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Auxiliary ligand-directed synthesis of 3D energetic coordination polymer from discrete complex: Enhanced energy density, thermal stability and energey performances

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Table S1. Selected bond lengths (Å) and bond angles (°) for **1** and **2**.

Complex 1			
Cu(1)-O(1)	1.9164(18)	Cu(1)-O(1) #1	1.9165(18)
Cu(1)-O(3)	1.9047(18)	Cu(1)-O(3)#1	1.9047(18)
O(1)-C(7)	1.276(3)	O(2)-C(7)	1.239(3)
O(3)-C(1)	1.290(3)	O(4)-N(1)	1.216(4)
O(5)-N(1)	1.216(3)	O(6)-N(2)	1.221(3)
O(7)-N(2)	1.227(3)	N(1)-C(2)	1.459(4)
N(2)-C(4)	1.448(4)	C(1)-C(2)	1.422(4)
C(1)-C(6)	1.421(4)	C(2)-C(3)	1.361(4)
C(3)-C(4)	1.381(4)	C(4)-C(5)	1.374(4)
C(5)-C(6)	1.389(4)	C(6)-C(7)	1.494(4)
N(3)-C(8)	1.476(4)	N(3)-C(9)	1.466(4)
O(1)-Cu(1)-O(1)#1	180.00(12)	C(6)-C(1)-C(2)	115.5(2)
O(3)#1-Cu(1)-O(1)	87.15(8)	C(1)-C(2)-N(1)	117.5(2)
O(3)-Cu(1)-O(1)#1	87.15(8)	C(3)-C(2)-N(1)	117.7(2)
O(3)#1-Cu(1)-O(1)#1	92.85(8)	C(3)-C(2)-C(1)	124.8(3)
O(3)-Cu(1)-O(1)	92.85(8)	C(2)-C(3)-C(4)	117.3(3)
O(3)-Cu(1)-O(3)#1	180.0	C(3)-C(4)-N(2)	119.0(3)
C(7)-O(1)-Cu(1)	129.77(18)	C(5)-C(4)-N(2)	119.7(3)
C(1)-O(3)-Cu(1)	125.87(18)	C(5)-C(4)-C(3)	121.3(3)
O(4)-N(1)-O(5)	124.3(3)	C(4)-C(5)-C(6)	121.4(3)
O(4)-N(1)-C(2)	117.8(3)	C(1)-C(6)-C(7)	123.1(2)
O(5)-N(1)-C(2)	117.9(3)	C(5)-C(6)-C(1)	119.6(2)
O(6)-N(2)-O(7)	122.8(3)	C(5)-C(6)-C(7)	117.3(2)
O(6)-N(2)-C(4)	119.1(3)	O(1)-C(7)-C(6)	120.0(2)
O(7)-N(2)-C(4)	118.1(3)	O(2)-C(7)-O(1)	121.2(3)
O(3)-C(1)-C(2)	118.4(2)	O(2)-C(7)-C(6)	118.9(2)
O(3)-C(1)-C(6)	126.0(2)	C(9)-N(3)-C(8)	113.7(2)
Complex 2			
Cu(1)-O(1)	1.909(2)	N(3)-C(8)	1.318(4)
Cu(1)-O(3)	1.900(2)	N(4)-N(5)	1.294(3)
Cu(1)-O(8)	1.881(2)	N(5)-N(6)	1.338(4)
Cu(1)-N(3)	1.976(2)	N(6)-Cu(2)#3	1.976(2)
Cu(2)-O(2)#1	1.971(2)	C(1)-C(6)	1.389(4)
Cu(2)-O(8)	1.879(2)	C(1)-C(7)	1.496(4)
Cu(2)-N(4)	2.036(2)	C(2)-C(1)	1.438(4)

