

Carbonyl-Bridged Energetic Materials: Biomimetic Synthesis, Organic Catalytic Synthesis, and Energetic Performances

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Electronic Supplementary Information

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S1. Materials and General Method

Bis(tetrazole)methane (H_2btm) was prepared according to our previous work.¹ All other materials were commercially available and were used without further purification. Elemental analyses (C, H, and N) were performed on a Flash EA 1112 fully automatic trace element analyzer. Densities were measured with an ULTRAPYC 1200e automatic density analyzer. Thermal stabilities were measured by means of differential scanning calorimetry (DSC) on a CDR-4 apparatus from Shanghai Precision & Scientific Instrument Co., Ltd. at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ from $50\text{ }^\circ\text{C}$ to $500\text{ }^\circ\text{C}$. The purities of the bulk samples were verified by X-ray powder diffraction (XRPD) measurements performed on a Bruker D8 advance diffractometer at 60 kV and 300 mA, employing Cu K_α radiation ($\lambda=1.5406\text{ \AA}$), at a scan speed of 5 min^{-1} and a step size of 0.02° in 2θ . Single-crystal X-ray diffraction data collections were carried out on a Rigaku AFC-10/Saturn 724+CCD diffractometer with graphite-monochromated Mo K_α radiation ($\lambda=0.71073\text{ \AA}$) using the multi-scan technique. The structures were determined by direct methods using SHELXS-97 and refined by full-matrix least-squares procedures on F^2 with SHELXL-97.² The positions of all non-hydrogen atoms were obtained from the difference Fourier map and subjected to anisotropic refinement by full-matrix least-squares on F^2 . Hydrogen atoms were obtained geometrically and treated as riding on the parent atoms or were constrained in the locations during refinements.

All structure characterization and performance testing, including elemental analyses, XPS, crystal structures, DSC, sensitivities, were carried out by using crystal products.

S2. Synthesis Method

G₂btm: H_2btm (5 mmol, 0.76 g) was dissolved in water (20 mL), and then a solution of G_2CO_3 (bisguanidinium carbonate, 5 mmol, 0.90 g) in water (10 mL) was added. After the addition, the mixture was stirred at room temperature for 10 min. It was then left to stand, whereupon crystals suitable for single-crystal X-ray diffraction measurement were obtained after 10 days. Yield: 1.14 g (92%). $^1\text{H NMR}$ (300 MHz, D_2O): δ 4.70, 4.35 ppm; $^{13}\text{C NMR}$ (75 MHz, D_2O): δ 160.30, 158.06, 21.12 ppm. IR (KBr): $\nu=3415, 3340, 3245, 1671, 1620, 1474, 1420, 1389, 1319, 1285, 1199, 1134, 1100, 1058, 1019, 949, 895, 753, 730, 667, 512\text{ cm}^{-1}$. Elemental analysis calcd (%) for $C_5H_{14}N_{14}$ (270.26): C 22.22, H 5.22, N 72.56; found: C 22.01, H 5.03, N 72.42.

G₂btk: G_2btm (10 mmol, 2.7 g) was dissolved in water (30 mL), and the solution was heated to $60\text{ }^\circ\text{C}$ for 30 min. It was then cooled to room temperature and left to stand. Pale-yellow crystals suitable for single-crystal X-ray diffraction measurement were obtained after 1 day. Yield: 0.59 g (21%). $^1\text{H NMR}$ (300 MHz, D_2O): δ 4.70 ppm; $^{13}\text{C NMR}$ (75 MHz, D_2O): δ 178.50, 160.84, 157.91 ppm. IR (KBr): $\nu=3405, 3401, 3331, 3189, 3107, 2216, 2072, 1709, 1672, 1591, 1490, 1389, 1368, 1174, 1105, 1052, 1010, 935, 748, 654, 557, 523\text{ cm}^{-1}$. Elemental analysis calcd (%) for $C_5H_{12}N_{14}O$ (284.24): C 21.13, H 4.26, N 68.99; found: C 21.01, H 4.11, N 68.81.

