Supplementary Information

Luminescent Zn-MOF for detection of explosives and development of fingerprints

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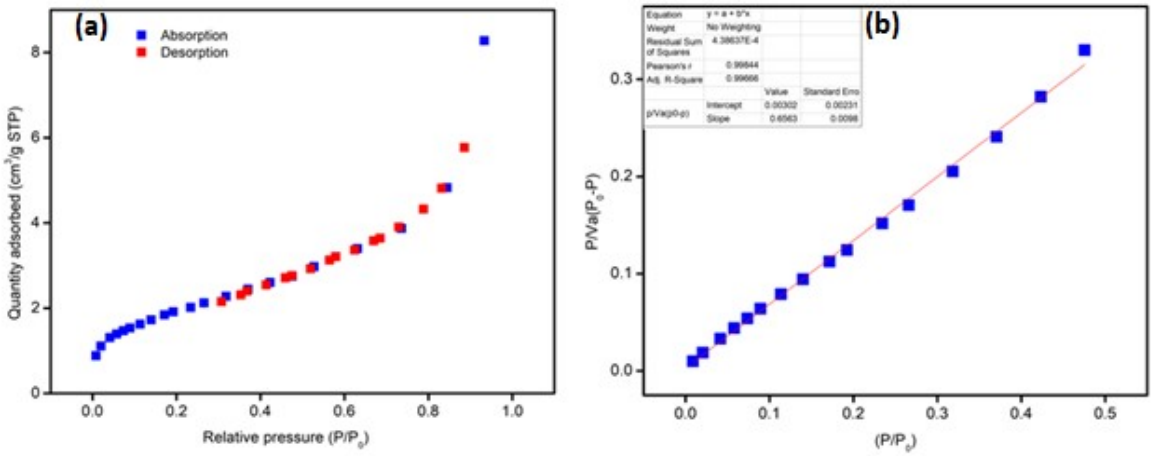


Figure S1: (a) N_2 adsorption (Blue) and desorption (Red) isotherms of thermally activated PUC1 measured. The samples were heated at 100°C under vacuum for 12 h before the sorption measurement. (b) BET plot.

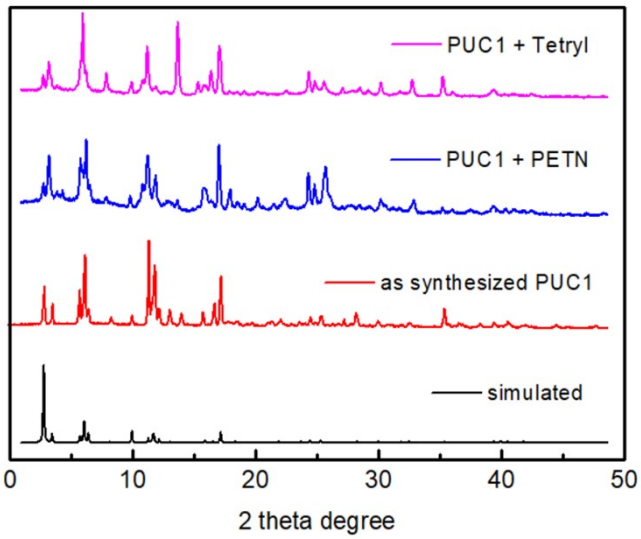


Figure S2: PXRD pattern of PUC1 before and after addition of PETN and Tetryl.

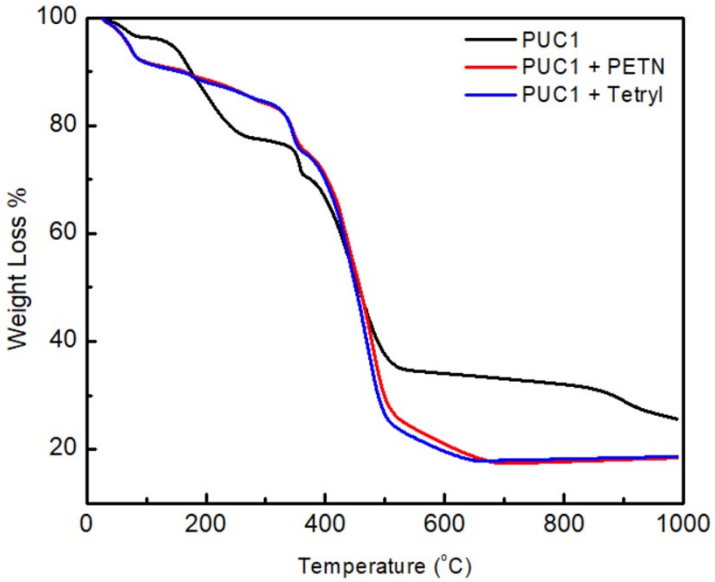


Figure S3: Thermogravimetric analysis curves of **PUC1** before and after treatment with PETN and Tetryl.

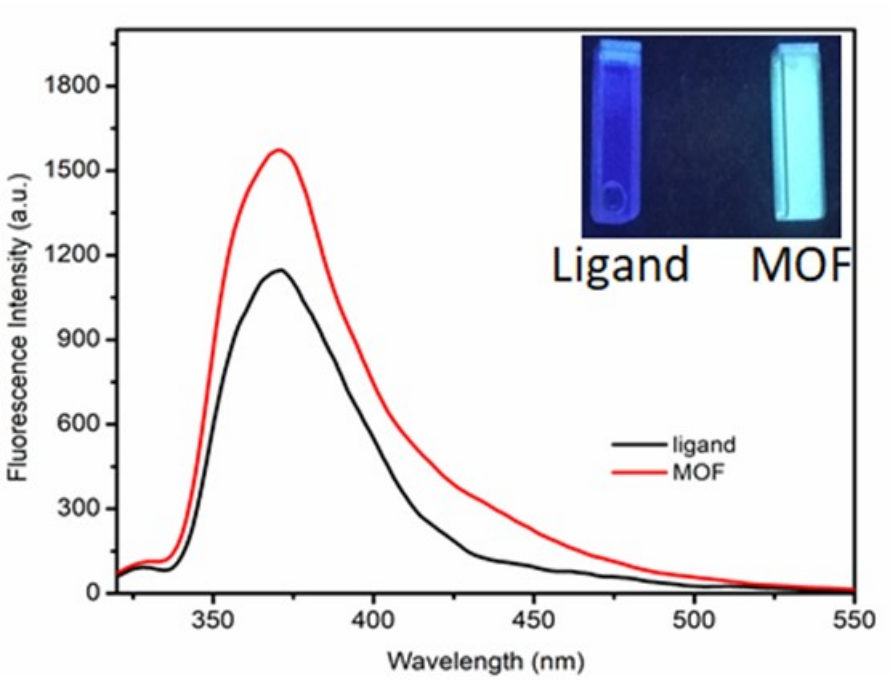


Figure S4: Fluorescence spectra of free ligand and PUC1 (inset) optical image of ligand and MOF in UV chamber.

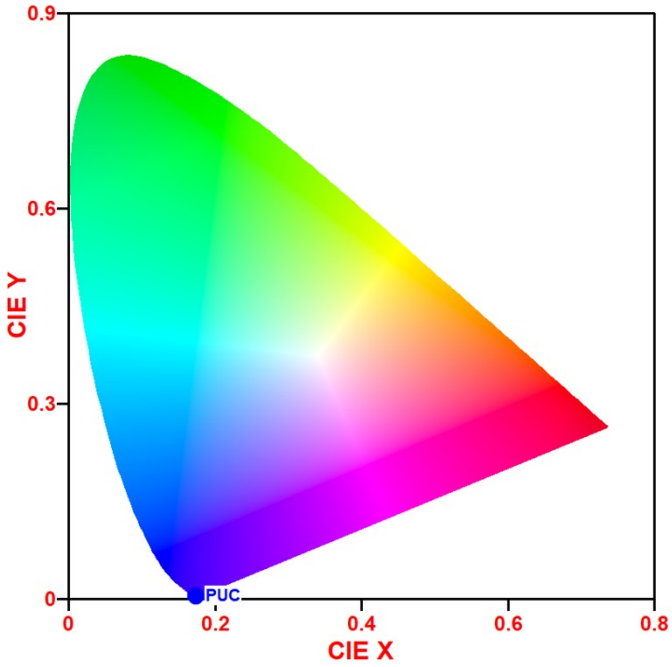
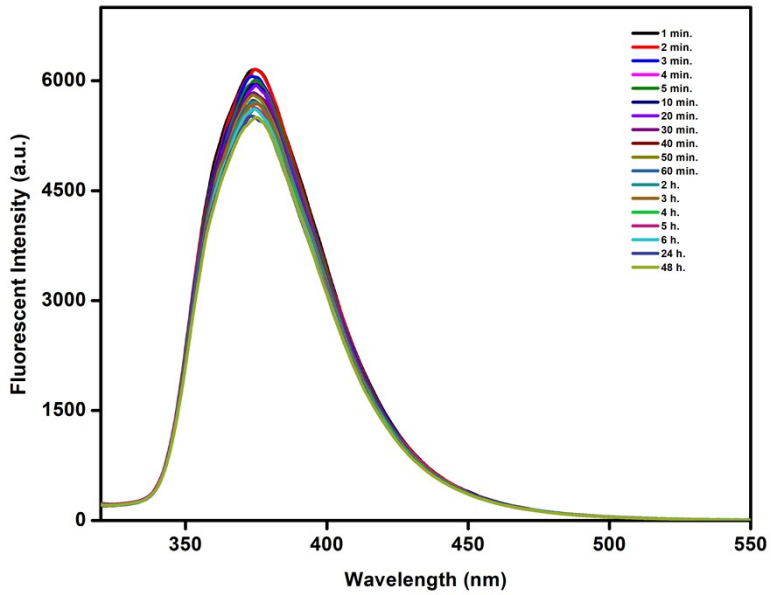


Figure S5: The CIE 1931 chromaticity diagram with CIE colour coordinates (0.170, 0.005).