Cu(2)-N(6)#2	1.976(2)	C(2)-C(3)	1.436(4)
O(1)-C(7)	1.266(4)	C(3)-N(1)	1.462(4)
O(2)-Cu(2)#1	1.971(2)	C(3)-C(4)	1.371(4)
O(3)-C(2)	1.280(3)	C(5)-N(2)	1.467(4)
O(4)-N(1)	1.226(4)	C(5)-C(4)	1.389(5)
O(5)-N(1)	1.224(4)	C(6)-C(5)	1.379(5)
N(2)-O(6)	1.216(5)	C(7)-O(2)	1.248(3)
N(2)-O(7)	1.208(4)	C(8)-N(6)	1.337(4)
N(3)-N(4)	1.351(3)		
O(1)-Cu(1)-N(3)	173.59(11)	N(3)-N(4)-Cu(2)	120.45(17)
O(3)-Cu(1)-O(1)	92.75(9)	N(5)-N(4)-Cu(2)	127.9(2)
O(3)-Cu(1)-N(3)	89.99(9)	N(5)-N(4)-N(3)	110.0(2)
O(8)-Cu(1)-O(1)	91.71(9)	N(4)-N(5)-N(6)	108.0(2)
O(8)-Cu(1)-O(3)	174.72(9)	N(5)-N(6)-Cu(2)#3	117.21(18)
O(8)-Cu(1)-N(3)	85.29(9)	C(8)-N(6)-Cu(2)#3	134.1(2)
O(2)#1-Cu(2)-N(4)	176.55(11)	C(8)-N(6)-N(5)	106.8(2)
O(2)#1-Cu(2)-N(6)#2	88.12(10)	C(2)-C(1)-C(7)	122.0(3)
O(8)-Cu(2)-O(2)#1	95.98(9)	C(6)-C(1)-C(2)	121.1(3)
O(8)-Cu(2)-N(4)	83.70(9)	C(6)-C(1)-C(7)	116.8(3)
O(8)-Cu(2)-N(6)#2	174.60(11)	O(3)-C(2)-C(1)	125.6(3)
N(6)#2- Cu(2)-N4	92.42(10)	O(3)-C(2)-C(3)	119.4(3)
C(7)-O(1)-Cu(1)	131.04(19)	C(3)-C(2)-C(1)	115.0(3)
C(7)-O(2)-Cu(2)#1	131.2(2)	C(2)-C(3)-N(1)	119.4(3)
C(2)-O(3)-Cu(1)	127.55(19)	C(4)-C(3)-N(1)	116.7(3)
Cu(2)-O(8)-Cu(1)	129.35(11)	C(4)-C(3)-C(2)	123.9(3)
O(4)-N(1)-C(3)	120.0(3)	C(3)-C(4)-C(5)	117.9(3)
O(5)-N(1)-O(4)	122.6(3)	C(4)-C(5)-N(2)	118.4(3)
O(5)-N(1)-C(3)	117.3(3)	C(6)-C(5)-N(2)	119.5(3)
O(6)-N(2)-C(5)	117.7(3)	C(6)-C(5)-C(4)	122.0(3)
O(7)-N(2)-C(5)	118.9(3)	C(5)-C(6)-C(1)	120.0(3)
O(7)-N(2)-O(6)	123.4(3)	O(1)-C(7)-C(1)	120.9(3)
N(4)-N(3)-Cu(1)	120.86(18)	O(2)-C(7)-O(1)	121.9(3)
C(8)-N(3)-Cu(1)	132.8(2)	O(2)-C(7)-C(1)	117.2(3)
C(8)-N(3)-N(4)	105.6(2)	N(3)-C(8)-N(6)	109.6(3)

Table S2. Hydrogen bonding distances and bond angles (Å, °) for **1**.

