Supporting Information

Nitrogen-Rich Tetranuclear Metal Complex as a New Structural Motif for Energetic Materials

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1. Tables

Table S1. Selected bond distances (Å) and bond angles (°).

Compound **1**			
Zn(1)–O(2W)	2.085(2)	Zn(2)–O(1W)	2.0716(19)
Zn(1)–N(10)	2.104(2)	Zn(2)–N(29)	2.133(2)
Zn(1)–N(25)	2.117(2)	Zn(2)–O(3W)	2.163(2)
Zn(1)–N(19)	2.191(2)	Zn(2)–N(20)	2.167(2)
Zn(1)–O(4W)	2.195(2)	Zn(2)–N(15)#1	2.185(2)
Zn(1)–N(26)	2.215(2)	Zn(2)–N(16)#1	2.211(2)
O(2W)–Zn(1)–N(10)	91.51(8)	O(1W)–Zn(2)–N(29)	93.16(8)
O(2W)–Zn(1)–N(25)	92.11(8)	O(1W)–Zn(2)–O(3W)	175.15(8)
N(10)–Zn(1)–N(25)	169.98(8)	N(29)–Zn(2)–O(3W)	86.76(8)
O(2W)–Zn(1)–N(19)	90.93(8)	O(1W)–Zn(2)–N(20)	92.14(7)
N(10)–Zn(1)–N(19)	93.68(7)	N(29)–Zn(2)–N(20)	94.11(7)
N(25)–Zn(1)–N(19)	95.61(8)	O(3W)–Zn(2)–N(20)	92.70(8)
O(2W)–Zn(1)–O(4W)	98.10(9)	O(1W)–Zn(2)–N(15)#1	97.15(8)
N(10)–Zn(1)–O(4W)	86.38(8)	N(29)–Zn(2)–N(15)#1	166.86(8)
N(25)–Zn(1)–O(4W)	83.86(9)	O(3W)–Zn(2)–N(15)#1	82.28(8)
N(19)–Zn(1)–O(4W)	170.97(9)	N(20)–Zn(2)–N(15)#1	93.63(7)
O(2W)–Zn(1)–N(26)	166.07(8)	O(1W)–Zn(2)–N(16)#1	88.86(8)
N(10)–Zn(1)–N(26)	101.30(7)	N(29)–Zn(2)–N(16)#1	96.07(8)
N(25)–Zn(1)–N(26)	76.18(7)	O(3W)–Zn(2)–N(16)#1	86.33(8)
N(19)–Zn(1)–N(26)	82.87(9)	N(20)–Zn(2)–N(16)#1	169.70(8)
O(4W)–Zn(1)–N(26)	88.26(9)	N(15)#1–Zn(2)–N(16)#1	76.08(7)
Compound **2**			
Mn(1)–O(1W)	2.144(5)	Mn(2)–O(3W)	2.158(5)
Mn(1)–O(2W)	2.197(5)	Mn(2)–O(4W)	2.201(6)