FigureS6: Fluorescence spectra of PUC1 with time up to 48 hours.

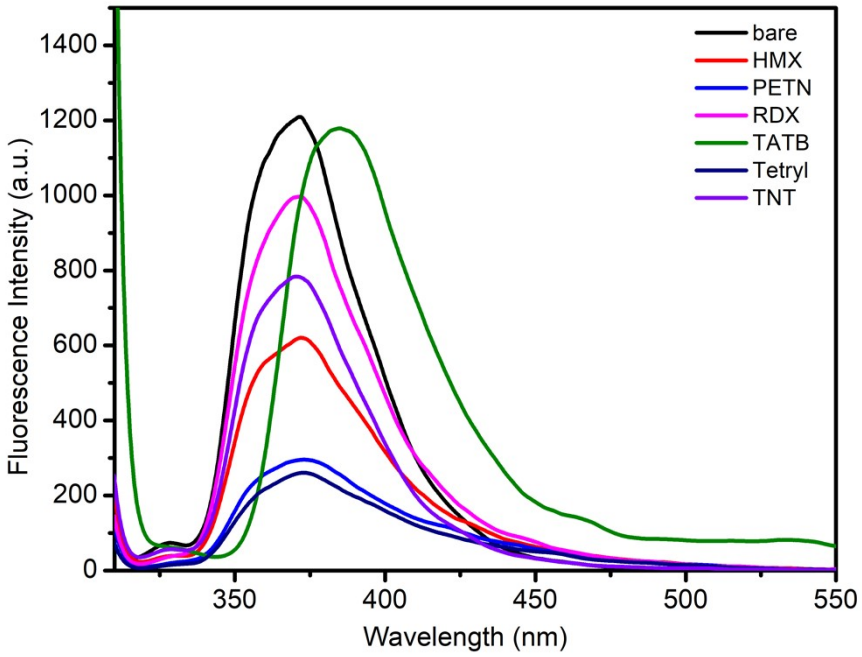


Figure S7: The fluorescence spectra of PUC1 before and after the addition of PETN, Tetryl, TATB, TNT, HMX and RDX (50μM).

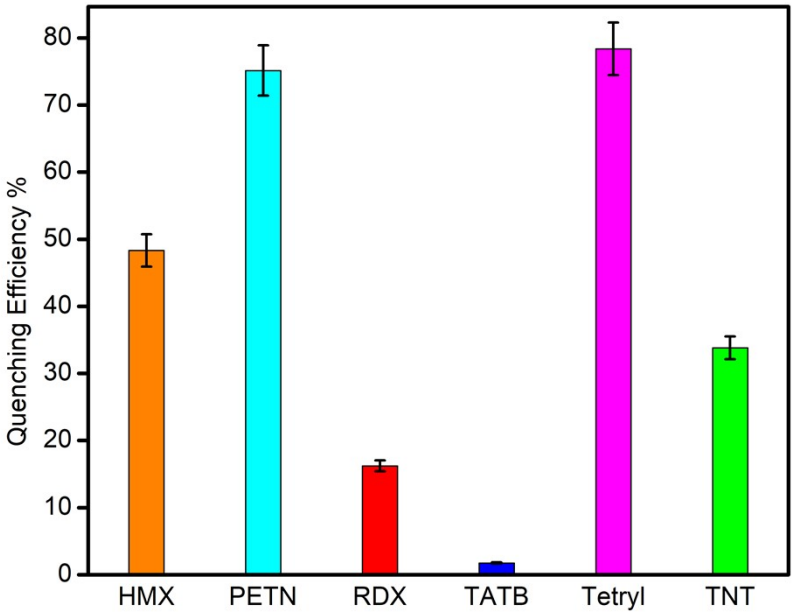


Figure S8: Quenching efficiency of different explosive compounds.

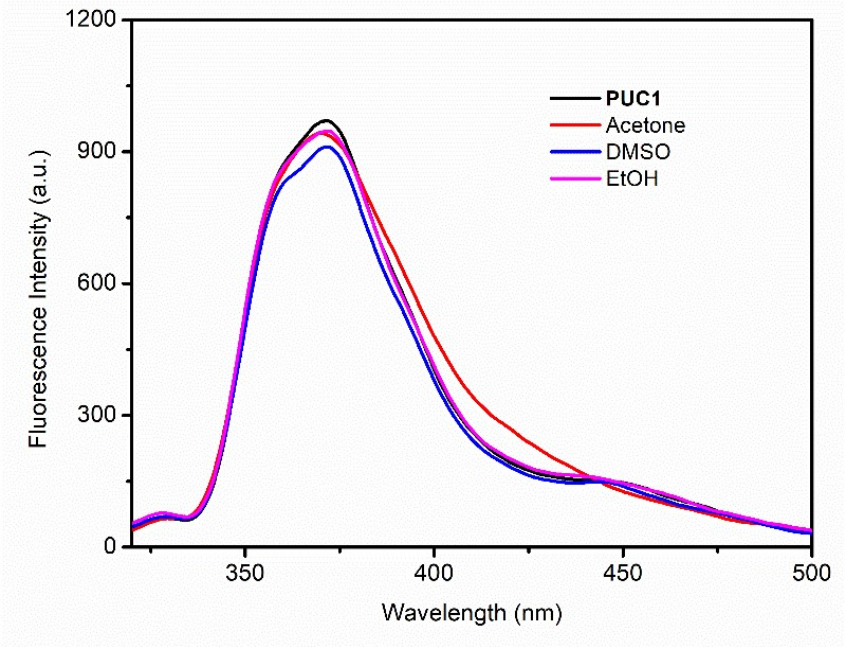


Figure S9: Fluorescence spectra of PUC1 before and after addition of different solvents.

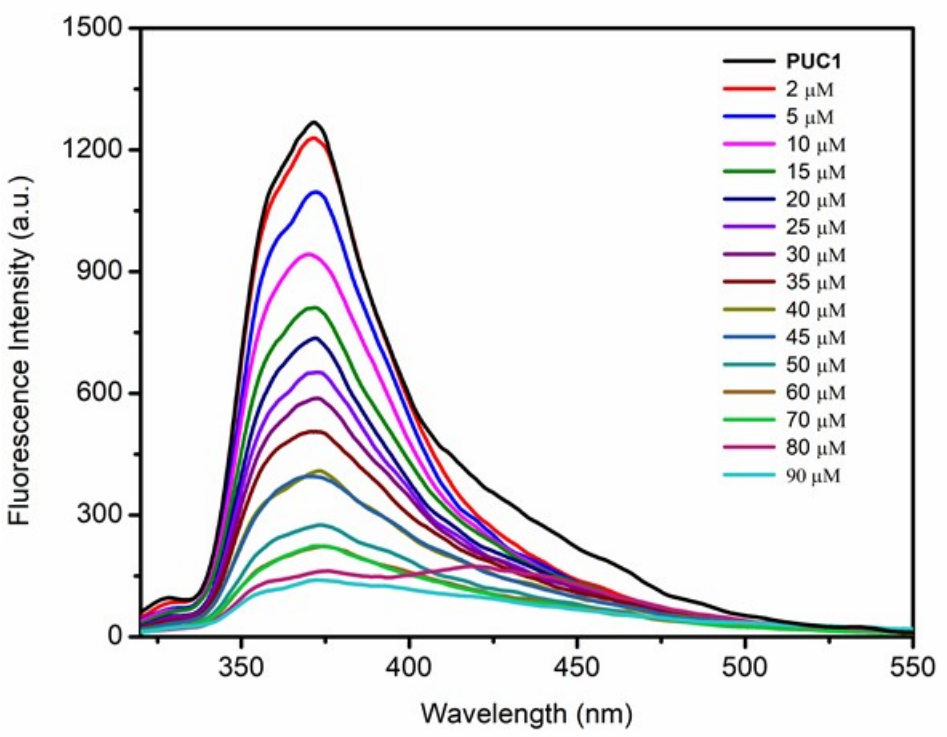


Figure S10: Fluorescence spectra of **PUC1** by gradual addition of PETN (90μM).