Donor–H···Acceptor	D – H	H···A	D···A	D – H···A
N3–H3A···O2	0.8896(27)	1.8751(27)	2.7645(38)	178.837(169)
N3–H3B···O2	0.8907(24)	2.2422(20)	2.8914(30)	129.466(147)

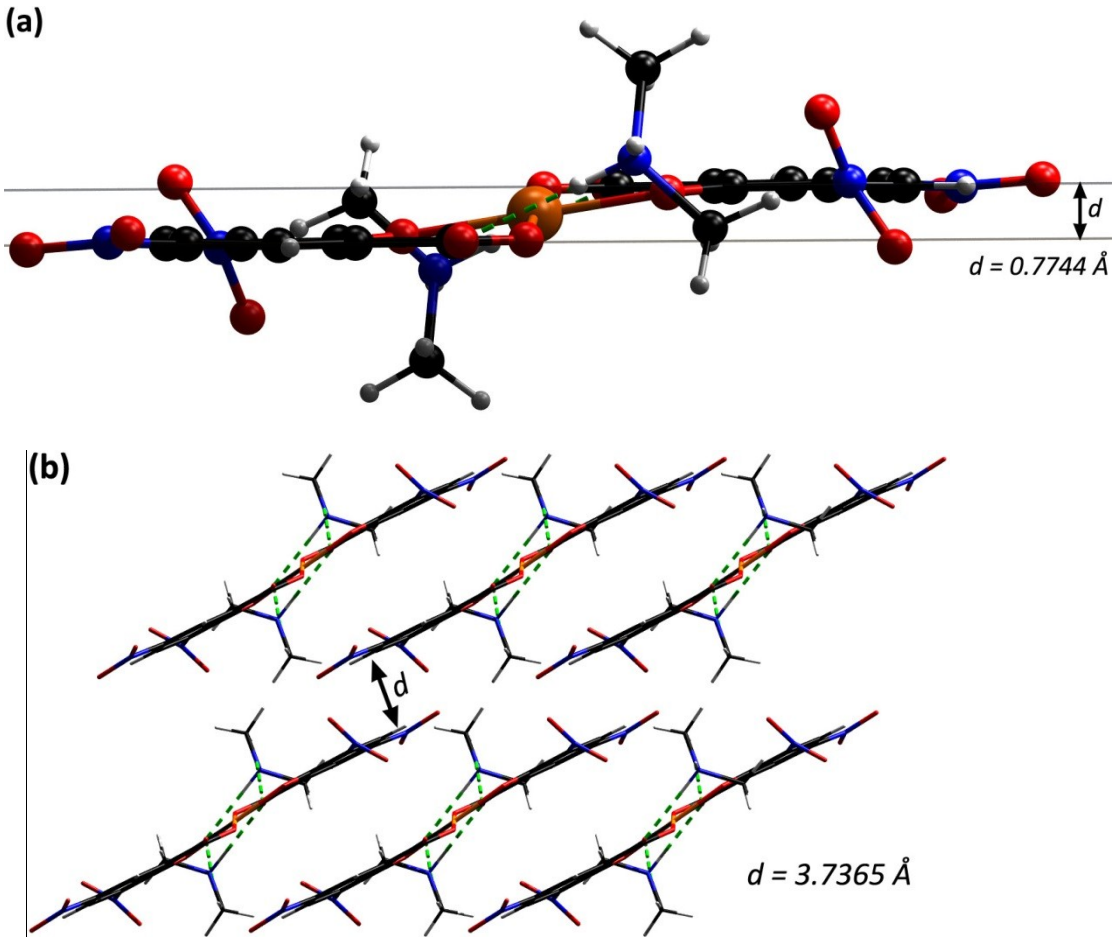


Figure S1. Side view of the discrete complex (a) and side view of one dimensional supramolecular structure of **1** (b)

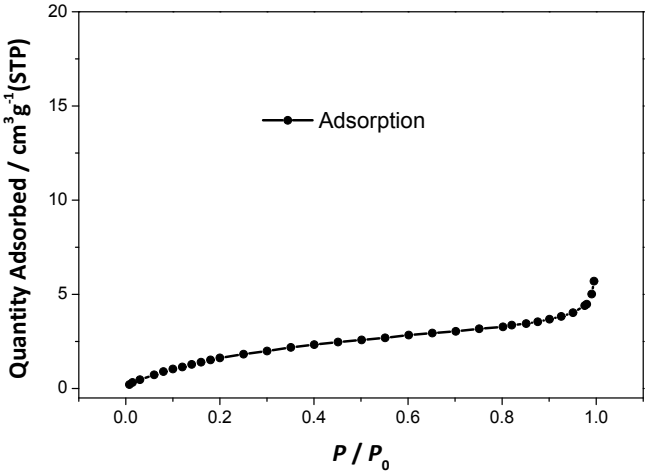


Figure S2. Nitrogen sorption curve of complex **2**.