Mn(1)–N(20)#1	2.246(5)	Mn(2)–N(10)	2.214(5)
Mn(1)–N(15)	2.257(5)	Mn(2)–N(24)	2.240(5)
Mn(1)–N(29)#1	2.265(5)	Mn(2)–N(23)	2.262(5)
Mn(1)–N(16)	2.277(5)	Mn(2)–N(19)	2.287(5)
O(1W)–Mn(1)–O(2W)	171.11(17)	O(3W)–Mn(2)–O(4W)	99.7(2)
O(1W)–Mn(1)–N(20)#1	89.32(18)	O(3W)–Mn(2)–N10	91.99(19)
O(2W)–Mn(1)–N(20)#1	86.14(19)	N(10)–Mn(2)–O(4W)	88.1(2)
O(1W)–Mn(1)–N(15)	99.61(18)	O(3W)–Mn(2)–N(24)	92.93(18)
O(2W)–Mn(1)–N(15)	84.17(19)	N(10)–Mn(2)–N(24)	85.5(2)
N(20)#1–Mn(1)–N(15)	169.13(19)	O(4W)–Mn(2)–N(24)	172.5(2)
O(1W)–Mn(1)–N(29)#1	94.32(17)	O(3W)–Mn(2)–N(23)	163.91(18)
O(2W)–Mn(1)–N(29)#1	93.36(18)	N(10)–Mn(2)–N(23)	88.7(2)
N(20)#1–Mn(1)–N(29)#1	90.56(17)	O(4W)–Mn(2)–N(23)	102.03(18)
N(15)–Mn(1)–N(29)#1	94.91(17)	N(24)–Mn(2)–N(23)	73.97(17)
O(1W)–Mn(1)–N(16)	87.53(17)	O(3W)–Mn(2)–N(19)	90.3(2)
O(2W) –Mn(1)–N(16)	85.83(18)	N(10) –Mn(2)–N(19)	169.8(2)
N(20)#1–Mn(1)–N(16)	100.84(17)	O(4W) –Mn(2)–N(19)	89.42(17)
N(15)-Mn(1)–N(16)	73.58(16)	N(24) –Mn(2)–N(19)	96.27(18)
N(29)#1–Mn(1)–N(16)	168.48(17)	N(23) –Mn(2)–N(19)	82.12(19)

Symmetry code: #1 $-x + 1, -y + 1, -z + 1$.

Table S2. Intermolecular π-π interaction distances (Å).

π-π interactions	**Plane A**	**Plane B**	**Distance**
Compound **1**			
Cg(A)•••Cg(B)	N16, N17, N18, N19, C15	N26, N27, N28, N29, C25	3.6005(15)
Cg(A)•••Cg(B)	N16A, N17A, N18A, N19A, C15A	N26 A, N27 A, N28 A, N29 A, C25A	3.6005(15)
Cg(A)•••Cg(B)	N10, N11, N12, N13, C11	N21C, N22C, N23C, N24C, C21C	3.9330(15)
Cg(A)•••Cg(B)	N10B, N11B, N12B, N13B, C11B	N21A, N22A, N23A, N24A, C21A	3.6275(15)
Cg(A)•••Cg(B)	N14, C12, C14, N15, C13	N24C, C22C, C24C, N25C, C23C	3.9817(16)
Cg(A)•••Cg(B)	N14B, C12B, C14B, N15B, C13B	N24A, C22A, C24A, N25A, C23A	3.8870(16)

Compound **2**			
Cg(A)•••Cg(B)	N16, N17, N18, N19, C15 N20,	N20, N21, N22, N23, C21	3.633(5)
Cg(A)•••Cg(B)	N16A, N17A, N18A, N19A, C15A	N20A, N21A, N22A, N23A, C21A	3.633(5)
Cg(A)•••Cg(B)	N10, N11, N12, N13, C11	N26C, N27C, N28C, N29C, C25C	3.957(5)
Cg(A)•••Cg(B)	N10B, N11B, N12B, N13B, C11B	N26A, N27A, N28A, N29A, C25A	3.659(5)
Cg(A)•••Cg(B)	N14, C12, C14, N15, C13	N24C, C22C, C24C, N25C, C23C	4.013(5)
Cg(A)•••Cg(B)	N14B, C12B, C14B, N15B, C13B	N24A, C22A, C24A, N25A, C23A	3.832(5)

Symmetry codes: (A) 1 – *x*, 1 – *y*, 1 – *z*. (B) 1.5 – *x*, –0.5 + *y*, 0.5 – *z*, (C) –0.5 + *x*, 1.5 – *y*, –0.5 + *z*.

Table S3. Hydrogen bond distances (Å) and bond angles (°).