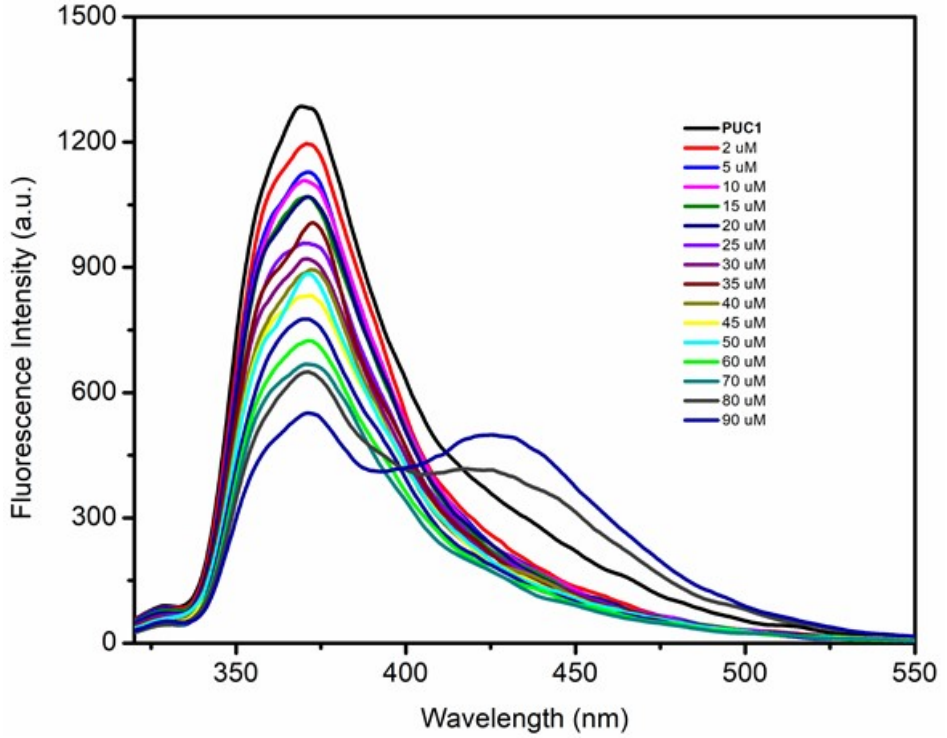


Figure S11: Fluorescence spectra of **PUC1** by gradual addition of Tetryl (90μM).

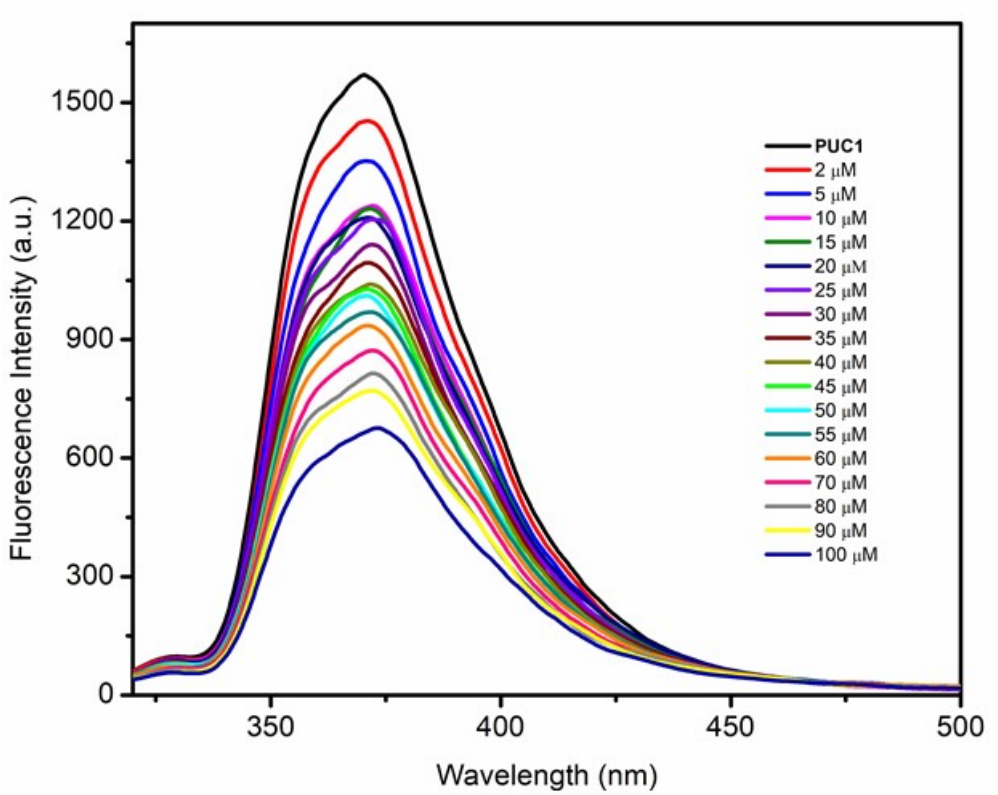


Figure S12: Fluorescence spectra of **PUC1** by gradual addition of TNT (100μM).

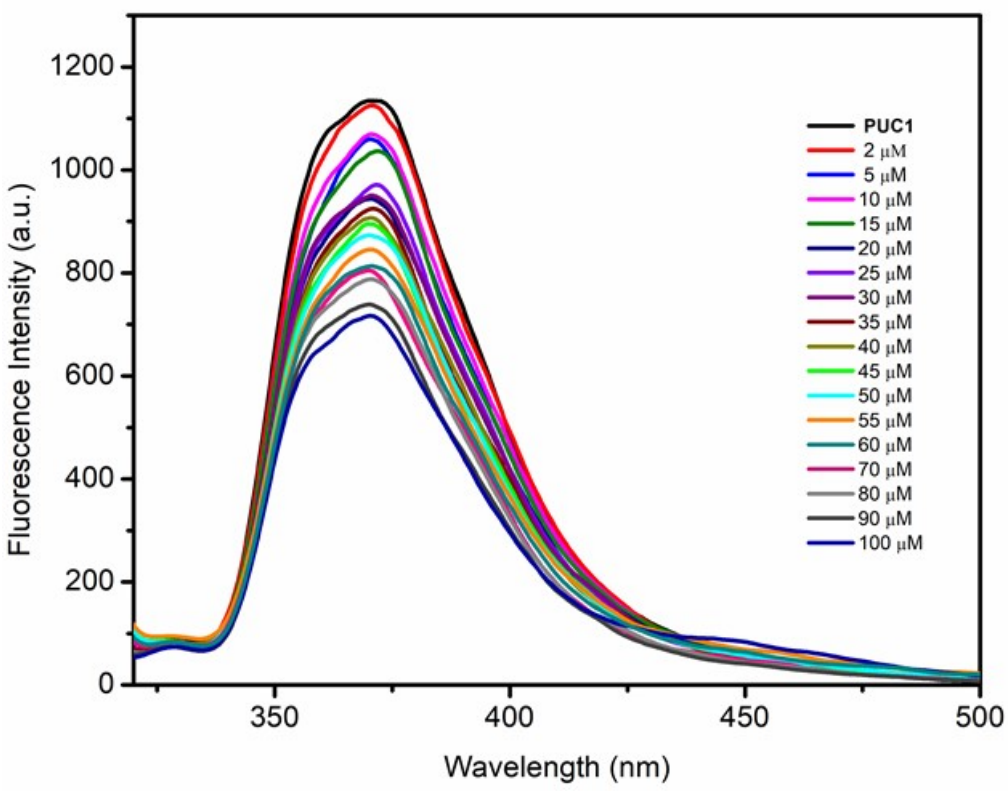


Figure S13: Fluorescence spectra of **PUC1** by gradual addition of HMX (100μM).

