

Supporting Information

Discriminative Detection of Nitro Aromatics Explosives by a Luminescent Metal-Organic Framework

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Theoretical Methods

First principles electronic structure studies within a gradient-corrected density functional framework were carried out to understand the experimental findings on the band gaps. Two kinds of theoretical studies were performed. Electronic structure calculations with the PBE exchange-correlation functional¹ were performed on periodic solids using the experimentally determined crystal structures to understand the origins of changes in the band gap energy. These calculations were performed using the Vienna Ab-Initio Simulation Package (VASP).² The projector augmented wave (PAW) pseudopotentials were used to describe the electron-ion interaction. The kinetic energy cut-off of 400 eV was found to give converged results and was used for the plane wave basis. The geometries in these studies used the experimentally determined crystal structures. Secondly, gradient-corrected calculations using the PBE functional³⁵ were performed on free clusters to understand the nature of bonding, using the Amsterdam Density Functional Package (ADF).³ Relativistic effects were taken in account using the Zeroth Order Regular Approximation, and the TZ2P basis set was used.⁴

References

- [1] Perdew, J. P.; Burke, K.; Enzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.
- [2] Kresse, G.; Furthmuller, J. *Phys. Rev. B* **1996**, *54*, 11169.
- [3] Te Velde, G.; Bichelhaupt, F. M.; van Gisbergen, S. J. A.; Fonseca, G. C.; Baerends, E. J.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931.
- [4] van Lenthe, E.; Baerends, E.J.; Snijders, J. G. *J. Comput. Chem.* **1993**, *99*, 4597.

Table S1. Crystallographic data parameters for structure of compound **1**.^a

Empirical formula	C ₃₄ H ₁₆ N ₂ O ₈ Zn ₂
Formula weight	711.23
Crystal system	Triclinic
Space group	<i>P</i> (-1) (no. 2)
Crystal size (mm)	0.200 x 0.150 x 0.150
a (Å)	12.9634(2)
b (Å)	13.1087(2)
c (Å)	13.8909(2)
α (°)	85.137(5)
β (°)	68.466(5)
γ (°)	84.926(4)
Volume (Å ³)	2183.7(5)
Z	2
Calculated density (g/cm ³)	1.082
Absorption coefficient (mm ⁻¹)	1.138
θ range (°)	1.562 to 27.826
Reflections collected	34603
Unique	9796
Parameters	405
Goodness-of-fit	0.937
Final R indices [I>2σ(I)]	R ₁ = 0.0929, wR ₂ = 0.2421
R indices (all data)	R ₁ = 0.1369, wR ₂ = 0.2614

^[a]R₁ = Σ||F₀| - |F_c|| / Σ|F₀|; wR₂ = {[w(F₀² - F_c²)²] / [w(F₀²)²]}^{1/2}; w = 1/[σ²(F₀)² + (aP)² + bP]; P = [max(F₀², 0) + 2(F_c)²]/3, where a = 0.1683 and b = 0.0000, respectively.

Table S2. Selected bond lengths in compound **1**.

Moiety	Bond lengths (Å)
Zn(1)-O(5)	2.0091
Zn(1)-O(1)	2.0197
Zn(1)-O(3)	2.0378
Zn(1)-O(7)	2.0898
Zn(1)-N(1)	2.0413
Zn(2)-O(2)	2.0201
Zn(2)-N(2)	2.0374
Zn(2)-O(8)	2.0419
Zn(2)-O(6)	2.0422
Zn(2)-O(4)	2.0454

Table S3. The CHN analysis for the compound **1'**

Compound	Theoretical (%)			Experimental (%)		
	C	H	N	C	H	N
1'	56.70	3.36	3.86	56.64	3.32	3.91

Table S4. The lifetime χ^2 values and the average lifetime for fluorescence decay of (A) compound **1** (B) compound **1** and NT (1.42 mM) and (C) **1** and NB (1.42 mM)

	A	B	C
χ^2 value	1.05	1.08	1.10
T_1 (ns)	11.29	8.73	8.01
α_1 (%)	30	9	5
T_2 (ns)	40.13	38.7	36.39
α_2 (%)	25	9	4
T_3 (ns)	1.34	0.51	0.397
α_3 (%)	44	83	92
Lifetime (ns)	31.52	29.8	25.35

Table S5. Theoretical band gap energies of available analytes.^a

Analytes	HOMO (ev)	LUMO (eV)	Band gap (eV)
TNP	-8.2374	-3.8978	4.3396
TNT	-8.4592	-3.4926	4.9666
1,3-DNB	-7.9855	-3.4311	4.5544
2,4-DNT	-7.7645	-3.2174	4.5471
NB	-7.5912	-2.4283	5.1629

^a Adapted from, *Angew. Chem. Int. Ed.* **2013**, *52*, 2881 –2885.