Donor–H···Acceptor	**d(D–H)**	**d(H···A)**	**d(D···A)**	**∠D---H···A**
Compound **1**				
O1W–H1WA···N28	0.77(3)	2.09(3)	2.828(3)	162(3)
O1W–H1WB···N13	0.95(5)	2.02(5)	2.886(3)	151(4)
O2W–H2WA···N22	0.77(5)	2.10(5)	2.860(3)	171(5)
O2W–H2WB···N11	0.74(9)	2.09(10)	2.824(10)	171(7)
N24–H5···N27	0.87(3)	2.11(3)	2.943(3)	161(3)
O3W–H3WA···N12	0.82(6)	2.04(6)	2.854(3)	177(7)
O3W–H3WB···N17 (Intra)	0.84(5)	2.26(5)	3.091(3)	178(6)
O4W–H4WA···N21	0.80(4)	2.19(4)	2.951(3)	158(4)
O4W–H4WA···N22	0.80(4)	2.57(3)	3.134(3)	129(3)
Compound **2**				
O1W–H1WA···N2	0.84(3)	2.07(5)	2.830(7)	150(5)
O1W–H1WB···N13	0.85(5)	2.13(5)	2.913(7)	154(5)
O2W–H2WA···N12	0.85(4)	2.01(4)	2.832(7)	163(6)
O2W–H2WB···N17(Intra)	0.84(6)	2.32(6)	3.139(7)	166(5)
O3W–H3WA···N27	0.77(8)	2.12(8)	2.883(8)	170(8)
O3W–H3WB···N11	0.87(11)	1.94(11)	2.760(7)	156(11)
O4W–H4WA···N27	0.71(12)	2.56(13)	3.116(7)	136(13)
O4W–H4WB···N27	0.90(8)	2.29(8)	3.182(8)	169(7)
N14–H14A···N18	0.98(6)	1.94(7)	2.921(7)	175(6)

Symmetry code: (A) 1 – *x*, 1 – *y*, 1 – *z*.

Table S4. Calculated parameters used in the detonation reactions for compounds **1** and **2**

	Compounds	ZnO/MnO_2	H_2O	NH_3	N_2	C	ΔE_{det}	ΔE_{det}	ΔH_{det}	ΔH_{det}
	hartree	hartree	hartree	hartree	hartree	hartree	hartree	$kcal \cdot g^{-1}$	$kcal \cdot g^{-1}$	$kcal \cdot cm^{-3}$
1	−1118.4725	−302.2548	−76.3787	−56.4983	−109.4493	−37.7441	1.5075	3.1158	3.558	7.499
2	−995.8487	−254.7155	−76.3787	−56.4983	−109.4493	−37.7441	1.6195	3.4668	3.953	7.780

1 hartree = 627.51 $Kcal \cdot mol^{-1}$

Notes:

Heats of detonation for compounds 1 and 2. All of the calculations were completed in the Materials Studio 6.0 package. Density functional theory (DFT) was used to compute the energy of detonation (ΔH_{det}), from which ΔE_{det} is estimated by using a linear correlation equations (ΔH_{det} = 1.127 ΔE_{det} + 0.046, r = 0.968). As in the reported literature[1], the DFT calculations for energetic materials were performed with the code DMOl3[2] under 3D periodic boundary conditions employing the Monkhorst-Pack multiple K-point sampling of the Brillouin zone[3] and the Perdew-BeckeEzerhoff (PBE) exchange-correlation function.[4] The complete detonation reactions are described by equations 1 and 2.

$ZnC_5H_6O_2N_{10} \rightarrow ZnO + H_2O + 4/3NH_3 + 13/3N_2 + 5C$ (1)

$MnC_5H_6O_2N_{10} \rightarrow MnO_2 + 2NH_3 + 4N_2 + 5C$ (2)