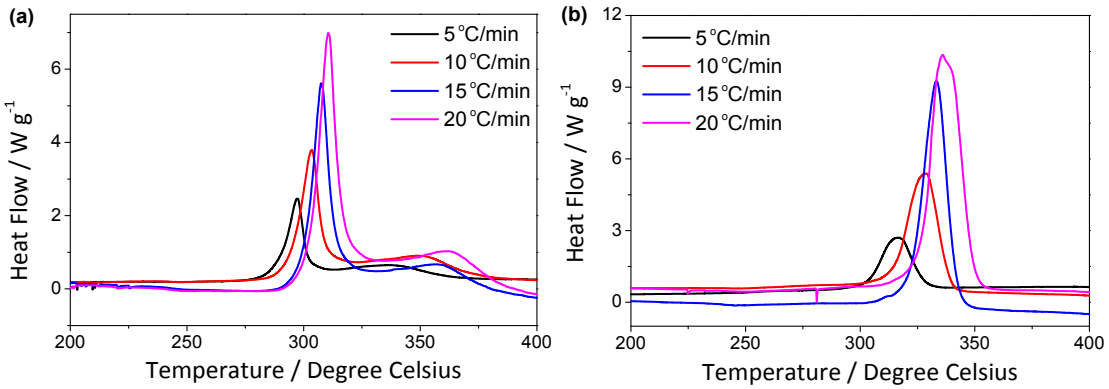


Figure S3. DSC curves of **1** (a) and **2** (b) at four different heating rates of 5, 10, 15, 20 °C/min.

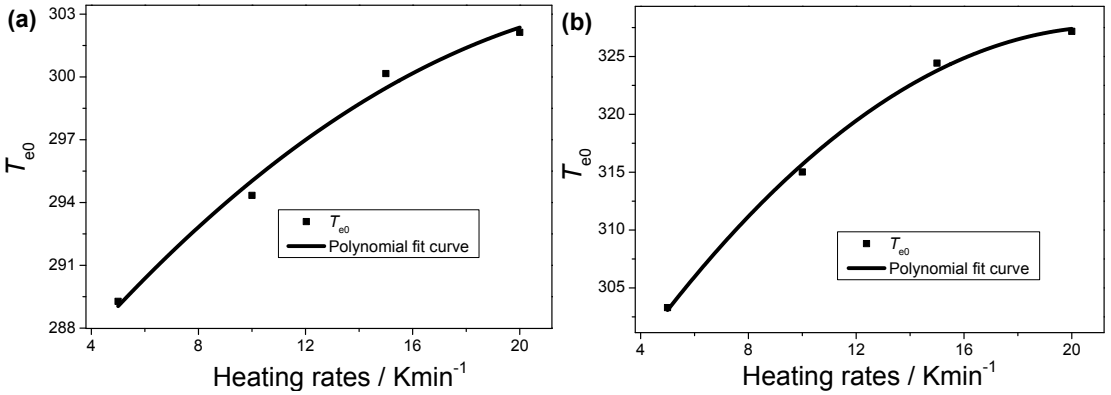
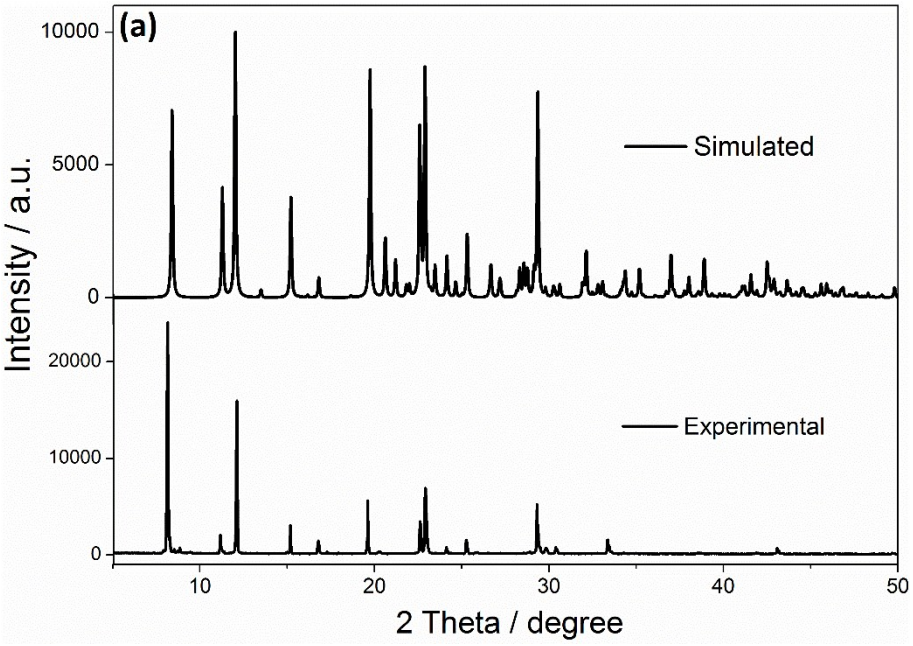