Table S6: The reduction potential values, calculated free energy, and the calculated LUMO energies for all analytes.

Nitro aromatics	E_{red} (Volts)	LUMO energy (eV)	ΔG^0 (kCalmol ⁻¹)	Dipole moment (Debye)
DNB	-0.79	-3.5684	-21.91	3.65
DNT	-0.895	-3.4634	-19.48	4.31
TNT	-0.73	-3.6284	-23.29	1.18
NB	-1.09	-3.2604	-14.16	3.95
NT	-1.13	-3.2284	-14.05	4.52

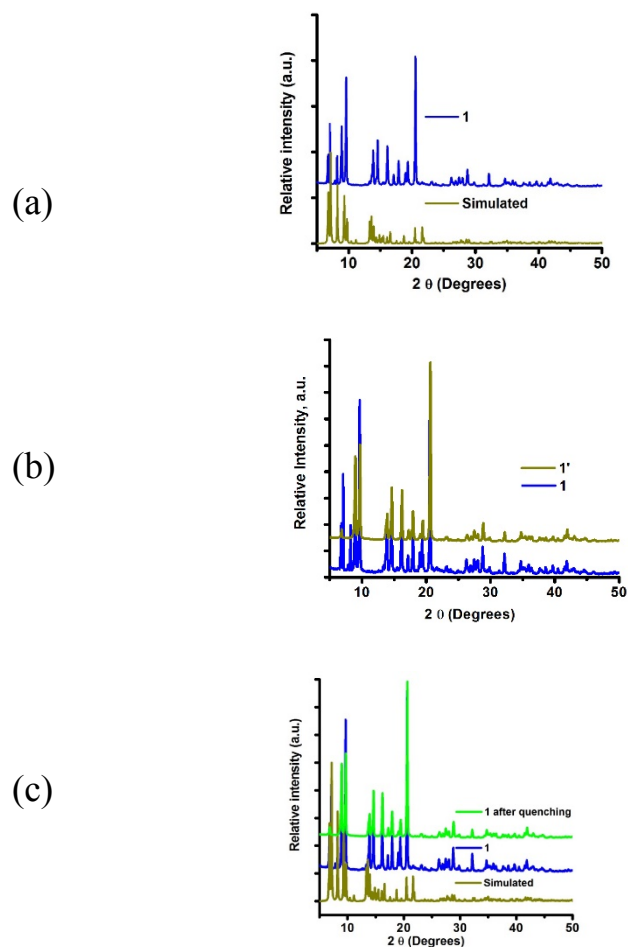


Figure S1. (a) Comparison of simulated and experimental PXRD pattern of compound **1** shows considerable bulk purity of the crystalline phase. Small change in XRD patterns of as-synthesize materials is observed due to solvent evaporation at room temperature. (b) PXRD of **1** and **1'**. In **1'** few peaks are slightly shifted due to distortion of the unit cell. (c) Comparison of PXRD pattern of **1** before and after quenching shows that there is no structural deformation after quenching interaction.

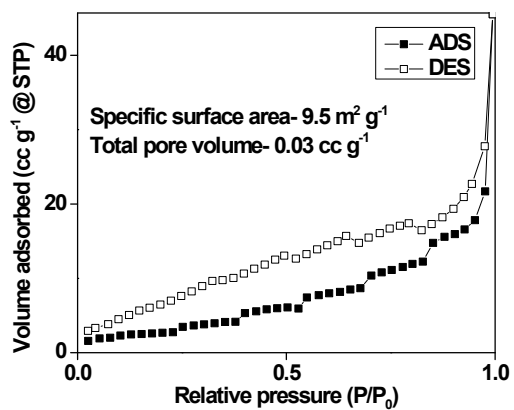


Figure S2. BET adsorption isotherm form 1' showing the adsorption desorption cycle for N₂ gas at 77 K.