AG₂btm: H_2btm (5 mmol, 0.76 g) was dissolved in water (20 mL), and then a solution of $AGHCO_3$ (aminoguanidinium hydrogencarbonate, 10 mmol, 1.36 g) in water (10 mL) was added. After the addition, the mixture was stirred at room temperature for 10 min and then left to stand. Crystals suitable for single-crystal X-ray diffraction measurement were obtained after 7 days. Yield: 1.32 g (88%). $^1\text{H NMR}$ (300 MHz, D_2O): δ 4.71, 4.43, 4.35 ppm; $^{13}\text{C NMR}$ (75 MHz, D_2O): δ 160.21, 159.02, 21.12 ppm. IR (KBr): $\nu=3462, 3360, 3170, 1677, 1638, 1476, 1388, 1284, 1202, 1156, 1133, 1107, 1058, 1026, 1005, 1005, 910, 753, 671, 539, 520\text{ cm}^{-1}$. Elemental analysis calcd (%) for $C_5H_{16}N_{16}$ (300.29): C 19.99, H 5.37, N 74.63; found: C 19.86, H 5.23, N 74.49.

[(G₂Cu(btm))₂]_n: G_2btm (3 mmol, 0.811 g) was dissolved in water (20 mL) and the solution was heated to $80\text{ }^\circ\text{C}$ for 10 min. A solution of $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (1 mmol, 0.1705 g) in water (5 mL) was then added dropwise, which led, after several minutes, to the deposition of a navy-blue precipitate. The mixture was stirred at $80\text{ }^\circ\text{C}$ for a further 30 min. It was then cooled to room temperature, and the navy-blue precipitate was collected by filtration, washed with water and ethanol, and dried in air. Crystals suitable for single-crystal X-ray diffraction measurement were obtained by slow crystallization from water over a period of 8 days. Yield: 0.382 g (79%). IR (KBr): $\nu=3410, 3179, 2966, 2924, 1657, 1567, 1508, 1481, 1431, 1404, 1291, 1234, 1222, 1191, 1136, 1125, 1114, 1091, 1030, 944, 791, 773, 547, 536\text{ cm}^{-1}$. Elemental analysis calcd (%) for $C_8H_{16}N_{22}Cu$ (483.91): C 19.86, H 3.33, N 63.68; found: C 19.79, H 3.22, N 63.56. The XPS spectrum of the crystalline sample shows evident satellite peaks of 933eV, suggesting Cu (II) in compound [(G₂Cu(btm))₂]_n.

(G₃Co(btm)(btk))₂: G_2btm (6 mmol, 1.621 g) was dissolved in water (20 mL) and the solution was heated at $80\text{ }^\circ\text{C}$ for 10 min. A solution of $\text{CoCl}_2\cdot 2\text{H}_2\text{O}$ (2 mmol, 0.3409 g) in water (5 mL) was added dropwise, whereupon a voluminous pink precipitate appeared immediately. After 2 min, the pink precipitate had redissolved to give a clear orange solution. The mixture was then cooled to room temperature. Crystals of $(G_3Co(btm)(btk))_2\cdot n\text{H}_2\text{O}$ suitable for single-crystal X-ray diffraction measurement were obtained by slow crystallization from water over a period of 7 days. After drying, $(G_3Co(btm)(btk))_2$ was obtained. Yield: 1.09 g (76%). IR (KBr): $\nu=3459, 3369, 3168, 1693, 1666, 1506, 1413, 1389, 1352, 1082, 931, 735, 646, 521\text{ cm}^{-1}$. Elemental analysis calcd (%) for $C_{12}H_{20}N_{33}CoO_2$ (717.44): C 20.09, H 2.81, N 64.43; found: C 19.94, H 2.68, N 64.31. The XPS spectrum of the crystalline sample shows evident satellite peaks of 780eV, suggesting Co (III) in compound $(G_3Co(btm)(btk))_2$.

