Electronic Supplementary Information (ESI) for

Relativistic Modulation of Supramolecular Halogen/Copper Interactions and Phosphorescence in Cu(I) Pyrazolate Cyclotrimers

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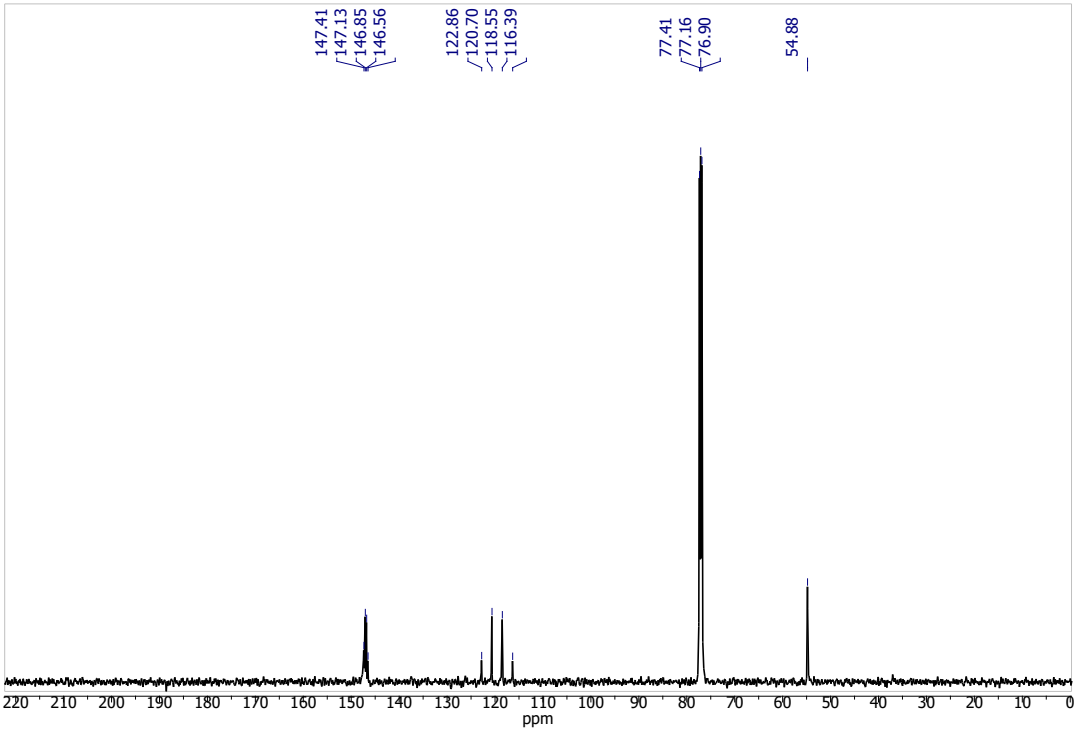


Figure S1. $^{13}C\{^{1}H\}$ NMR spectrum of **1-I** in $CDCl_3$.

