Supporting Information (SI)

Luminescent Copper(I) Halide and Pseudohalide Diimine Complexes: Simple Structures But Complicated Excited State Behavior

Jörn Nitsch,[a] Christian Kleeberg,[b] Roland Fröhlich,[c] and Andreas Steffen*[a]

[a] *Institut für Anorganische Chemie, Julius-Maximilians- Universität Würzburg, Am Hubland, 97074 Würzburg, Germany*
[b] *Institut für Anorganische und Analytische Chemie, Technische Universität Carolo-Wilhelmina zu Braunschweig, Hagenring 30, 38106 Braunschweig, Germany*
[c] *Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Corrensstr. 40, 48149 Münster, Germany*

Table of contents

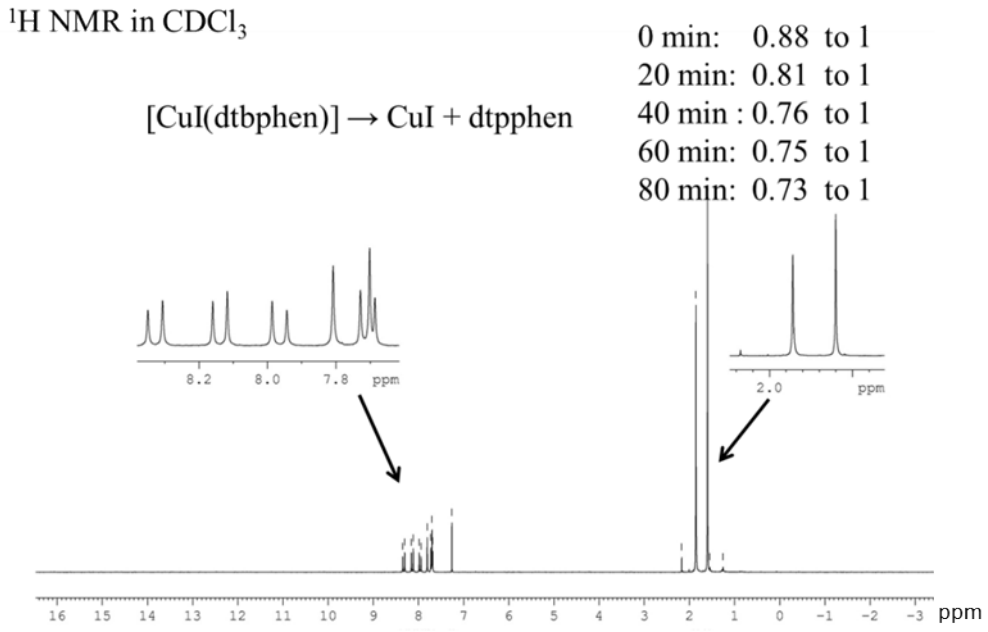

Figure S1. ^{1}H NMR (200 MHz) spectrum of [CuI(dtbphen)] (**1**) in deuterated chloroform with signals corresponding to **1** at 8.34 ppm, 7.96 ppm, 7.81 ppm, 1.86 ppm and signals of free dtbphen at 8.14 ppm, 7.74-7.67 ppm and 1.60 ppm. Time resolved measurements show the decomposition of **1** in solution, as indicated by the decreasing ratio between the signals of the *tert*-butyl protons of the complex and the free ligand.

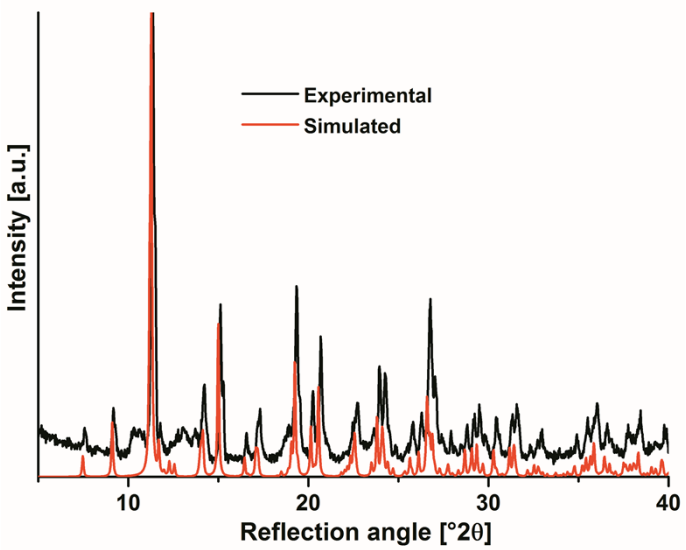

Figure S2. Experimental powder diffraction pattern (black) and predicted powder diffraction pattern calculated on the basis of the crystal structure of **5** · MeCN (red).

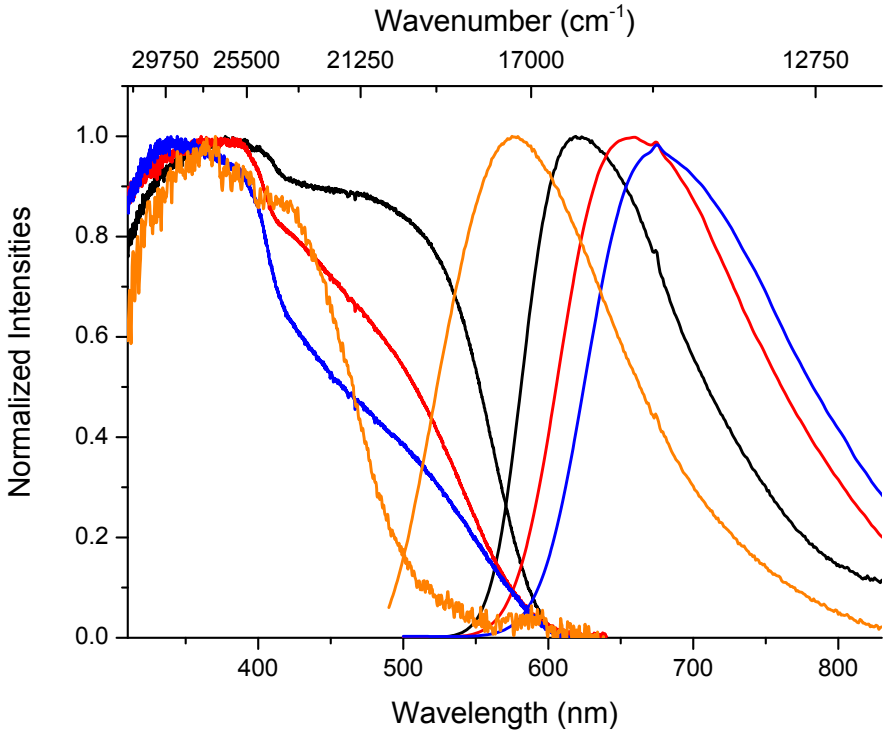

Figure S3. Normalized solid state absorption (left) and emission (right) spectra of complexes **1** (black), **2** (red), **3** (blue) and **4** (orange).

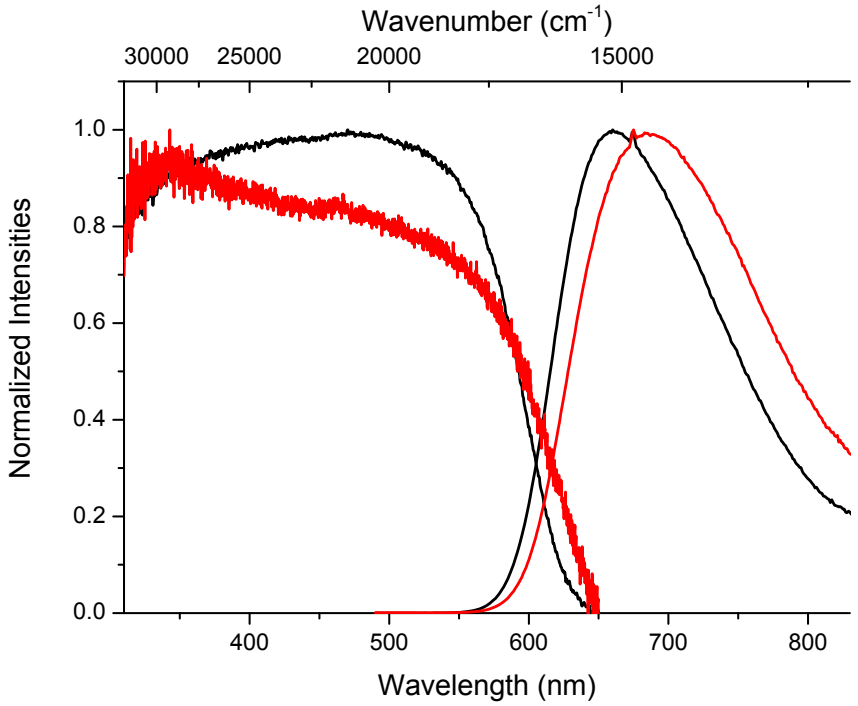

Figure S4. Normalized solid state absorption (left) and emission (right) spectra of complexes **5** (black) and **6** (red).

