Supporting Information

Solid state luminescence of copper(ı) (pseudo)halide complexes with neocuproine and aminomethylphosphanes derived from morpholine and thiomorpholine.

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Table S1. NMR spectra of chalcogenide derivatives of $P(CH_2N(CH_2CH_2)_2S)_3$ (**2**), $P(CH_2N(CH_2CH_2)_2O)_3$ (**1**), $P(CH_2N(CH_2CH_2)_2CH_3)_3$ (**3**) and $P(CH_2N(CH_2CH_2)_2CH_2CH_3)_3$ (**4**). (oxides: **a**, sulphides: **b**, selenides: **c**)

Table S2. NMR spectra of $[CuI(dmp)P(CH_2N(CH_2CH_2)_2O)_3]$ (**1I**), $[CuI(dmp)P(CH_2N(CH_2CH_2)_2S)_3]$ (**2I**), $[CuNCS(dmp)P(CH_2N(CH_2CH_2)_2O)_3]$ (**1T**) and $[CuNCS(dmp)P(CH_2N(CH_2CH_2)_2S)_3]$ (**2T**) and ligands: $P(CH_2N(CH_2CH_2)_2O)_3$ (**1**), $P(CH_2N(CH_2CH_2)_2S)_3$ (**2**) and dmp ($CDCl_3$, 298 K)

Figure S1 Molecular orbitals (and spin density) for 1I (6-31G** except I - 6-311G(d,p) and Cu - LanL2Dz with Los Alamos ECP)

Figure S2. Molecular orbitals (and spin density) for 2I(6-31G** except I - 6-311G(d,p) and Cu - LanL2Dz with Los Alamos ECP)

Figure S3. Molecular orbitals (and spin density) for 1T (6-31G** except I - 6-311G(d,p) and Cu - LanL2Dz with Los Alamos ECP)

Figure S4. Molecular orbitals (and spin density) for 2T (6-31G** except I - 6-311G(d,p) and Cu - LanL2Dz with Los Alamos ECP)

Table S3. DFT geometries obtained with a larger basis set (Cu: 6-311+G**; I: 6-311G**; N, P, O and S: 6-31+G**; C, H: 6-31G** for NBO charges: 6-311+G** except I: 6-311G**) -LEFT and a simple basis set: 6-31G(d,p) except I - 6-311G** and Cu - LanL2Dz with Los Alamos ECP - RIGHT of the iodo and isothiocyanato copper(ı) complexes with dmp and **1** or **2** in ground singlet and triplet states

Figure S5. Molecular geometries in ground singlet and first triplet states determined with DFT methods (B3Lyp/Cu: 6-311+G*; I: 6-311G**; N, P, O and S: 6-31+G**;C, H: 6-31G**)

Table S4. UV-Vis transitions (in nanometres) from TDDFT calculations obtained with a simple basis set (6-31G** except I: 6-311G(d,p) and Cu: LanL2Dz with Los Alamos ECP)

Figure S6. Molecular orbitals for the optimized geometries (6-311+G** except I: 6-311G**)

Table S1.

NMR spectra of chalcogenide derivatives of $P(CH_2N(CH_2CH_2)_2S)_3$ (**2**), $P(CH_2N(CH_2CH_2)_2O)_3$ (**1**), $P(CH_2N(CH_2CH_2)_2CH_3)_3$ (**3**) and $P(CH_2N(CH_2CH_2)_2CH_2CH_3)_3$ (**4**). (oxides: **a**, sulphides: **b**, selenides: **c**)