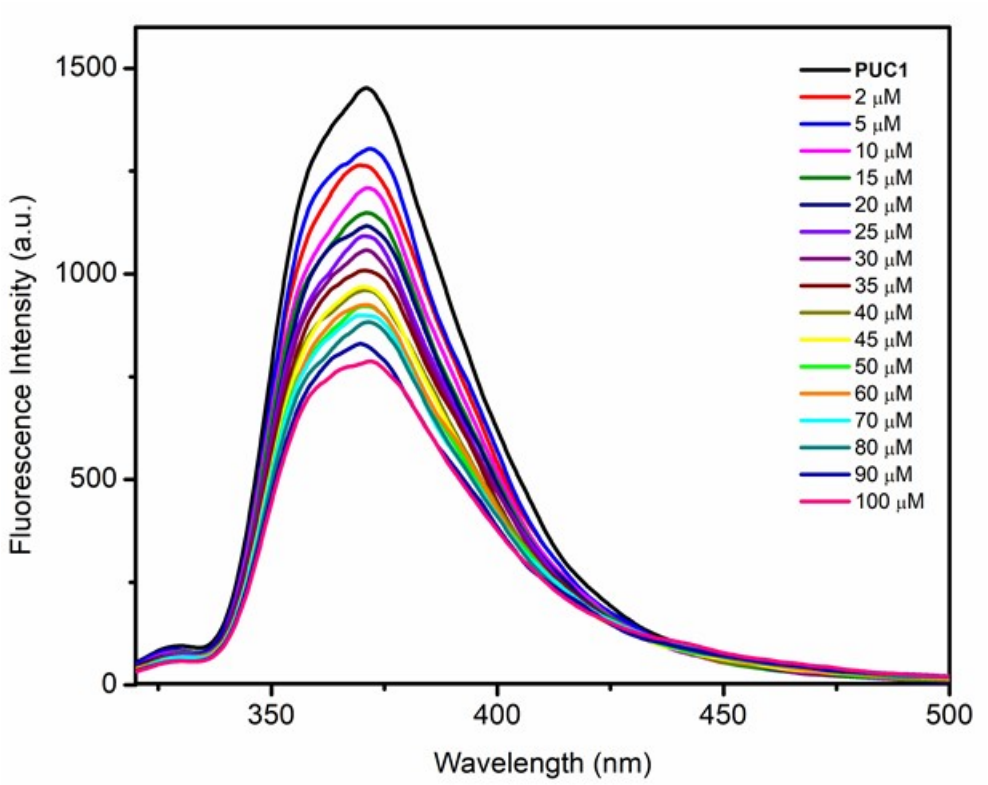


Figure S14: Fluorescence spectra of **PUC1** by gradual addition of RDX (100μM).

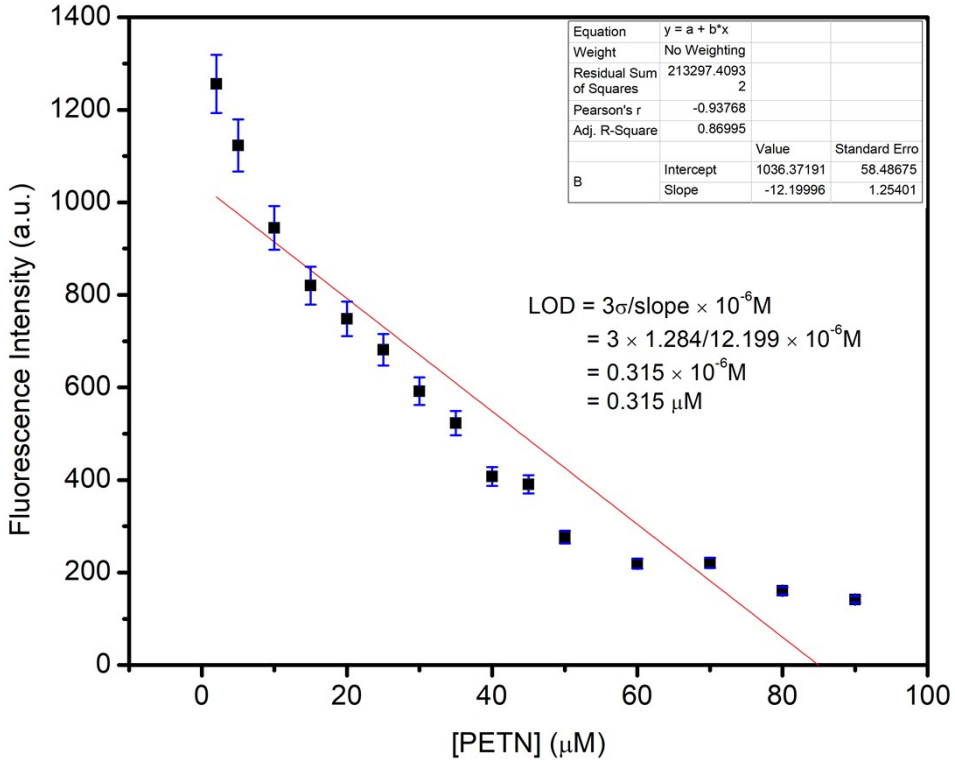


Figure S15: Estimation of limit of detection of **PUC1** for PETN.

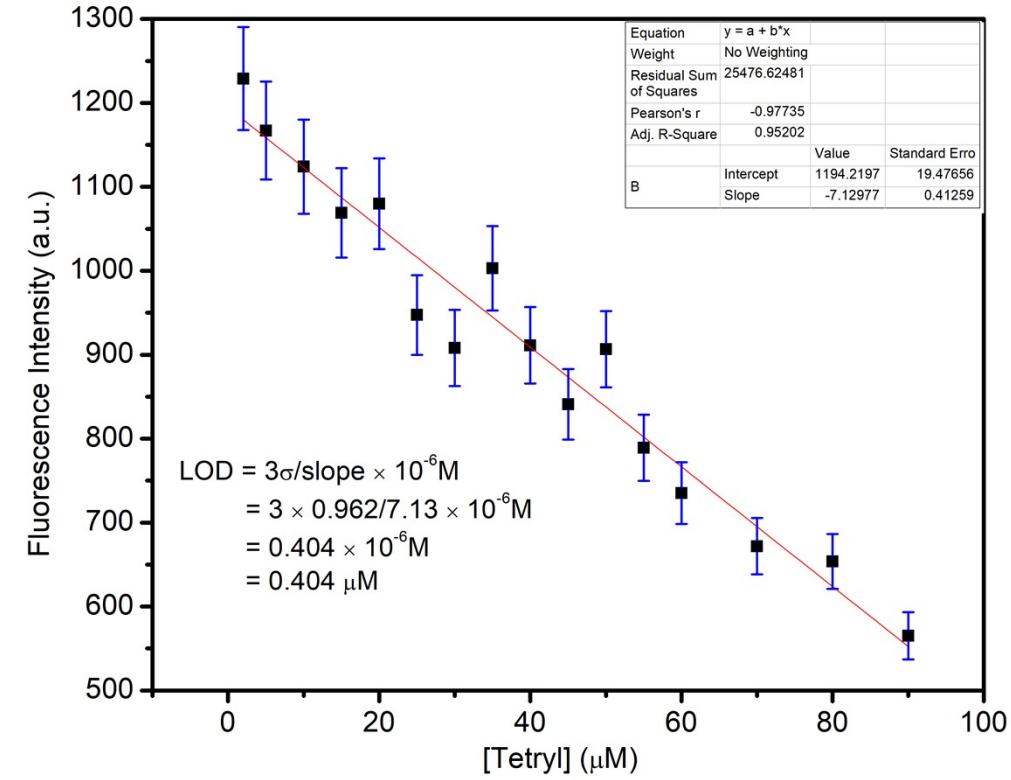


Figure S16: Estimation of limit of detection of **PUC1** for Tetryl.

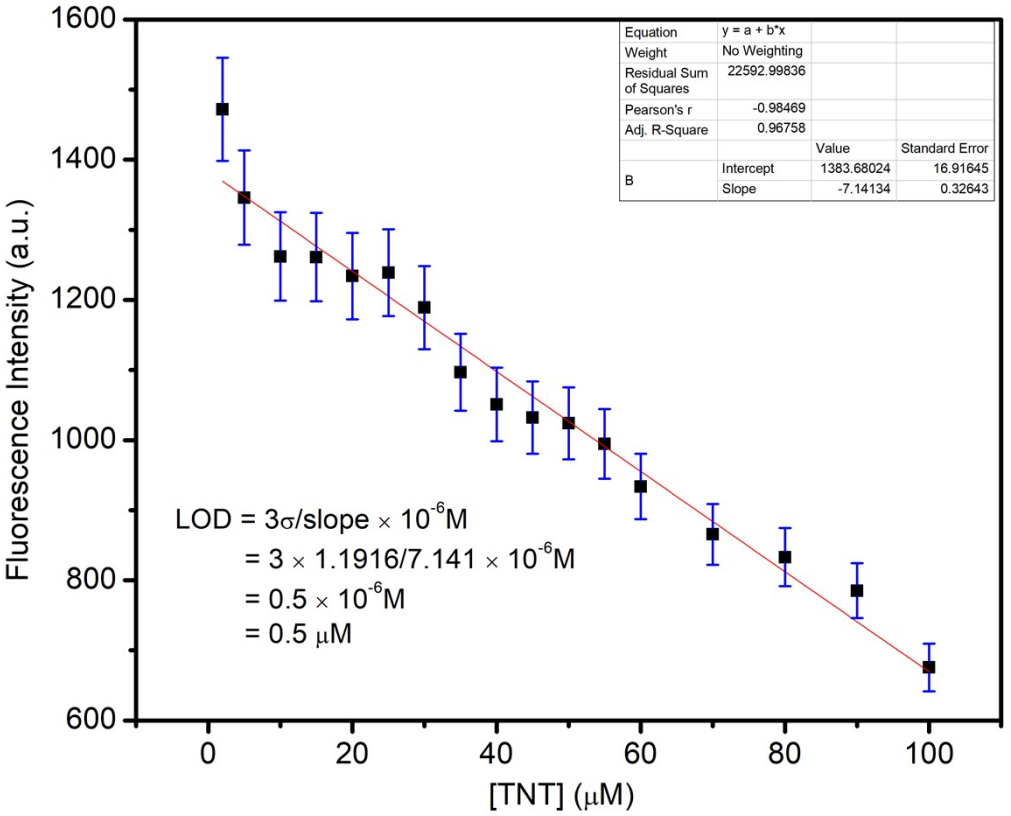


Figure S17: Estimation of limit of detection of **PUC1** for TNT.