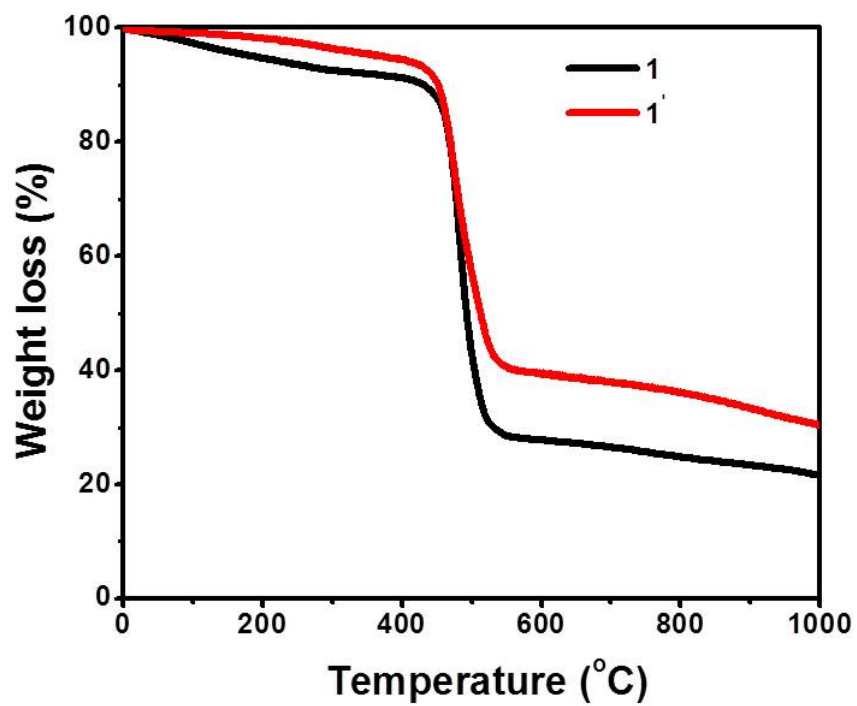


Figure S3. Thermal Gravimetric Analysis (TGA) curve of compound **1** and **1'**.

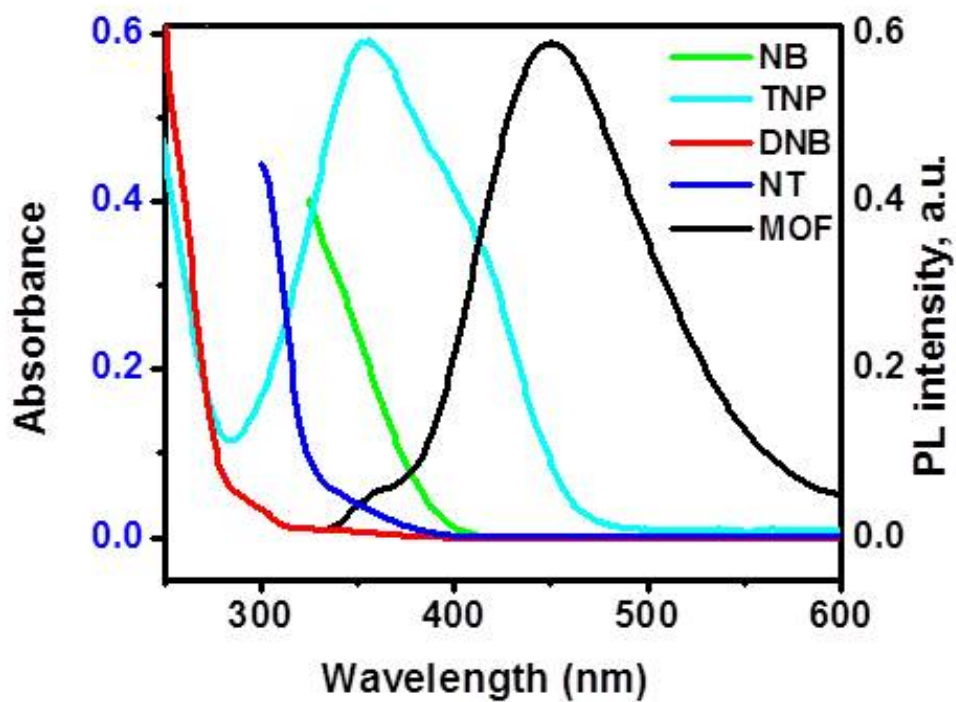


Figure S4. The absorption spectra of nitro aromatics and the emission spectra of the compound **1**.

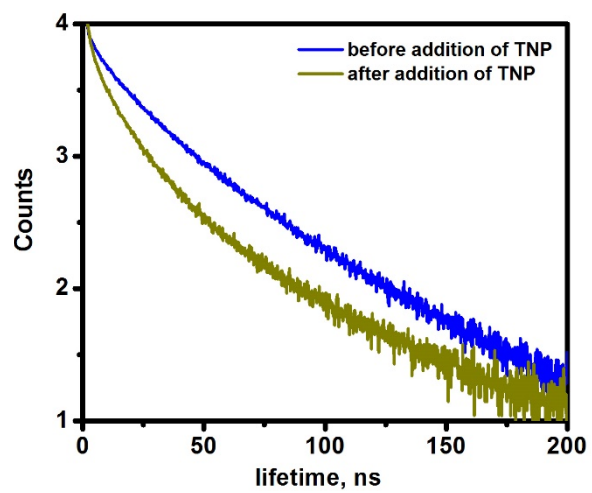


Figure S5. Fluorescence decay profile of **1**, before and after addition of TNP.