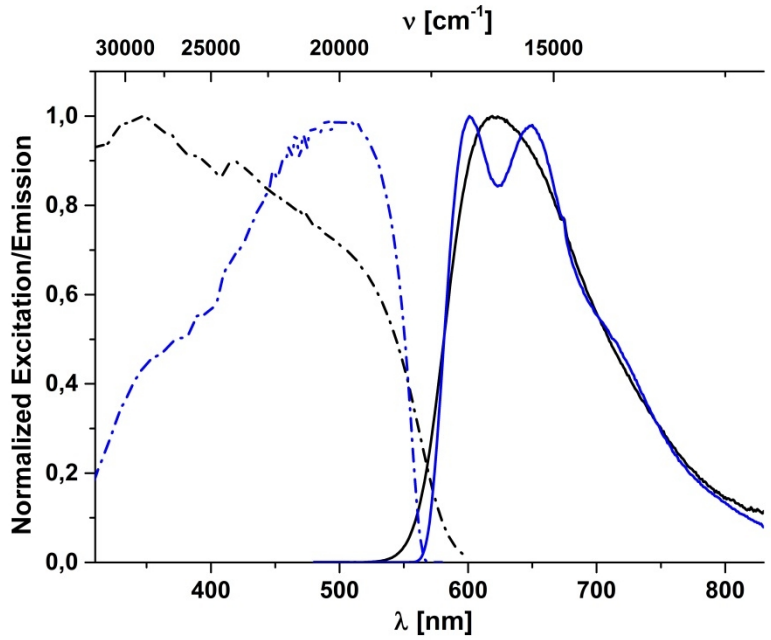

Figure S5. Normalized solid state excitation (dashed) and emission (solid) spectra of [CuI(dtbphen)] (**1**) at room temperature (black) and at 4 K (blue).

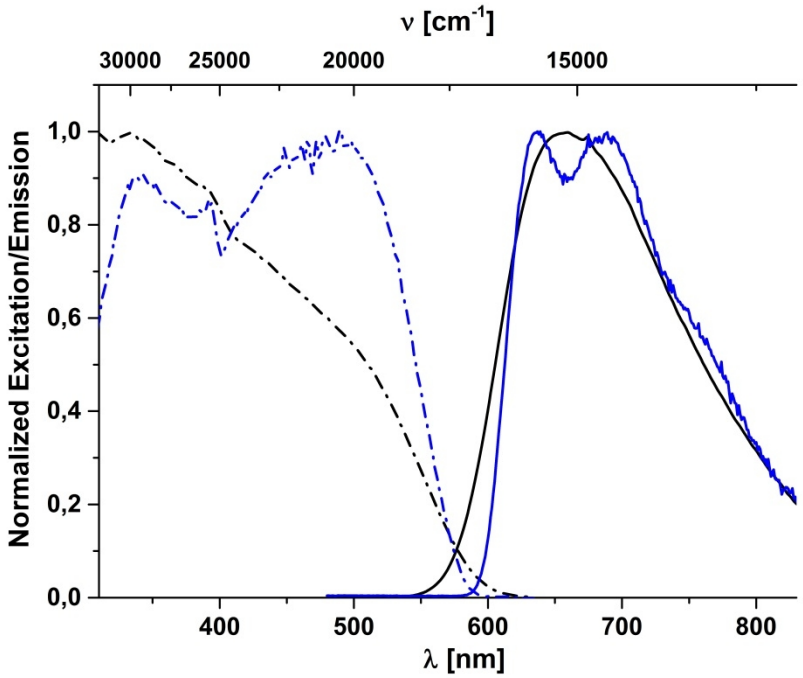

Figure S6. Normalized solid state excitation (dashed) and emission (solid) spectra of [CuBr(dtbphen)] (**2**) at room temperature (black) and at 4 K (blue).

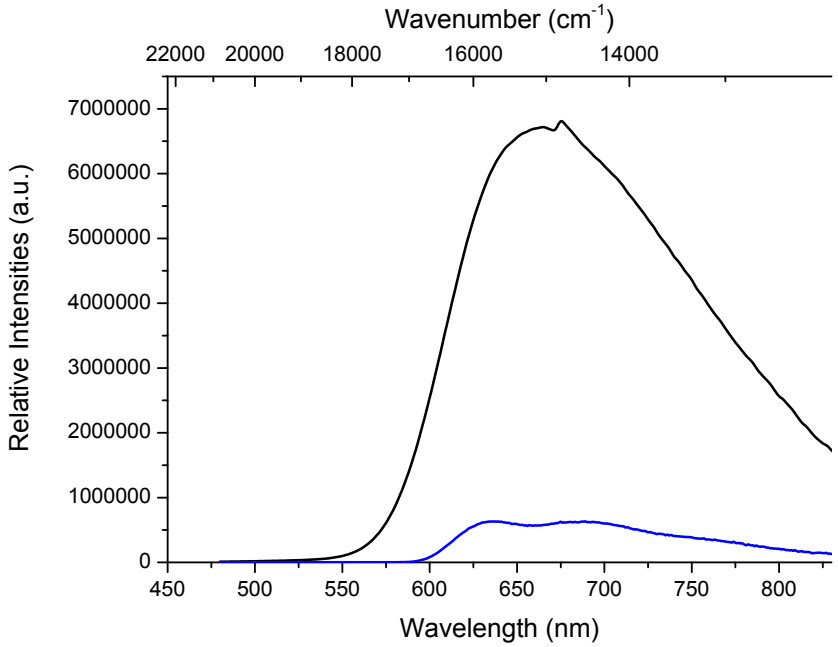

Figure S7. Variable temperature emission spectra of [CuBr(dtbphen)] (**2**) (298 K black and 77 K blue) recorded in the solid state.

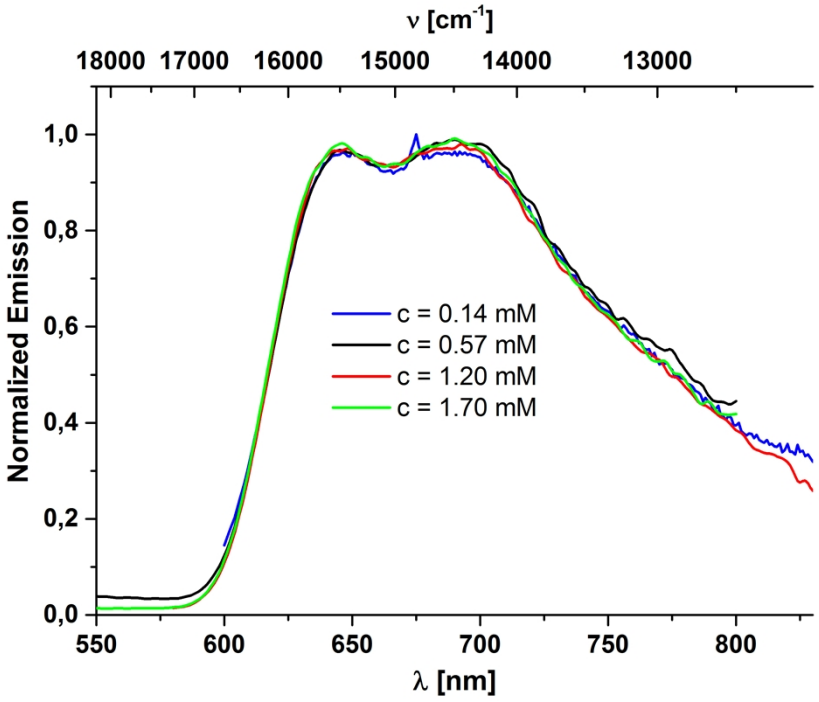

Figure S8. Normalized concentration dependent emission spectra of [CuBr(dtbphen)] (**2**) at 77 K in a frozen glass of 2-MeTHF.

