Electronic Supplementary Information

for

Alkyl Pyridinium Iodocyanocuprate(I) Chains $(RPy)_2[Cu_2I_3(CN)]$: Insight into Structural, Electronic and Spectroscopic Properties

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Figure S1. X-ray Structure of **2**, anion shown as ball and stick, cation shown as wireframe. A: chain structure; B: unit cell viewed between *a*- and *c*-axes. Color scheme: orange = Cu, purple = I, grey = C, blue = N.

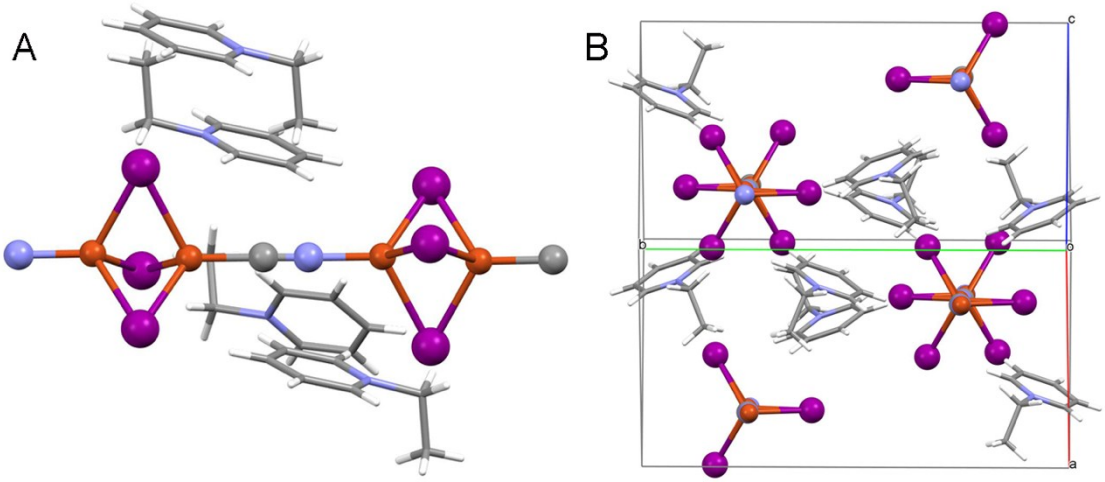


Figure S2. X-ray Structure of **4**, anion shown as ball and stick, cation shown as wireframe. A: chain structure with disorder shown in one pair of cations as non-connected atoms; B: unit cell viewed down *a*-axis. Color scheme: orange = Cu, purple = I, grey = C, blue = N.

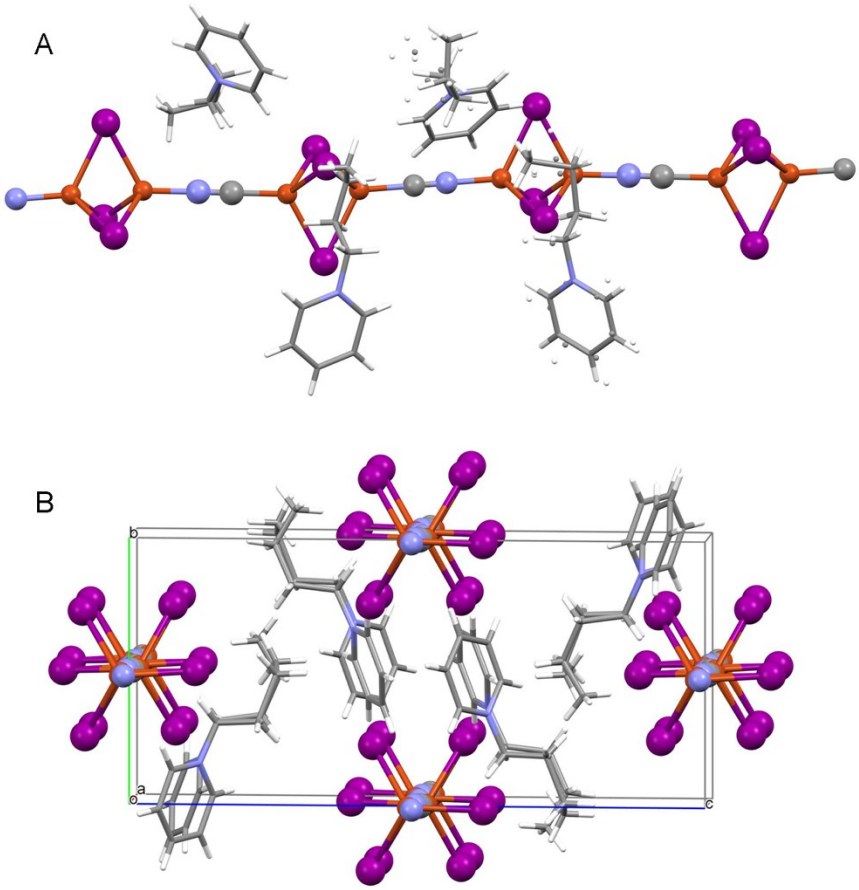


Figure S3. Chain Overlay for **1**–**4**. C/N atoms at ends of four-unit chain segments co-located. Color key: blue = **1**, red = **2**, green = **3**, orange = **4**.

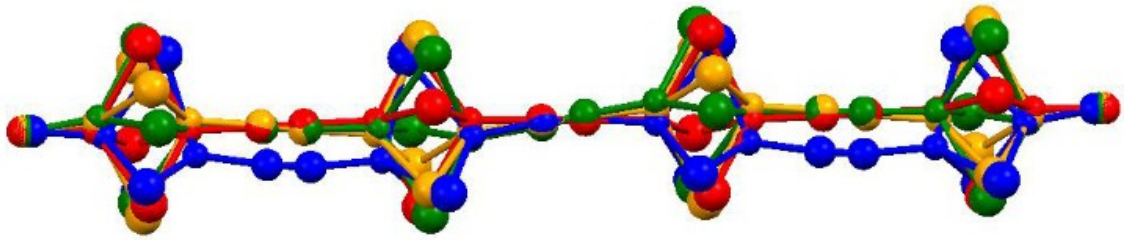


Figure S4. PXRD Overlay for **1**, $(MePy)_2[Cu_2I_3CN]$.

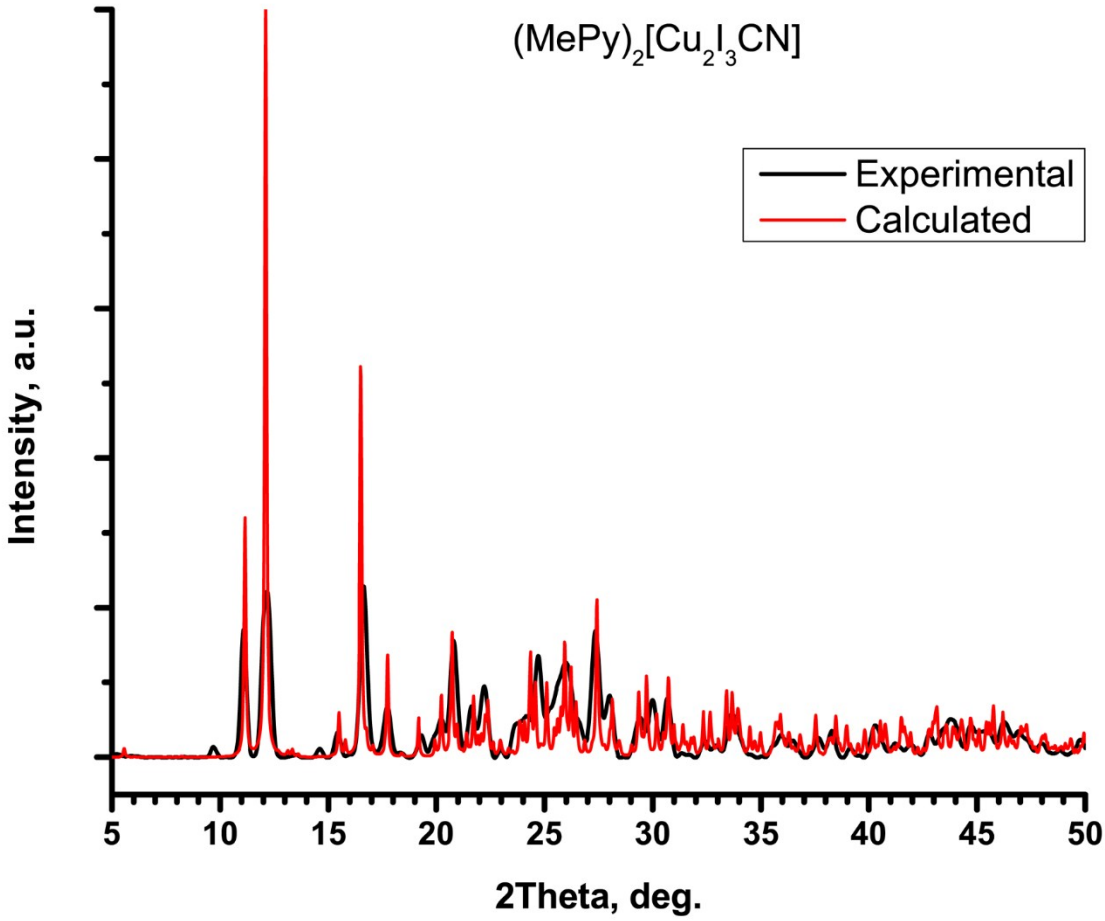


Figure S5. PXRD Overlay for **2**, $(EtPy)_2[Cu_2I_3CN]$.