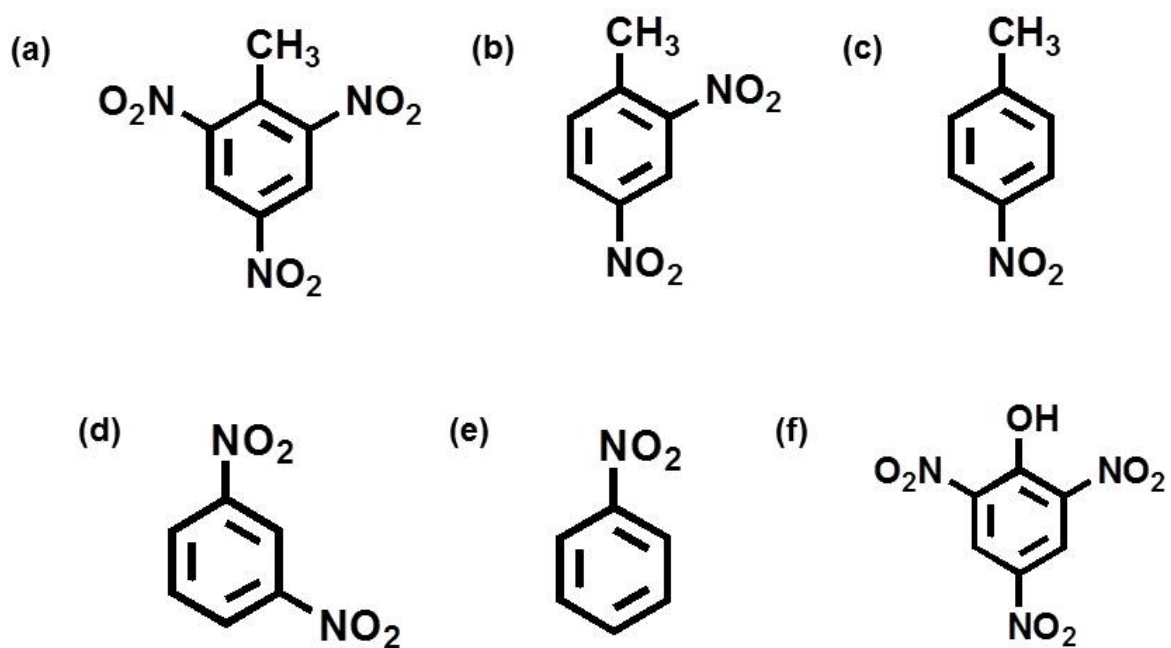


Figure S6. Chemical structure of (a) TNT, (b) DNT, (c) NT, (d) DNB, (e) NB and (f) TNP.

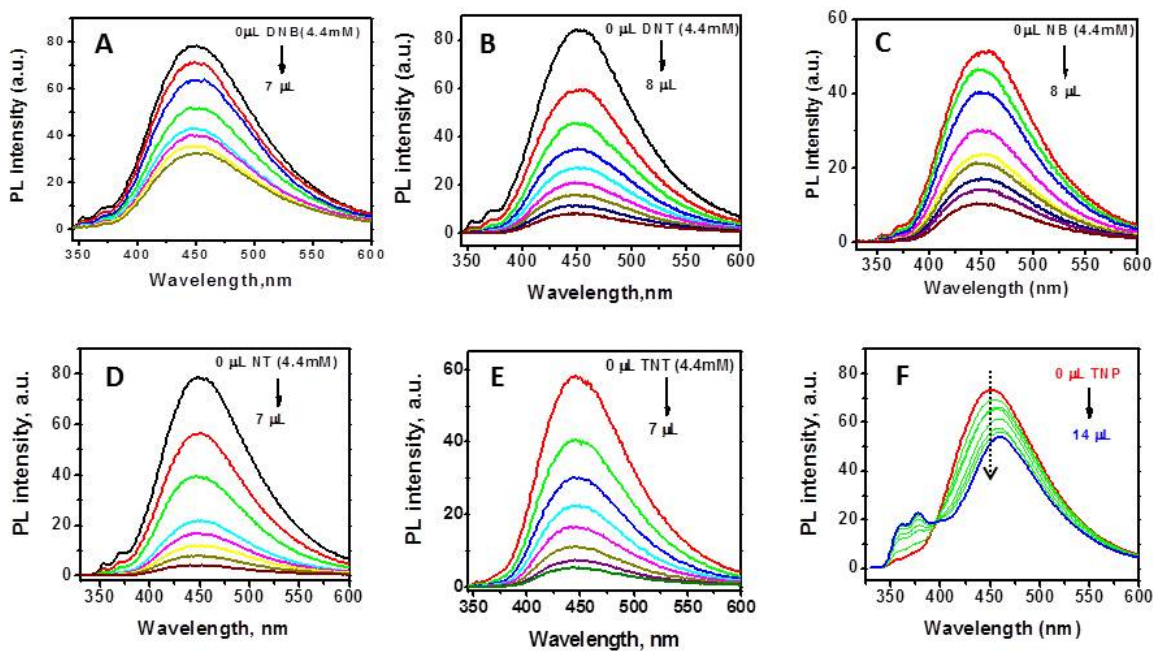


Figure S7. The quenching titrations of compound **1** by incremental addition of nitroaromatics. (A) DNB, (B) DNT, (C) NB, (D) NT, (E) TNT, and (F) TNP.