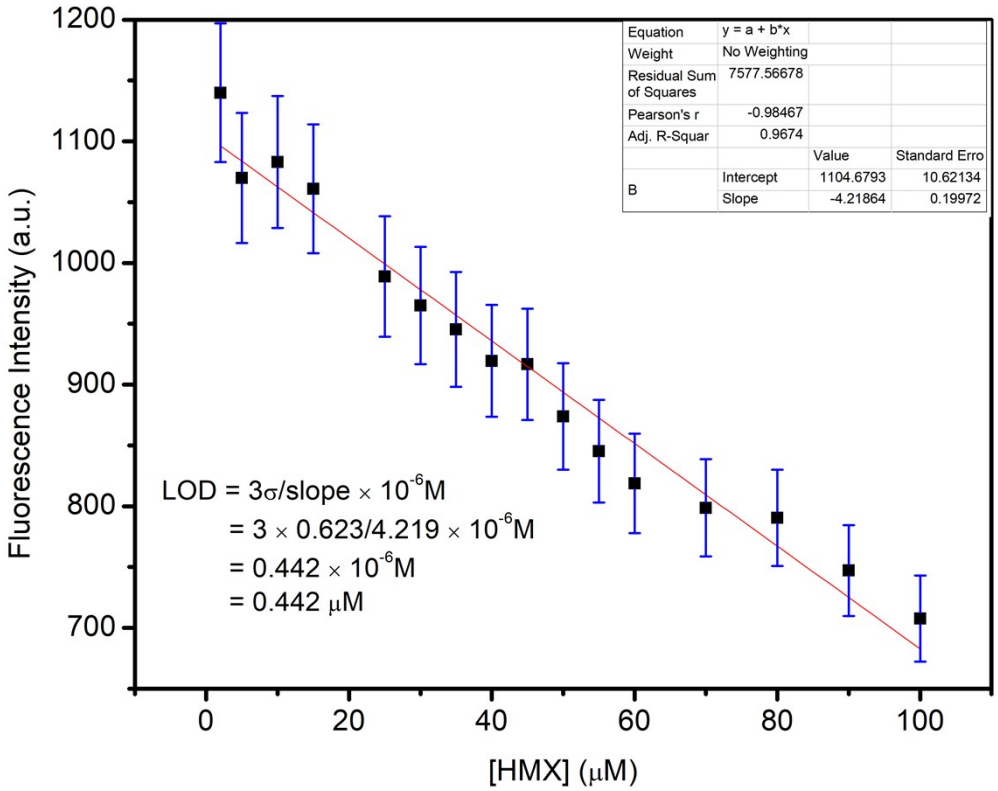


Figure S18: Estimation of limit of detection of **PUC1** for HMX.

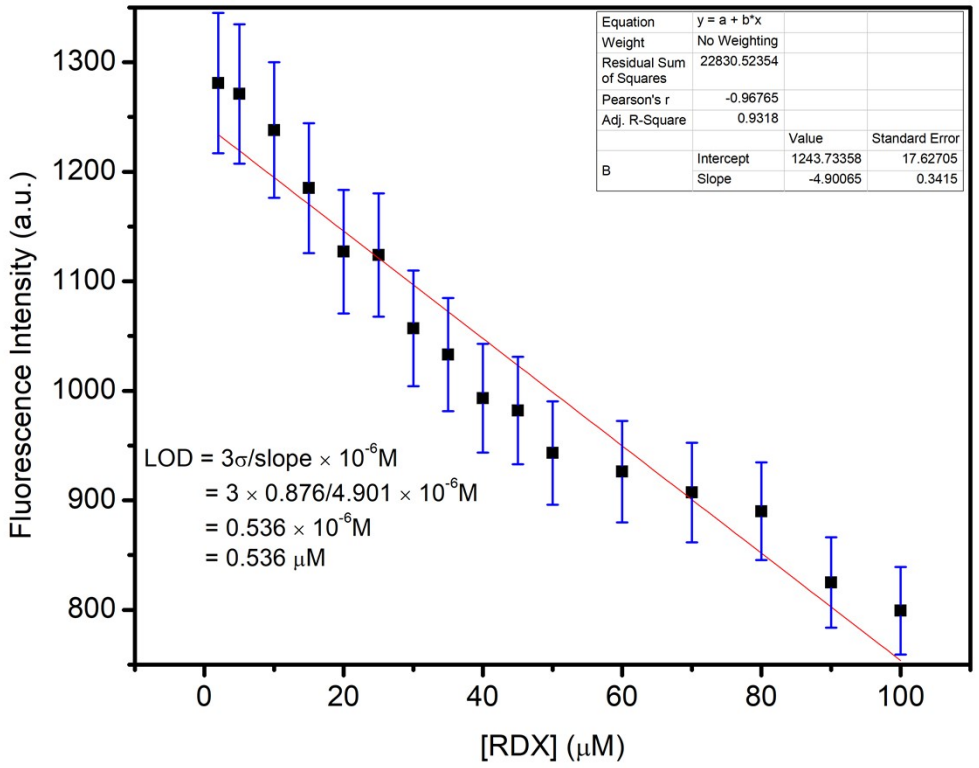


Figure S19: Estimation of limit of detection of **PUC1** for RDX.

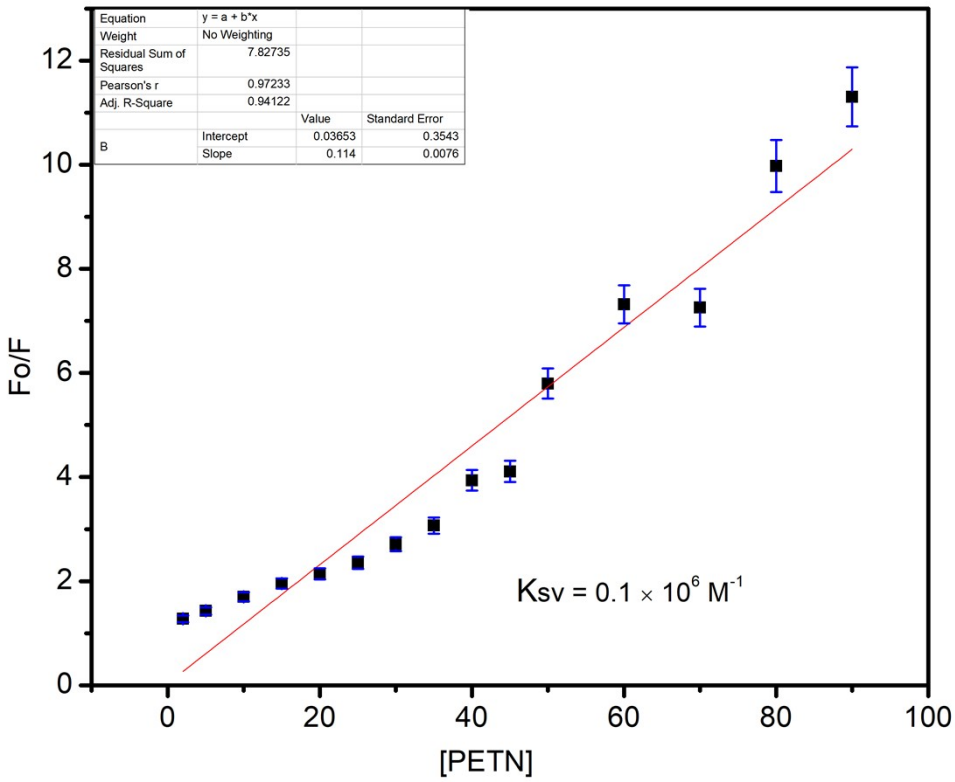


Figure S20: Stern-Volmer plots of **PUC1** by gradual addition of PETN (90µM).