Table S5. Comparison of nitrogen content, heat of detonation, detonation velocity and detonation pressure of some reported energetic MOFs with **1** and **2**

explosive	N^a	$\Delta H_{det}{}^b$	D^c	P^d	Ref
2	47.75	3.953	9.064	38.18	This work
1	46.12	3.558	9.610	44.57	This work
CHP	33.49	1.250	8.225	31.73	*J. Am. Chem. Soc.* **2012**, *134*, 1422–1425
NHP	33.49	1.370	9.184	39.69	*J. Am. Chem. Soc.* **2012**, *134*, 1422–1425
CHHP	23.58	0.750	6.205	17.96	*Chem. Eur. J.* **2013**, *19*, 1706–1711
ZnHHP	23.61	0.700	7.016	23.58	*Chem. Eur. J.* **2013**, *19*, 1706–1711
CuATRZ	53.35	3.618	9.160	35.68	*Angew. Chem. Int. Ed.* **2013**, *52*, 14031–14035
AgATRZ	43.76	1.381	7.773	29.70	*Angew. Chem. Int. Ed.* **2013**, *52*, 14031–14035
CoBTA	59.85	2.658	8.657	32.18	*Chem. Eur. J.* **2014**, *20*, 1–6
$[Pb(Htztr)_2(H_2O)]_n$	39.4	1.36	7.72	31.6	*J. Mater. Chem. A*, **2014**, *2*, 11958–11965
$[Pb(H_2tztr)(O)]_n$	27.2	0.26	8.12	40.1	*J. Mater. Chem. A*, **2014**, *2*, 11958–11965
$[Cu(Htztr)_2(H_2O)_2]_n$	52.72	2.128	8.18	30.57	*Green Chem.*, ***2015**, 17, 831–836*
$[Cu(tztr)\cdot H_2O]_n$	45.23	1.322	7.92	31.99	*Green Chem.*, ***2015**, 17, 831–836*
$[Cu(Htztr)]_n$	49.08	3.958	10.40	56.48	*Green Chem.*, ***2015**, 17, 831–836*
$[Cu_4Na(Mtta)_5(CH_3CN)]_n$	40.08	2.37	7.23	24.4	*Dalton Trans.*, ***2015**, 44, 2333–2339*
$[Cu_3(MA)_2(N_3)_3]_n$	47.55	2.47	8.47	35.32	*Chem. Eur. J.* ***2015**, 21, 1–6*

[a] Nitrogen content. [b] The heat of detonation. [c] Detonation velocity. [d] Detonation pressure. $[Pb(Htztr)_2(H_2O)]_n$: $PbC_6H_6N_{14}O$, M = 497.45; $[Pb(H_2tztr)(O)]_n$: $PbC_3H_3N_7O$, M_r = 360.31; $[Cu(Htztr)_2(H_2O)_2]_n$: $CuC_6H_8N_{14}O_2$, M_r = 371.8; $[Cu(tztr)H_2O]_n$: $CuC_3H_3N_7O$, M_r = 216.65; $[Cu_4Na(Mtta)_5(CH_3CN)]_n$: $Cu_4NaN_{21}C_{12}H_{18}$, M_r = 735; $[Cu_3(MA)_2(N_3)_3]_n$: $C_3H_6Cu_3N_{15}$, M_r = 442.85. The other reported energetic MOFs have been illustrated in the manuscript.

Notes:

Detonation properties for compounds 1 and 2. Detonation performance of the related energetic materials (**1** and **2**) here was evaluated by the empirical Kamlet formula, as

$$D = 1.01\ \Phi^{1/2}\ (1 + 1.30\rho)$$

$$P = 1.558\ \Phi\rho^2$$

$$\Phi = 31.68\ N(MQ)^{1/2}$$

$$Q = -[\Delta H_f(\text{denotation products}) - \Delta H_f(\text{explosive})]/\text{formula weight of explosive}$$

where D represents detonation velocity ($km \cdot s^{-1}$) and P is detonation pressure (GPa), ρ is the density of explosive ($g \cdot cm^{-3}$). Φ, N, M and Q are characteristic parameters of an explosive. N is the moles of detonation gases per gram of explosive, M is the average molecular weight of these gases and Q is the heat of detonation ($kJ \cdot g^{-1}$). The formation of metal oxides as solid was assumed to be governed by the deficiency of oxygen.