	2 ($CDCl_3$)				**2** (acetone-d_6)				**1** (acetone-d_6) [(a)]				**3** (acetone-d_6) [(a)]				**4** (acetone-d_6) [(a)]			
Compound Type:		**2a**	**2b**	**2c**		**2a**	**2b**	**2c**		**1a**	**1b**	**1c**		**3a**	**3b**	**3c**		**4a**	**4b**	**4c**
σ(P)	-60.30	48.73	44.53	27.62	-61.76	46.46	43.53	27.93 705.97	-62.77	44.22	42.38	26.31	-60.87	45.02	43.26	27.44	-61.12	44.93	43.26	27.35
σ(Se) ^1J(SeP)				-322 701.90				-314.8 704.68				-303.9 709.76				-307.3 707.45				-306.4 707.50
σ(C^1) (d) $^1J(C^1P)$	59.41 5.6	53.75 81.9	57.14 66.4	56.90 58.9	59.88 5.7	54.76 81.5	57.95 66.40	57.74 59.4	59.31 4.3	55.01 81.2	58.01 67.0	57.78 59.8	58.69 3.5	54.30 81.9	57.49 67.6	57.27 60.3	59.03 4.7	54.38 82.2	57.61 67.6	57.25 60.0
σ(C^2) (d) $^3J(C^2P)$	56.25 8.0	57.04 7.5	57.33 7.1	57.33 6.6	57.32 8.5	58.00 7.5	58.22 6.6	58.23 7.1	56.11 8.1	56.83 7.4	56.95 7.2	56.91 6.9	55.21 7.9	56.32 7.4	56.36 6.9	56.34 6.8	55.73 8.0	56.53 7.4	56.62 6.9	56.47 6.5
σ(C^3) (s)	27.93	27.92	27.86	27.78	28.61	28.57	28.43	28.37	67.57	67.61	67.52	67.45	55.73	56.17	56.02	55.93	53.84	53.93	53.82	53.62
σ(C^4) (s)	-	-	-	-	-	-	-	-	-	-	-	-	46.25	46.37	46.30	46.34	52.88	52.89	52.85	52.73
σ(C^5)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	12.71	12.67	12.65	12.64
σ(H^1) (d) $^2J(H^1P)$	2.59 2.7	2.78 6.7	2.96 4.7	3.11 4.1	2.63 3.1	2.82 6.8	3.01 4.9	3.16 4.1	2.64 2.9	2.82 7.2	3.03 5.2	3.18 4.6	2.58 3.0	2.75 7.2	2.97 5.4	3.12 4.4	2.58 2.9	2.75 7.1	2.97 5.2	3.12 4.6
σ(H^2)	2.78	2.87	-	3.00	2.77	2.88	2.98	3.00	2.49	2.61	2.72	2.74	2.50	2.62	2.73	2.74	2.50	2.62	2.73	2.75
σ(H^3)	2.63	2.62	2.64	2.65	2.60	2.62	2.63	2.63	3.58	3.59	3.59	3.60	2.31	2.32	2.34	2.33	2.36	2.37	2.38	2.38
σ(H^4) $^3J(H^4H^5)$	-	-	-	-	-	-	-	-	-	-	-	-	2.15	2.15	2.16	2.15	2.29 7.17	2.29 7.20	2.30 7.20	2.30 7.14
σ(H^5) $^3J(H^4H^5)$	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.99 7.20	0.99 7.20	0.99 7.15	0.99 7.14

(a) data from: R. Starosta, B. Bażanów, W. Barszczewski, *Dalton Trans.,* **2010**, *39*, 7548-7555

Table S2.

NMR spectra of [CuI(dmp)P($CH_2N(CH_2CH_2)_2O)_3$] (**1I**), [CuI(dmp)P($CH_2N(CH_2CH_2)_2S)_3$] (**2I**), [CuNCS(dmp)P($CH_2N(CH_2CH_2)_2O)_3$] (**1T**) and [CuNCS(dmp)P($CH_2N(CH_2CH_2)_2S)_3$] (**2T**) and ligands: P($CH_2N(CH_2CH_2)_2O)_3$ (**1**), P($CH_2N(CH_2CH_2)_2S)_3$ (**2**) and dmp ($CDCl_3$, 298 K)

	1[(a)]	**2**	**dmp**[(a)]	**1I**[(a)]	**2I**	**1T**	**2T**
P	-62.8	-60.3		-28.5*	-29.6*	-29.9*	-29.9*
C^{NCS}						130.65	Not observed
$C^{1\text{-}P}$	56.79 (4.3)	59.41 (5.6)		55.8*	55.50*	56.50*	57.10*
$C^{2\text{-}P}$	55.71 (8.1)	56.25 (8.0)		55.53 (4.7)*	56.98 (5.65)	55.39 (6.59)	56.66 (7.06)
$C^{3\text{-}P}$	67.57	27.93		66.71	27.81	66.80	27.77
H^{1P}	2.64 (2.95)	2.59 (2.7)		2.88	2.86	2.74*	2.74
H^{2P}	2.49	2.78		2.52	2.74	2.44*	2.79
H^{3P}	3.58	2.63		3.48	2.39	3.44*	2.55
$C^{2,9}$			**159.07**	**159.14**	**159.09**	**158.58**	**158.69**
$C^{3,8}$			123.29	124.92	125.00	124.89	125.05
$C^{4,7}$			136.07	136.59	136.66	136.69	136.79
$C^{5,6}$			125.22	125.41	125.48	125.42	125.55
$C^{11,12}$			145.03	142.88	142.87	142.74	142.84
$C^{13,14}$			126.58	127.09	127.13	126.95	127.07
$C^{15,16}$			25.64	27.60	27.66	27.10	27.19
$H^{3,8}$			7.42 (8.16)	7.64 (8.16)	7.63 (8.35)	7.62 (8.16)	7.68 (8.16)
$H^{4,7}$			8.04 (8.16)	8.25 (8.16)	8.24 (8.15)	8.23 (8.16)	8.27 (8.28)
$H^{5,6}$			7.62	7.79	7.77	7.73	7.80
$H^{15,16}$			2.90	3.24	3.19	3.13	3.13