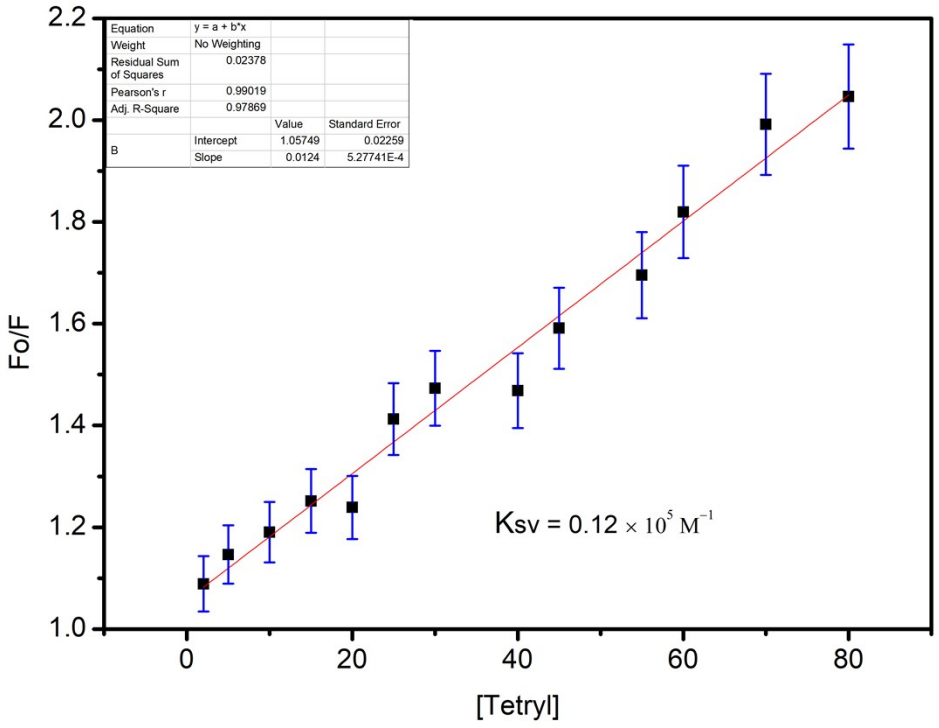


Figure S21: Stern-Volmer plots of **PUC1** by gradual addition of Tetryl (90µM).

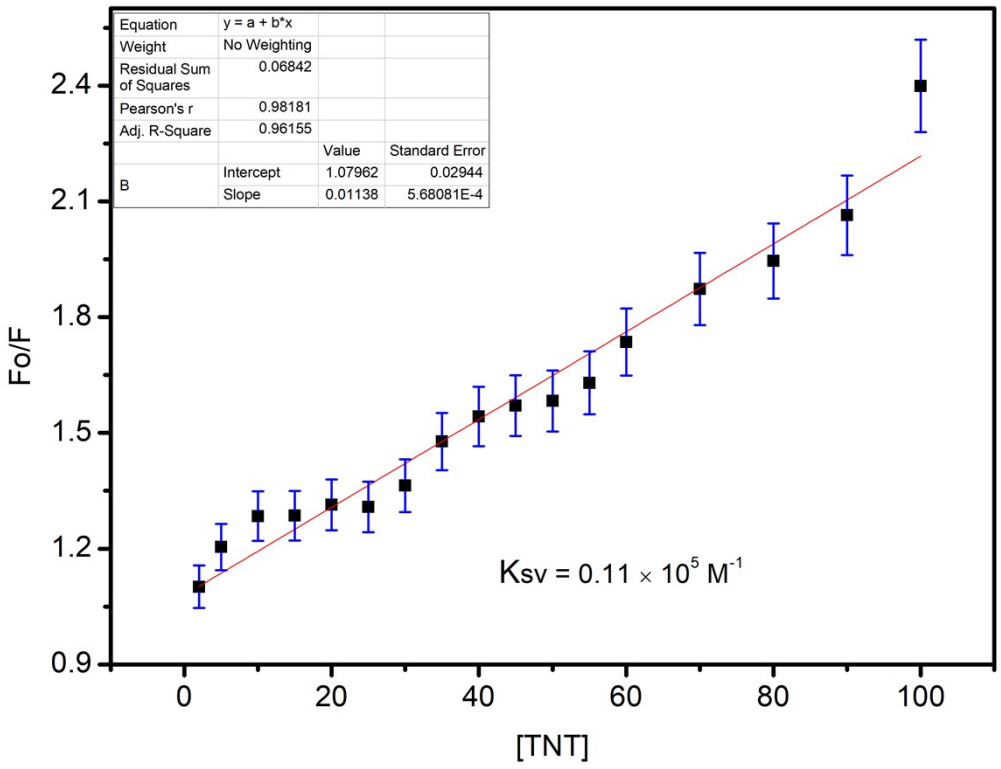


Figure S22: Stern-Volmer plots of **PUC1** by gradual addition of TNT (100µM).

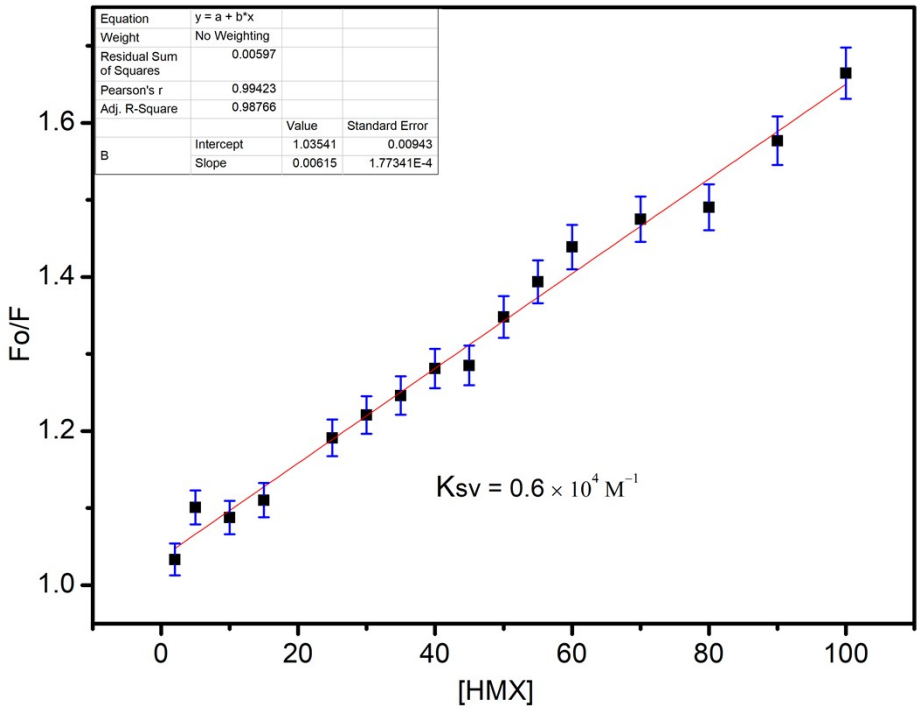


Figure S23: Stern-Volmer plots of **PUC1** by gradual addition HMX (100µM).

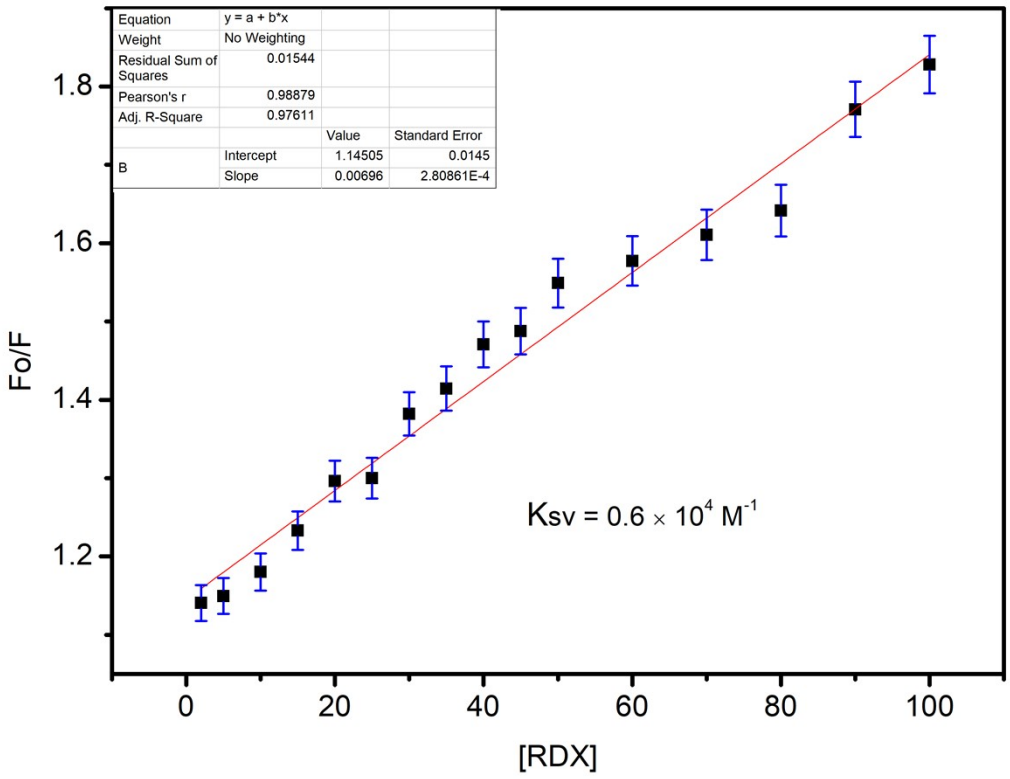


Figure S24: Stern-Volmer plots of **PUC1** by gradual addition of RDX (100μM).

