Supporting Information

Comparative Study of Two Copper Perchlorate Hydrazide Complexes: Impact of Coordination Chemistry on Laser Sensitivity and Energetic Properties

Contents

Experimental

Caution!

Some of the studied compounds have the potential to be energetic materials that are heat, friction, and impact sensitive. To safeguard personal safety throughout the whole experiment, appropriate protective equipment (goggles, safety shields, rubber gloves, etc.) must be used.

Materials and Equipment

The analytical grade reagents used in the experiment were bought from Aladdin and Azov and utilized without additional purification.

Differential scanning calorimetry (DSC3, METTLER TOLEDO) was used to study the thermal behavior of synthesized compound under a nitrogen environment and a heating rate of 10 $^{\circ}C \cdot min^{-1}$, and the gas atmosphere was N_2. Single crystal X-ray diffraction data was collected by using Rigaku supernova single X-ray diffractometer area detector. The laser performance test is measured by Diode Laser (Changchun laser technology co., LTD. LR-ISP-980/1~1000mW. Spectral Line width (nm): < 3, Output Power (mW): 1~1000, Beam Diameter at Aperture (mm): 5.0 x 5.0, Modulating Repetition: 100KHz TTL / 10KHz Analogue. Operating parameters: theoretical maximal output power Pmax = 40 W; theoretical pulse length τmax = 49571 μs. wavelength λ = 808 nm. Frequency F = 1Hz.). The mechanical sensitivities (including impact sensitivity and friction sensitivity) of the material were determined by the standard step method of the drop weight device with a BAM DFH-10 device with a weight drop of 2 kg.

Hot Needle Tests

Approximately 2 mg of the compound was dispersed on the operating table in a powdered state. The tiny iron needle is heated, and then slowly approached the compound, while recording the detonation process of the compound with a high-speed camera.

Detonation Initiation

The test device used to breakdown of the lead plate, the material inside can be divided into two parts: the first part is filled with compound ECC-1 or ECC-2 (10 mg, charge pressure is 120 MPa); the second component is RDX (20 mg, charge pressure is 120 MPa). The lead plate has a thickness of 2 mm.

Laser Performance Tests

Weigh 5 mg samples (pressure of fixation is 3 MPa), a total of 5 parts, and place them in sample tubes. Use a semiconductor laser to trigger the sample. Determine the minimum trigger energy by adjusting the action time and power. Take the average value as the final test value.

Supplementary Figures

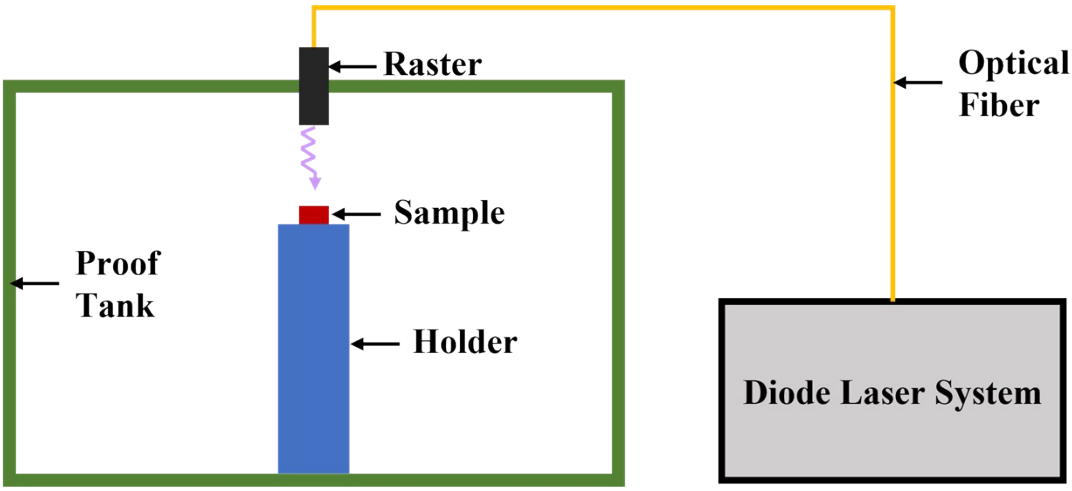

Figure S1. Schematic diagram of laser initiation tests.