(a) data from: R. Starosta, M. Puchalska, J. Cybińska, M. Barys, A.V. Mudring, *Dalton Trans.*, 2011, **40**, 2459-2468

Figure S1

Molecular orbitals (and spin density) for 1I (6-31G** except I - 6-311G(d,p) and Cu - LanL2Dz with Los Alamos ECP)

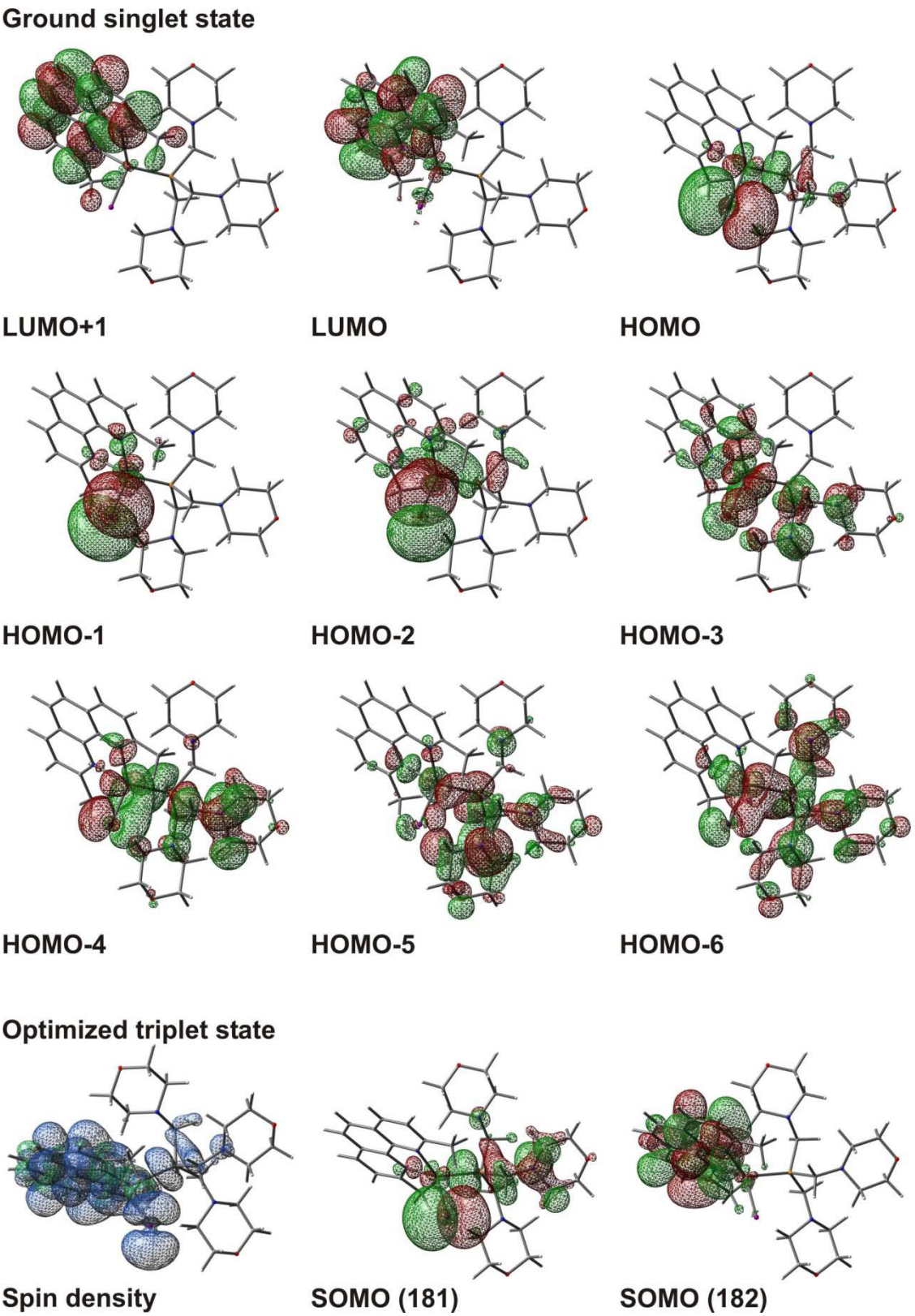

Figure S2.

Molecular orbitals (and spin density) for 2I(6-31G** except I - 6-311G(d,p) and Cu - LanL2Dz with Los Alamos ECP)

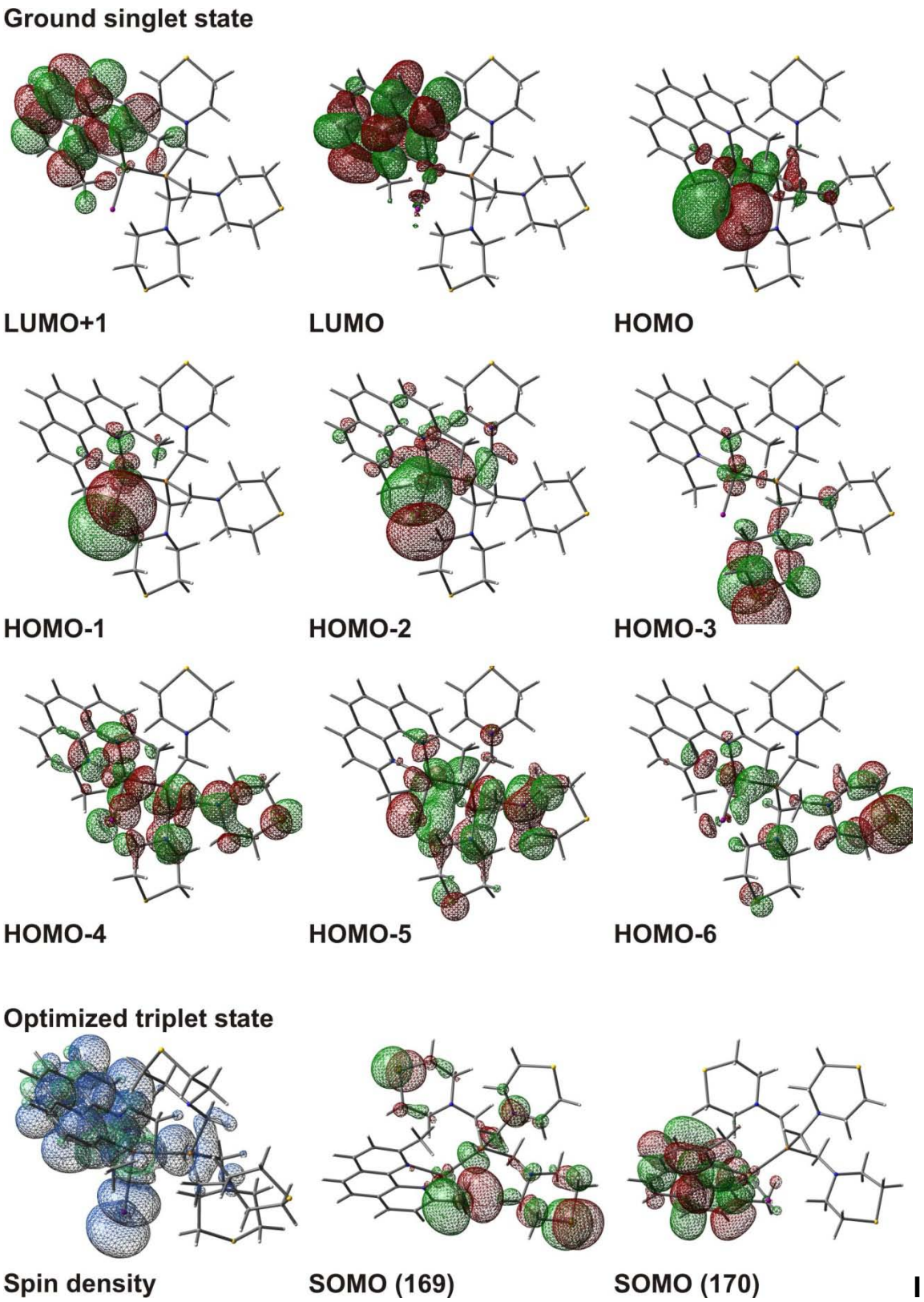

Figure S3.

