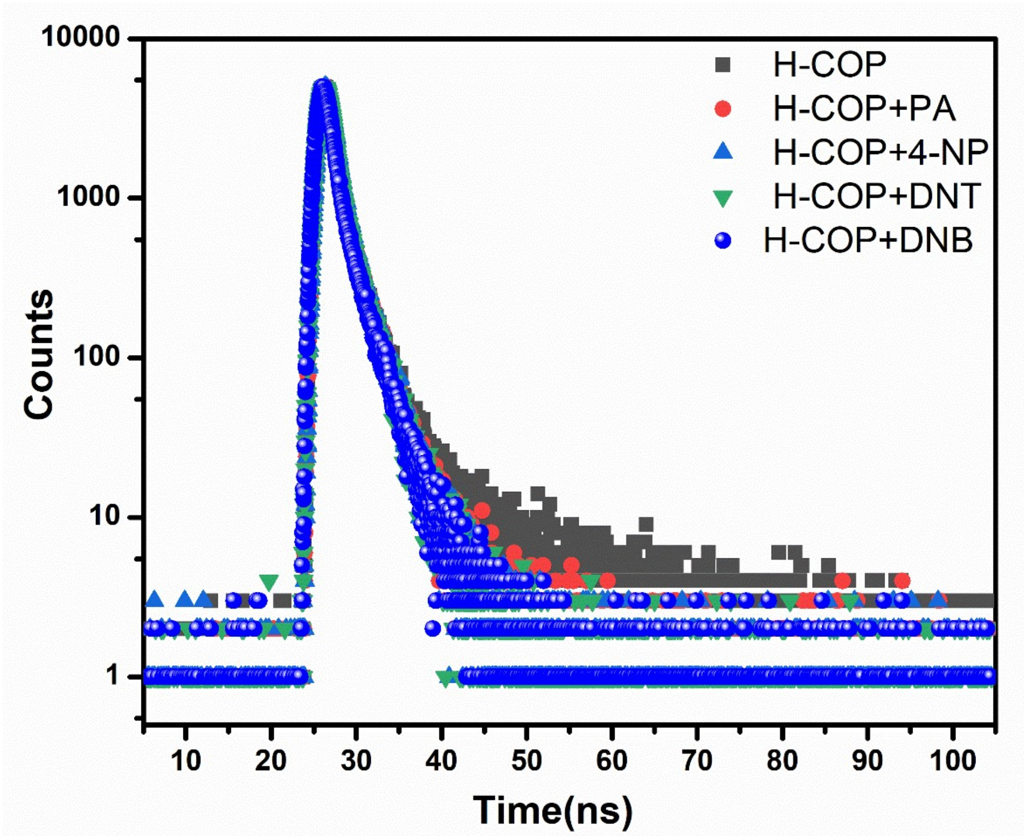

Fig. S12 The **H-COP** average luminescence lifespan decay profile with different common explosives (λ_{ex} =378 nm & λ_{em} =500 nm).

Table S3. TCSPC calculation of H-COP and nitro explosives analytes

Samples	T1 (ns)	T2 (ns)	B1	B2	A1=[B1/SumB]	A2=[B2/SumB]	<I> (ns)
H-COP	1.5649	5.1379	69.50	30.50	0.695	0.305	2.65
H-COP + PA	0.1611	2.1364	5.66	94.34	0.056	0.9434	2.02
H-COP + 4-NP	0.7828	2.5102	40.44	59.59	0.4044	0.5959	1.81
H-COP + DNT	0.8033	2.5831	47.67	52.33	0.4767	0.5233	1.73
H-COP + DNB	0.8779	2.6575	53.64	46.36	0.5364	0.4636	1.72

xi. Table. S4 DFT calculations using B3LYP/6-31G*[17]

Analytes	HOMO (eV)	LUMO (eV)	Band gap (eV)
H-COP	-5.605	-2.35	3.255
PA	-8.4592	-3.4726	4.986
4-NP	-7.577	-2.499	5.078
2,4-DNT	-8.09	-2.97	5.12
1,3-DNB	-8.32	-3.14	5.18

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