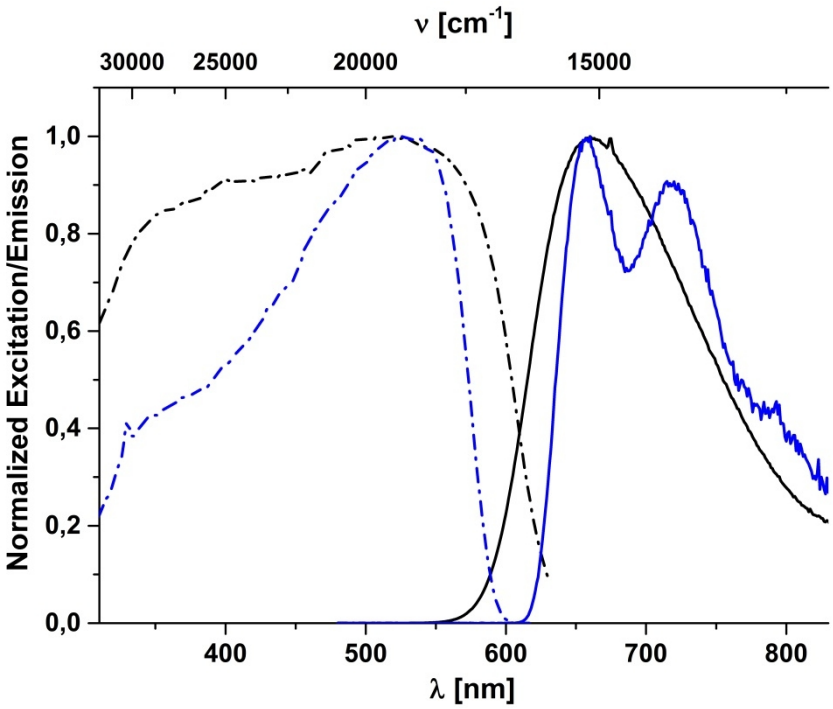

Figure S9. Normalized solid state excitation (dashed) and emission (solid) spectra of $[Cu_2(\mu^2\text{-}I)_2(dmphen)_2]$ (**6**) at room temperature (black) and at 22 K (blue).

Table S1. Geometric parameters obtained from single crystal X-ray diffraction experiments compared to the parameters obtained from the calculated optimized structures.

Entry	d(Cu-X) [Å] exp.	d(Cu-X) [Å] calc.	d(Cu-N) [Å] exp.	d(Cu-N) [Å] calc.	τ(Cu-X) [°] exp.[c)]	τ(Cu-X) [°] calc.[c)]
1	2.443	2.476	2.064, 2.086	2.102	48.7	48.2
2[a)]	2.298	2.318	2.065, 2.086	2.099	40.6	35.5
3	2.147	2.246	2.075, 2.093	2.091	39.4	6.4
4m[b)]	1.853	1.894	2.030, 2.054	2.099	61.7	12.5

[a)] From Reference [1]

[b)] $[CuCN(dtbphen)\times CuCN]_\infty$ (**4**) was replaced by its monomeric fragment [CuCN(dtbphen)] (**4m**)

[c)] defined as follows: angle between plane (N1, N10, C13, C14) and plane (N1, Cu, X)

Table S2. Cartesian coordinates of the optimized ground state (S_0) of complex **1**

C	4.74195100	0.04369000	1.59063500
C	3.41230200	-0.33414000	0.91077800
C	2.54441600	-1.06304100	1.94886500
C	3.44919600	2.04954800	-0.01761200
C	3.70836900	-1.26900300	-0.28041700
C	2.70050900	0.90923300	0.37385400
C	2.81214800	3.17241400	-0.49597400
C	1.40294200	3.19913700	-0.56160200
C	0.67443500	4.35441200	-0.99511100
C	0.72243600	2.02412300	-0.16396400
C	-0.68894900	4.35248100	-0.99457300
C	-0.72960000	2.02191700	-0.16381800
C	-2.54354500	-1.07026400	1.95009800
C	-1.41381500	3.19504600	-0.56072300
C	-2.70425600	0.90067400	0.37382400
C	-2.82286200	3.16421300	-0.49411700
C	-3.41191600	-0.34565800	0.90934400
C	-4.74501600	0.02628500	1.58559400
C	-3.45640200	2.03920300	-0.01604500
C	-3.70086600	-1.28224400	-0.28225700
H	5.16387100	-0.84966200	2.06572700
H	4.60425700	0.80312300	2.37160900
H	5.49614500	0.40611300	0.88170600
H	3.10771700	-1.90868200	2.36201400
H	4.53124700	2.03618600	0.05887200
H	2.26621600	-0.39831300	2.77679900
H	4.23540700	-2.16397900	0.07484400
H	3.38422300	4.04681800	-0.80554700
H	4.34579900	-0.77222900	-1.02389900
H	1.62975900	-1.47813400	1.50891400
H	2.78533500	-1.59746300	-0.77062900
H	1.23207600	5.23425500	-1.31407700
H	-2.27141400	-0.40422600	2.77901500
H	-1.62523800	-1.48089100	1.51349900
H	-1.24934200	5.23074400	-1.31305900
H	-3.10395200	-1.91873600	2.36139900
H	-4.61297300	0.78669200	2.36660500
H	-3.39767300	4.03713800	-0.80279400
H	-5.16402200	-0.86880100	2.05998600
H	-4.53834800	2.02277700	0.06120500
H	-5.49896500	0.38481800	0.87441700
H	-2.77523300	-1.60687100	-0.77010400
H	-4.22484400	-2.17939600	0.07202700
H	-4.33862800	-0.78849900	-1.02746000
N	1.37107500	0.90573000	0.25541100
N	-1.37481100	0.90131200	0.25490800
Cu	-0.00052800	-0.67645700	0.05880800
I	0.00662600	-2.94590500	-0.93093200

Table S3. Cartesian coordinates of the optimized T_1 state of complex **1**

C	4.7514850	-0.1156480	1.4393970
C	3.3848140	-0.4239350	0.8011240
C	2.5399060	-1.1277390	1.8784400
C	3.4277910	2.0129800	0.0764280
C	3.6265860	-1.3505560	-0.4072700
C	2.6915000	0.8547050	0.3202610
C	2.8087570	3.1984830	-0.3635080
C	1.4231840	3.2386630	-0.4813920
C	0.6806410	4.4188950	-0.8360430
C	0.7009210	2.0436130	-0.1965810
C	-0.6819430	4.4187350	-0.8359720
C	-0.7015760	2.0434510	-0.1965250
C	-2.5396310	-1.1285350	1.8783150
C	-1.4241660	3.2383200	-0.4812550
C	-2.6918400	0.8540020	0.3203530
C	-2.8097210	3.1977900	-0.3632540
C	-3.3847270	-0.4249430	0.8010060
C	-4.7515930	-0.1172880	1.4391560
C	-3.4284400	2.0120990	0.0766480
C	-3.6259640	-1.3515450	-0.4075120
H	5.1690660	-1.0434630	1.8490940
H	4.6681140	0.6074640	2.2602680
H	5.4797050	0.2633590	0.7130660
H	3.0827200	-2.0005710	2.2617920
H	4.5002280	2.0030100	0.2314710
H	2.3336150	-0.4548410	2.7200200
H	4.0836320	-2.2923310	-0.0761330
H	3.4031100	4.0876590	-0.5691530
H	4.3060320	-0.8736410	-1.1245940
H	1.5834300	-1.5077000	1.5004560
H	2.6987080	-1.5976480	-0.9313380
H	1.2356720	5.3233390	-1.0838690
H	-2.3336480	-0.4556480	2.7199780
H	-1.5829760	-1.5080930	1.5003590
H	-1.2372130	5.3230460	-1.0837430
H	-3.0821310	-2.0016200	2.2615350
H	-4.6686150	0.6057660	2.2601180
H	-3.4043090	4.0868280	-0.5688180
H	-5.1688480	-1.0453170	1.8487010
H	-4.5008680	2.0018480	0.2317270
H	-5.4798760	0.2615010	0.7127760
H	-2.6979080	-1.5982540	-0.9314530
H	-4.0827100	-2.2935210	-0.0765340
H	-4.3054690	-0.8748190	-1.1249040
N	1.3437670	0.8536070	0.1220880
N	-1.3441070	0.8532880	0.1221570
Cu	-0.0000710	-0.5538020	-0.0114670
I	0.0005480	-2.9028990	-0.8235640