S3 Single-Crystal Structure

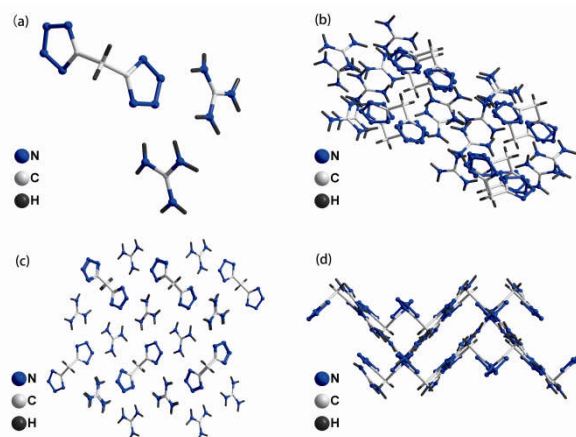


Figure S1. (a) Crystal structure of G₂btm. (b) Crystal packing of G₂btm viewed from the crystallographic a axis. (c) Crystal packing of G₂btm viewed from the crystallographic b axis. (d) Crystal packing of G₂btm viewed from the crystallographic c axis.

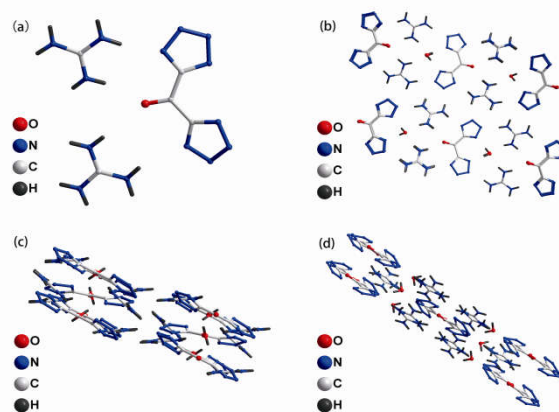


Figure S2. (a) Crystal structure of G₂btk. (b) Crystal packing of G₂btk viewed from the crystallographic a axis. (c) Crystal packing of G₂btk viewed from the crystallographic b axis. (d) Crystal packing of G₂btk viewed from the crystallographic c axis.

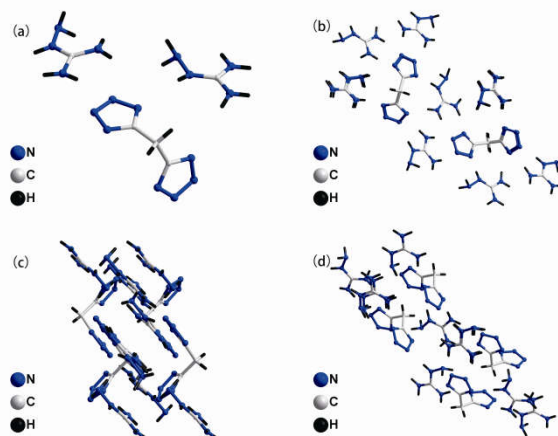


Figure S3. (a) Crystal structure of AG₂btm. (b) Crystal packing of AG₂btm viewed from the crystallographic a axis. (c) Crystal packing of AG₂btm viewed from the crystallographic b axis. (d) Crystal packing of AG₂btm viewed from the crystallographic c axis.

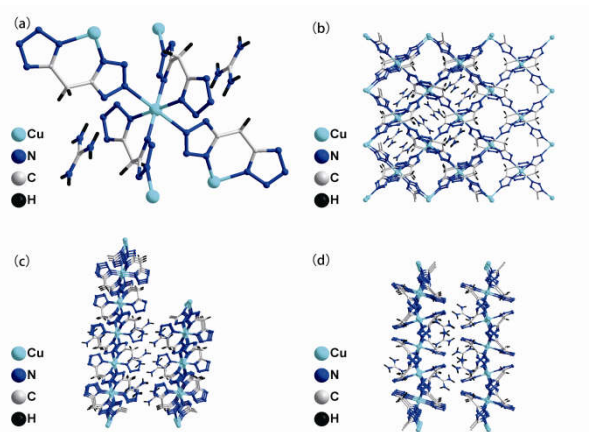


Figure S4. (a) Crystal structure of $\{[(G)_2(Cu(btm)_2)]\}_n$. (b) Crystal packing of $\{[(G)_2(Cu(btm)_2)]\}_n$ viewed from the crystallographic a axis. (c) Crystal packing of $\{[(G)_2(Cu(btm)_2)]\}_n$ viewed from the crystallographic b axis. (d) Crystal packing of $\{[(G)_2(Cu(btm)_2)]\}_n$ viewed from the crystallographic c axis.