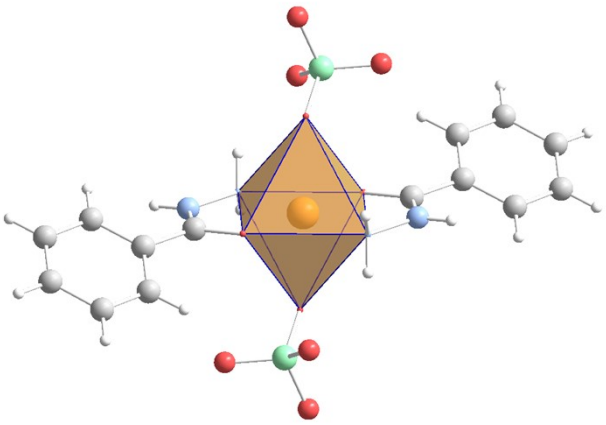

Figure S2. Single-crystal structure of ECCs-1 and its coordination octahedra.

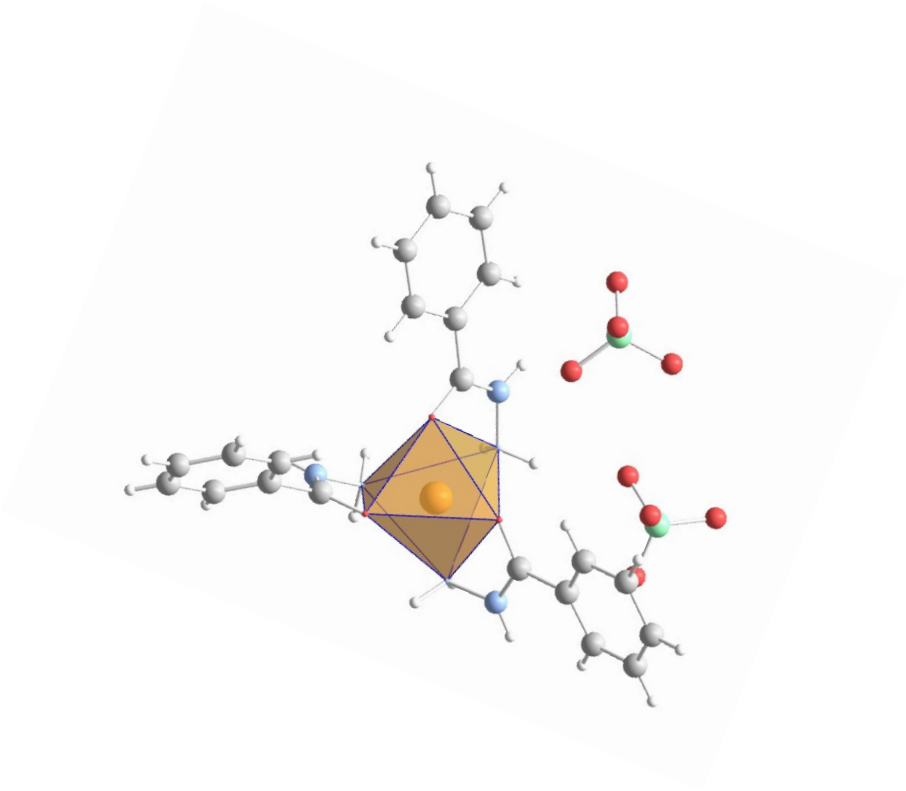

Figure S3. Single-crystal structure of ECCs-2 and its coordination octahedra.