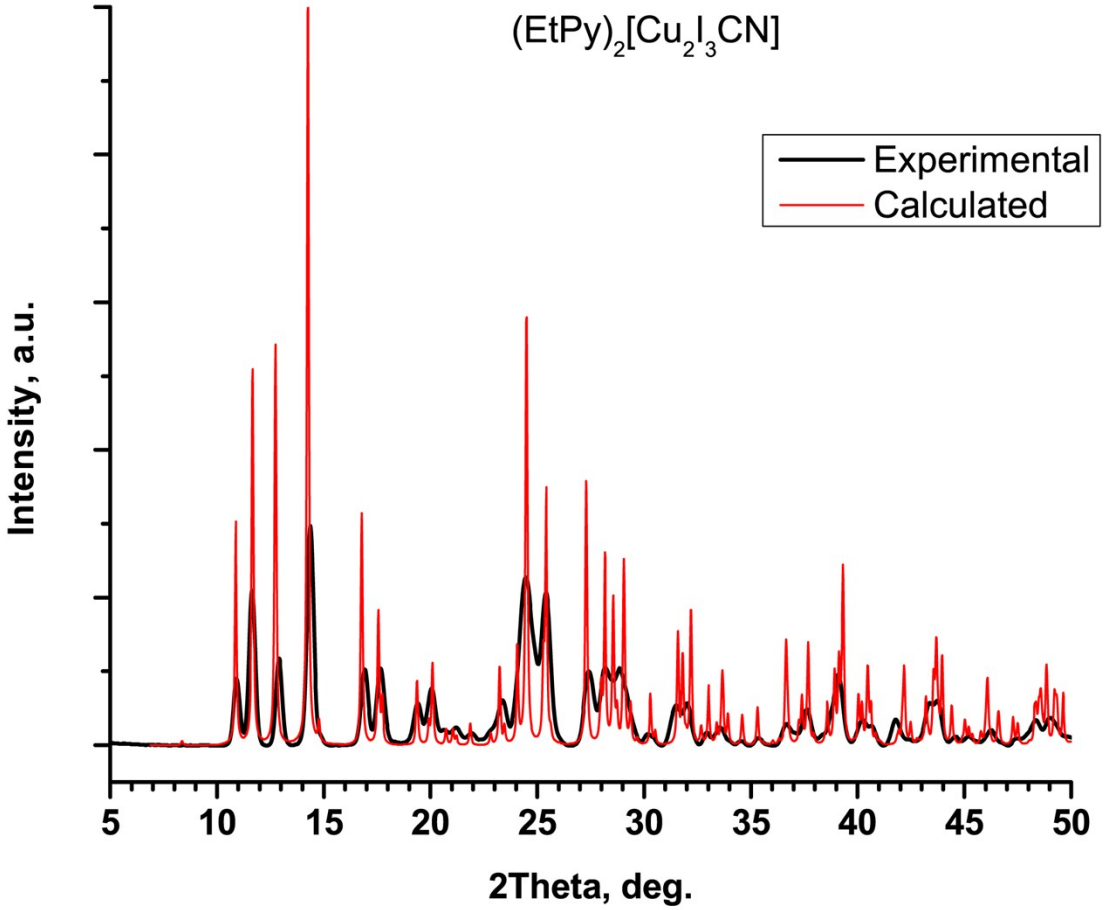


Figure S6. PXRD Overlay for **3**, $(PrPy)_2[Cu_2I_3CN]$.

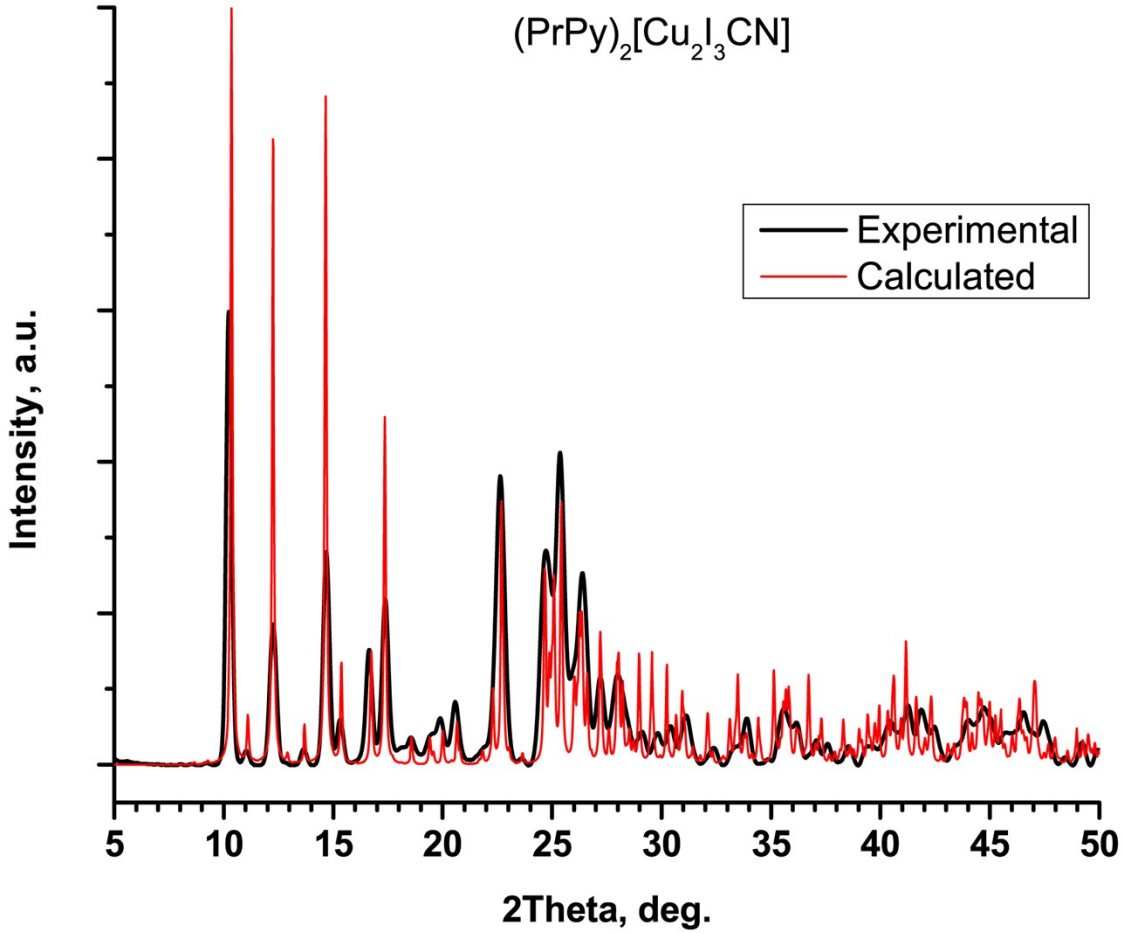


Figure S7. PXRD Overlay for **4**, $(BuPy)_2[Cu_2I_3CN]$.

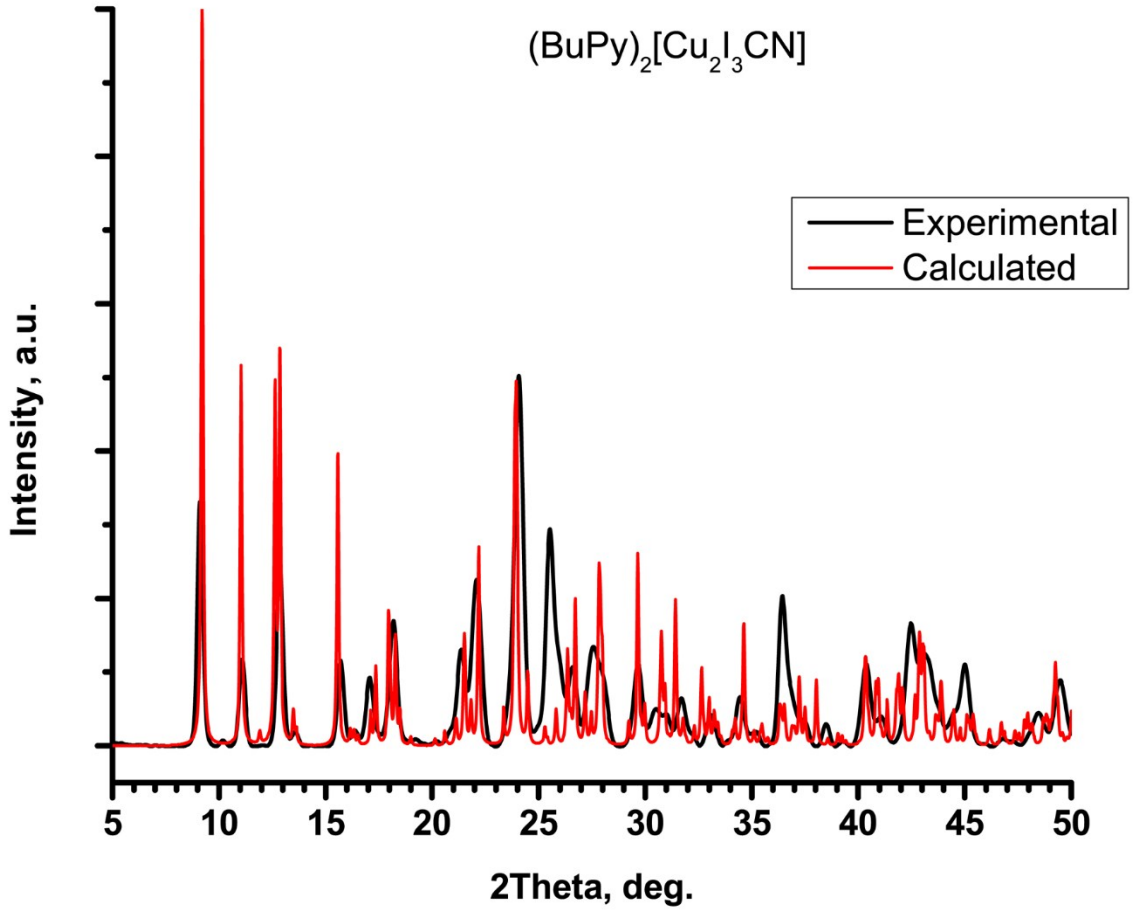


Figure S8. IR Spectrum for **1**.