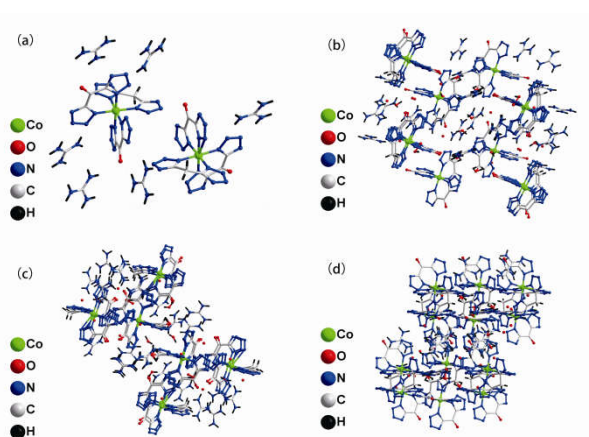


Figure S5. (a) Crystal structure of $(G)_3[Co(btm)(btk)_2]$. (b) Crystal packing of $(G)_3[Co(btm)(btk)_2]$ viewed from the crystallographic a axis. (c) Crystal packing of $(G)_3[Co(btm)(btk)_2]$ viewed from the crystallographic b axis. (d) Crystal packing of $(G)_3[Co(btm)(btk)_2]$ viewed from the crystallographic c axis.

Table S1. Crystal data and structure refinement details for the five compounds.

Compd.	G ₂ btm	G ₂ btk	AG ₂ btm	{[G] ₂ [Cu(btm) ₂]} _n	{[G] ₃ [Co(btm)(btk) ₂]}
CCDC	1496932	1496933	1496934	1464521	1496935
Formula sum	C ₅ H ₁₄ N ₁₄	C ₅ H ₁₄ N ₁₄ O ₂	C ₃ H ₁₆ N ₁₆	C ₈ H ₁₆ CuN ₂₂	C ₁₂ H _{28.73} CoN ₃₃ O _{6.63}
Formula weight (g mol ⁻¹)	270.30	302.30	300.34	483.97	800.47
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space-group	Pbcn (No. 60)	Pbcn (No. 60)	P21 (No. 4)	P21/c (No. 14)	P-1 (No. 2)
Cell parameters	a=14.452(4)Å, b=4.6313(13)Å, c=17.861(5)Å	a=3.6071(14)Å, b=19.316(8)Å, c=18.825(8)Å	a=4.4701(14)Å, b=17.557(6)Å, c=8.400(3)Å; β=93.512(3)°	a=10.6585(4)Å, b=7.138(3)Å, c=9.7203(8)Å; β=95.092(5)°	a=11.9362(16)Å, b=12.6704(17)Å, c=24.704(4)Å; α=75.697(7)°, β=76.691(8)°, γ=65.697(5)°
Cell volume (Å ⁻³)	1195.5(6)	1311.6(9)	658.0(4)	899.22(9)	3264.4(8)
Z	4	4	2	2	2
Calc. density (g cm ⁻³)	1.502	1.531	1.516	1.787	1.618
Mu(MoKa) [/mm]	0.11	0.124	0.116	1.271	0.616
F(000)	568	632	316	494	1626
Crystal Size [mm]	0.24x0.24x0.33	0.06x0.22x0.41	0.07x0.32x0.53	0.15 × 0.15 × 0.02	0.21 × 0.23 × 0.44
Radiation[Angstrom] MoKa	0.71073	0.71073	0.71073	0.71073	0.71073
Theta Min-Max [Deg]	2.8, 31.5	3.0, 30.0	2.4, 31.5	3.0, 26.0	2.3, 29.1
Dataset	-20:18; -6:6; -26:25	-4:5; -25:27; -25:26	-6:6; -25:25; -12:12	-13:12; -7:10; -11:8	-16:16; -17:17; -33:32
Tot., Uniq. Data, R(int)	11071, 3594, 0.03	10577, 1893, 0.034	6559, 3615, 0.02	4198, 1756, 0.030	35741, 17232, 0.033
Observed data [I > 2.0 sigma(I)]	3266	1640	2975	1544	14361
R, wR2, S	0.0396, 0.0920, 1.00	0.0483, 0.1255, 1.00	0.0342, 0.0603, 1.00	0.0312, 0.0762, 1.04	0.0757, 0.2039, 1.00