Molecular orbitals (and spin density) for 1T (6-31G** except I - 6-311G(d,p) and Cu - LanL2Dz with Los Alamos ECP)

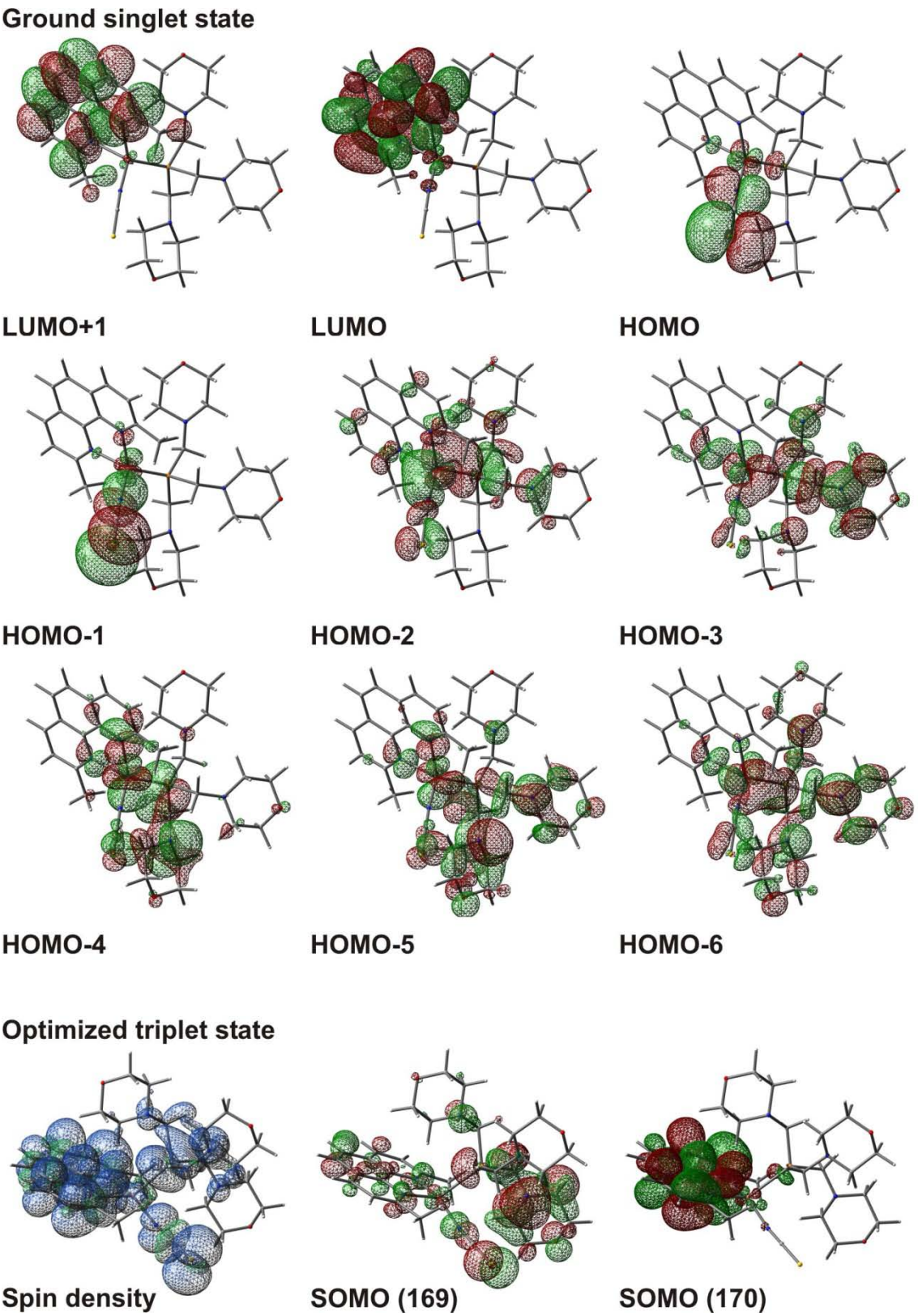

Figure S4.