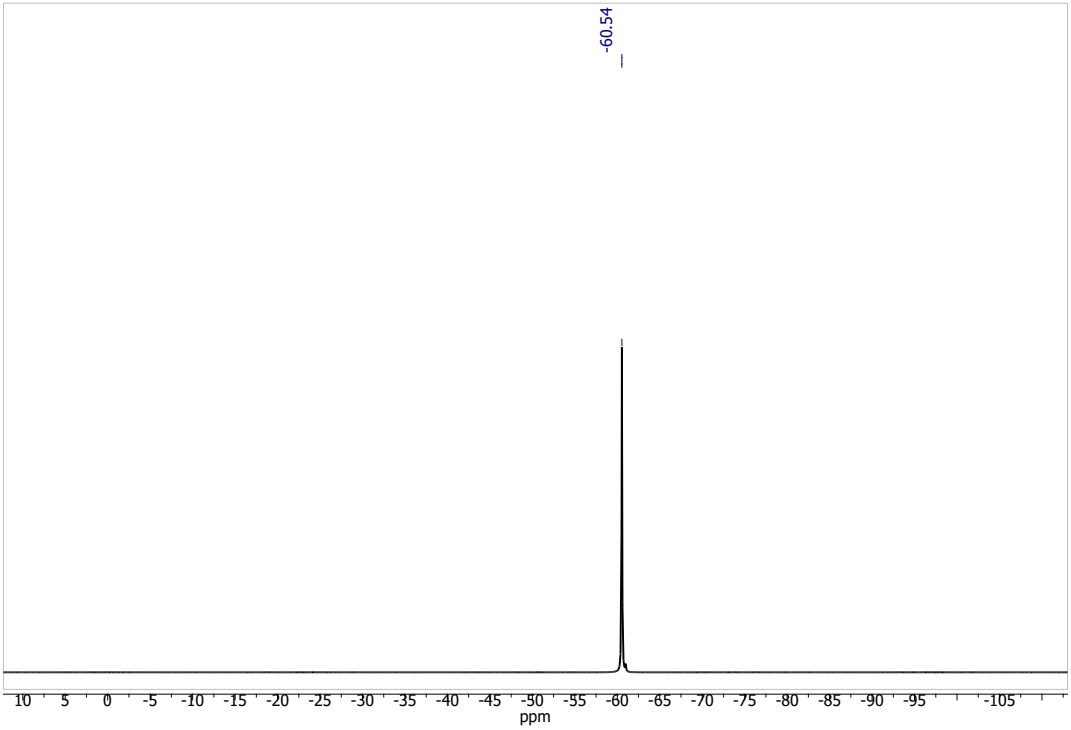


Figure S2. ^{19}F NMR spectrum of **1-I** in $CDCl_3$.

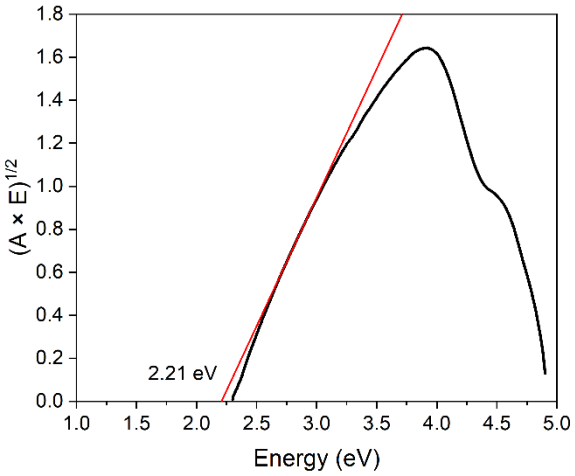


Figure S3. Diffuse reflectance UV-vis spectrum of K-M function versus E (eV) of **1-Cl**.

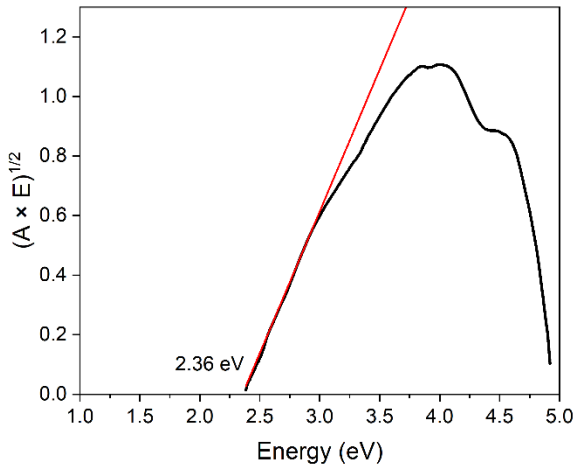


Figure S4. Diffuse reflectance UV-vis spectrum of K-M function versus E (eV) of **1-Br**.