S4. X-ray Powder Diffraction

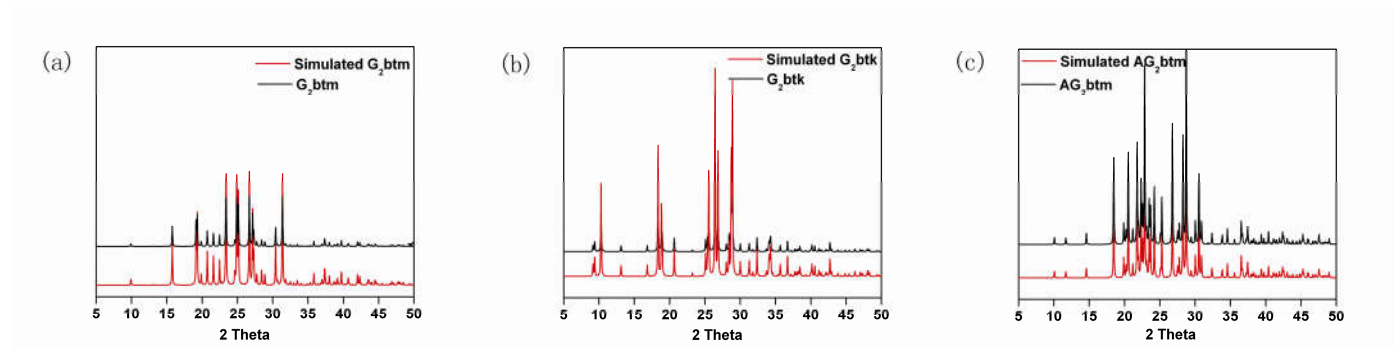


Figure S6. (a) X-ray powder diffraction (XRPD) pattern of G₂btm. (b) XRPD pattern of G₂btk. (c) XRPD pattern of AG₂btm.

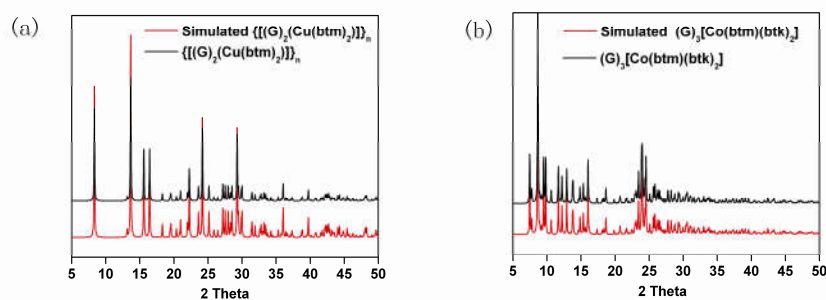


Figure S7. (a) XRPD curve of {[G]₂[Cu(btm)₂]}_n. (b) XRPD curve of (G)₃[Co(btm)(btk)₂].

S5. Sensitivity

Sensitivity: The impact sensitivity (IS) and friction sensitivity (FS) were tested according to the method described in ref. 3.