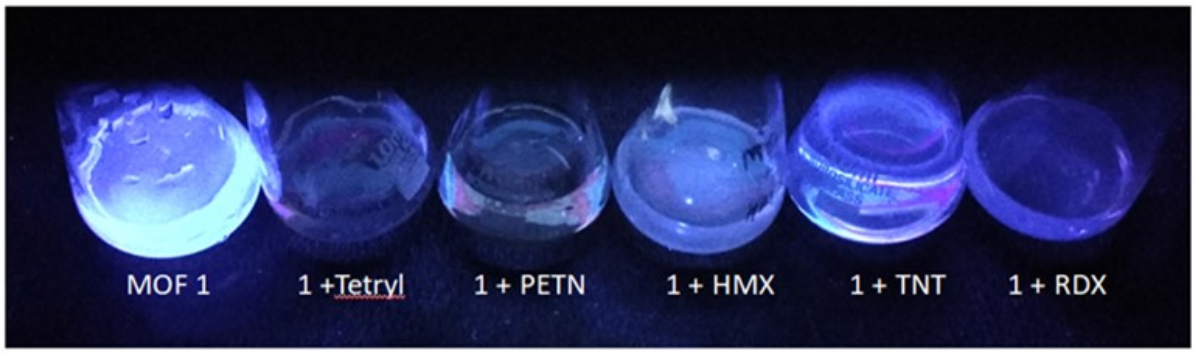


Figure S25: Optical images of PUC1 before and after the addition of analytes under UV light (λ_{ext}=365).

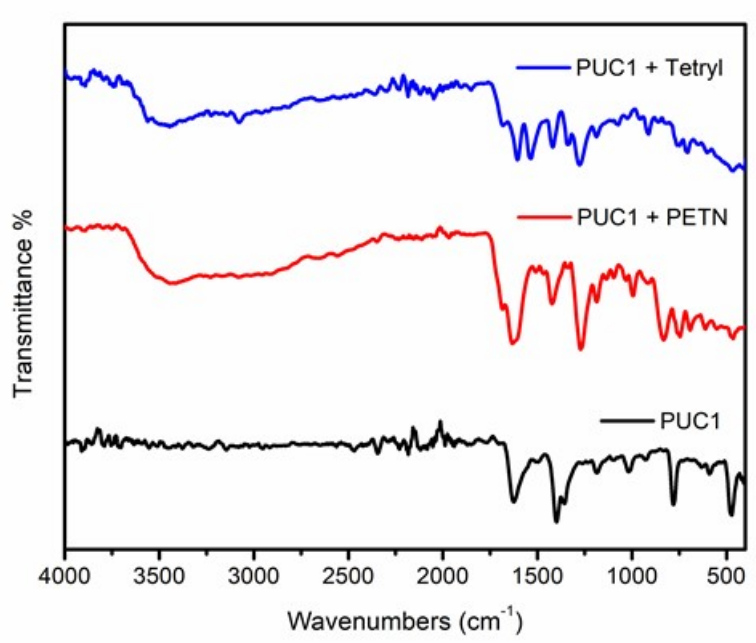


Figure S26: FTIR spectra of **PUC1** before and after addition of PETN and Tetryl.

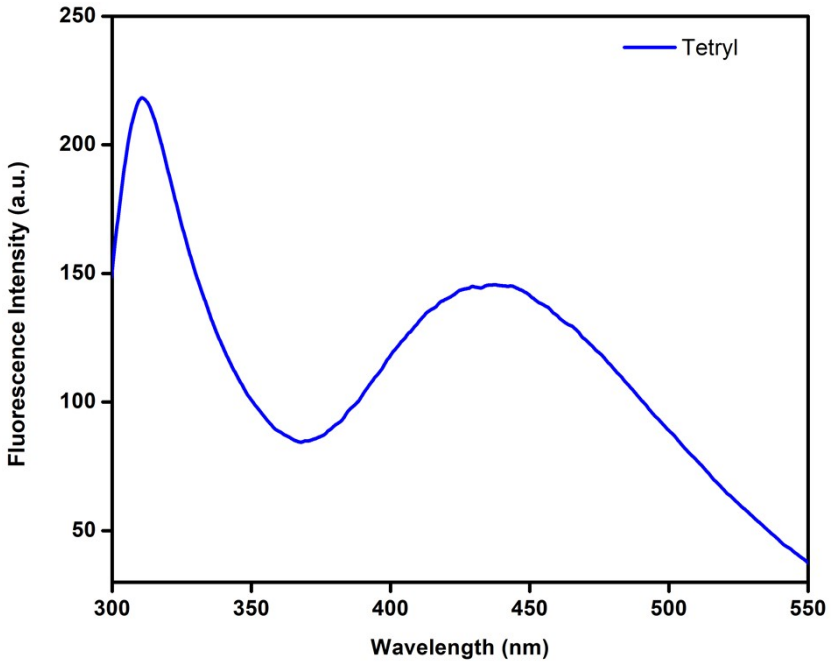
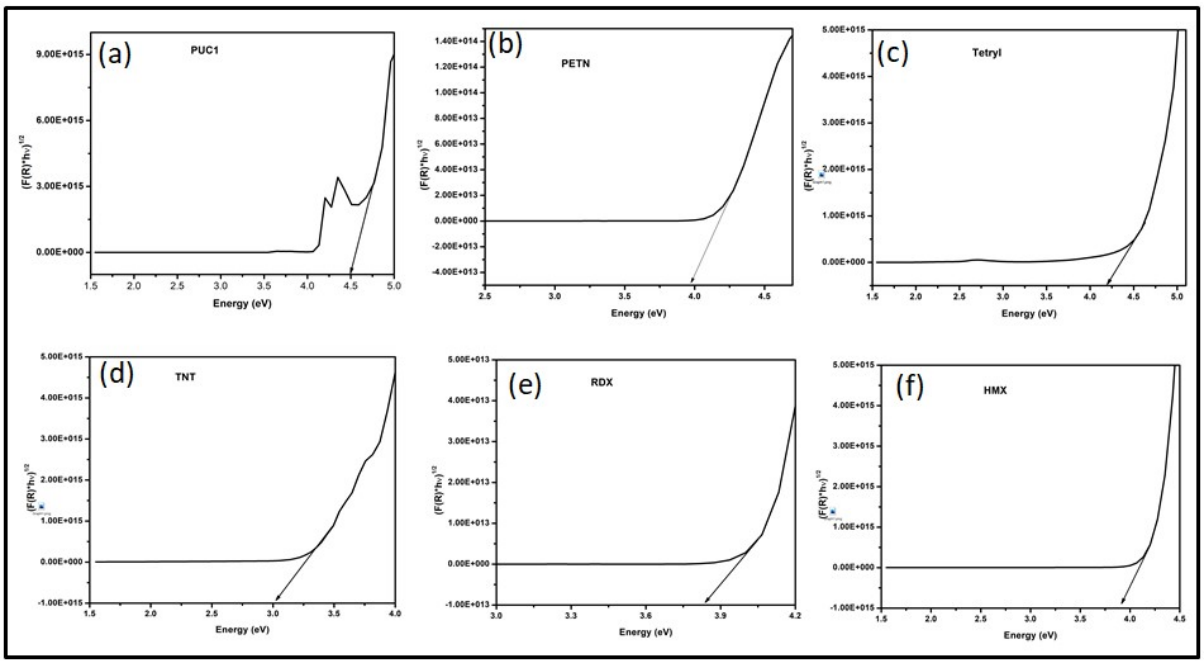


Figure S27: Fluorescence spectra of Tetryl only.

Figure S28: Tauc plots of (a) PUC1; (b) PETN; (c) Tetryl; (d) TNT; (e) RDX and (f) HMX.