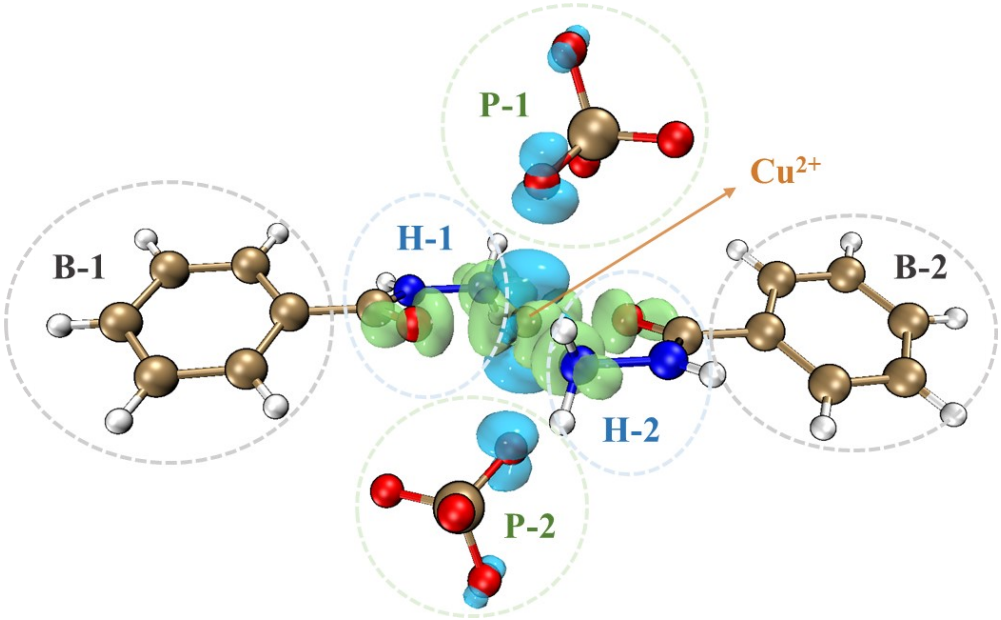

Figure S4. Fragments division of ECCs-1.

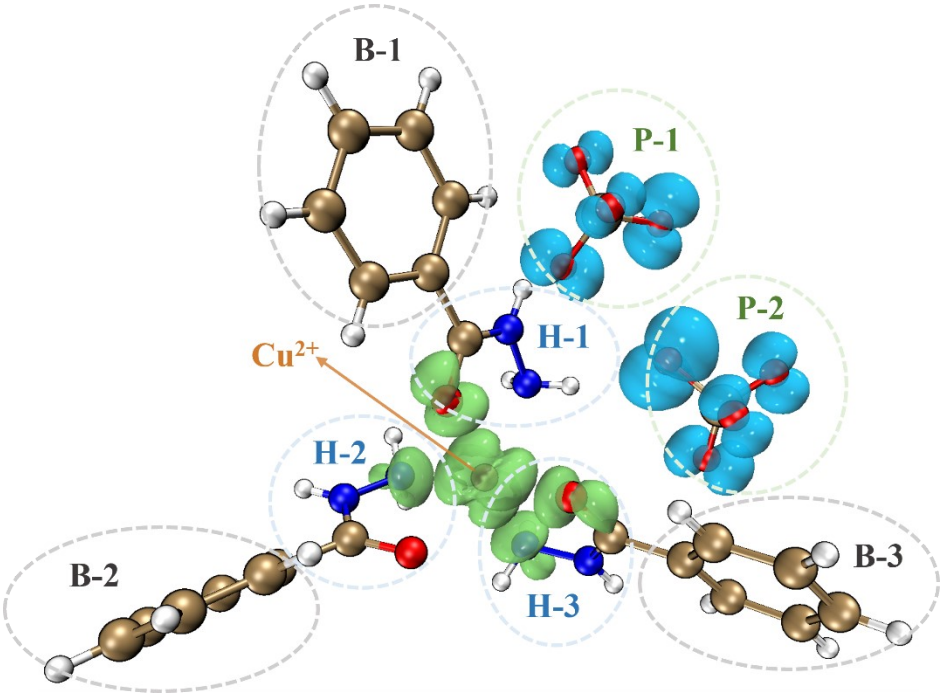

Figure S5. Fragments division of ECCs-2.

Supplementary Table S1-S2

Table S1. Crystallographic data for **ECCs-1** and **ECCs-2**.

	ECCs-1	ECCs-2
CCDC Number	2410968	2410865
Formula Weight	534.75	670.90
Temperature / K	119.75(10)	120.0(10)
Crystal System	monoclinic	monoclinic
Space Group	$P2_1/c$	$P2_1/c$
a / Å, b / Å, c / Å	9.9076(8), 7.1785(5), 14.717(2)	15.0312(6), 9.3081(4), 19.6029(8)
α/°, β/°, γ/°	90.00, 108.113(12), 90.00	90.00, 101.075(4), 90.00
Volume / $Å^3$	994.8(2)	2691.6(2)
Z	2	4
ρ_{calc} / mg mm^{-3}	1.785	1.656
μ / mm^{-1}	1.429	1.080
F(000)	542	1372
Crystal Size / mm^3	0.33 × 0.26 × 0.08	0.25 × 0.23 × 0.14
2Θ Range for Data Collection	5.82 to 51.98°	6.1 to 52°
Reflections Collected	4325	12668
Independent Reflections	1915[R(int) = 0.0411 (inf-0.9Å)]	5219[R(int) = 0.0626 (inf-0.9Å)]
Data/Restraints/Parameters	1915/0/142	5219/0/370
Goodness-of-Fit on F^2	1.060	1.050
Final R Indexes [All Data]	R_1 = 0.0490, wR_2 = 0.0840	R_1 = 0.1064, wR_2 = 0.2031
Largest Diff. Peak/Hole / e $Å^{-3}$	0.397/-0.374	1.636/-0.802
Flack Parameters	N	N
Completeness	0.9974	0.9963

Table S2. Hydrogen bonding data for **ECCs-1**.