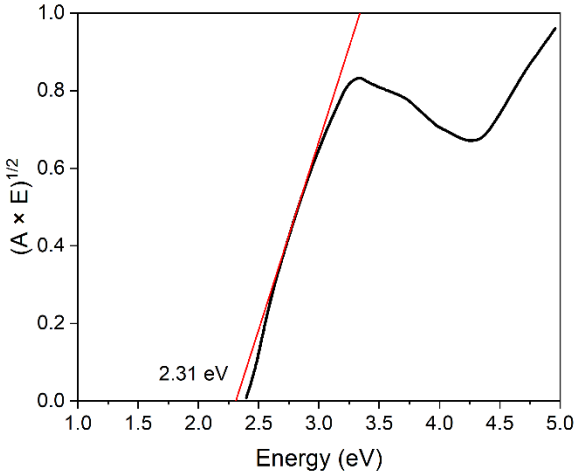


Figure S5. Diffuse reflectance UV-vis spectrum of K-M function versus E (eV) of **1-I**.

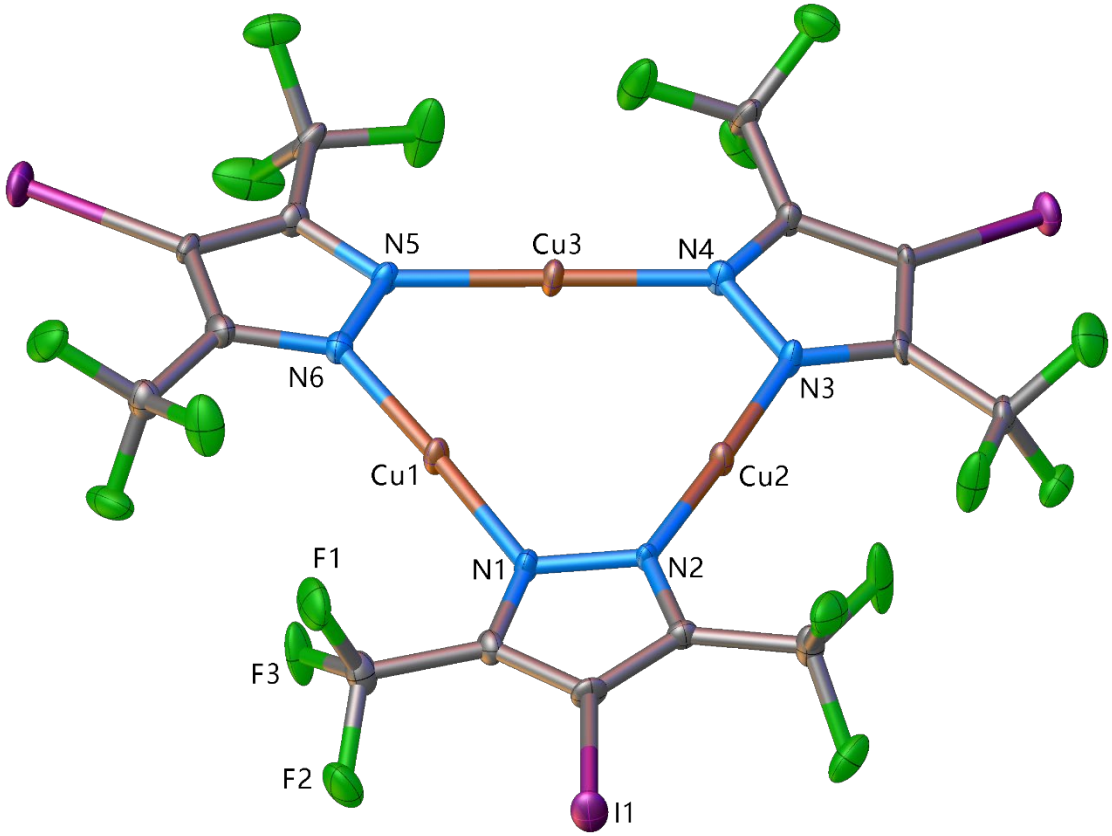


Figure S6. Molecular structure (ORTEP at 50%) of **1-I**.