S6. Thermal Stability Measurements (DSC)

To investigate the thermal stabilities of compounds **1** and **2**, their DSC traces were recorded at a linear heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$ in flowing N_2 (flow rate 20 mL min^{-1}). The curves are shown in Figure S8. For compounds **1** and **2**, their onset temperatures of first intense exothermic processes appear at 224.6 and $223.3\text{ }^{\circ}\text{C}$, respectively.

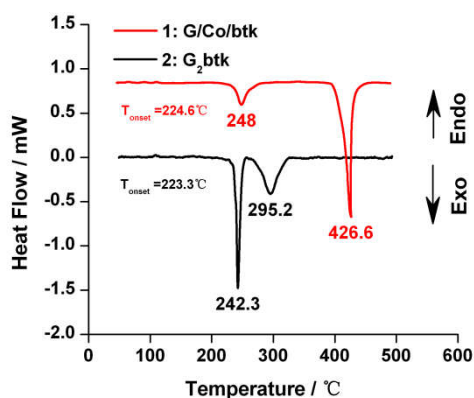


Figure S8. DSC curves of compounds **1** and **2**.

S7. Theoretical Calculations on Compounds **1** and **2**

Heats of formation ($\Delta_f H^\circ$) and enthalpies of combustion ($\Delta_c H^\circ$) are two important parameters for energetic materials. They are calculated based on measurements of constant volume combustion energy ($\Delta_c U^\circ$). The experimental results for $\Delta_c U^\circ$ of compounds **1** and **2** are shown in the following table (Table S2). The standard molar enthalpy of combustion ($\Delta_c H^\circ$) can be obtained according to the formula (Eq. (1)):

$$\Delta_c H = \Delta_c U + \Delta n RT \quad (\text{Eq. 1})$$

where $\Delta n = \Delta n_i$ (products, g) - Δn_j (reactants, g); Δn_i (mol) and Δn_j (mol) are the total molar amounts of gases in the products and reactants, respectively. Heats of formation ($\Delta_f H^\circ$, kJ mol^{-1}) at 298 K were calculated through adoption of the Hess thermochemical cycle on the basis of the combustion reactions (Eqs. (2) & (3)). The heats of formation ($\Delta_f H$) of the combustion products, CO_2 (g) and H_2O (l), are $-393.51\text{ kJ mol}^{-1}$ and $-285.83\text{ kJ mol}^{-1}$, respectively.

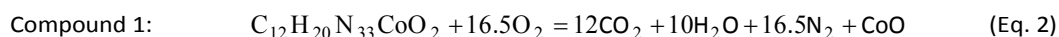


Table S2. Thermodynamic parameters of **1** and **2**.

Compd.	$\Delta_c U^\circ$ (MJ Kg^{-1})	$\Delta_c U^\circ$ (kJ mol^{-1})	$\Delta_c H^\circ$ (kJ mol^{-1})	$\Delta_f H^\circ$ (kJ mol^{-1})
1	10.9383	-7847.6	-7817.9	453.38
2	12.2959	-3495.0	-3483.9	198.34