Donor	H	Acceptor	D-H /Å	H…A /Å	D…A /Å	D-H…A/°
N(1)	H(1A)	O(3)	0.92	2.30	3.067(3)	141
N(1)	H(1A)	O(4)	0.92	2.39	3.075(3)	131
N(1)	H(1B)	O(4)	0.92	2.00	2.869(3)	157
N(2)	H(2)	O(3)	0.88	2.10	2.851(3)	143
C(4)	H(4)	O(2)	0.95	2.57	3.413(4)	151

Table S3. Hydrogen bonding data for **ECCs-2**.

Donor	H	Acceptor	D-H /Å	H…A /Å	D…A /Å	D-H…A/°
N(3)	H(3A)	O(19)	0.92	2.43	3.064(7)	126
N(3)	H(3B)	O(36)	0.92	2.02	2.922(7)	167
N(4)	H(4)	O(25)	0.88	2.13	2.868(6)	141
N(7)	H(7A)	O(36)	0.92	2.22	3.105(7)	162
N(7)	H(7B)	O(19)	0.92	2.41	2.937(7)	116
N(7)	H(7B)	O(28)	0.92	2.56	3.284(7)	136
N(7)	H(7B)	O(18)	0.92	2.51	3.013(6)	115
N(8)	H(8)	O(23)	0.88	2.43	3.235(7)	152
N(8)	H(8)	O(35)	0.88	2.50	3.082(7)	124
N(10)	H(10)	O(23)	0.88	2.09	2.929(6)	158
N(13)	H(13A)	O(18)	0.92	2.09	2.987(6)	164
N(13)	H(13B)	O(19)	0.92	2.21	3.011(7)	145
N(13)	H(13B)	O(28)	0.92	2.52	2.938(7)	108
C(22)	H(22)	O(1)	0.95	2.42	2.745(7)	100
C(24)	H(24)	O(2)	0.95	2.46	2.780(7)	100
C(30)	H(30)	O(9)	0.95	2.45	3.393(8)	173

Table S4. Contribution of each non-hydrogen atom to hole and electron in ECCs-1.

Atoms	Hole	Electron	Overlap	Diff.
1(Cu)	85.54 %	75.38 %	80.30 %	-0.1017
2(Cl)	0.26 %	-0.00 %	0.00 %	-0.0026
3(O)	0.95 %	0.00 %	0.02 %	-0.0095
4(O)	0.06 %	0.00 %	0.01 %	-0.0006
5(N)	0.02 %	0.29 %	0.08 %	0.0026
7(O)	0.93 %	5.51 %	2.26 %	0.0458
8(N)	1.13 %	5.64 %	2.52 %	0.0451
11(C)	0.05 %	0.21 %	0.10 %	0.0016
12(C)	-0.02 %	-0.02 %	0.00 %	-0.0001
14(C)	0.02 %	0.02 %	0.02 %	0.0001
16(O)	0.09 %	0.00 %	0.00 %	-0.0009
17(C)	0.01 %	0.02 %	0.01 %	0.0002
19(C)	0.00 %	-0.00 %	0.00 %	0
21(C)	-0.01 %	0.51 %	0.00 %	0.0052
22(C)	0.01 %	0.04 %	0.02 %	0.0003
24(O)	3.73 %	-0.00 %	0.00 %	-0.0373
25(Cl)	0.26 %	-0.00 %	0.00 %	-0.0026
26(O)	0.95 %	0.00 %	0.02 %	-0.0095
27(O)	0.06 %	0.00 %	0.01 %	-0.0006
28(N)	0.02 %	0.29 %	0.08 %	0.0026
30(O)	0.93 %	5.51 %	2.26 %	0.0458
31(N)	1.13 %	5.64 %	2.52 %	0.0451
34(C)	0.05 %	0.21 %	0.10 %	0.0016
35(C)	-0.02 %	-0.02 %	0.00 %	-0.0001

Table S5. Contribution of each non-hydrogen atom to hole and electron in ECCs-2.