Figure S4. Polynomial fit curves of **1** (a) and **2** (b) for calculating self-accelerating decomposition temperature.

Table S3. Detonation Products of **1** and **2** predicted by EXPLO5

1				**2**			
Detonation products	mol/mol	mol/kg	Mol %	Detonation products	mol/mol	mol/kg	Mol %
C(d)	1.402267E01	2.306648E01	46.0720	C(d)	4.197973E00	9.535213E00	28.6120
H_2O	8.084113E00	1.329790E01	26.5606	N_2	2.985538E00	6.781305E00	20.3485
N_2	2.917767E00	4.799559E00	9.5864	Cu(l)	2.000000E00	4.542769E00	13.6314
CO_2	1.721872E00	2.832380E00	5.6573	CO_2	1.779698E00	4.042380E00	12.1299
CO	1.235419E00	2.032192E00	4.0590	H_2O	1.644891E00	3.736181E00	11.2111
Cu(l)	1.000000E00	1.644942E00	3.2855	CO	1.216321E00	2.762734E00	8.2901
CH_2O_2	6.178591E-01	1.016343E00	2.0300	CH_2O_2	7.895664E-01	1.793409E00	5.3814
H_2	3.209896E-01	5.280094E-01	1.0546	H_2	2.477643E-02	5.627682E-02	0.1689
CH_4	3.044221E-01	5.007569E-01	1.0002	NH_3	1.741347E-02	3.955268E-02	0.1187
NH_3	1.580286E-01	2.599480E-01	0.5192	HCN	1.130091E-02	2.566871E-02	0.0770
C_2H_6	3.696948E-02	6.081267E-02	0.1215	CH_4	3.426248E-03	7.782327E-03	0.0234
C_2H_4	7.512026E-03	1.235685E-02	0.0247	C_2H_4	5.437066E-04	1.234967E-03	0.0037
HCN	6.411212E-03	1.054607E-02	0.0211	C_2H_6	2.393438E-04	5.436420E-04	0.0016
C(gr)	1.381486E-03	2.272465E-03	0.0045	CH_3OH	1.127736E-04	2.561522E-04	0.0008