Table S4. Cartesian coordinates of the optimized ground state (S_0) of complex **2**

Br	-0.00075800	-3.08079500	-0.90296700
Cu	0.00014900	-0.91381100	-0.08022200
N	-1.37656000	0.65282900	0.16075900
N	1.37685600	0.65250100	0.16045300
C	-2.70889000	0.63896300	0.26210100
C	-3.45421000	1.82398400	0.03948100
C	-3.41909300	-0.67425100	0.59602900
C	-2.64459700	-1.44897900	1.67206500
C	3.45461500	1.82370000	0.04128900
C	0.68104400	4.24275500	-0.59027700
C	1.40732200	3.03682700	-0.32421500
C	2.70916400	0.63849400	0.26239300
C	0.72668900	1.81709100	-0.09398400
C	3.41910900	-0.67513100	0.59524000
C	-0.72619000	1.81719200	-0.09418300
C	-1.40662600	3.03688500	-0.32519200
C	2.64500300	-1.44995500	1.67152100
C	-0.68012400	4.24276300	-0.59086300
C	3.51620000	-1.50967900	-0.69527700
C	2.81499500	3.00273400	-0.26491500
C	-4.83807000	-0.42232900	1.12728900
C	-2.81435500	3.00282800	-0.26693300
C	-3.51738800	-1.50930800	-0.69407200
C	4.83856700	-0.42415700	1.12560200
H	-4.53621000	1.80110400	0.10910600
H	-3.20703600	-2.35001400	1.94527000
H	-2.50555100	-0.84334000	2.57688500
H	-1.66336600	-1.78373700	1.31531800
H	4.53655600	1.80078800	0.11173600
H	1.24240400	5.15637200	-0.78083700
H	2.50717000	-0.84471500	2.57679100
H	3.20703100	-2.35155200	1.94371700
H	1.66322000	-1.78380800	1.31543600
H	-1.24130600	5.15637900	-0.78194500
H	2.52439100	-1.76272500	-1.08671100
H	4.03870600	-2.45155200	-0.48477500
H	4.08095000	-0.97239500	-1.46867500
H	3.38417300	3.91440200	-0.44430300
H	-5.27354200	-1.37985600	1.43529800
H	-5.50527100	-0.00102300	0.36546700
H	-4.84133300	0.24138100	2.00194100
H	-3.38338500	3.91440700	-0.44724100
H	-2.52590600	-1.76295600	-1.08595900
H	-4.08233700	-0.97209000	-1.46736700
H	-4.04021900	-2.45084400	-0.48286500
H	5.50541400	-0.00280100	0.36349200
H	5.27377500	-1.38206000	1.43281200
H	4.84280800	0.23909000	2.00060500

Table S5. Cartesian coordinates of the optimized T_1 of complex **2**

Br	-0.00001239	-2.85751786	-1.10298225
Cu	0.00000836	-0.78254310	-0.10449692
N	-1.33917477	0.61920825	0.12153669
N	1.33916409	0.61921672	0.12155247
C	-2.68919960	0.54674313	0.28190169
C	-3.44120534	1.72248990	0.05920996
C	-3.34951853	-0.76902501	0.68932219
C	-2.46926517	-1.53538457	1.68949141
C	3.44119459	1.72248915	0.05916023
C	0.70012554	4.19805638	-0.59809823
C	1.42150025	3.01871501	-0.35148355
C	2.68919535	0.54674798	0.28189446
C	0.72051576	1.79712113	-0.13772934
C	3.34953342	-0.76901165	0.68933056
C	-0.72053195	1.79711794	-0.13773092
C	-1.42152116	3.01871499	-0.35146306
C	2.46917630	-1.53551800	1.68929403
C	-0.70015311	4.19805735	-0.59808525
C	3.61740086	-1.62971205	-0.55947603
C	2.85024611	2.92033140	-0.27569264
C	-4.69415202	-0.50554089	1.38636698
C	-2.85026321	2.92033551	-0.27563631
C	-3.61709951	-1.62982973	-0.55947483
C	4.69402599	-0.50548329	1.38662510
H	-4.52141287	1.67750388	0.15696805
H	-3.00765516	-2.41861794	2.05489655
H	-2.20986565	-0.90969897	2.55215937
H	-1.54261200	-1.91768177	1.24126395
H	4.52140616	1.67749809	0.15687814
H	1.24884731	5.12182898	-0.77357431
H	2.20951318	-0.90989048	2.55192417
H	3.00760772	-2.41869261	2.05478144
H	1.54266368	-1.91792647	1.24086890
H	-1.24887956	5.12183084	-0.77354259
H	2.69453936	-1.85763910	-1.10306370
H	4.08045100	-2.58339285	-0.27251630
H	4.30018968	-1.11162849	-1.24431762
H	3.45937588	3.80562525	-0.45074888
H	-5.10386790	-1.45752667	1.74534235
H	-5.43854837	-0.07434494	0.70753268
H	-4.58266095	0.16264140	2.24932954
H	-3.45939531	3.80563636	-0.45064873
H	-2.69412395	-1.85770779	-1.10289040
H	-4.29981987	-1.11185442	-1.24446723
H	-4.08011020	-2.58353415	-0.27253056
H	5.43849921	-0.07417235	0.70794777
H	5.10375977	-1.45746533	1.74559223
H	4.58233740	0.16262176	2.24962161

Table S6 Cartesian coordinates of the optimized ground state (S_0) of complex **2π**

C	-3.265574	4.835264	-1.781337
C	-3.540270	3.688731	0.406693
C	-3.337278	3.471904	-1.093249
C	-4.529578	2.728906	-1.696870
C	-0.849611	3.313295	-1.627559
C	-2.058950	2.670962	-1.299518
C	0.274328	2.580951	-1.891110
C	1.405155	3.524233	1.390817
C	3.987514	4.684801	1.181853
C	0.183853	2.999542	1.715132
C	4.049802	3.205297	-0.810970
C	3.849977	3.239107	0.704461
C	0.217947	1.183488	-1.837961
C	2.474224	2.679992	1.044186
C	-1.006443	0.614333	-1.442019
C	0.005966	1.611130	1.739726
C	-1.223462	0.998776	2.115672
C	1.333615	0.359418	-2.156229
C	-4.927478	-2.425088	-1.419931
C	4.933762	2.425360	1.412530
C	1.116235	0.826932	1.379960
C	-1.113551	-0.821731	-1.379095
C	-1.332805	-0.348494	2.160232
C	1.227337	-0.988144	-2.112478
C	-0.001072	-1.603331	-1.737729
C	-3.844140	-3.239934	-0.712401
C	-2.468212	-2.677873	-1.046598
C	1.006162	-0.608842	1.444446
C	-0.219083	-1.175119	1.841821
C	-4.047665	-3.211801	0.802587
C	-3.978561	-4.683945	-1.195614
C	-0.175611	-2.992133	-1.712662
C	-1.396140	-3.519582	-1.389908
C	-0.278269	-2.572376	1.897311
C	2.054422	-2.667871	1.304518
C	0.844139	-3.307358	1.634567
C	4.525176	-2.731072	1.701129
C	3.330974	-3.471554	1.098067
C	3.532615	-3.689317	-0.401946
C	3.256968	-4.834686	1.786413
H	-4.228318	5.330140	-1.642216
H	-2.503097	5.491906	-1.358012
H	-3.093194	4.732976	-2.855311
H	-4.488480	4.201995	0.587401
H	-5.430748	3.334084	-1.575345
H	-2.737512	4.312045	0.811791
H	-0.810005	4.391993	-1.663955
H	-4.373293	2.561281	-2.765301
H	-3.575782	2.738903	0.938795
H	-4.718617	1.769198	-1.213027
H	3.318109	5.371144	0.660447
H	1.541084	4.594502	1.388059
H	-0.648186	3.645938	1.970433
H	3.332213	3.866785	-1.304914
H	1.208737	3.061201	-2.159593
H	5.006423	5.036630	1.001185
H	3.800897	4.769232	2.256175
H	5.050196	3.570436	-1.052958
H	-2.077010	1.620142	2.361521
H	3.962574	2.195989	-1.220714
H	-4.904633	-1.366355	-1.155685
H	-4.810444	-2.506609	-2.503645
H	2.270875	0.823207	-2.441881