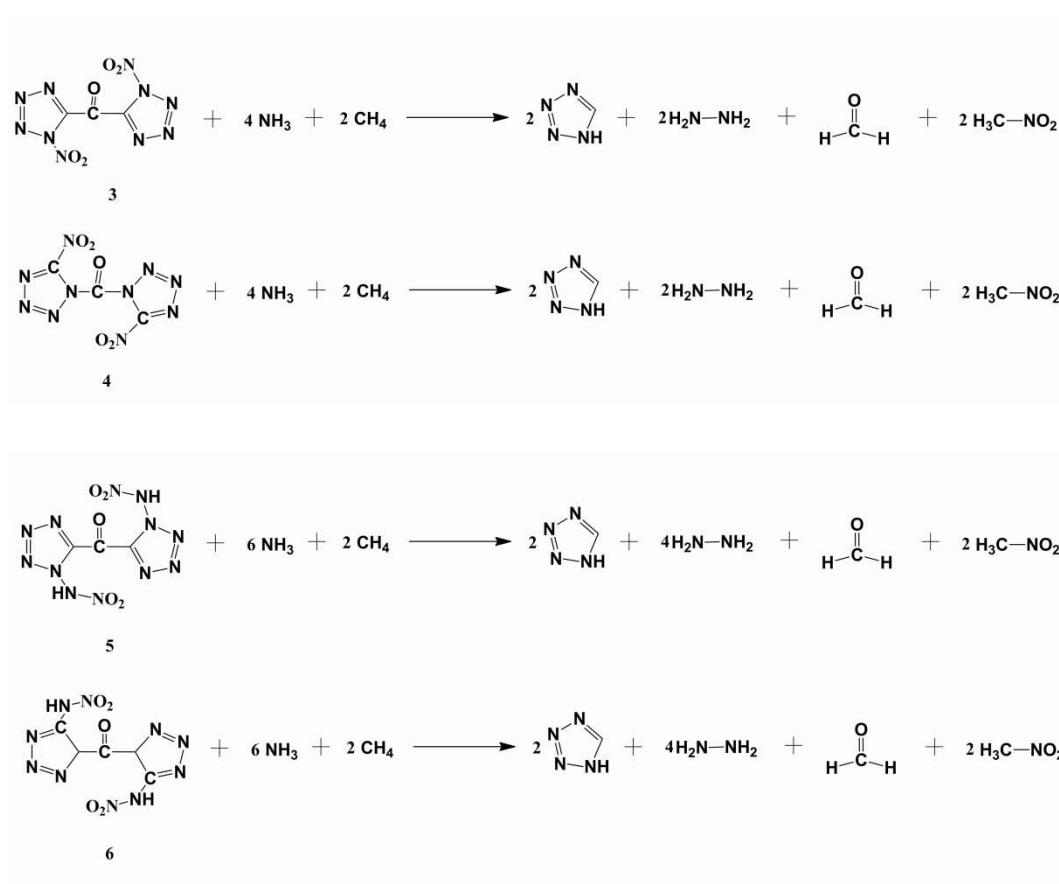
The heats of detonation of compounds **1** and **2** were calculated based on different methods. The heat of detonation of compound **1**, which contains a metal, was obtained by a simple method (Eq. 4) reported by Pang et al. in 2014.⁴ The heat of detonation of compound **2** was obtained from the classical K-J equation (Eq. 5).⁵⁻⁶

$$\text{Compound 1: } Q = \frac{-[\Delta_f H(\text{products}) - \Delta_f H(\text{explosives})]}{M} \quad (\text{Eq. 4})$$

$$\text{Compound 2: } Q = \frac{57.8 \times C + 0.239 \times \Delta_f H(\text{explosives})}{M} \quad (\text{Eq. 5})$$

Here, $\Delta_f H(\text{products})$ and $\Delta_f H(\text{explosives})$ are the heats of formation of detonation products and explosives, respectively; M is the molecular weight of the explosive, and C is the number of O atoms therein.

S8. Gaussian Calculations on Four Designed Compounds



Scheme S1. Isodesmic reaction for compounds **3**, **4**, **5**, and **6**.

Geometric optimizations of the structures and frequency analyses were carried out using the B3LYP functional with the 6-31+G** basis set, and single-point energies were calculated at the MP2/6-311++G** level.⁷⁻⁹ (1 a.u.=627.509*4.18 kJ mol⁻¹).

Table S3. Calculated (B3LYP/6-31+G**/MP2/6-311++G**) total energies (E₀), zero-point energies (ZPE), values of the correction (H_r), and heats of formation (HOF) for compounds **3**, **4**, **5** and **6**.

Compound	E ₀	ZPE	H _r	HOF (kJ mol ⁻¹)
N ₂ H ₄	-111.207661	0.052611	0.0039	95.44[a]
NH ₃	-56.21468	0.034372	0.00382	-46.14[a]
tetrazole	-256.814368203	0.046861	0.004432	237[b]
CH ₄	-40.208579	0.044793	0.00386	-17.6[c]
CH ₃ NO ₂	-243.602855	0.049836	0.005294	-74.8[c]
HCHO	-113.900922825	0.026665	0.030477	-113.8195787[b]
3	-1032.1179708	0.084936	0.100289	120.5745278[b]
4	-1032.17715933	0.086067	0.101179	-29.37519569[b]
5	-1142.20363658	0.120183	0.137386	235.8691431[b]
6	-1142.27878515	0.120199	0.137438	38.93373751[b]

a From ref. 10. b Calculated from G2. c From ref. 11.