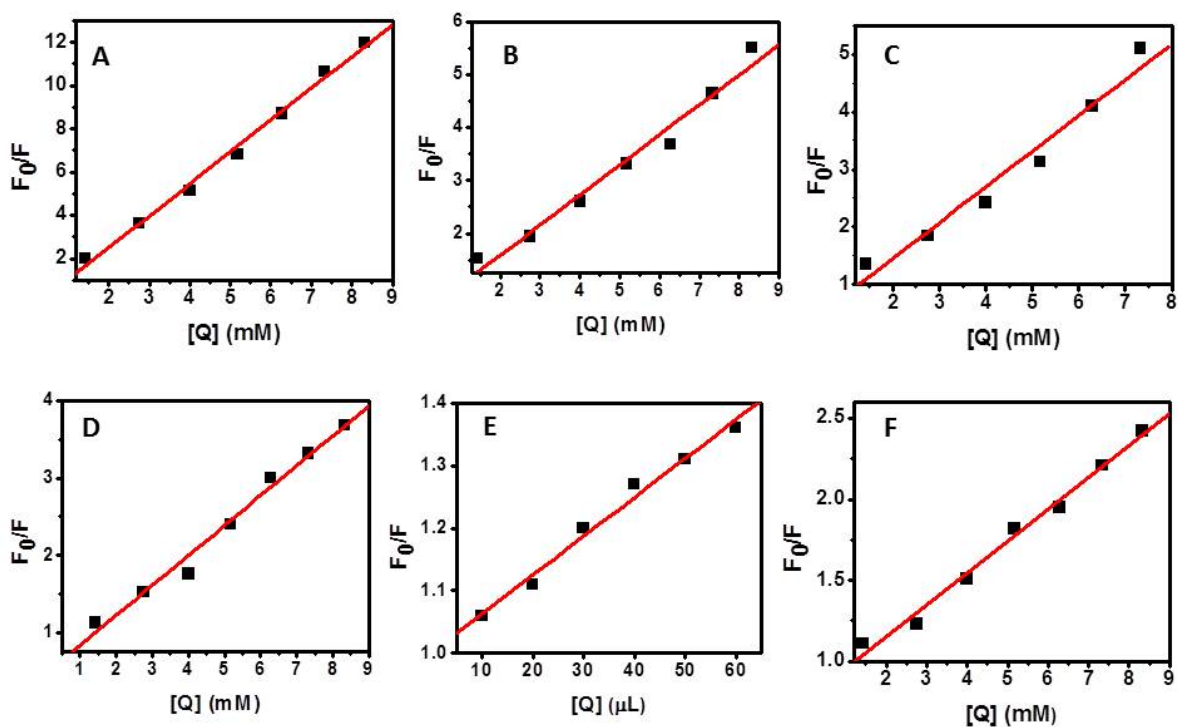


Figure S8. The relative change in the fluorescence intensity of **1** as the function of concentration of various nitroaromatics (Stern-Volmer plot), where (A) NT, (B) DNT, (C) TNT, (D) NB, (E) DNB, (F) TNP.

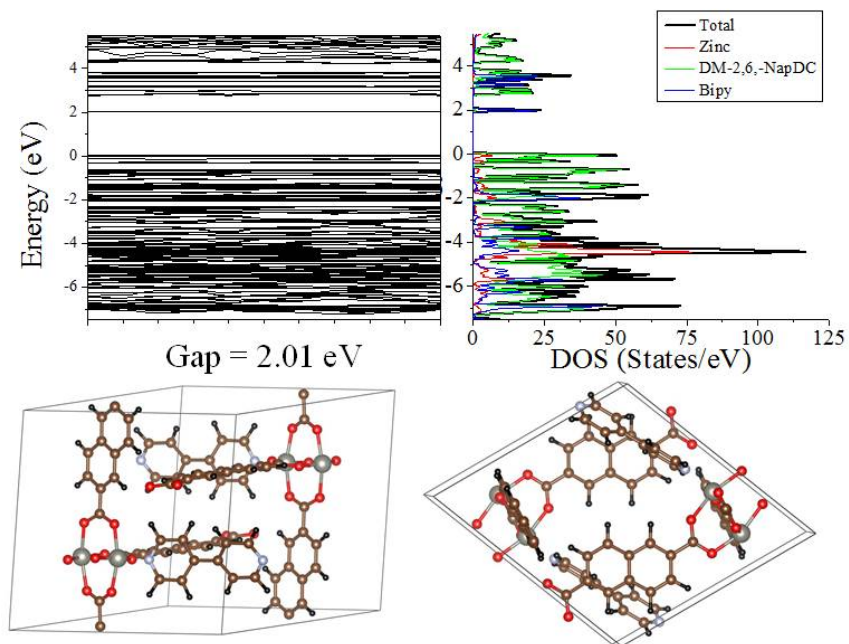


Figure S9. The band structure and density of states of the compound **1**.