H	5.919376	2.806587	1.139045
H	-5.912793	-2.811411	-1.152217
H	-2.270448	-0.810365	2.447613
H	4.820304	2.512569	2.496175
H	4.906079	1.365271	1.154300
H	-3.964117	-2.203289	1.214875
H	-5.047412	-3.581097	1.041276
H	2.082670	-1.607213	-2.358229
H	-3.791542	-4.764463	-2.270222
H	-4.996897	-5.038520	-1.016724
H	-3.328814	-3.872272	1.296079
H	-1.213418	-3.050273	2.167467
H	0.658107	-3.636789	-1.966886
H	-3.308576	-5.371426	-0.676464
H	-1.529234	-4.590211	-1.386389
H	4.716374	-1.772001	1.216886
H	3.565959	-2.739995	-0.934990
H	4.369444	-2.562835	2.769531
H	0.802708	-4.385906	1.672882
H	2.730112	-4.314196	-0.805098
H	5.424772	-3.338584	1.579706
H	4.481326	-4.201303	-0.583569
H	3.086608	-4.731844	2.860646
H	2.492137	-5.489534	1.364499
H	4.218297	-5.331830	1.645710
N	-2.099957	1.352714	-1.166021
N	2.296441	1.364217	1.004233
N	-2.293255	-1.361739	-1.005587
N	2.097980	-1.349872	1.168827
Cu	-3.417726	0.051547	-0.091455
Cu	3.419221	-0.054833	0.094126
Br	-4.973352	0.459976	1.541635
Br	4.976161	-0.464983	-1.537979

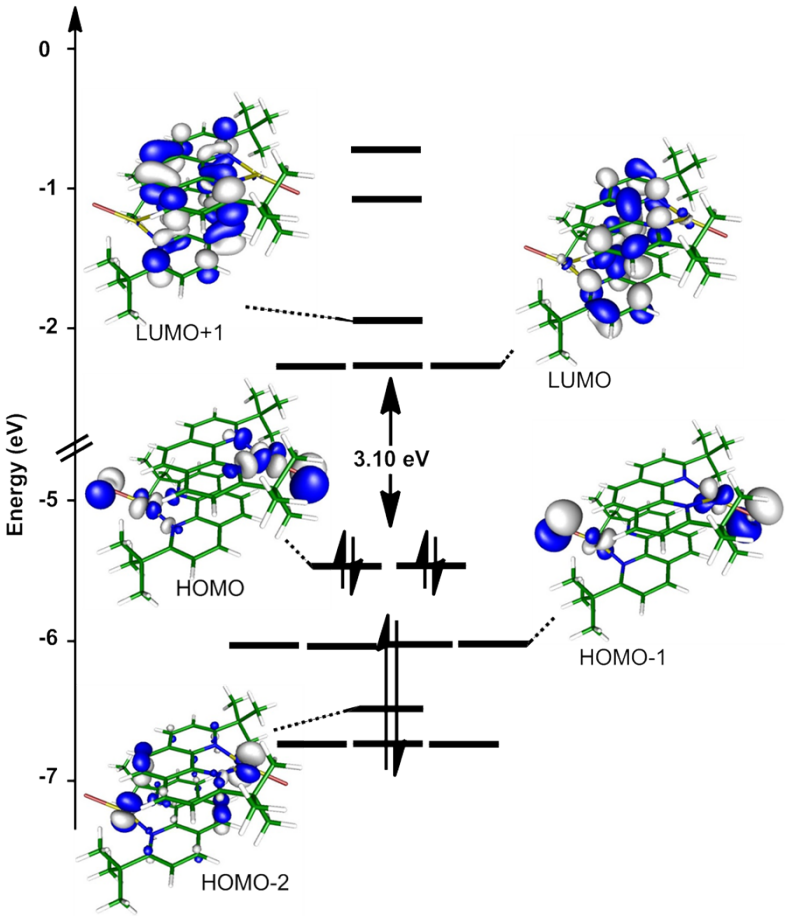

Figure S10. Molecular orbital diagram of **2π** showing selected frontier orbitals.

Table S7. Cartesian coordinates of the optimized T_1 of complex **2π**

C	-3.265574	4.835264	-1.781337
C	-3.540270	3.688731	0.406693
C	-3.337278	3.471904	-1.093249
C	-4.529578	2.728906	-1.696870
C	-0.849611	3.313295	-1.627559
C	-2.058950	2.670962	-1.299518
C	0.274328	2.580951	-1.891110
C	1.405155	3.524233	1.390817
C	3.987514	4.684801	1.181853
C	0.183853	2.999542	1.715132
C	4.049802	3.205297	-0.810970
C	3.849977	3.239107	0.704461
C	0.217947	1.183488	-1.837961
C	2.474224	2.679992	1.044186
C	-1.006443	0.614333	-1.442019
C	0.005966	1.611130	1.739726
C	-1.223462	0.998776	2.115672
C	1.333615	0.359418	-2.156229
C	-4.927478	-2.425088	-1.419931
C	4.933762	2.425360	1.412530
C	1.116235	0.826932	1.379960
C	-1.113551	-0.821731	-1.379095
C	-1.332805	-0.348494	2.160232
C	1.227337	-0.988144	-2.112478

C	-0.001072	-1.603331	-1.737729
C	-3.844140	-3.239934	-0.712401
C	-2.468212	-2.677873	-1.046598
C	1.006162	-0.608842	1.444446
C	-0.219083	-1.175119	1.841821
C	-4.047665	-3.211801	0.802587
C	-3.978561	-4.683945	-1.195614
C	-0.175611	-2.992133	-1.712662
C	-1.396140	-3.519582	-1.389908
C	-0.278269	-2.572376	1.897311
C	2.054422	-2.667871	1.304518
C	0.844139	-3.307358	1.634567
C	4.525176	-2.731072	1.701129
C	3.330974	-3.471554	1.098067
C	3.532615	-3.689317	-0.401946
C	3.256968	-4.834686	1.786413
H	-4.228318	5.330140	-1.642216
H	-2.503097	5.491906	-1.358012
H	-3.093194	4.732976	-2.855311
H	-4.488480	4.201995	0.587401
H	-5.430748	3.334084	-1.575345
H	-2.737512	4.312045	0.811791
H	-0.810005	4.391993	-1.663955
H	-4.373293	2.561281	-2.765301
H	-3.575782	2.738903	0.938795
H	-4.718617	1.769198	-1.213027
H	3.318109	5.371144	0.660447
H	1.541084	4.594502	1.388059
H	-0.648186	3.645938	1.970433
H	3.332213	3.866785	-1.304914
H	1.208737	3.061201	-2.159593
H	5.006423	5.036630	1.001185
H	3.800897	4.769232	2.256175
H	5.050196	3.570436	-1.052958
H	-2.077010	1.620142	2.361521
H	3.962574	2.195989	-1.220714
H	-4.904633	-1.366355	-1.155685
H	-4.810444	-2.506609	-2.503645
H	2.270875	0.823207	-2.441881
H	5.919376	2.806587	1.139045
H	-5.912793	-2.811411	-1.152217
H	-2.270448	-0.810365	2.447613
H	4.820304	2.512569	2.496175
H	4.906079	1.365271	1.154300
H	-3.964117	-2.203289	1.214875
H	-5.047412	-3.581097	1.041276
H	2.082670	-1.607213	-2.358229
H	-3.791542	-4.764463	-2.270222
H	-4.996897	-5.038520	-1.016724
H	-3.328814	-3.872272	1.296079
H	-1.213418	-3.050273	2.167467
H	0.658107	-3.636789	-1.966886
H	-3.308576	-5.371426	-0.676464
H	-1.529234	-4.590211	-1.386389
H	4.716374	-1.772001	1.216886
H	3.565959	-2.739995	-0.934990
H	4.369444	-2.562835	2.769531
H	0.802708	-4.385906	1.672882
H	2.730112	-4.314196	-0.805098
H	5.424772	-3.338584	1.579706
H	4.481326	-4.201303	-0.583569
H	3.086608	-4.731844	2.860646
H	2.492137	-5.489534	1.364499
H	4.218297	-5.331830	1.645710
N	-2.099957	1.352714	-1.166021