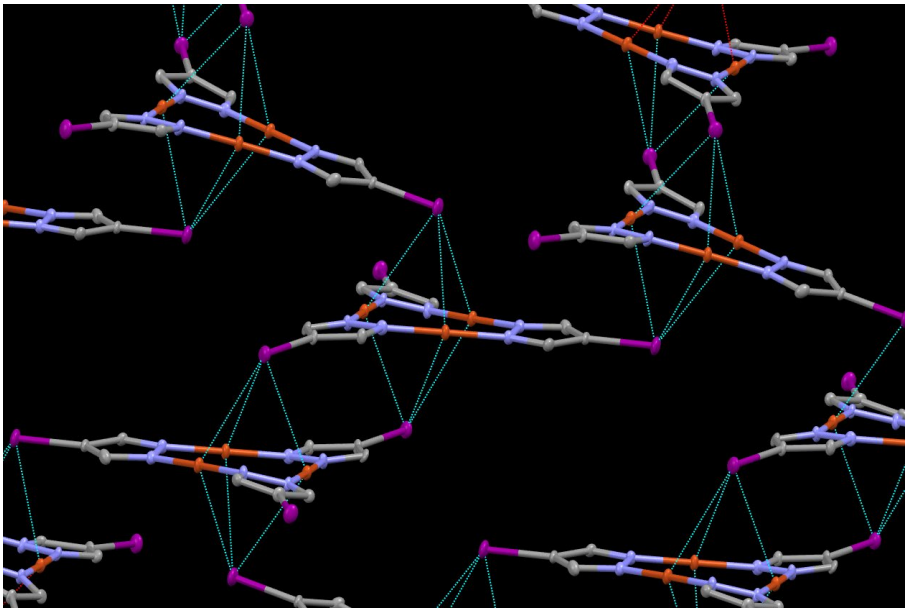


Figure S7. Figure showing inter-trimer Cu···I interactions (F and some C atoms have been omitted for clarity)

Table S1. Crystal data and refinement parameters of 1-I.

Empirical formula	$C_{15}Cu_3F_{18}I_3N_6$
CCDC No.	2204230
Formula weight	1177.53
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.2314(5)
b/Å	14.3123(7)
c/Å	20.1811(10)
α/°	90
β/°	97.717(2)
γ/°	90
Volume/Å^3	2642.2(2)
Z	4
ρ_{calc}g/cm^3	2.96
μ/mm^{-1}	6.047
F(000)	2160
Crystal size/mm^3	0.27 × 0.23 × 0.19
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.14 to 61.174
Index ranges	$-13 \le h \le 13$, $-20 \le k \le 20$, $-28 \le l \le 28$
Reflections collected	57828
Independent reflections	8101 [R_{int} = 0.0391, R_{sigma} = 0.0237]
Data/restraints/parameters	8101/0/406
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0625, wR_2 = 0.1446
Final R indexes [all data]	R_1 = 0.0710, wR_2 = 0.1497
Largest diff. peak/hole / e Å^{-3}	3.38/-1.88

Table S2. Selected bond lengths (Å) and angles (°) of **1-I**.

Cu1-N1	1.872(7)	Cu3-N5	1.893(7)
Cu1-N6	1.883(7)	N1-Cu1-N6	176.9(3)
Cu2-N2	1.888(7)	N3-Cu2-N2	177.8(3)
Cu2-N3	1.887(7)	N5-Cu3-N4	179.8(3)
Cu3-N4	1.893(7)		

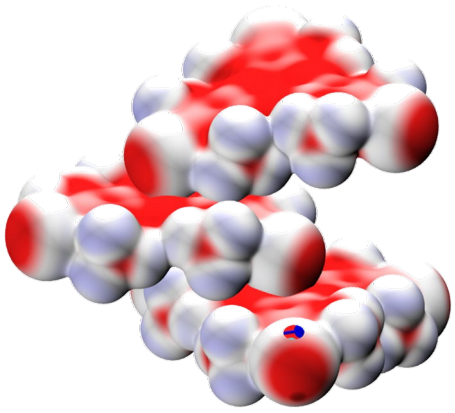


Figure S8. Electrostatic potential (ESP) mapping on the iso-electron-density surface (0.002 e^-) of three monomer-of-trimer stacked molecules in the supramolecular structure of the iodo complex from -0.03 (blue) to +0.03 (red) a.u.