CH_3OH	9.793492E-04	1.610973E-03	0.0032	NO	1.087433E-04	2.469978E-04	0.0007
CH_2O	2.263054E-05	3.722593E-05	0.0001	H	5.084138E-05	1.154803E-04	0.0003
H	1.552765E-05	2.554208E-05	0.0001	NH_2	3.318150E-05	7.536796E-05	0.0002
NH_2	8.455732E-06	1.390919E-05	0.0000	N_2H_4	2.066034E-05	4.692758E-05	0.0001
N_2H_4	6.864814E-06	1.129222E-05	0.0000	CNO	2.018195E-05	4.584098E-05	0.0001
CHNO	2.697322E-06	4.436939E-06	0.0000	CH_2O	9.262425E-06	2.103853E-05	0.0001
NO	1.071993E-06	1.763367E-06	0.0000	CHNO	4.891444E-06	1.111035E-05	0.0000
CNO	8.256931E-08	1.358218E-07	0.0000	N	8.217843E-07	1.866589E-06	0.0000
Cu	9.323864E-09	1.533722E-08	0.0000	NO_2	4.552569E-07	1.034064E-06	0.0000
N	1.080368E-09	1.777144E-09	0.0000	Cu	2.100433E-07	4.770893E-07	0.0000
N_2O	7.620254E-10	1.253488E-09	0.0000	N_2O	1.859664E-07	4.224013E-07	0.0000
Cu(s)	1.670430E-10	2.747761E-10	0.0000	Cu(s)	4.439412E-10	1.008361E-09	0.0000
NO_2	1.273661E-10	2.095099E-10	0.0000	C(gr)	3.834479E-10	8.709578E-10	0.0000
$Cu(OH)_2(s)$	6.189807E-12	1.018188E-11	0.0000	$Cu_2O(l)$	7.820999E-11	1.776450E-10	0.0000
$Cu_2O(l)$	4.426277E-12	7.280970E-12	0.0000	CuO(s)	1.679147E-11	3.813989E-11	0.0000
CuO(s)	1.694401E-12	2.787192E-12	0.0000	$Cu(OH)_2(s)$	9.640567E-12	2.189744E-11	0.0000
$Cu_2O(s)$	9.248207E-13	1.521277E-12	0.0000	CuO	7.385997E-12	1.677644E-11	0.0000
CuO	1.188547E-14	1.955092E-14	0.0000	$Cu_2O(s)$	7.051131E-12	1.601583E-11	0.0000



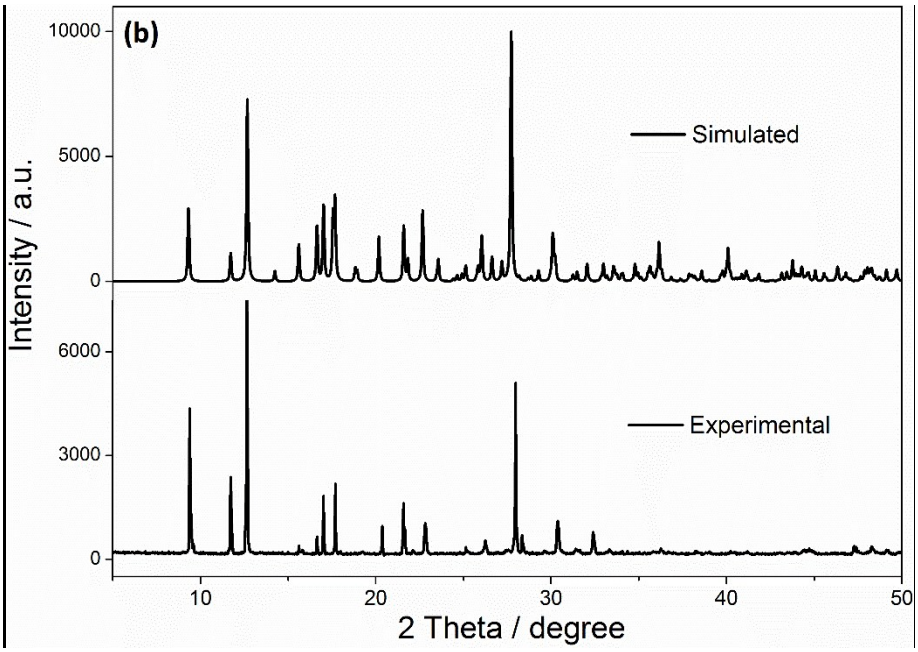


Figure S5. PXRD pattern of **1** (a) and **2** (b).