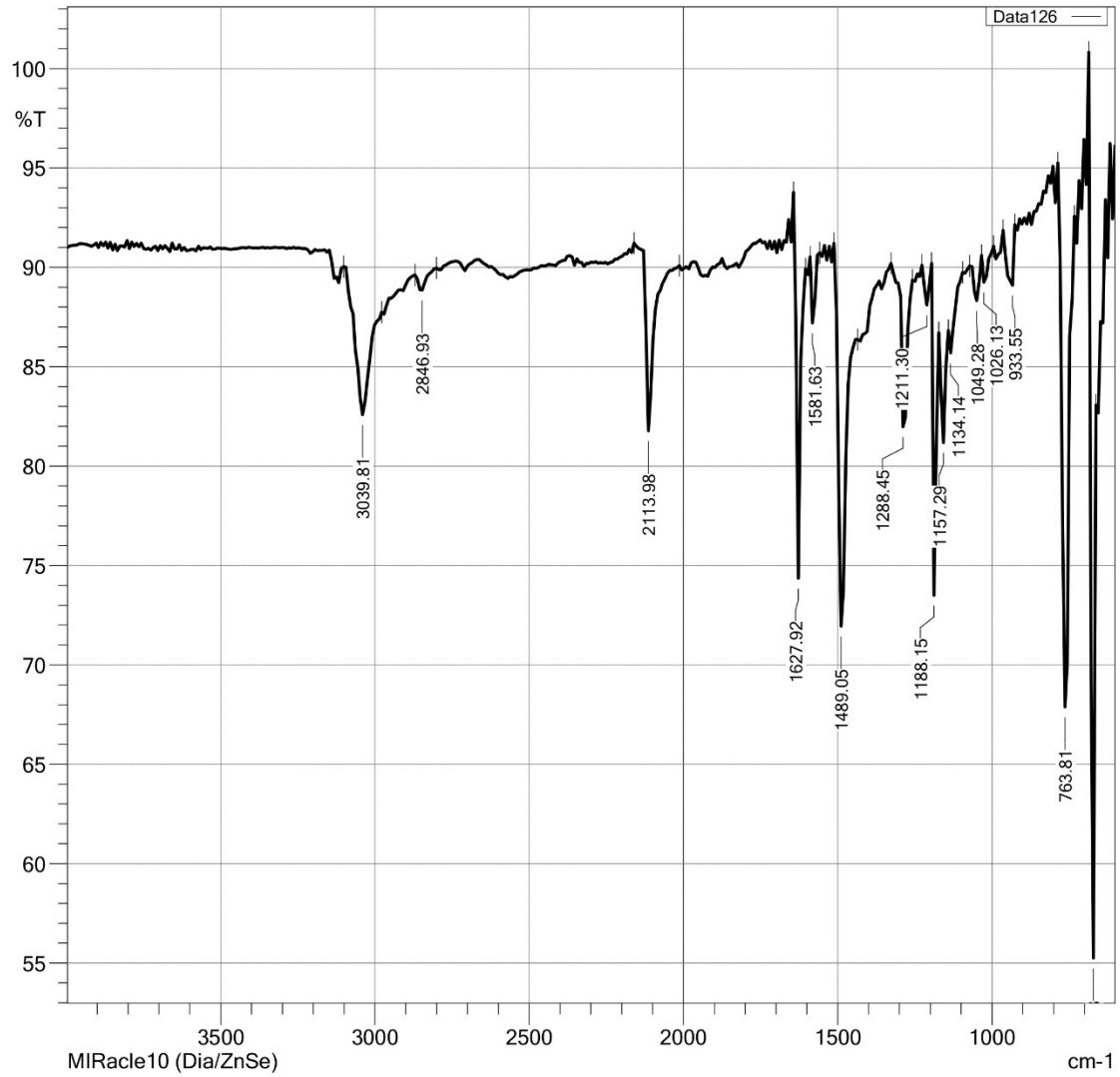


Figure S9. IR Spectrum for **2**.

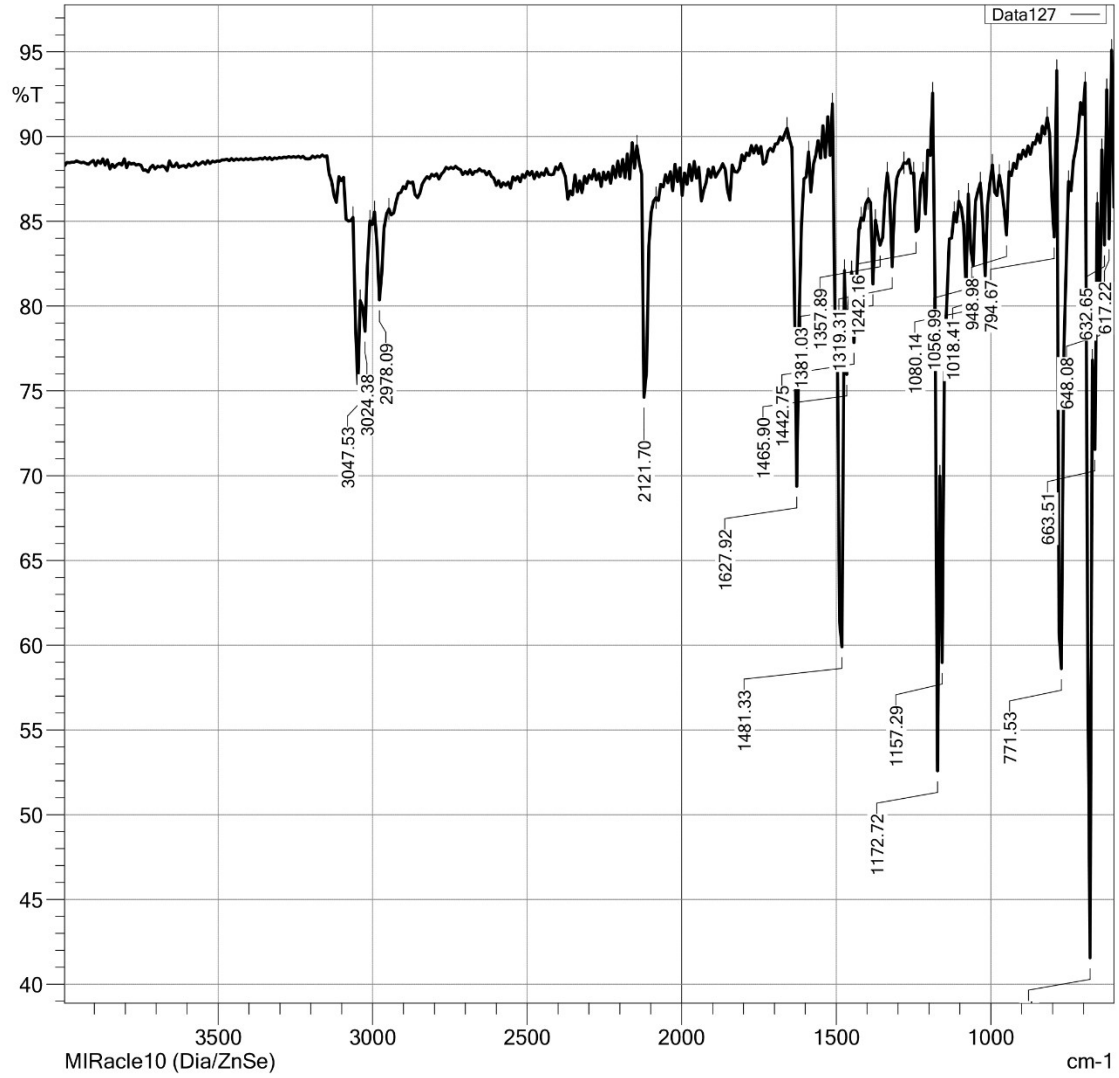


Figure S10. IR Spectrum for **3**.

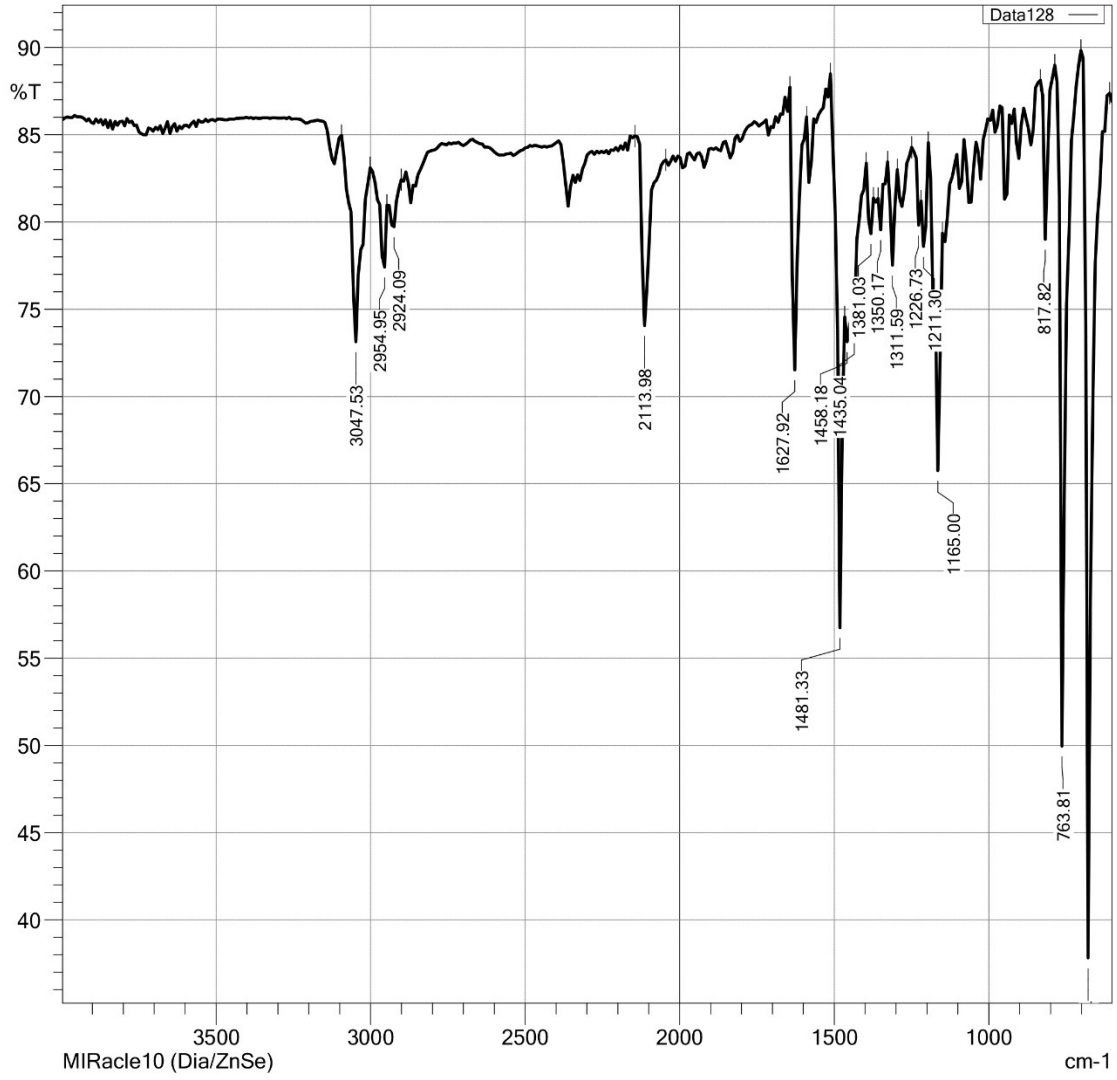


Figure S11. IR Spectrum for **4**.