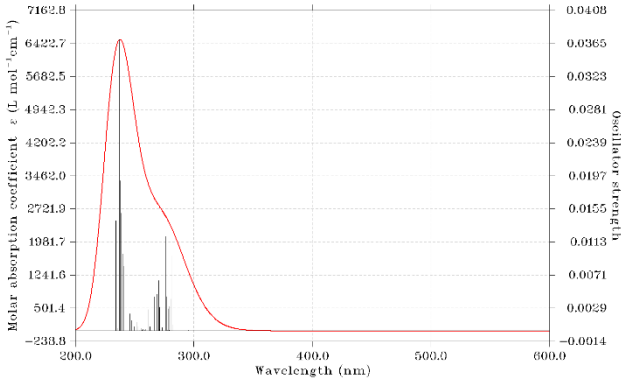


Figure S9. Simulated absorption spectrum of **1-Cl**.

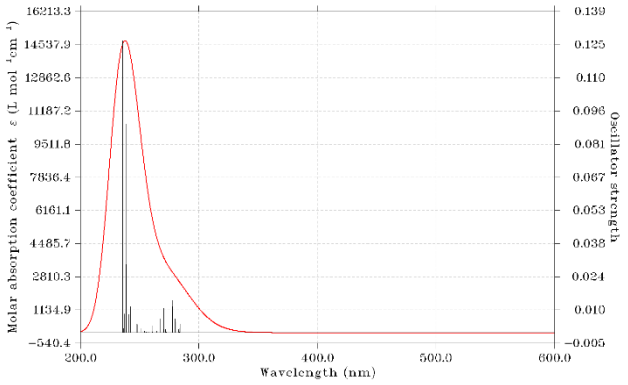


Figure S10. Simulated absorption spectrum of **1-Br**.

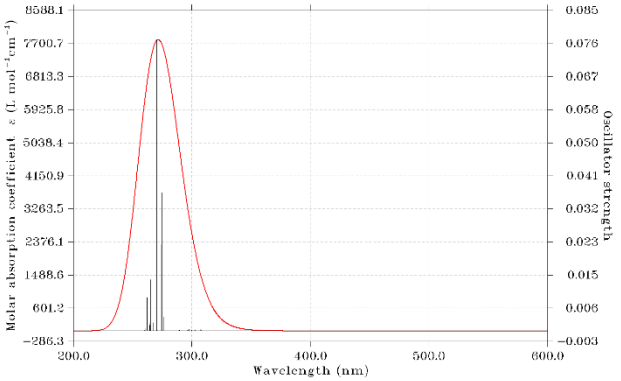


Figure S11. Simulated absorption spectrum of **1-I**.

Table S3. Spin-orbit coupling matrix elements (SOCME) of **1-Cl** between first 10 singlet and first 20 triplet excited states. Bordered are possible inter-system crossing (ISC) pathways.

μ	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10	T11	T12	T13	T14	T15	T16	T17	T18	T19	T20
S1	81	153	36	28	63	1	106	38	26	20	24	44	40	83	38	10	15	41	148	66
S2	84	51	62	34	100	6	178	21	19	14	36	66	40	76	74	22	72	59	174	147
S3	101	90	38	45	117	4	86	20	12	33	60	53	48	47	58	35	32	18	97	110
S4	19	12	128	122	60	24	76	59	35	31	48	154	148	16	133	95	73	17	78	182
S5	27	26	116	130	53	22	97	9	15	30	52	188	87	60	119	100	66	25	61	187
S6	18	22	177	139	107	26	22	50	35	18	95	214	80	24	52	17	22	28	26	17
S7	15	15	145	73	36	14	34	54	5	8	19	102	155	41	106	50	112	27	72	286
S8	28	39	27	8	99	3	37	35	100	63	78	68	69	15	12	27	66	15	37	51
S9	15	31	144	79	203	20	45	46	52	11	23	170	42	10	12	16	29	31	48	18
S10	34	25	56	31	17	9	7	70	60	75	54	78	58	13	50	68	12	12	76	21

Table S4. Spin-orbit coupling matrix elements (SOCME) of **1-Br** between first 10 singlet and first 20 triplet excited states. Bordered are possible inter-system crossing (ISC) pathways.