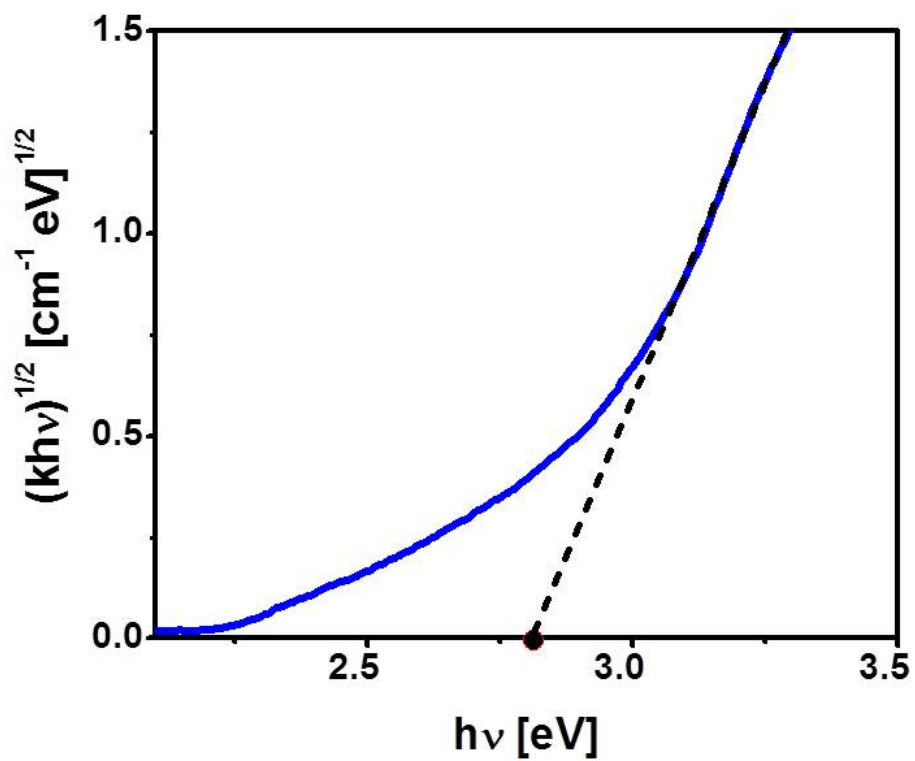


Figure S10. Tauc plots showing the band gap energy ($E_{bg} = 2.81 \text{ eV}$) determined from the optical absorption spectra of compound **1**.

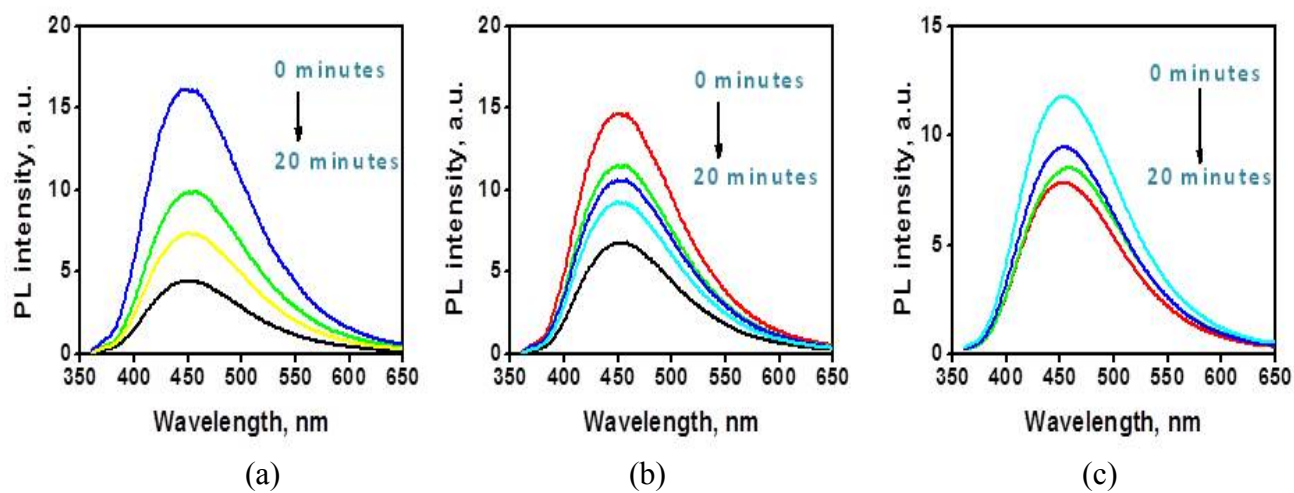


Figure S11. The quenching study of compound **1** in solid state by the exposure of vapors of analytes (a) DNB (b) NB (c) NT in different time intervals.