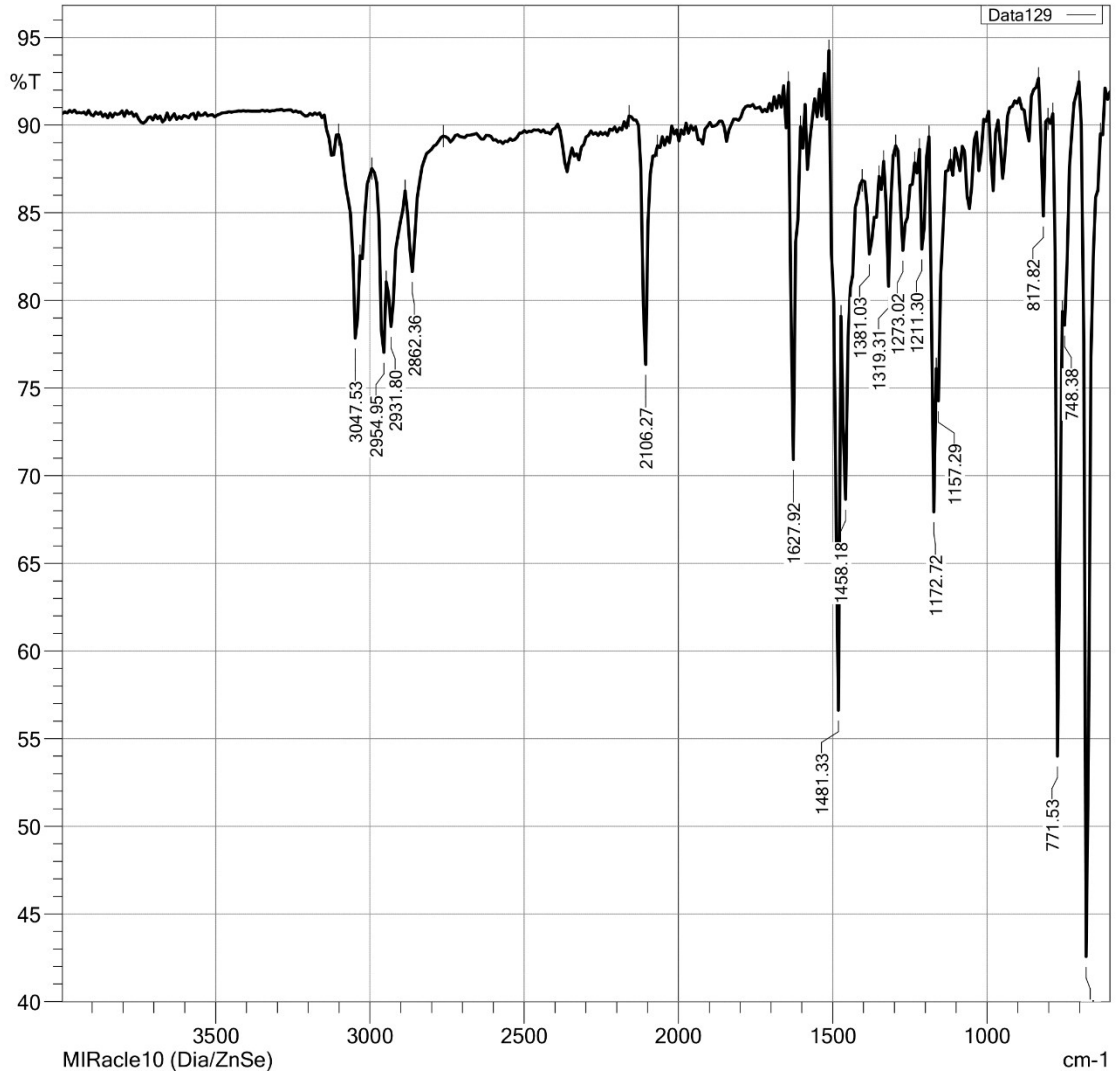


Figure S12. Hirshfeld surfaces of **1**−**4**. Instances of close atom···atom distances are indicated by regions of red. Surface ranges: −0.2000 to +1.0000 au. Surfaces generated on experimental structures.

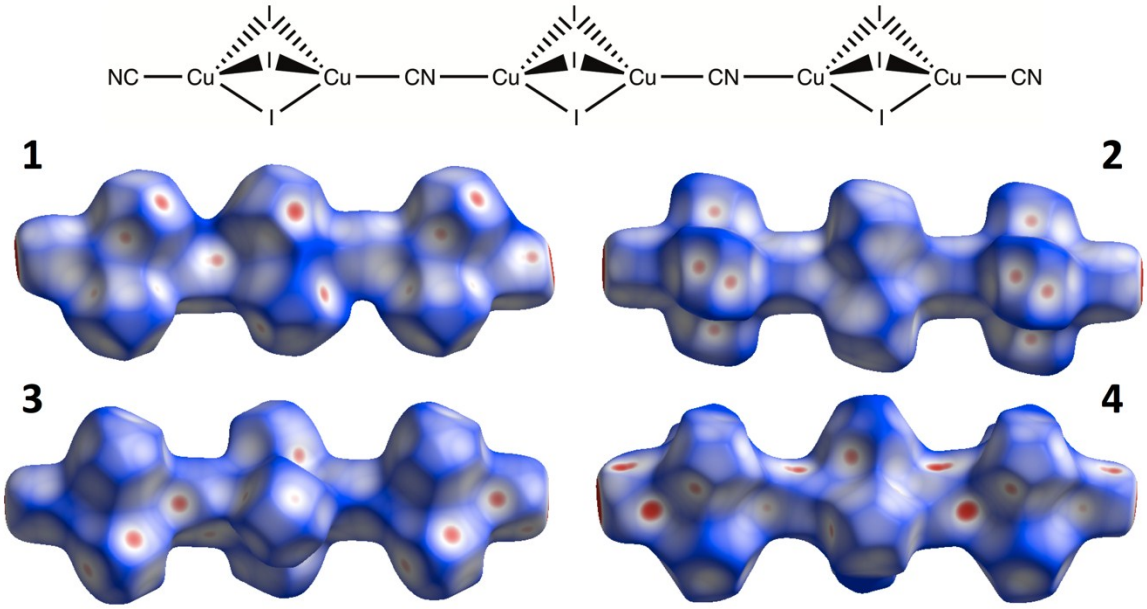


Figure S13. Fingerprint plots of close atom···atom contacts derived from **1-4** Hirshfeld surfaces.

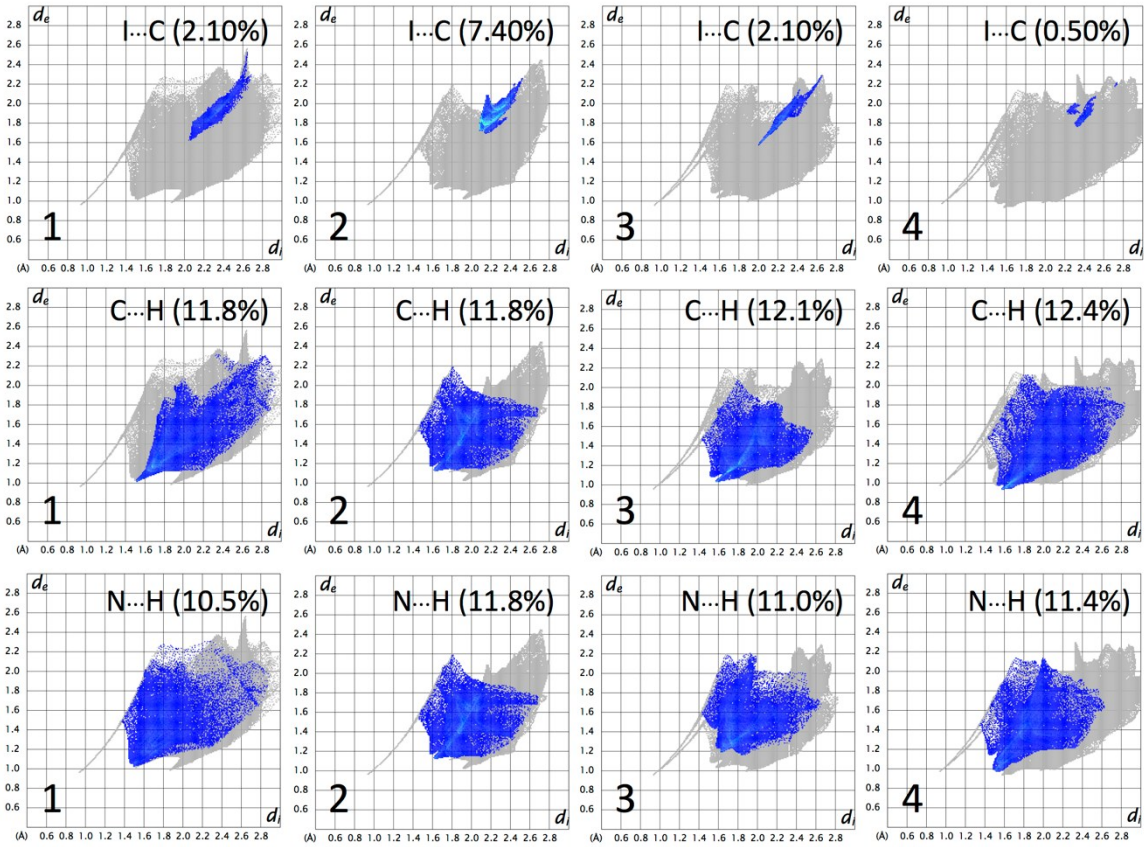


Figure S14. Diffuse reflectance spectra (Left) and Tauc plots (right) of **1-4**.