	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10	T11	T12	T13	T14	T15	T16	T17	T18	T19	T20
S1	113	150	81	44	13	100	5	25	31	38	23	21	46	34	75	126	102	78	85	78
S2	87	127	125	27	31	15	5	69	61	35	26	12	42	26	93	137	75	56	109	53
S3	11	68	149	81	57	247	4	13	18	4	17	75	77	63	24	38	67	187	126	56
S4	8	98	173	70	40	10	8	9	10	4	32	128	7	42	5	26	63	160	12	75
S5	12	32	106	49	115	80	5	17	31	17	2	43	178	211	20	73	51	47	179	102
S6	17	26	113	125	149	63	4	16	13	36	45	171	174	76	20	38	34	38	107	105
S7	24	16	94	236	126	24	7	34	40	30	46	223	81	39	32	52	70	76	54	57
S8	17	62	86	152	125	74	5	9	55	38	66	212	92	59	32	60	49	58	57	91
S9	63	114	91	58	59	16	4	99	67	30	13	58	20	77	91	152	127	61	135	30
S10	12	44	65	32	60	71	6	92	109	92	31	69	30	5	7	23	24	41	45	65

Table S5. Spin-orbit coupling matrix elements (SOCME) of **1-I** between first 10 singlet and first 20 triplet excited states. Bordered are possible inter-system crossing (ISC) pathways.

	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10	T11	T12	T13	T14	T15	T16	T17	T18	T19	T20
S1	63	92	284	98	184	160	35	181	399	1135	57	114	284	82	93	8	29	16	77	150
S2	107	296	181	40	74	82	219	223	243	436	29	58	68	28	74	7	16	7	28	27
S3	151	464	93	77	128	136	245	107	258	677	11	94	43	58	77	14	8	10	41	76
S4	325	110	166	16	37	253	50	34	35	154	6	13	7	8	12	4	8	4	15	20
S5	52	255	93	71	56	48	21	96	110	108	21	78	10	25	9	17	3	18	16	43
S6	90	38	105	37	94	149	56	33	78	103	118	42	58	36	14	22	5	15	29	18
S7	99	168	126	51	59	151	73	53	73	114	97	90	33	44	16	13	8	28	15	38
S8	5	57	4	195	187	16	46	78	9	45	38	215	35	92	23	25	1	15	47	21
S9	69	237	107	48	46	93	75	100	30	213	23	63	58	12	36	16	20	102	69	77
S10	107	367	122	9	62	151	51	125	44	38	41	80	69	57	37	28	5	70	55	89