N	2.296441	1.364217	1.004233
N	-2.293255	-1.361739	-1.005587
N	2.097980	-1.349872	1.168827
Cu	-3.417726	0.051547	-0.091455
Cu	3.419221	-0.054833	0.094126
Br	-4.973352	0.459976	1.541635
Br	4.976161	-0.464983	-1.537979

Table S8 Cartesian coordinates of the optimized ground state (S_0) of complex **3**

Cu	13.34598600	9.50106100	2.64759100
Cl	14.59403300	10.36697800	0.99254800
N	12.75939100	10.00853600	4.58995000
C	13.11484300	11.05888400	5.36370200
C	11.84317500	9.09485000	5.03829600
C	11.50001300	7.96736400	4.18979400
N	12.10226400	7.85024100	2.96552900
C	10.25538900	5.92780100	3.81243200
C	14.14604100	12.06169200	4.83647700
C	11.81890700	6.80191100	2.15986300
C	11.22202400	9.20903100	6.31031300
C	10.26509500	8.23261300	6.74873500
C	9.94229500	7.17177900	5.95045600
C	12.52300600	11.22075700	6.64768800
C	10.55517900	7.01768700	4.66130600
C	13.56892900	12.76793200	3.58528000
C	11.58983600	10.31338900	7.11248400
C	15.45690700	11.31918800	4.48435200
C	10.87964900	5.82062000	2.58404100
C	12.51175200	6.69626800	0.79761900
C	12.08470900	7.89839000	-0.07978000
C	14.47876400	13.14267600	5.88566100
C	14.04603600	6.68731800	0.99649500
C	12.12054900	5.40043700	0.05752800
H	9.53755300	5.18018800	4.13455100
H	9.80807600	8.35524600	7.72530700
H	9.22171000	6.42822000	6.27522500
H	12.80758100	12.06125900	7.26242700
H	13.38946300	12.06416100	2.76925700
H	12.63504700	13.28932800	3.82751500
H	14.29121100	13.50479500	3.21913600
H	11.13731400	10.43840700	8.09104100
H	15.31005300	10.59419000	3.68038000
H	16.19875300	12.04191300	4.12964100
H	15.86461400	10.80648100	5.36377800
H	10.65438100	4.98549600	1.93814900
H	12.40906300	8.84903600	0.34970800
H	12.55633600	7.81467200	-1.06430000
H	10.99681000	7.91405400	-0.21728000
H	14.90031600	12.71562100	6.80314300
H	15.23117900	13.81491400	5.46284500
H	13.60691900	13.75443900	6.14474600
H	14.40400400	7.61959700	1.43952400
H	14.35389200	5.84518400	1.62777900
H	14.53708300	6.58839600	0.02305400
H	12.39890200	4.50092000	0.61900400
H	11.04988100	5.35954100	-0.17379100
H	12.65828700	5.37024000	-0.89469700

Table S9. Cartesian coordinates of the optimized ground state (S_0) of complex **4m**

C	7.65933500	17.94869800	34.08197900
C	7.17439900	18.20730400	35.39503200
H	7.65545200	17.73966100	36.24077800
C	6.09653500	19.04872500	35.59619100
H	5.72539000	19.24108700	36.59778800
C	5.47551500	19.67243400	34.48992000
C	6.00066600	19.38049200	33.20373800
C	5.40925100	20.01906800	32.04299500
C	4.32455700	20.91542500	32.23076900
C	3.79389700	21.53549000	31.07645600
H	2.96200700	22.22578500	31.17341500
C	4.34259300	21.26493100	29.83710600
H	3.94432100	21.74677500	28.95699500
C	5.42969900	20.35537700	29.70654000
C	4.36554200	20.57101200	34.63923700
H	3.98398800	20.76424100	35.63655100
C	3.80849200	21.17266200	33.54579200
H	2.97262600	21.85658200	33.65133100
H	7.60215700	15.21036500	33.71773200
H	7.91744600	15.98531000	32.14327600
C	6.03556000	20.04432100	28.33383200
C	7.56265900	20.28754600	28.36870500
H	8.05952600	19.64134800	29.09531900
H	7.98961900	20.05793700	27.38720300
H	7.78729600	21.33375300	28.60798800
C	5.72728900	18.56957700	27.97441700
H	4.64534200	18.40017900	27.91869500
H	6.16401400	18.33266700	26.99885300
H	6.16066700	17.87926200	28.70049500
C	5.43987100	20.94090500	27.22852700
H	5.60494500	22.00671900	27.42488000
H	5.93630800	20.70090700	26.28367200
H	4.36773200	20.76707300	27.08234900
C	8.34959300	17.07299400	29.83069400
N	7.05672600	18.52907700	33.01982900
N	5.92859600	19.74677800	30.80601700
N	8.96624100	16.34800100	29.11752200
Cu	7.37898900	18.23718700	30.96586900
C	8.84831200	17.00971100	33.85256200
C	9.49376200	16.56757100	35.18235600
H	10.35600900	15.93405300	34.95434600
H	9.85755400	17.41841200	35.77014000
H	8.81159300	15.97281900	35.80039700
C	8.34895400	15.74194100	33.11596000
H	9.19246400	15.06700300	32.93838200
C	9.93183500	17.73183400	33.01774600
H	9.55740200	18.02566100	32.03494900
H	10.30067400	18.62212300	33.54081800
H	10.77510100	17.05362100	32.85255500

Table S10. Cartesian coordinates of the optimized ground state (S_0) of complex **5**

C	5.3205584	-2.8308422	-0.0017740
C	6.6029985	-0.6816611	-0.0014210
C	4.0903863	-3.4629053	-0.0013400
C	5.3706444	-1.4192791	-0.0010680
C	6.6028425	0.6829511	-0.0006500
C	2.9211432	-2.6762162	-0.0001560
C	4.1372413	-0.7228591	0.0000720
C	5.3703224	1.4202941	0.0004690
C	4.1370743	0.7235971	0.0007610
C	-4.0908933	-3.4627883	0.0049640
C	5.3199404	2.8318432	0.0013050
C	-2.9215482	-2.6762682	0.0033710
C	-5.3209874	-2.8305632	0.0041400
C	4.0896323	3.4636393	0.0023760
C	2.9205622	2.6767012	0.0025150
C	-5.3708814	-1.4190011	0.0017640
C	-4.1373893	-0.7227451	0.0003470
C	-6.6031355	-0.6812061	0.0007490
C	-4.1370193	0.7237131	-0.0020090
C	-6.6027925	0.6834021	-0.0015450
C	-5.3701704	1.4205811	-0.0029730
C	-2.9202162	2.6766222	-0.0054150
C	-5.3195764	2.8321182	-0.0053130
C	-4.0891683	3.4637313	-0.0065550
H	6.2467455	-3.4049813	-0.0026520
H	7.5417816	-1.2348471	-0.0022930
H	4.0094533	-4.5476713	-0.0018760
H	7.5414976	1.2363551	-0.0008960
H	1.9367471	-3.1424182	0.0001780
H	-4.0101073	-4.5475643	0.0068000
H	-1.9372161	-3.1426002	0.0039460
H	6.2460045	3.4061803	0.0011050
H	-6.2472465	-3.4045843	0.0052930
H	4.0084583	4.5483873	0.0030980
H	1.9360751	3.1427072	0.0033570
H	-7.5419926	-1.2342651	0.0018440
H	-7.5413736	1.2369321	-0.0023140
H	-1.9356551	3.1424692	-0.0063700
H	-6.2455485	3.4066003	-0.0061160
H	-4.0078433	4.5484683	-0.0083770
N	2.9389742	-1.3518411	0.0005740
N	2.9386582	1.3523201	0.0016700
N	-2.9392012	-1.3518771	0.0011100
N	-2.9385172	1.3522461	-0.0031850
Cu	1.2968221	0.0002270	0.0014550
Cu	-1.2968691	-0.0004590	-0.0008700
I	-0.0014740	0.0014080	2.2916492
I	0.0015640	-0.0030220	-2.2910562