For **1**

$\rho = 2.108\ g \cdot cm^{-3}$

$Q = \Delta H_{det} = 3.5576\ Kcal \cdot g^{-1} = 14870.8\ J \cdot g^{-1}$

$N = 20/(3\times303.6) = 0.0220\ mol \cdot g^{-1}$

$M = (18.02\times3+17.03\times4+28.01\times13)/20 = 24.32\ g \cdot mol^{-1}$

$P = 1.55\times(2.108)^2\times[0.0220\times(24.32\times3557.6)^{1/2}] = 1.55\times(2.108)^2\times6.471 = 44.57\ GPa$

$D = 1.01\times(6.471)^{1/2}\times(1+1.30\times2.108) = 9.610\ km \cdot s^{-1}$

For **2**

$\rho = 1.968\ g \cdot cm^{-3}$

$Q = \Delta H_{det} = 3.9531\ Kcal \cdot g^{-1} = 16523.958\ J \cdot g^{-1}$

$N = 6/293.15 = 0.0205\ mol \cdot g^{-1}$

$M = (17.03\times2+28.01\times4)/6 = 24.35\ g \cdot mol^{-1}$

$P = 1.55\times(1.968)^2\times[0.0205\times(24.35\times3953.1)^{1/2}] = 1.55\times(1.968)^2\times6.36 = 38.18\ GPa$

$D = 1.01\times(6.36)^{1/2}\times(1+1.30\times1.968) = 9.064\ km \cdot s^{-1}$

2. Graphics

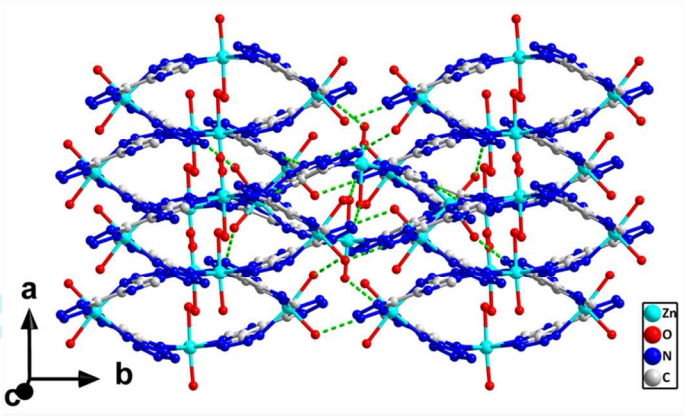

Figure S1. Schematic representation of 0-D to 3-D supramolecular architecture *via* hydrogen bonds in **1**