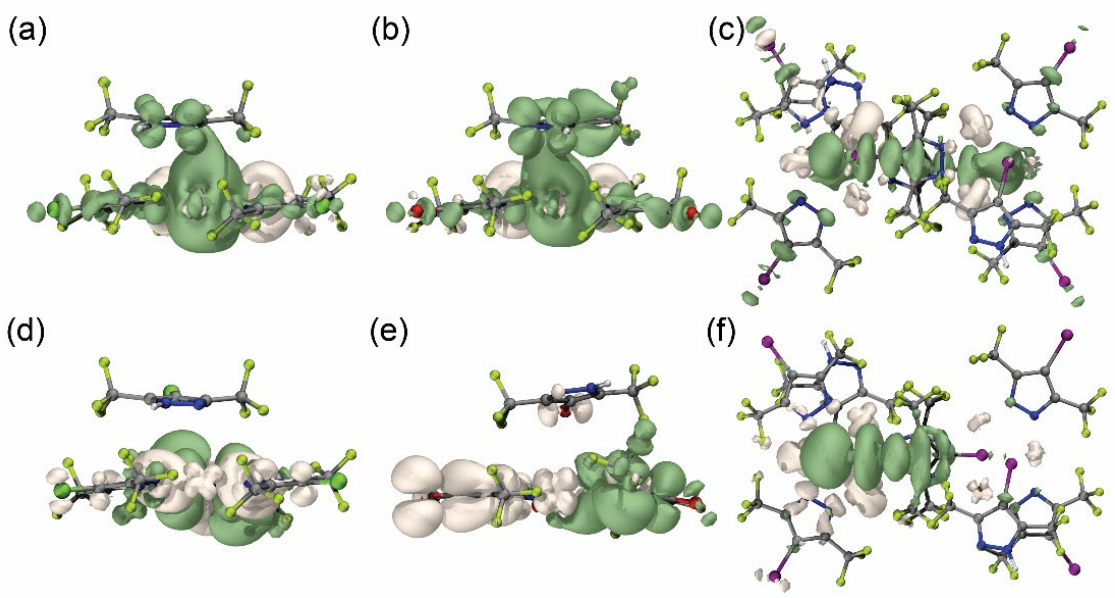
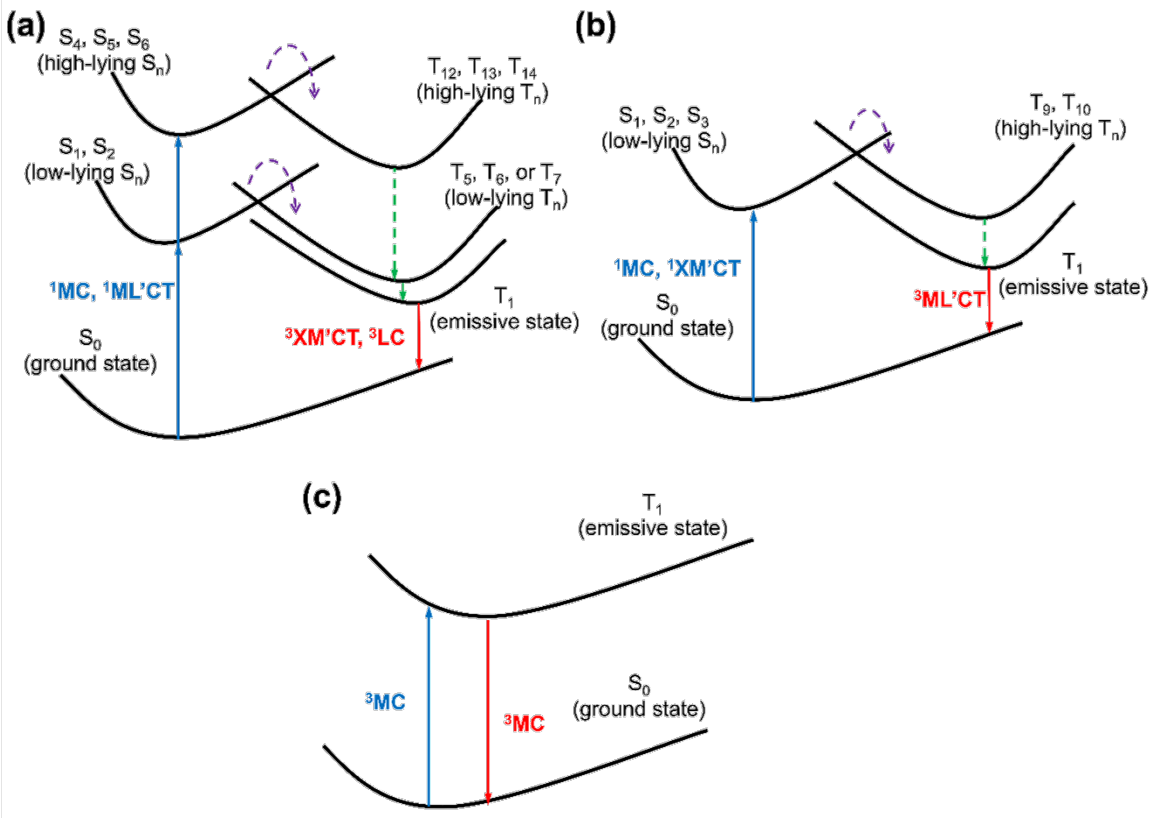