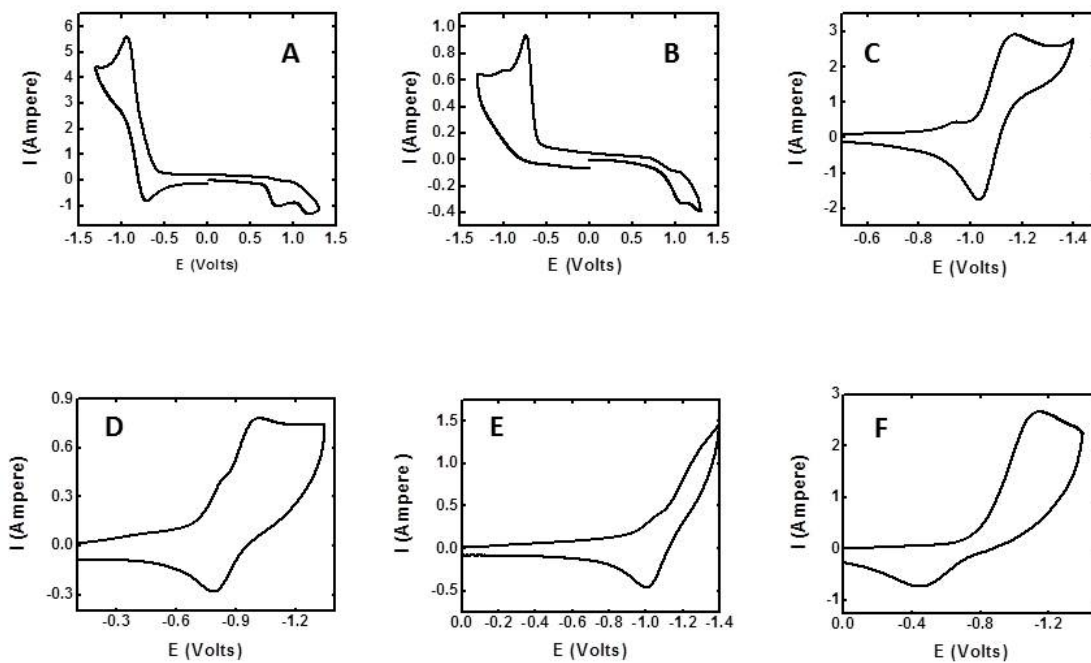


Figure S12. The electrochemical studies of **1** and all the nitro aromatics (A) **1**, (B) TNT, (C) NB, (D) DNT, (E) NT, and (F) DNB.