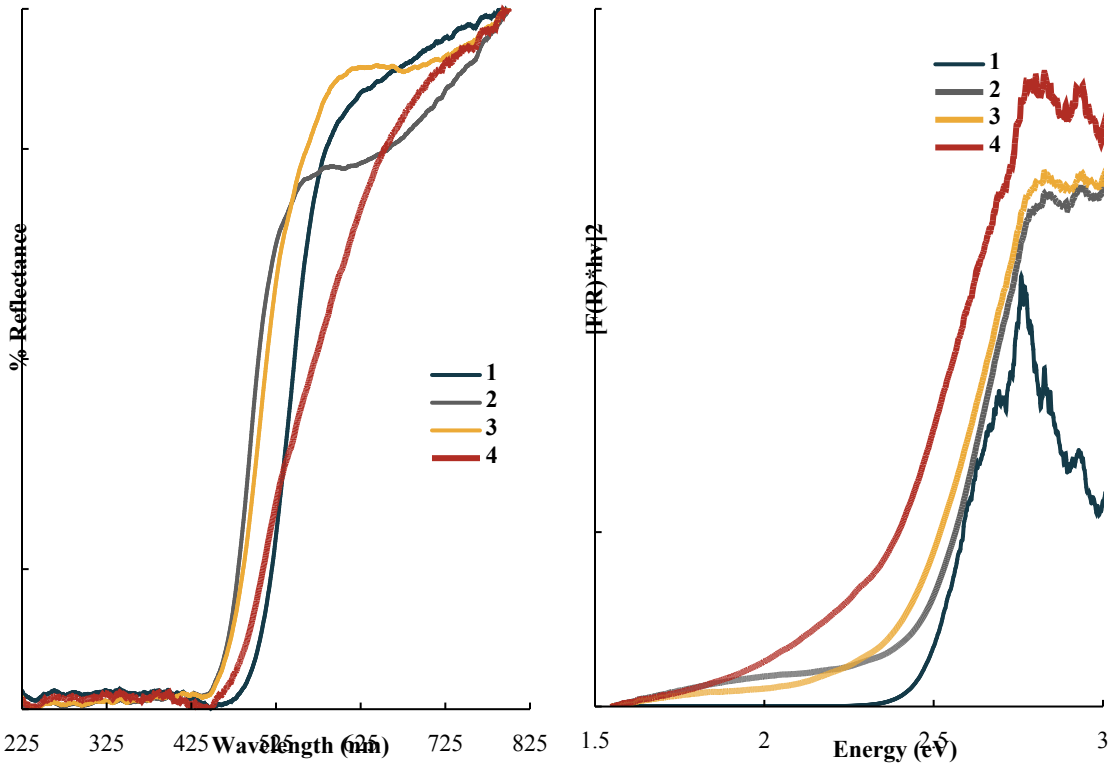


Figure S15. B3LYP/LANL2DZ calculated ground state model of **1**.

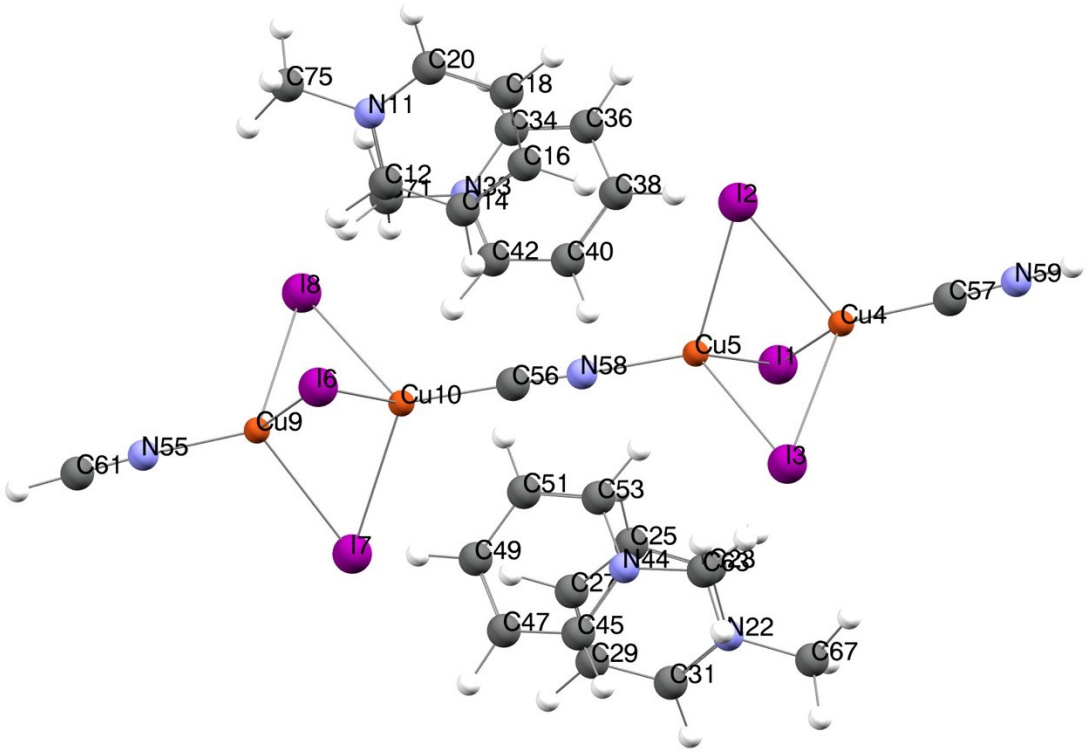


Table S1. Select B3LYP/LANL2DZ calculated ground state bond lengths of model **1**.

Atom1	Atom2	Calc.	Exp.
Cu4	Cu5	2.5370	2.4820
Cu9	Cu10	2.5120	2.4820
C12	C14	1.4000	1.3740
C14	C16	1.4047	1.3876
C18	C16	1.4171	1.3710
C18	C20	1.3907	1.3820
C20	N11	1.3787	1.3544
C23	C25	1.4007	1.3734
C23	N22	1.3666	1.3451
C25	C27	1.4043	1.3876
C27	C29	1.4181	1.3703
C29	C31	1.3899	1.3826
C34	N33	1.3715	1.3469
C36	C34	1.3959	1.3683
C38	C36	1.4134	1.3733
C38	C40	1.4090	1.3819
C40	C42	1.3979	1.3687
C42	N33	1.3723	1.3463
C45	C47	1.3965	1.3683
C47	C49	1.4123	1.3733
C51	C49	1.4098	1.3819
C53	C51	1.3965	1.3687
C63	N44	1.4952	1.4701
C75	N11	1.4948	1.4700

Atom1	Atom2	Calc.	Exp.
Cu10	C56	1.9339	1.9063
Cu10	I6	2.9550	2.9258
Cu4	C57	1.9205	1.9182
Cu4	I1	2.8029	2.6573
Cu5	N58	1.9724	1.9053
Cu9	I7	2.8085	2.7997
Cu9	I8	2.8996	2.7494
Cu9	N55	1.9910	1.9173
I1	Cu5	2.9278	2.9258
I2	Cu4	2.8465	2.7997
I2	Cu5	2.7896	2.6573
I3	Cu4	2.9822	2.7494
I3	Cu5	2.8443	2.6918
I6	Cu9	2.7896	2.6573
I7	Cu10	2.8177	2.6573
I8	Cu10	2.9138	2.6918
N11	C12	1.3678	1.3444
N22	C31	1.3790	1.3536
N22	C67	1.4958	1.4701
N33	C71	1.4960	1.4700
N44	C45	1.3709	1.3469
N44	C53	1.3719	1.3463
N55	C61	1.1711	1.2936
N58	C56	1.1928	1.1596
N59	C57	1.1870	1.2936

Figure S16. B3LYP/LANL2DZ calculated ground state model of **2**.

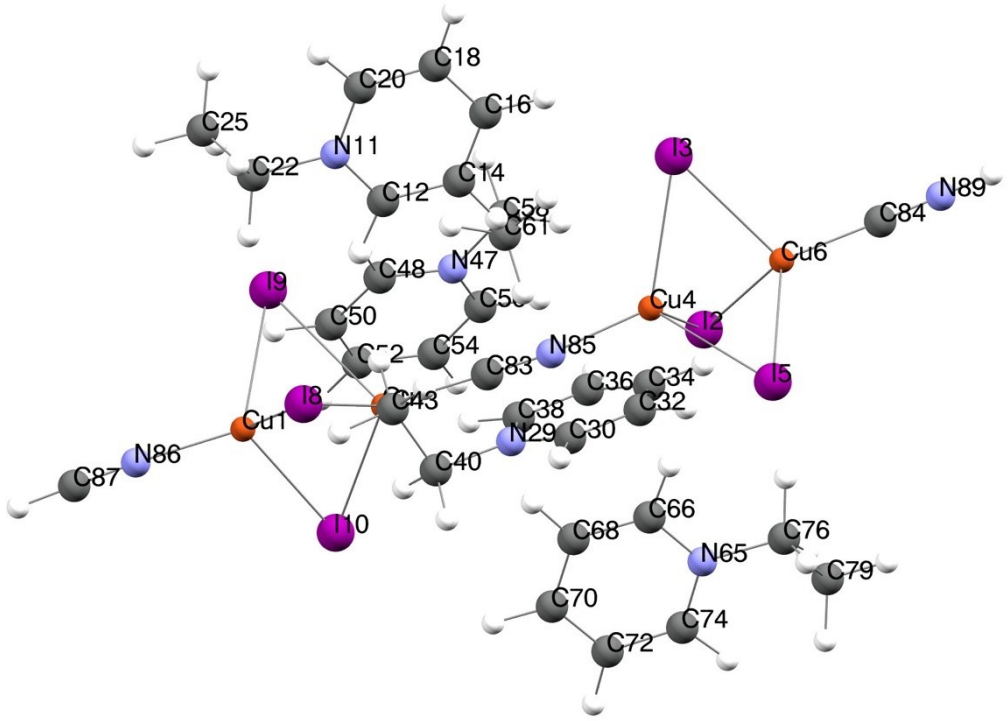


Table S2. Select B3LYP/LANL2DZ calculated ground state bond lengths of model **2**.