Table S11. Cartesian coordinates of the optimized T_1 of complex **5**

C	5.2573856	-2.8251820	-0.0013876
C	6.5342664	-0.6772370	-0.0007740
C	4.0165250	-3.4685919	-0.0013089
C	5.3040750	-1.4220340	-0.0007466
C	6.5331083	0.6867517	-0.0001279
C	2.8542415	-2.6871355	-0.0005698
C	4.0709985	-0.7112583	-0.0000319
C	5.3016352	1.4293773	0.0005869
C	4.0697737	0.7164576	0.0006003
C	-4.0169350	-3.4684953	0.0023647
C	5.2524506	2.8324336	0.0012880
C	-2.8545659	-2.6872144	0.0015976
C	-5.2577357	-2.8249247	0.0019641
C	4.0105025	3.4736285	0.0019812
C	2.8495792	2.6900188	0.0019184
C	-5.3042348	-1.4217710	0.0008217
C	-4.0710789	-0.7111455	0.0001118
C	-6.5343398	-0.6768134	0.0003372
C	-4.0696925	0.7165690	-0.0010356
C	-6.5330332	0.6871749	-0.0007841
C	-5.3014741	1.4296400	-0.0015130
C	-2.8492530	2.6899389	-0.0028001
C	-5.2520989	2.8326890	-0.0026900
C	-4.0100897	3.4737231	-0.0033553
H	6.1845460	-3.3973976	-0.0019412
H	7.4743473	-1.2286130	-0.0013187
H	3.9367080	-4.5528628	-0.0018049
H	7.4722451	1.2397365	-0.0001432
H	1.8722667	-3.1595151	-0.0005011
H	-3.9372552	-4.5527760	0.0032536
H	-1.8726537	-3.1597178	0.0018957
H	6.1786004	3.4062910	0.0012960
H	-6.1849672	-3.3970219	0.0025279
H	3.9287806	4.5577600	0.0025617
H	1.8667797	3.1607033	0.0024587
H	-7.4744824	-1.2280838	0.0008835
H	-7.4721083	1.2402649	-0.0011496
H	-1.8663912	3.1604993	-0.0033068
H	-6.1781774	3.4066645	-0.0030801
H	-3.9282302	4.5578440	-0.0042882
N	2.8634077	-1.3559368	0.0000731
N	2.8610334	1.3588998	0.0012268
N	-2.8635635	-1.3559833	0.0004941
N	-2.8608758	1.3588523	-0.0016608
Cu	1.2861939	-0.0008098	0.0008361
Cu	-1.2861983	-0.0015300	-0.0005420
I	-0.0010204	-0.0038822	2.2459929
I	0.0010213	-0.0052941	-2.2457190

Table S12. Vertical electronic excitation energies and main transitions describing selected Franck-Condon states of 1 obtained by TD-DFT calculations

State	Energy [eV]	Energy [nm]	Oscillator strength *f*	Transitions (%)[a]	Classification
S_1	2.83	438	0.0003	H→L (77), H-3→L (18)	^{1}XMLCT
S_2	3.32	374	0.0020	H→L+1 (83)	^{1}XMLCT
S_3	3.48	356	0.0087	H-1→L (87)	^{1}XMLCT
S_4	3.56	348	0.0416	H-2→L (85)	^{1}XMLCT
S_6	3.99	311	0.0266	H-2→L+1 (88)	^{1}XMLCT
S_{13}	4.56	272	0.0178	H-4→L+1 (58), H-7→L (27), H-6→L+1 (7)	^{1}MLCT
S_{14}	4.70	264	0.0433	H-6→L+1 (42), H-4→L+1 (30), H-7→L (19)	^{1}XMLCT
S_{19}	4.94	251	0.5469	H-7→L (32), H-6→L+1 (23)	^{1}XMLCT
T_1	2.00	620	-	H-4→L+1 (25), H-6→L+1 (17), H→L (11), H-7→L (11), H-3→L (7), H-2→L+1 (6)	^{3}XMLCT
T_2	2.36	525	-	H→L (59), H-3→L (16)	^{3}XMLCT

[a] Only major contributions >5% are given; H = HOMO, L = LUMO

Table S13. Vertical electronic excitation energies and main transitions describing selected Franck-Condon states of 3 obtained by TD-DFT calculations

State	Energy [eV]	Energy [nm]	Oscillator strength *f*	Transitions (%)[a]	Classification
S_1	2.60	477	0.0000	H→L (89)	^{1}XMLCT
S_2	3.21	386	0.0002	H→L+1 (92)	^{1}XMLCT
S_3	3.25	382	0.0009	H-1→L (82), H-2→L (10)	^{1}XMLCT
S_4	3.60	345	0.0294	H-2→L (74), H-1→L (9), H-8→L (7)	^{1}XMLCT
S_8	4.09	303	0.0215	H-2→L+1 (80), H-1→L+1 (6), H-8→L+1 (5)	^{1}XMLCT
S_{15}	4.77	260	0.3453	H-7→L(27), H-6→L+1 (19), H→L+9 (9), H→L+5 (7)	^{1}XMLCT
T_1	2.45	505	-	H→L (86)	^{3}XMLCT
T_2	2.57	482	-	H-6→L+1 (52), H-7→L (14), H-10→L (5)	^{3}XMLCT

[a] Only major contributions >5% are given; H = HOMO, L = LUMO.

Table S14. Vertical electronic excitation energies and main transitions describing the first 50 Franck-Condon singlet states of 2π obtained by TD-DFT calculations

State	Energy (cm-1)	Wavelength (nm)	fosc	T2 (au**2)	TX (au)	TY (au)	TZ (au)
1	21842.3	457.8	0.000345013	0.00520	-0.05396	-0.04627	-0.01214
2	21852.7	457.6	0.000304825	0.00459	0.05028	0.04372	0.01235
3	26452.9	378.0	0.000184534	0.00230	0.00161	0.00147	-0.04787
4	26487.0	377.5	0.003201862	0.03980	-0.00527	-0.00622	0.19932
5	27895.6	358.5	0.023695304	0.27964	0.51169	-0.07684	-0.10911
6	27987.3	357.3	0.000277312	0.00326	-0.05514	0.00845	0.01224
7	29749.8	336.1	0.000304107	0.00337	-0.04932	0.00983	0.02892
8	29792.8	335.7	0.037469159	0.41404	-0.54270	0.11338	0.32658
9	30127.6	331.9	0.000187037	0.00204	-0.03330	-0.02912	0.00933
10	30133.8	331.9	0.000145430	0.00159	-0.02656	-0.02935	0.00472
11	30590.2	326.9	0.000001177	0.00001	-0.00279	-0.00095	-0.00200
12	30625.0	326.5	0.014070423	0.15125	0.38073	0.07939	0.00034
13	30922.6	323.4	0.000007374	0.00008	0.00312	-0.00049	-0.00828
14	31184.8	320.7	0.012507120	0.13204	0.11690	-0.07468	-0.33585
15	31381.4	318.7	0.000000369	0.00000	-0.00167	-0.00104	0.00005
16	31785.2	314.6	0.000679813	0.00704	0.05844	0.05992	-0.00592
17	31809.8	314.4	0.000128117	0.00133	0.02559	0.02578	-0.00250
18	32346.0	309.2	0.003087328	0.03142	0.10828	-0.13416	-0.04123
19	33211.3	301.1	0.001808050	0.01792	0.00723	-0.06488	-0.11688
20	33255.9	300.7	0.000014381	0.00014	-0.00116	-0.00355	-0.01133
21	33441.4	299.0	0.000508600	0.00501	-0.05245	0.01861	-0.04370
22	33454.1	298.9	0.001567712	0.01543	-0.09641	0.03243	-0.07128
23	34272.9	291.8	0.052380842	0.50315	-0.18167	-0.68520	0.02541
24	34696.9	288.2	0.003038214	0.02883	-0.06799	-0.14210	0.06334
25	34707.9	288.1	0.000480670	0.00456	-0.02626	-0.05711	0.02465
26	35169.2	284.3	0.005575422	0.05219	0.10489	-0.18933	0.07310
27	35445.8	282.1	0.000000927	0.00001	0.00214	0.00187	0.00074
28	35487.4	281.8	0.009219944	0.08553	-0.27580	-0.08581	-0.04587
29	35541.3	281.4	0.000001611	0.00001	0.00370	-0.00076	0.00080
30	35952.4	278.1	0.000020794	0.00019	-0.01343	0.00052	-0.00313
31	36009.9	277.7	0.003659797	0.03346	-0.17270	0.04972	-0.03407
32	36257.8	275.8	0.000000808	0.00001	0.00174	0.00198	-0.00061
33	36307.4	275.4	0.000000744	0.00001	0.00027	0.00258	-0.00015
34	36418.3	274.6	0.001002892	0.00907	0.04705	0.08220	0.00976
35	37220.0	268.7	0.000000017	0.00000	0.00003	0.00036	-0.00013
36	37395.8	267.4	0.000051412	0.00045	0.01808	-0.00567	-0.00967
37	37575.9	266.1	0.025496397	0.22338	-0.39720	0.16175	0.19862
38	37734.5	265.0	0.039790957	0.34715	0.16933	0.56434	0.00160
39	38821.4	257.6	0.004206590	0.03567	0.04284	0.18390	0.00443
40	38835.2	257.5	0.006768823	0.05738	0.04906	0.23437	0.00657
41	39040.4	256.1	0.000022749	0.00019	0.00469	0.01303	0.00030
42	39216.2	255.0	0.000015300	0.00013	0.00043	0.01126	0.00125
43	39781.8	251.4	0.034630146	0.28658	0.42610	-0.21234	-0.24480
44	39897.9	250.6	0.261033452	2.15388	-0.27533	-1.44119	-0.03230
45	40260.9	248.4	0.000023043	0.00019	0.00539	0.01245	-0.00207
46	40465.2	247.1	0.000112618	0.00092	0.00165	-0.02944	-0.00686
47	40510.5	246.8	0.002259425	0.01836	0.05780	-0.10964	-0.05476
48	40538.8	246.7	0.000159509	0.00130	-0.00454	0.03570	0.00064
49	40574.9	246.5	0.001874893	0.01521	-0.04253	0.11022	-0.03544
50	40653.7	246.0	0.000788476	0.00639	-0.02916	-0.07400	0.00767