Figure S12. Electron density difference (EDD) maps of the lowest-singlet excited states (S_1) of (a) **1-Cl**, (b) **1-Br**, and (c) **1-I** from the other view. EDD maps of the lowest-triplet excited states (T_1) of (d) **1-Cl**, (e) **1-Br**, and (f) **1-I** from the other view. White and green regions refer to the decrease and increase of electron density, respectively.



Scheme S1. Proposed Jablonski diagram for (a) **1-Cl**, **1-Br**, (b) **1-I**, and (c) **1-H**. Blue solid line: excitation, purple dashed line: inter-system crossing (ISC), green dashed line: internal conversion (IC), red solid line: phosphorescence.

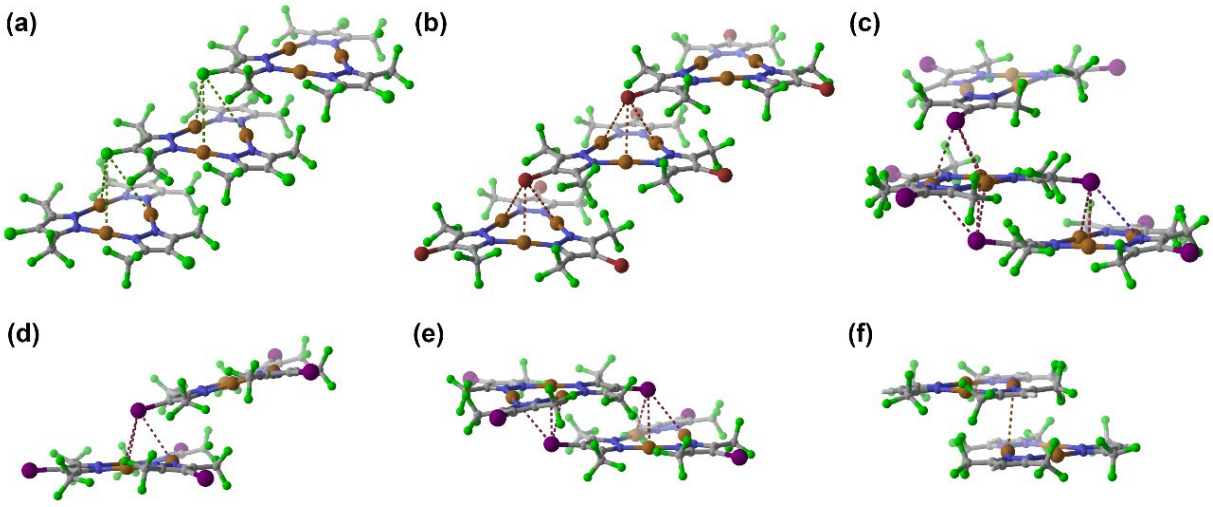


Figure S13. Illustrations of energy decomposition analyses (EDA) models. (a) trimer-of-trimer of **1-Cl** with 2*1 Cu_3…Cl, (b) trimer-of-trimer of **1-Br** with 2*1 Cu_3…Br, (c) trimer-of-trimer of **1-I** with 2 Cu_3…I + 1 Cu_3…I, (d) dimer-of-trimer of **1-I** with 1 Cu_3…I, (e) dimer-of-trimer of **1-I** with 2 Cu_3…I, (h) dimer-of-trimer $Cu_3[3,5\text{-}(CF_3)_2Pz]_3$.