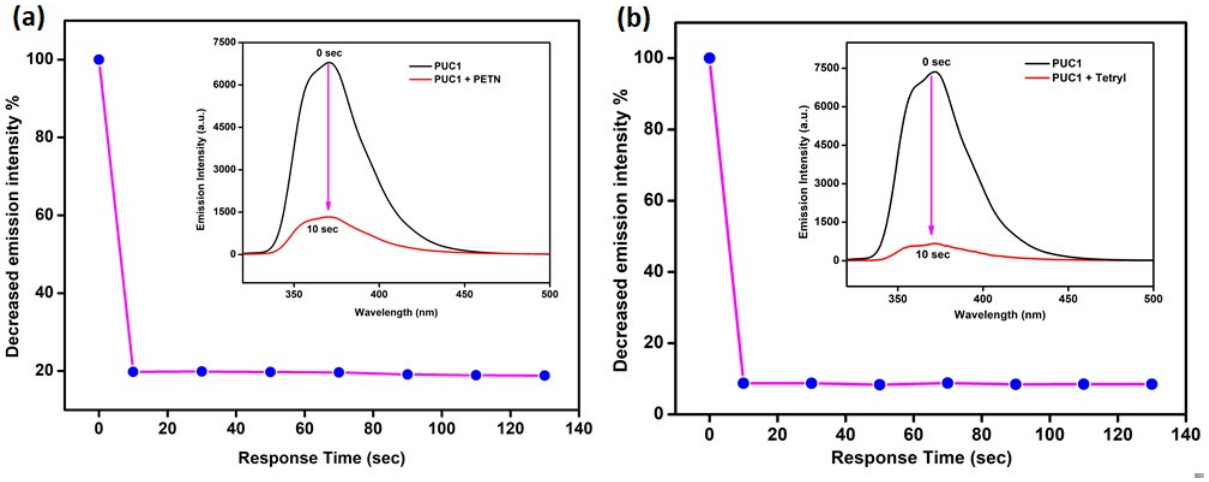


Figure S29: Plot of decrease in the emission intensity percentage at different time intervals for (a) PETN and (b) Tetryl. Inset shows the fluorescence spectra of PUC1 before (0 s) and after (10 s) the addition of analytes.

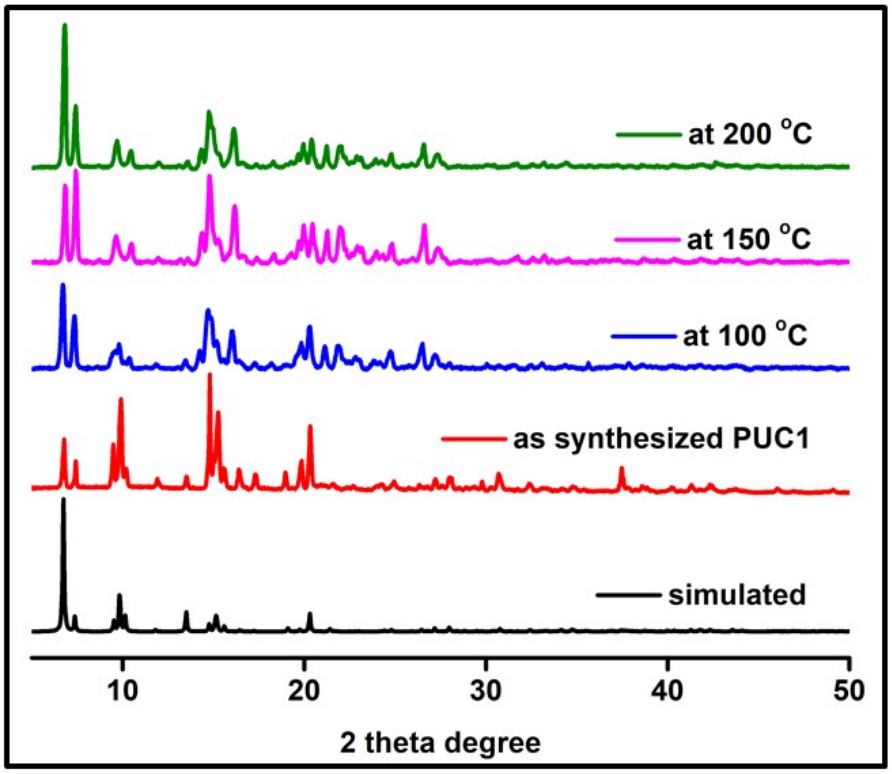


Figure S30: PXRD spectra of PUC1 at different temperatures i.e. 100, 150 and 200 °C.

Table S1: List of Crystallographic parameters for PUC1.

Identification code	**PUC1**
CCDC	2038686
Empirical formula	$C_{123}H_{52}N_8O_{32}Zn_8$
Formula weight	2676.85
Temperature/K	293(2)
Crystal system	monoclinic
Space group	C2/m
a/Å	18.1819(3)
b/Å	18.8056(4)
c/Å	23.9801(4)
α/°	90
β/°	92.003(2)
γ/°	90
Volume/Å^3	8194.3(3)
Z	2
ρ_{calc}g/cm^3	1.085
μ/mm^{-1}	1.209
F(000)	2684.0
Crystal size/mm^3	0.12 × 0.10 × 0.08
Radiation	MoKα (λ =
Index ranges	-23 ≤ h ≤ 22, -16 ≤ k ≤ 24, -31 ≤ l ≤ 27
Reflections collected	37268
Independent reflections	9018 [R_{int} = 0.0655, R_{sigma} = 0.0474]
Data/restraints/parameters	9018/150/514
Goodness-of-fit on F^2	1.098
Final R indexes [I>=2σ (I)]	R_1 = 0.0961, wR_2 = 0.2741
Final R indexes [all data]	R_1 = 0.1159, wR_2 = 0.2850

Largest diff. peak/hole / e $Å^{-3}$ 2.05/-2.47

Table S2: List of selected bond lengths for PUC1.

Atom	Atom	Length/Å
Zn3	$Zn4^{1}$	2.9602(13)
Zn3	$O5^{2}$	2.019(6)
Zn3	O5	2.019(6)
Zn3	$O8^{3}$	2.019(6)
Zn3	$O8^{1}$	2.019(6)
Zn3	N2	2.024(7)
Zn1	Zn2	2.9690(13)
Zn1	$O2^{4}$	2.039(5)
Zn1	$O2^{5}$	2.039(5)
Zn1	$O3^{2}$	2.023(6)
Zn1	O3	2.023(6)
Zn1	$N4^{6}$	2.064(8)
Zn4	O7	2.009(6)
Zn4	$O7^{7}$	2.009(5)
Zn4	$O6^{5}$	2.038(6)
Zn4	$O6^{8}$	2.038(6)
Zn4	N3	2.025(8)
Zn2	O4	2.015(5)
Zn2	$O4^{2}$	2.015(5)
Zn2	$O1^{4}$	2.050(5)
Zn2	$O1^{5}$	2.050(5)
Zn2	N1	2.022(8)

Table S3: Band Gap table of PUC1 and other analytes, calculated using tauc plot:

Analyte	Band gap (eV)
PUC1	4.5
Tetryl	4.2
PETN	3.95
HMX	3.9
RDX	3.8
TNT	3.0

Table S4: Comparison with the earlier reported methods.

Probes	**Sensing analyte**	**Sensing Method**	**K_{sv} value**	**LOD**	**Reference**
Eu-MOF	Tetryl	Fluorescence	1.09×10^4	0.1 – 0.5mM	[1]
Modified AuNPs	TNT & Tetryl	Colorimetric	------	1.76 & 1.74pM	[2]
QDs	TNT	Fluorescence	------	≈ 1.2 μg/mL	[3]
AuNPs composite	PETN	Surface Plasmon Resonance(SPR)	------	200fM	[4]
Silica@TTF	Tetryl & TNT	Fluorescence	------	3.5 & 26μM	[5]
3-mercepto,2-butanone	Tetryl & TNT	Surface enhanced Raman scattering (SERS)	------	17.2 & 6.81ng/ml^{-1}	[6]
AuNPs-4-ATP + NED	PETN	Colorimetric	-----	0.12mg/L	[7]
AuNPs	PETN	Colorimetric	-----	0.169μM/L	[8]
[Zn(NDA)(AMP)] (PUC1)	PETN, Tetryl	Fluorescence	0.1×10^6, 0.12×10^5 M^{-1}	0.315, 0.404μM	Present work

References:

1 N. He, M. Gao, D. Shen, H. Li, Z. Han and P. Zhao, *Forensic Sci. Int.*, 2019, **297**, 1–7.

2 N. Ular, A. Üzer, S. Durmazel, E. Erça and R. Apak, , DOI:10.1021/acssensors.8b00709.

3 W. J. Peveler, A. Roldan, N. Hollingsworth, M. J. Porter and I. P. Parkin, , DOI:10.1021/acsnano.5b06433.

4 M. Riskin, Y. Ben-amram, R. Tel-vered, V. Chegel, J. Almog and I. Willner, 2011, 3082–3088.

5 Y. Salinas, R. Martínez-Máñez, J. O. Jeppesen, L. H. Petersen, F. Sancenón, M. D. Marcos, J. Soto, C. Guillem and P. Amorós, *ACS Appl. Mater. Interfaces*, 2013, **5**, 1538–1543.

6 K. Milligan, N. C. Shand, D. Graham and K. Faulds, *Anal. Chem.*, 2020, **92**, 3253–3261.

7 A. Üzer, U. Yalçın, Z. Can, E. Erçağ and R. Apak, *Talanta*, 2017, **175**, 243–249.

8 Z. Taefi, F. Ghasemi and M. R. Hormozi-Nezhad, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.*, , DOI:10.1016/j.saa.2019.117803.