X-Ray diffraction: All crystals were rapidly transferred into inert perfluoroether oil mounted on top of a glass fiber (**1**) human hair (**2**, **4**) and transferred to the cold nitrogen gas stream of the diffractometer.[2a] Data set of **1** was collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT;[2b] data reduction Denzo-SMN;[2c] absorption correction, Denzo;[2d] structure solution SHELXS-97;[2e] structure refinement SHELXL-97 and graphics, XP.[2f,g] The data sets for **2** and **4** were collected on an Oxford Diffraction Xcalibur E instrument using monochromated MoKα radiation. The data were integrated and an empirical absorption correction was performed employing the CrysAlisPro software.[2h] The structures were solved employing SHELXS-97 and refined anisotropically for all non-hydrogen atoms by full-matrix least squares on all F^2 using SHELXL-97.[2e,f] During refinement and analysis of the crystallographic data the programs WinGX, PLATON, Ortep-3 and POV-Ray were used.[2i,j,k,l]

X-ray crystal structure analysis of 1 (CCDC No. 1006445): Compound **1** crystallized with two independent molecules per asymmetric unit. formula $C_{20}H_{24}CuIN_2$, M = 482.85, yellow crystal, 0.23 x 0.13 x 0.05 mm, a = 20.4147(4), b = 9.7229(2), c = 19.5841(3) Å, V = 3887.25(13) Å^3, ρ_{calc} = 1.650 gcm^{-3}, μ = 2.715 mm^{-1}, empirical absorption correction ($0.574 \leq T \leq 0.876$), Z = 8, orthorhombic, space group $Pca2_1$ (No. 29), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 16417 reflections collected ($\pm h$, $\pm k$, $\pm l$), 6417 independent (R_{int} = 0.050) and 5971 observed reflections [$I>2\sigma(I)$], 446 refined parameters, max./min. residual electron density 2.20/-0.54 e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

X-ray crystal structure analysis of 2 (CCDC No. 1006215): Compound **2** crystallized with one independent molecule per asymmetric unit. formula $C_{20}H_{24}BrCuN_2$, M = 435.86, dark orange crystal, 0.36 x 0.44 x 0.48 mm, a = 9.6421(3), b = 19.6933(5), c = 19.7231(5) Å, V = 3745.12(18) Å^3, ρ_{calc} = 1.546 gcm^{-3}, μ = 3.303 mm^{-1}, multi-scan absorption correction ($0.771 \leq T \leq 1.000$), Z = 8, orthorhombic, space group *Pbca* (No. 61), λ = 0.71073 Å, T = 100(2) K, ω scans, 143456 reflections collected ($-13 \leq h \leq 13$, $-27 \leq k \leq 27$, $-27 \leq l \leq 27$), 5456 independent (R_{int} = 0.0703) and 4443 observed reflections [$I>2\sigma(I)$], 223 refined parameters, max. (min.) residual electron density 0.533/–0.490 e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

X-ray crystal structure analysis of 4 (CCDC No. 1006216): Compound **4** crystallized with one independent molecule per asymmetric unit. formula $C_{22}H_{24}Cu_2N_2$, M = 471.53, dark orange crystal, 0.44 x 0.42 x 0.33 mm, a = 8.5167(3), b = 12.2692(3), c = 20.6552(5) Å, β = 94.754(3)°, V = 2150.90(11) Å^3, ρ_{calc} = 1.456 gcm^{-3}, μ = 1.991 mm^{-1}, multi-scan absorption correction ($0.854 \leq T \leq 1.000$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 100(2) K, ω scans, 42497 reflections collected ($-11 \leq h \leq 11$, $-17 \leq k \leq 16$, $-28 \leq l \leq 28$), 5951 independent (R_{int} = 0.0502) and 4858 observed reflections [$I>2\sigma(I)$], 277 refined parameters (24 restraints), max./min. residual electron density 0.406/–0.293 e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms. Two sites are occupied by disordered

CN moieties and were refined employing a split atom model; a ISOR restraints were applied to the disordered atom pairs.

X-ray powder diffractometric: investigations were done using a Bruker D8 Discover (DA VINCI® design) powder diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) with a copper tube operated at 40 kV and 40 mA (unsplit $K\alpha_1$+$K\alpha_2$ doublet, mean wavelength λ = 154.19 pm). A focusing Goebel mirror and a 0.6 mm fixed divergence slit were mounted in the primary beam path, the receiving slit in the secondary beam path was used with 7.5 mm opening. 2.5° axial Soller slits were used in both beam paths. Detection was done with a LynxEye® (Bruker AXS) 1D-detector using the full detector range of 192 channels.

Measurements were done in 'Coupled Two Theta/Theta' mode, with a 2θ range of 5 – 60°, a step width of 0.025° and 0.25 seconds measurement time per step.

Data collection and processing was done with the software packages DIFFRAC.Suite (V2 2.2.690, Bruker AXS 2009-2011) and DIFFRAC.EVA (Version 3.0, Bruker AXS 2010-2013).

[1] Pallenberg, A. J.; Koenig, K. S.; Barnhart, D. M., *Inorg. Chem.* **1995**, *34*, 2833-2840.

[2] (a) Stalke, D. *Chem. Soc. Rev.* **1998**, *27*, 171-178. (b) Nonius B.V., **1998**. (c) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307-326. (d) Otwinowski, Z.; Borek, D.; Majewski, W.; Minor, W. *Acta Crystallogr*. **2003**, *A59*, 228-234. (e) Sheldrick, G. M. *Acta Crystallogr*. **1990**, *A46*, 467-473. (f) Sheldrick, G. M. *Acta Crystallogr*. **2008**, *A64*, 112-122. (g) BrukerAXS, **2000**. (h) CrysAlisPro, Agilent Technologies, Version 1.171.34.44 – 1.171.36.24, **2010**–**2012**. (i) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837–838. (j) Spek, A. L. PLATON - A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, **1998**. (k) Farrugia, L. J. *J. Appl. Cryst* (2012), **45**, 849-854. (l) Persistence of Vision Pty. Ltd. (2004), Persistence of Vision Raytracer (Version 3.6), Retrieved from http://www.povray.org/download/