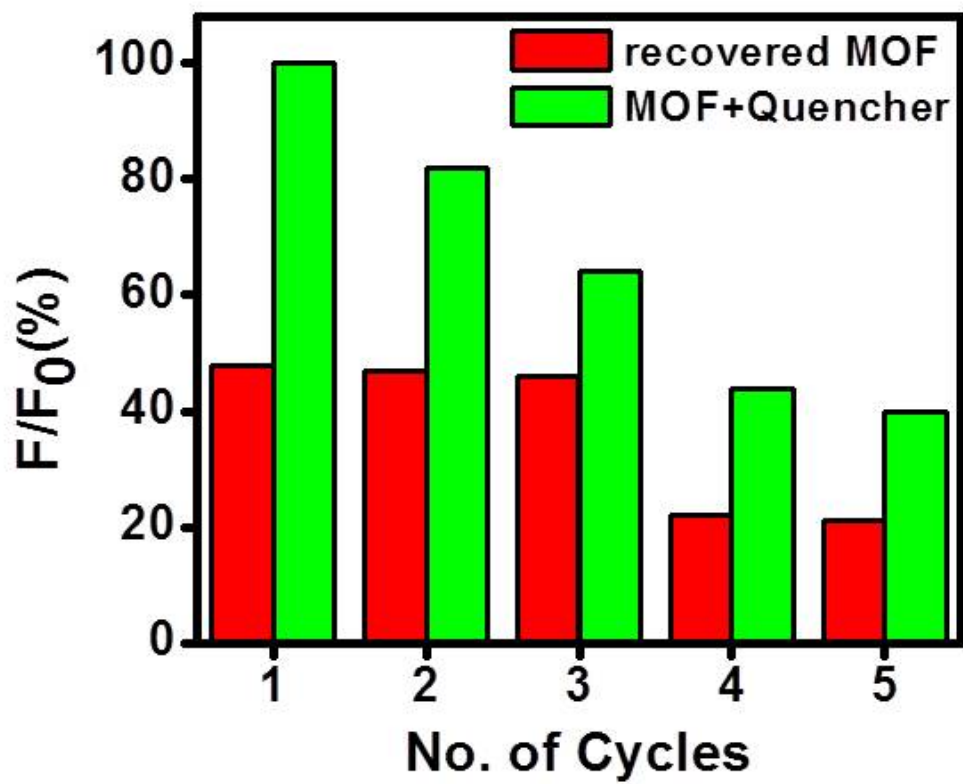


Figure S13. Shows the recyclability of compound 1.

Topological Analysis

Topological analysis using TOPOS software identified that the structure has a new topological network with uninodal 10-c net, which can be presented as a Schläfli symbol $3^{12}.4^{28}.5^5$ (td10 = 2721).(Ref. S1).

Ref. S1. Blatov, A. V.; Proserpio, D. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2009**, *65*, 202.

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1:C34 H16 N2 O8 Zn2

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Topology for Zn1

Atom Zn1 links by bridge ligands and has

Common vertex with	R (A-A)					f
Zn 2	0.1331	0.3278	-0.6102	(0 0 -1)	11.098A	1
Zn 1	1.2076	0.3213	0.1611	(1 0 0)	12.963A	1
Zn 1	-0.7924	0.3213	0.1611	(-1 0 0)	12.963A	1
Zn 2	-0.8669	0.3278	0.3898	(-1 0 0)	13.095A	1
Zn 1	0.2076	1.3213	0.1611	(0 1 0)	13.109A	1
Zn 1	0.2076	-0.6787	0.1611	(0 -1 0)	13.109A	1
Zn 2	0.1331	-0.6722	0.3898	(0 -1 0)	13.176A	1
Zn 2	1.1331	0.3278	0.3898	(1 0 0)	13.500A	1
Zn 2	0.1331	1.3278	0.3898	(0 1 0)	13.701A	1

Common face with R (A-A)

Zn 2 0.1331 0.3278 0.3898 (0 0 0) 2.968A 4

Topology for Zn2

Atom Zn2 links by bridge ligands and has

Common vertex with	R (A-A)					f
Zn 1	0.2076	0.3213	1.1611	(0 0 1)	11.098A	1
Zn 2	-0.8669	0.3278	0.3898	(-1 0 0)	12.963A	1
Zn 2	1.1331	0.3278	0.3898	(1 0 0)	12.963A	1
Zn 1	1.2076	0.3213	0.1611	(1 0 0)	13.095A	1
Zn 2	0.1331	1.3278	0.3898	(0 1 0)	13.109A	1
Zn 2	0.1331	-0.6722	0.3898	(0-1 0)	13.109A	1
Zn 1	0.2076	1.3213	0.1611	(0 1 0)	13.176A	1
Zn 1	-0.7924	0.3213	0.1611	(-1 0 0)	13.500A	1
Zn 1	0.2076	-0.6787	0.1611	(0-1 0)	13.701A	1

Common face with R (A-A)

Zn 1 0.2076 0.3213 0.1611 (0 0 0) 2.968A 4

Structural group analysis

Structural group No 1

Structure consists of 3D framework with ZnO4NC17H8

There are 2 interpenetrating nets

FISE: Full interpenetration symmetry elements

1: -1

PIC: [1,0,0][0,1,0][0,0,1] (PICVR=1)

Zt=1; Zn=2

Class IIa Z=2

Coordination sequences

Zn1: 1 2 3 4 5 6 7 8 9 10

Num 10 30 66 114 178 254 346 450 570 702

Cum 11 41 107 221 399 653 999 1449 2019 2721

Zn2: 1 2 3 4 5 6 7 8 9 10

Num 10 30 66 114 178 254 346 450 570 702

Cum 11 41 107 221 399 653 999 1449 2019 2721

TD10=2721

Vertex symbols for selected sublattice

Zn1 Point symbol: {3¹².4²⁸.5⁵}

Extended point symbol:

[3.3.3.3.3.3.3.3.3.3.3.3.3.3.4.4.4.4.4.4.4.4.4.4.4.4.4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).5.5.5.5.5(4)]

Zn2 Point symbol: {3¹².4²⁸.5⁵}

Extended point symbol:

[3.3.3.3.3.3.3.3.3.3.3.3.3.3.4.4.4.4.4.4.4.4.4.4.4.4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).4(3).5.5.5.5.5(4)]

Point symbol for net: {3¹².4²⁸.5⁵}

10-c net; uninodal net

Database with topological types was not loaded. Check 'Classification' flag.

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