Atom1	Atom2	Calc.	Exp.
Cu1	Cu7	2.5298	2.4840
Cu4	Cu6	2.5321	2.4840
C12	C14	1.4020	1.4023
C14	C16	1.4044	1.4065
C16	C18	1.4115	1.4153
C18	C20	1.3931	1.3944
C22	C25	1.5388	1.5391
C30	C32	1.3940	1.3950
C32	C34	1.4115	1.4134
C34	C36	1.4074	1.4096
C36	C38	1.3989	1.3996
C40	C43	1.5365	1.5392
C48	C50	1.3955	1.3988
C50	C52	1.4081	1.4088
C52	C54	1.4074	1.4104
C54	C56	1.3956	1.3987
C58	C61	1.5322	1.5367
C66	C68	1.4028	1.4030
C68	C70	1.4042	1.4039
C70	C72	1.4110	1.4132
C72	C74	1.3948	1.3939
C76	C79	1.5362	1.5376
C83	N85	1.1912	1.1929
C84	N89	1.1846	1.1880
N65	C66	1.3658	1.3675
N65	C74	1.3686	1.3699
N65	C76	1.5088	1.5113

Atom1	Atom2	Calc.	Exp.
Cu1	I10	2.7843	2.7819
Cu1	I8	2.8733	2.8746
Cu1	I9	2.7862	2.7998
Cu1	N86	1.9995	2.0023
Cu4	I5	2.8821	2.8797
Cu4	N85	1.9794	1.9803
Cu6	C84	1.9188	1.9197
Cu7	C83	1.9285	1.9302
Cu7	I10	2.7521	2.7484
Cu7	I8	2.9445	2.9583
Cu7	I9	3.1645	3.1723
I2	Cu4	2.9169	2.9119
I2	Cu6	2.8971	2.8947
I3	Cu4	2.7671	2.7768
I3	Cu6	2.8301	2.8391
I5	Cu6	2.8616	2.8636
N11	C12	1.3667	1.3692
N11	C20	1.3694	1.3712
N11	C22	1.5120	1.5098
N29	C30	1.3694	1.3711
N29	C38	1.3703	1.3721
N29	C40	1.5086	1.5105
N47	C48	1.3639	1.3676
N47	C56	1.3697	1.3702
N47	C58	1.5188	1.5205
N86	C87	1.1697	1.1711

Figure S17. B3LYP/LANL2DZ calculated ground state model of **3**.

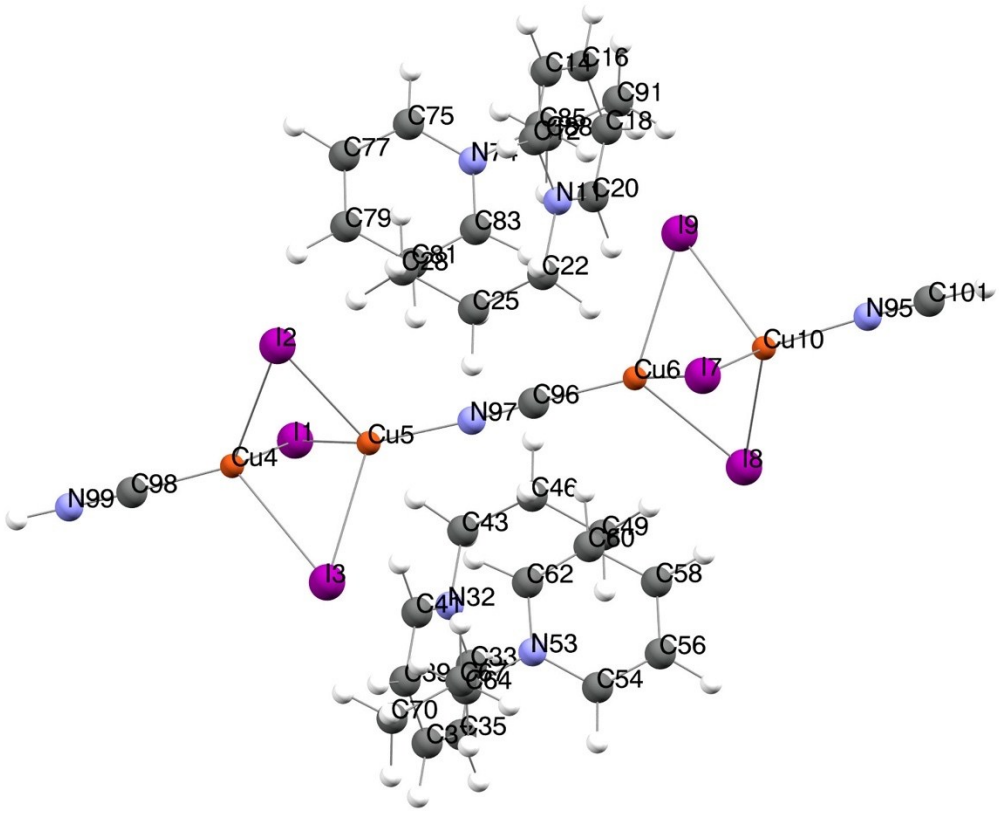


Table S3. Select B3LYP/LANL2DZ calculated ground state bond lengths of model **3**.

Atom1	Atom2	Calc.	Exp.
Cu4	Cu5	2.5741	2.4820
Cu6	Cu10	2.5990	2.4820
C12	C14	1.3977	1.3740
C14	C16	1.4140	1.3880
C16	C18	1.4086	1.3700
C18	C20	1.4031	1.3826
C22	C25	1.5471	1.5140
C25	C28	1.5440	1.5254
C33	C35	1.3969	1.3740
C35	C37	1.4141	1.3885
C37	C39	1.4083	1.3700
C39	C41	1.4028	1.3836
C43	C46	1.5473	1.5137
C46	C49	1.5442	1.5258
C54	C56	1.3975	1.3683
C56	C58	1.4142	1.3735
C58	C60	1.4116	1.3811
C60	C62	1.3992	1.3701
C64	C67	1.5464	1.5002
C67	C70	1.5466	1.5215
C75	C77	1.3972	1.3690
C77	C79	1.4148	1.3733
C79	C81	1.4101	1.3812
C81	C83	1.3998	1.3694
C85	C88	1.5466	1.4993
C88	C91	1.5458	1.5221
C96	N97	1.1938	1.1606
C98	N99	1.1935	1.1466
Cu6	I9	2.8365	2.6918

Atom1	Atom2	Calc.	Exp.
Cu6	I8	2.7383	2.6573
I1	Cu4	2.7967	2.6573
I1	Cu5	3.0580	2.9258
I2	Cu4	2.8135	2.7995
I2	Cu5	2.7759	2.6570
I3	Cu4	2.9906	2.7503
I3	Cu5	2.8231	2.6926
I7	Cu10	2.7318	2.6573
I8	Cu10	2.7979	2.7995
I9	Cu10	2.9321	2.7503
N11	C12	1.3712	1.3445
N11	C20	1.3704	1.3545
N11	C22	1.5115	1.4933
N32	C33	1.3715	1.3442
N32	C41	1.3700	1.3531
N32	C43	1.5109	1.4933
N53	C54	1.3726	1.3469
N53	C62	1.3737	1.3458
N53	C64	1.5077	1.4958
N74	C75	1.3720	1.3469
N74	C83	1.3741	1.3463
N74	C85	1.5078	1.4951
N95	C101	1.1741	1.1466
Cu10	N95	2.0078	1.9183
Cu4	C98	1.9231	1.9182
Cu5	N97	1.9680	1.9053
Cu6	C96	1.9340	1.9053
Cu6	I7	3.5131	2.9264

Figure S18. B3LYP/LANL2DZ calculated ground state model of **4**.

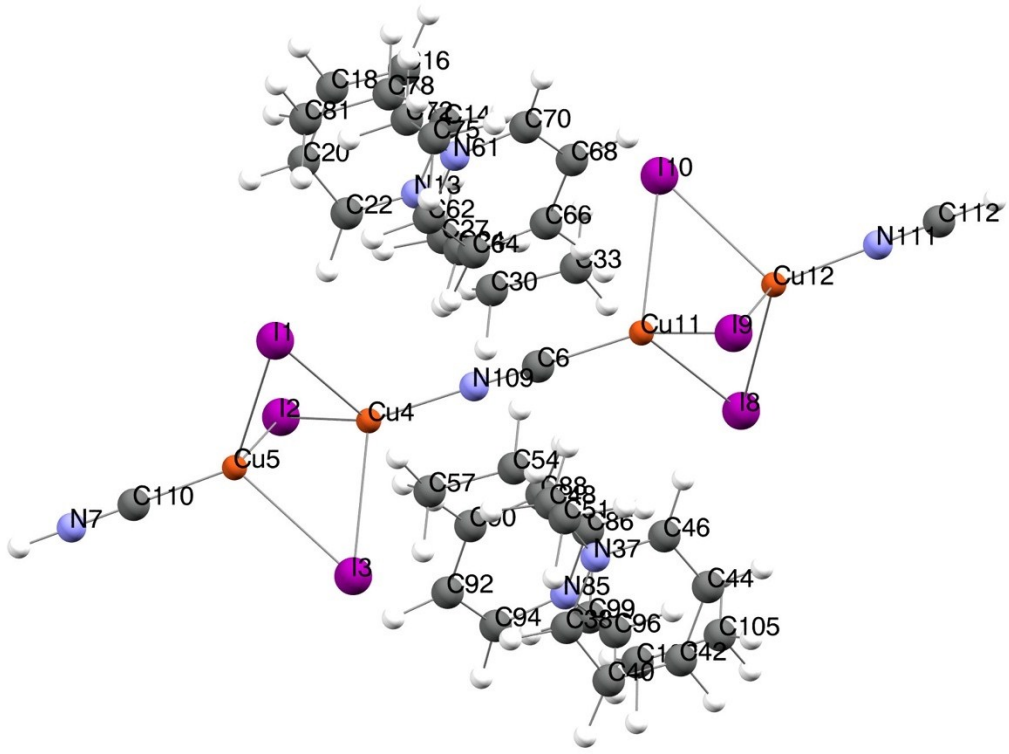


Table S4. Select B3LYP/LANL2DZ calculated ground state bond lengths of model **4**.