Atoms	Hole	Electron	Overlap	Diff.
1(Cu)	0.08 %	74.97 %	2.47 %	0.7489
2(O)	0.00 %	6.69 %	0.09 %	0.0669
3(O)	0.02 %	4.98 %	0.27 %	0.0496
4(N)	0.00 %	5.30 %	0.06 %	0.053
7(N)	0.00 %	0.31 %	0.02 %	0.0031
9(C)	0.00 %	0.00 %	0.00 %	0
11(O)	0.00 %	0.13 %	0.01 %	0.0013
12(N)	0.04 %	0.22 %	0.09 %	0.0018
15(N)	0.02 %	0.17 %	0.05 %	0.0015
17(N)	0.00 %	0.17 %	0.01 %	0.0016
19(C)	0.00 %	0.48 %	0.05 %	0.0048
20(C)	0.00 %	0.82 %	0.05 %	0.0082
21(N)	0.00 %	4.11 %	0.05 %	0.0411
24(C)	0.00 %	0.46 %	0.03 %	0.0046
25(C)	0.00 %	0.02 %	0.01 %	0.0002
26(C)	0.00 %	0.10 %	0.01 %	0.001
28(C)	0.00 %	0.10 %	0.02 %	0.0009
29(C)	0.01 %	0.00 %	0.00 %	0
31(C)	0.01 %	0.26 %	0.05 %	0.0025
32(C)	0.00 %	0.03 %	0.01 %	0.0003
34(C)	0.01 %	0.02 %	0.02 %	0.0001
36(C)	0.00 %	0.08 %	0.02 %	0.0008
38(C)	-0.00 %	0.00 %	0.00 %	0
40(C)	0.01 %	0.01 %	0.01 %	0.0001
42(C)	0.00 %	0.03 %	0.00 %	0.0003
44(C)	0.01 %	0.00 %	0.00 %	0
46(C)	0.00 %	0.00 %	0.00 %	0
48(C)	0.01 %	0.00 %	0.00 %	0
50(C)	0.01 %	0.01 %	0.01 %	0

52(C)	0.01 %	0.00 %	0.00 %	0
54(C)	0.01 %	0.01 %	0.01 %	0
56(Cl)	0.11 %	0.00 %	0.01 %	-0.001
57(O)	4.28 %	0.00 %	0.07 %	-0.0428
58(O)	3.53 %	0.00 %	0.03 %	-0.0353
59(O)	16.82 %	0.00 %	0.15 %	-0.1682
60(O)	13.19 %	0.01 %	0.33 %	-0.1319
61(Cl)	0.51 %	0.00 %	0.01 %	-0.0051
62(O)	5.37 %	0.00 %	0.05 %	-0.0537
63(O)	7.72 %	0.00 %	0.03 %	-0.0772
64(O)	11.51 %	0.00 %	0.07 %	-0.1151
65(O)	36.41 %	0.00 %	0.11 %	-0.3641

Table S6. Transferred electrons between fragments in **ECCs-1**.

Donors	Receptors						
	P-1	P-2	B-1	B-2	H-1	H-2	Cu^{2+}
P-1	0	0	0.00015	0.00015	0.00612	0.00612	0.03835
P-2	0	0	0.00015	0.00015	0.00612	0.00612	0.03835
B-1	0	0	0	0	0.00007	0.00007	0.00043
B-2	0	0	0	0	0.00007	0.00007	0.00043
H-1	0	0	0.00006	0.00006	0.00251	0.00251	0.01571
H-2	0	0	0.00006	0.00006	0.00251	0.00251	0.01571
Cu^{2+}	0.00001	0.00001	0.00247	0.00247	0.10284	0.10284	0.6448

The unit for all data in the table is ***e***.

Table S7. Transferred electrons between fragments in **ECCs-2**.

Donors	Receptors								
	P-1	P-2	B-1	B-2	B-3	H-1	H-2	H-3	Cu^{2+}
P-1	0.00001	0.00236	0.00019	0.00177	0.02867	0.01801	0.0436	0.28444	0.00001
P-2	0.00001	0.00383	0.00031	0.00287	0.04649	0.0292	0.0707	0.46122	0.00001
B-1	0	0	0	0	0.00002	0.00001	0.00003	0.00022	0
B-2	0	0	0	0	0.00003	0.00002	0.00005	0.0003	0
B-3	0	0	0	0	0.00004	0.00002	0.00006	0.00036	0
H-1	0	0.00002	0	0.00001	0.00024	0.00015	0.00037	0.00241	0
H-2	0	0	0	0	0.00001	0	0.00001	0.00005	0
H-3	0	0	0	0	0.00002	0.00001	0.00002	0.00015	0
Cu^{2+}	0	0.00001	0	0	0.00006	0.00004	0.00009	0.00061	0

The unit for all data in the table is ***e***.