The density, as an important parameter for energetic materials, was obtained using an improved equation (Eq. 6) proposed by Politzer et al. considering intermolecular interactions within the crystal:¹²

$$d = \alpha \left(\frac{M}{v(0.001)} \right) + \beta (v \sigma_{\text{Tot}}^2) + \gamma \quad (\text{Eq. 6})$$

where $v(0.001)$ is the volume in cm³/molecule and is encompassed by the 0.001 a.u. contour of the electronic density; M is the molecular mass in g/molecule; $v \sigma_{\text{Tot}}^2$ is derived from the molecular electrostatic potential calculation; and α , β , and γ are coefficients assigned through fitting Eq. (6) to the experimental densities of a series of 36 energetic compounds.¹²

Table S4. Calculated densities of four designed energetic compounds.

Compound	V (cm ³) ^a	M (g mol ⁻¹) ^b	d (g cm ⁻³) ^c
3	129.303	256.09	1.981
4	133.097	256.09	1.924
5	153.044	286.13	1.869
6	150.007	286.13	1.907

^a Calculated average volume based on 100 times volume calculation. ^b Molecular weight. ^c Density of compound.

Detonation performances of four designed energetic compounds, including detonation velocity (D) and detonation pressure (P), were computed by the empirical K-J formula (Eqs. (7)–(10)):⁵⁻⁶

$$D = 1.01\Phi^{1/2}(1 + 1.30d) \quad (\text{Eq. 7})$$

$$P = 1.558\Phi d^2 \quad (\text{Eq. 8})$$

$$\Phi = 31.68N(MQ)^{1/2} \quad (\text{Eq. 9})$$

$$Q = \frac{28.96 \times b + 94.05 \times \left(\frac{c}{2} - \frac{b}{4}\right) + 0.239 \times \Delta_f H}{M'} \quad (\text{Eq. 10})$$

where D is the detonation velocity (km s^{-1}), P is the detonation pressure (Gpa), ρ is the density of the explosive (g cm^{-3}), N is the number of moles of detonation gases per gram of explosive (mol g^{-1}), M is the average molecular weight of the gaseous products (g mol^{-1}), M' is the molecular weight of the explosives (g mol^{-1}), Q is the heat of detonation (kcal g^{-1}), $\Delta_f H$ is heat of formation (kJ mol^{-1}), and b and c are the amounts of hydrogen (H) and oxygen (O) atoms. The detonation reactions are described as follows (Eqs. (11)-(14)).

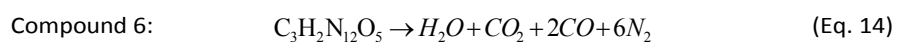
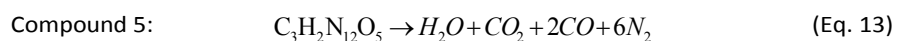
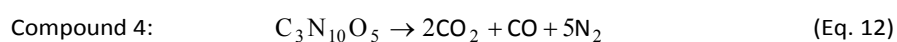
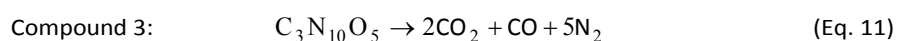


Table S5. The detonation parameters of four energetic materials.

Compound	d (g cm^{-3})	N (mol g^{-1})	M (g mol^{-1})	Q (kcal g^{-1})	D (km s^{-1})	P (GPa)
3	1.98	0.03124	32.0000	1.0310	8.55	34.4
4	1.92	0.03124	32.0000	0.8901	7.94	29.1
5	1.87	0.03495	28.6000	1.0557	8.56	33.1
6	1.91	0.03495	28.6000	0.8911	8.30	31.8

S9. References

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