Atom1	Atom2	Calc.	Exp.
Cu4	Cu5	2.5310	2.4910
Cu11	Cu12	2.5090	2.4910
C102	C105	1.5497	1.5292
Cu5	C110	1.9239	1.9194
N7	C110	1.1892	1.1502
N111	C112	1.1736	1.1600
N13	C14	1.3733	1.3916
C14	C16	1.3999	1.3879
C16	C18	1.4150	1.3890
C18	C20	1.4106	1.3888
C20	C22	1.4034	1.3927
N13	C22	1.3697	1.3897
N13	C24	1.5113	1.4768
C24	C27	1.5480	1.4806
C30	C33	1.5501	1.5292
N37	C38	1.3730	1.3916
C38	C40	1.3997	1.3879
C40	C42	1.4153	1.3890
C42	C44	1.4110	1.3888
C44	C46	1.4033	1.3925
N37	C46	1.3699	1.3905
N37	C48	1.5110	1.4768
C48	C51	1.5485	1.4806
C54	C57	1.5504	1.5302
N61	C62	1.3731	1.3916
C62	C64	1.4010	1.3879
C64	C66	1.4125	1.3891
C66	C68	1.4168	1.3888
N61	C70	1.3786	1.3906

Atom1	Atom2	Calc.	Exp.
C6	Cu11	1.9381	1.9108
I10	Cu11	2.8934	2.6920
I8	Cu11	2.8758	2.6737
I9	Cu11	2.9272	2.7750
I10	Cu12	2.8556	2.7642
I8	Cu12	2.8335	2.6774
I9	Cu12	2.8196	2.7866
I1	Cu4	2.8264	2.6737
I2	Cu4	2.8940	2.7750
I3	Cu4	2.8466	2.6920
I1	Cu5	2.8889	2.6774
I2	Cu5	2.8444	2.7866
I3	Cu5	2.9025	2.7642
C6	N109	1.1950	1.1532
Cu4	N109	1.9775	1.9108
Cu12	N111	1.9936	1.8700
N61	C72	1.5080	1.4759
C72	C75	1.5501	1.4807
C78	C81	1.5505	1.5302
N85	C86	1.3744	1.3916
C86	C88	1.4011	1.3879
C88	C90	1.4127	1.3891
C90	C92	1.4174	1.3888
C92	C94	1.3964	1.3927
N85	C94	1.3798	1.3899
N85	C96	1.5083	1.4759
C96	C99	1.5491	1.4807
C68	C70	1.3955	1.3925

Figure S19. TD-DFT B3LYP/LANL2DZ calculated UV-vis spectra of **1**−**4**.

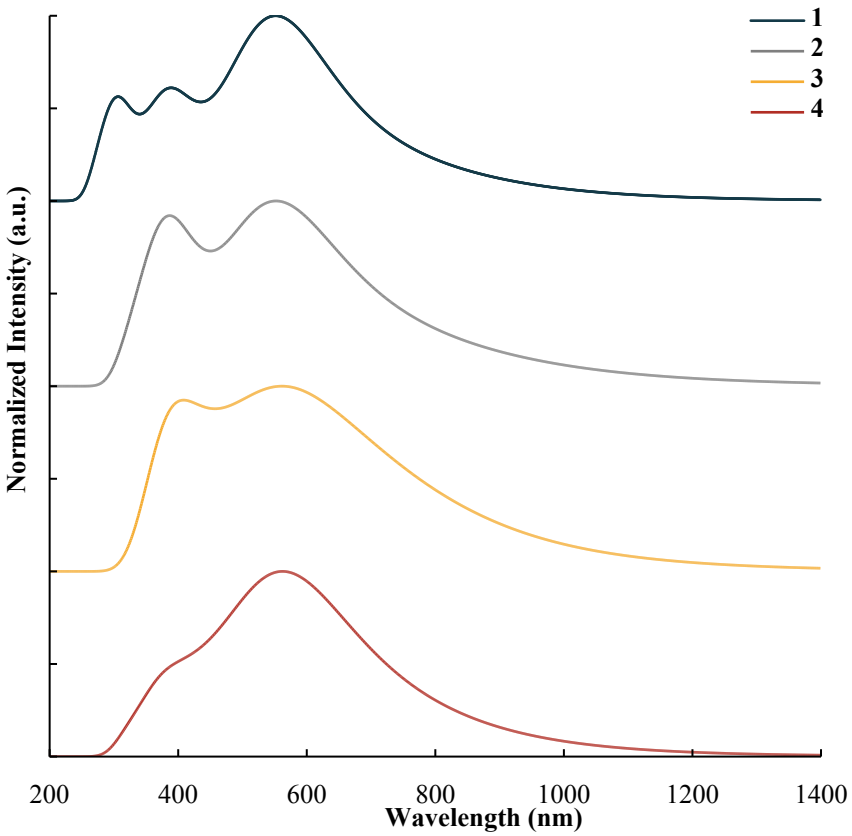


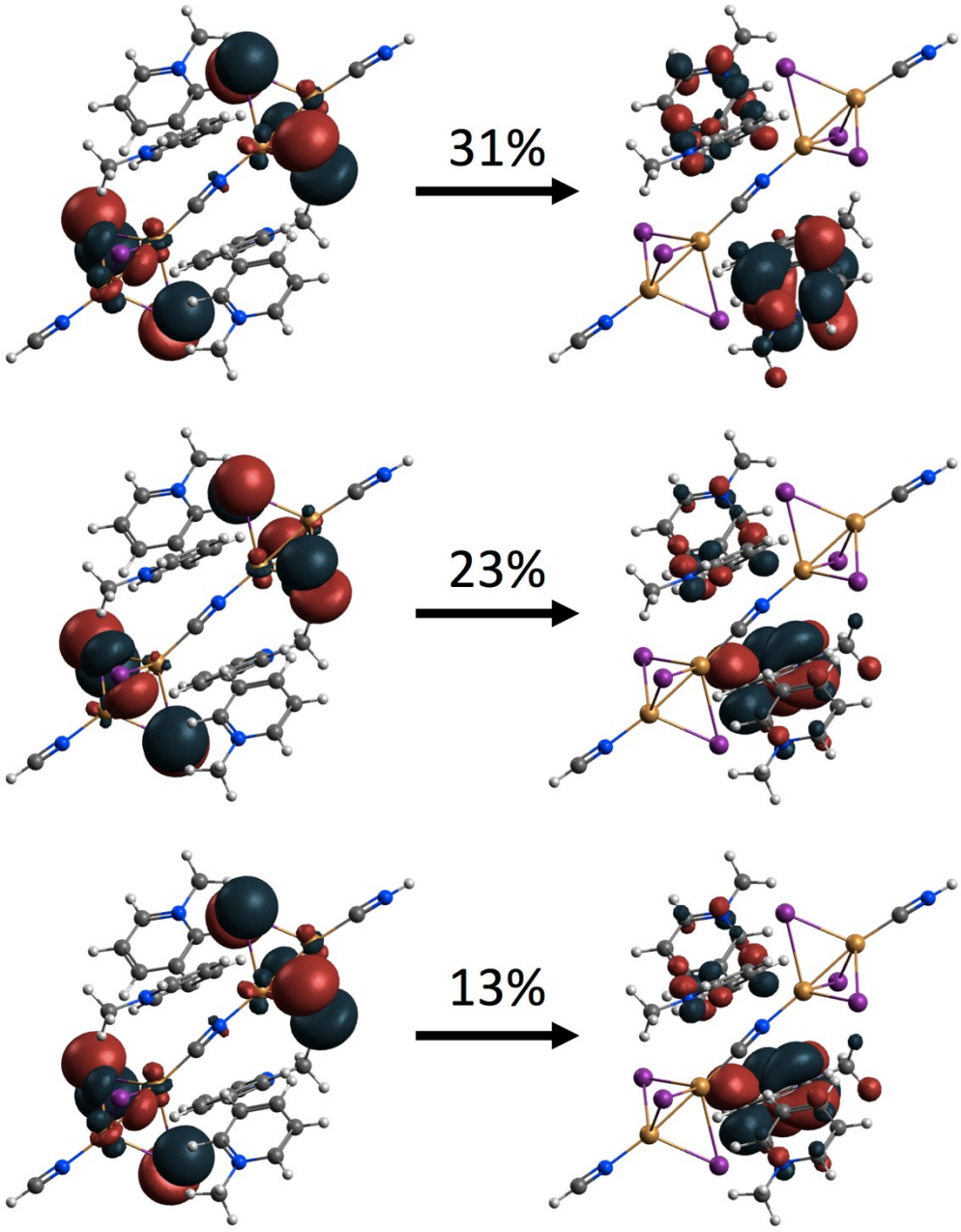
Table S5. Select TD-DFT B3LYP/LANL2DZ calculated excited states for **1**−**4** where f-oscillation > 0.01.

Compound	State	Energy	Oscillation
1	27	592.80 nm	0.0206
	31	577.79 nm	0.0151
	34	568.30 nm	0.0248
	36	563.79 nm	0.0166
	39	554.57 nm	0.0134
	44	537.53 nm	0.0160
	119	392.76 nm	0.0121
2	29	608.03 nm	0.0133
	48	545.01 nm	0.0131
	135	385.41 nm	0.0155
3	26	667.14 nm	0.0188
	38	585.92 nm	0.0127
	128	400.02 nm	0.0153
	134	392.42 nm	0.0184
4	26	620.19 nm	0.0153
	29	595.70 nm	0.0248
	30	581.81 nm	0.0221
	31	575.91 nm	0.0139
	34	565.23 nm	0.0109

Table S6. TD-DFT B3LYP/LANL2DZ calculated transitions for the lowest energy singlet excited states for **1**−**4**.

Complex	State	Transition			Coefficient	Percent Contribution
1	27	HOMO-6	→	LUMO	0.37563	31%
		HOMO-7	→	LUMO+3	0.32479	23%
		HOMO-6	→	LUMO+3	−0.24567	13%
		HOMO-6	→	LUMO+2	0.24140	13%
		HOMO-7	→	LUMO	−0.22810	11%
		HOMO-8	→	LUMO	0.15514	5%
		HOMO-6	→	LUMO+1	−0.13492	4%
2	29	HOMO-11	→	LUMO	0.60127	75%
		HOMO-12	→	LUMO	−0.24966	13%
		HOMO-9	→	LUMO	0.19681	8%
		HOMO-8	→	LUMO	0.14885	5%
3	26	HOMO-7	→	LUMO+1	0.56058	69%
		HOMO-8	→	LUMO+1	0.34779	26%
		HOMO-10	→	LUMO+1	−0.14819	5%
4	26	HOMO-7	→	LUMO+1	0.66236	96%
		HOMO-10	→	LUMO+1	0.13946	4%

Figure S20. TD-DFT B3LYP/LANL2DZ isodensity representations for transitions of the lowest energy singlet excited states for **1**.