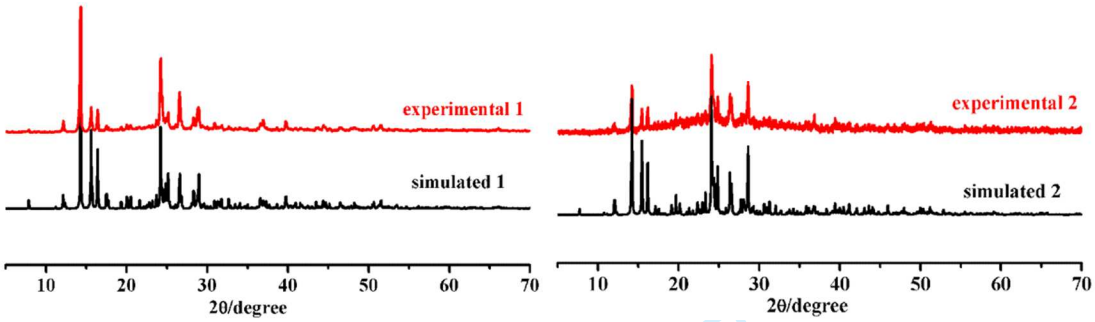

Figure S2. Powdered *X*-ray diffraction (PXRD) patterns of **1** and **2**

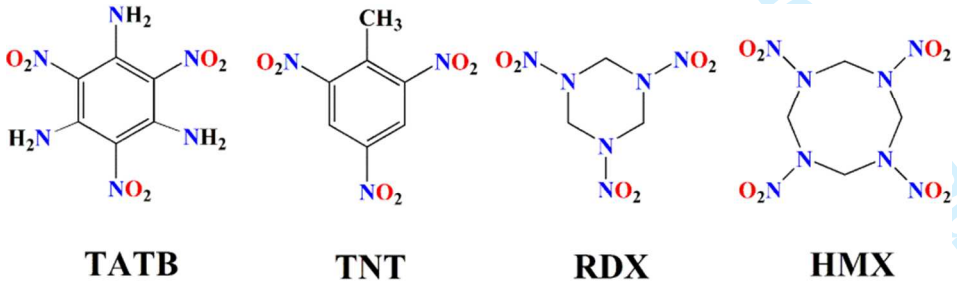

Figure S3. The structures of four classical explosive materials: triaminotrinitrobenzene (TATB), trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX), cyclotetramethylenetetranitramine (HMX).

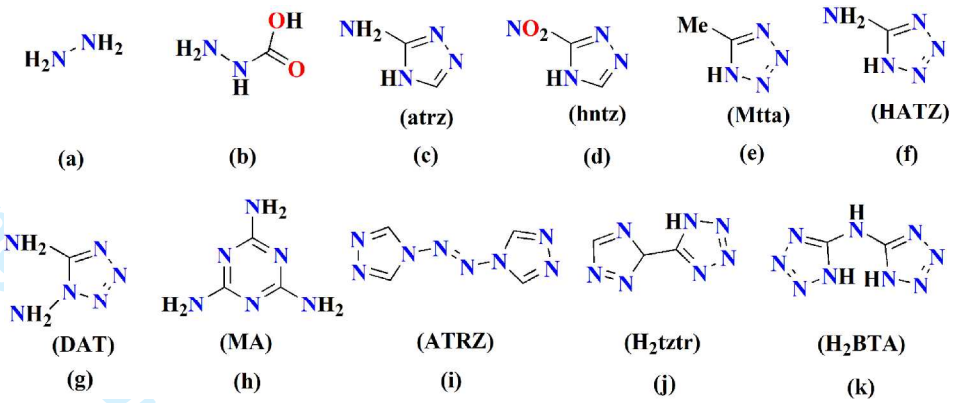

Figure S4. Selected nitrogen-rich ligands used in the synthesis of the reported 1D, 2D and 3D energetic MOFs: (a) hydrazine, (b) hydrazinecarboxylate, (c) 3-amino-1*H*-1,2,4-triazole (atrz), (d) 3-nitro-1*H*-1,2,4-triazole (Hntz), (e) 5-methyltetrazole (Mtta), (f) 5-aminotetrazole (HATZ), (g) 1,5-diaminotetrazole (DAT), (h) melamine (MA), (i) 4,4′-azo-1,2,4-triazole (ATRZ), (j) 3-(tetrazole-5-yl)triazole (H_2tztr), (k) N,N-bis(1*H*-tetrazole-5-yl)-amine (H_2BTA).

3. References:

[1] (a) Bushuyev, O. S.; Brown, P.; Maiti, A.; Gee, R. H.; Peterson,; Weeks, G. R. B. L.; Hope-Weeks, L. J. *J. Am. Chem. Soc.* **2012**, 134, 1422–1425. (b) Zhang, S.; Liu, X.; Yang, Q.; Su, Z.; Gao, W.; Wei, Q.; Xie, G.; Chen S.; Gao, S. *Chem.–Eur. J.* **2014**, 20, 7906–7910.

[2] Delley, B. *J. Chem. Phys*. **1990**, 92, 508–517.

[3] Monkhorst, H. J.; Pack, J. D. *Phys. Rev. B* **1976**, 13, 5188–5192.

[4] Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett*., **1996**, 77, 3865–3868.