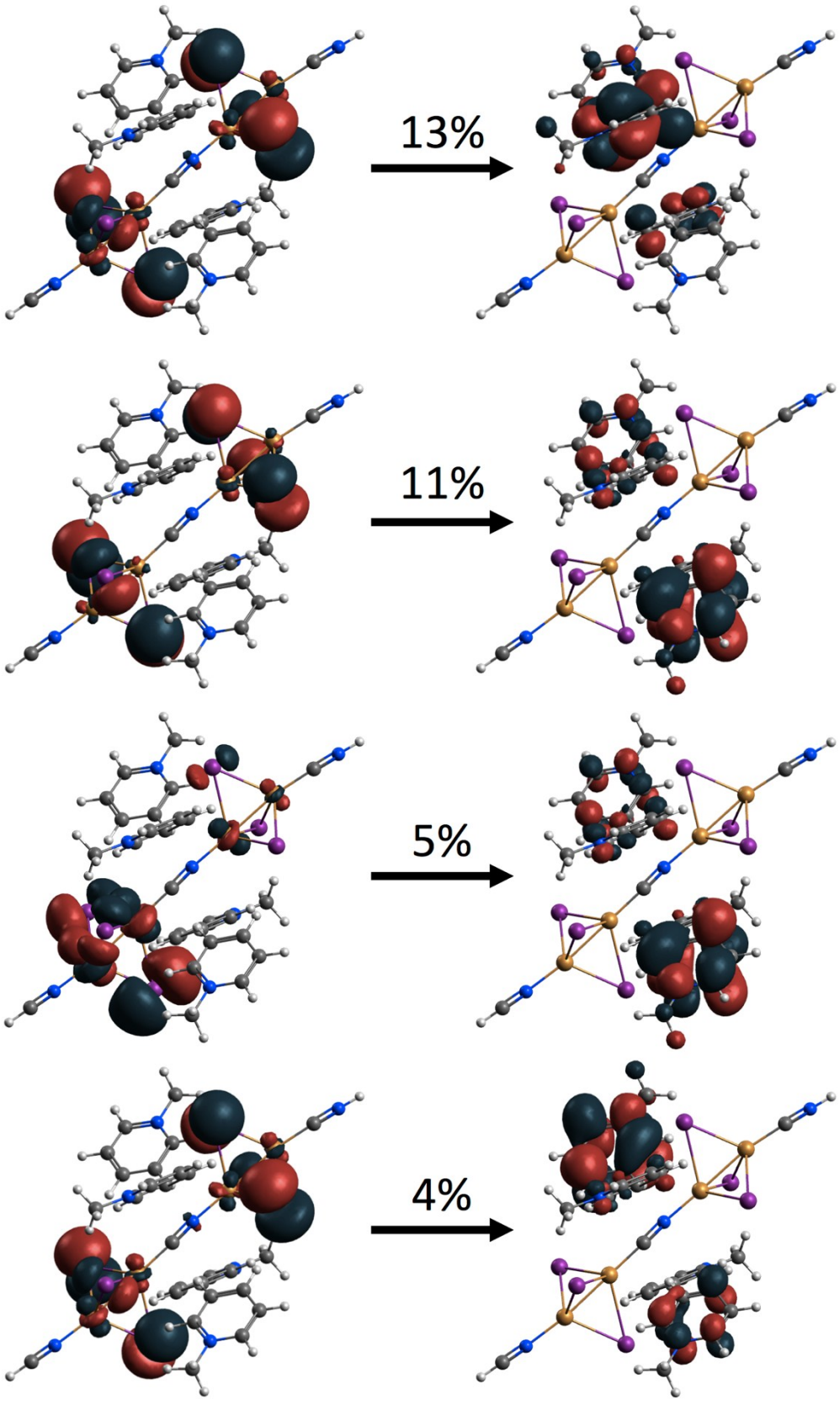

13%
11%
5%
4%

Figure S21. TD-DFT B3LYP/LANL2DZ isodensity representations for transitions of the lowest energy singlet excited states for **2**.

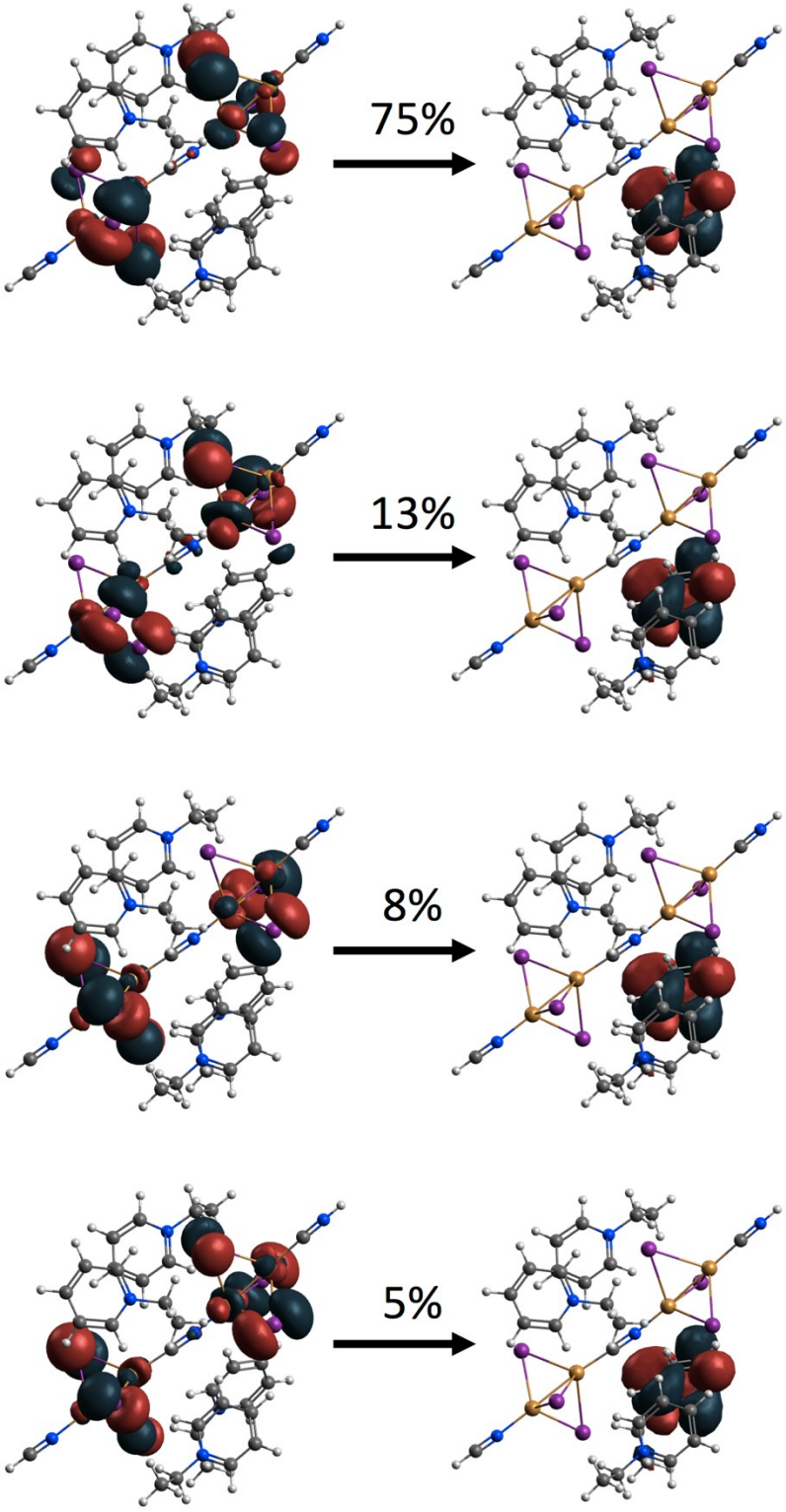


Figure S22. TD-DFT B3LYP/LANL2DZ isodensity representations for transitions of the lowest energy singlet excited states for **3**.

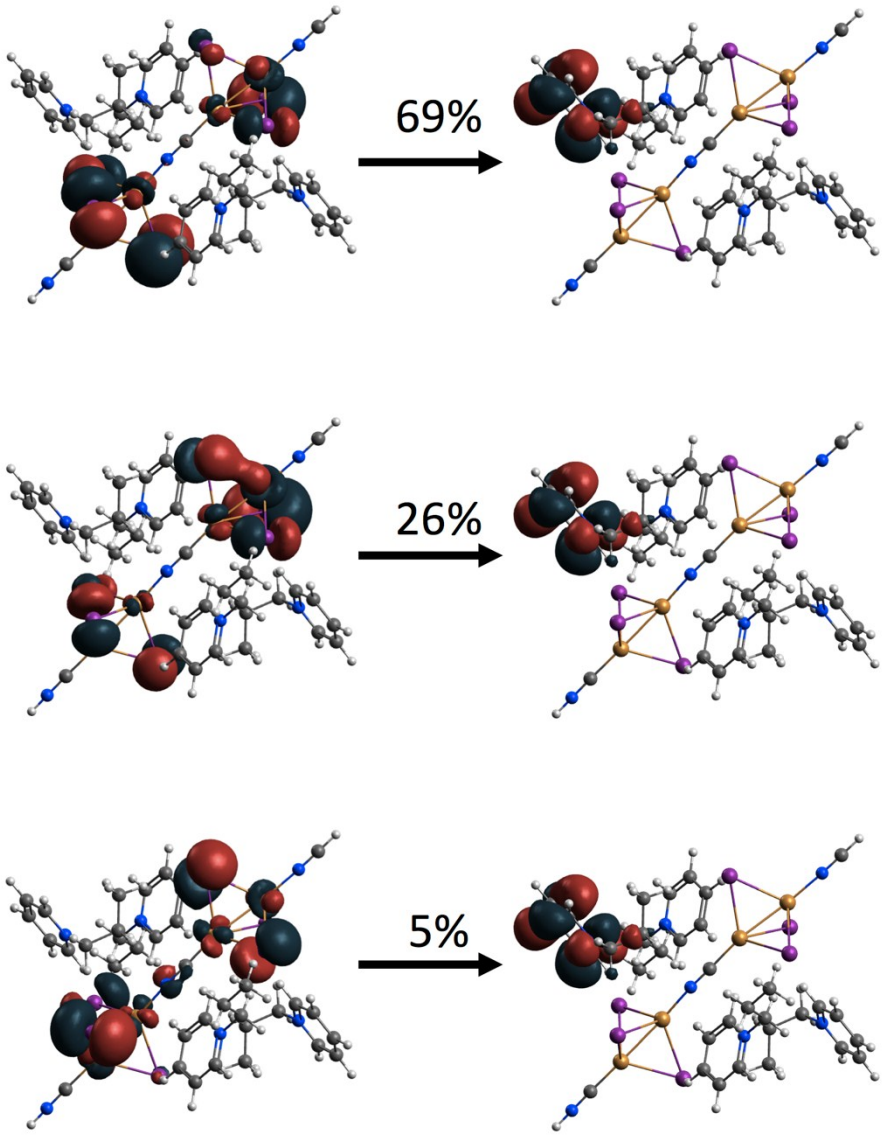


Figure S23. TD-DFT B3LYP/LANL2DZ isodensity representations for transitions of the lowest energy singlet excited states for **4**.