Molecular orbitals (and spin density) for 2T (6-31G** except I - 6-311G(d,p) and Cu - LanL2Dz with Los Alamos ECP)

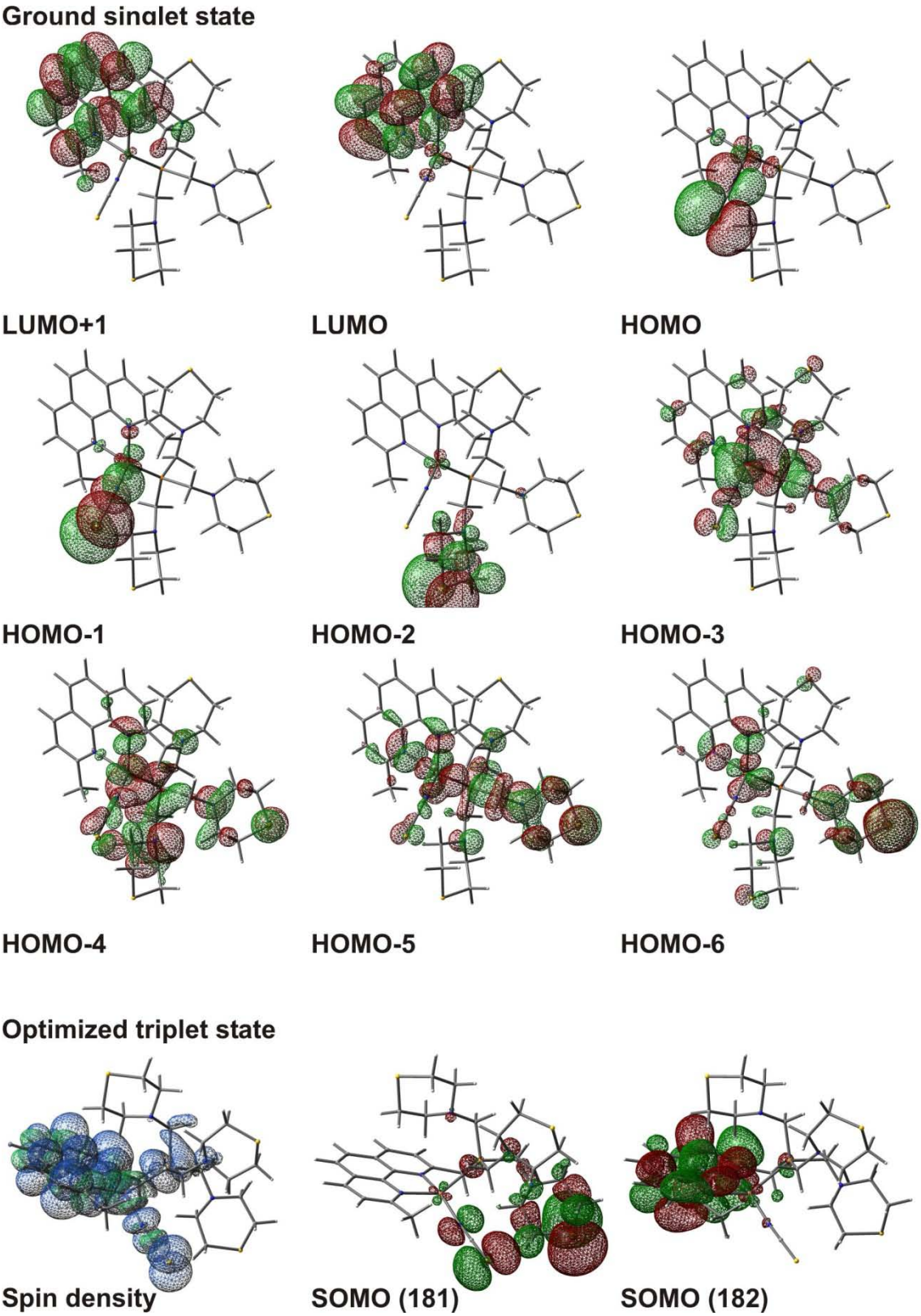

Table S3.

DFT geometries obtained with a larger basis set (Cu: 6-311+G**; I: 6-311G**; N, P, O and S: 6-31+G**; C, H: 6-31G**) -LEFT and a simple basis set: 6-31G(d,p) except I - 6-311G** and Cu - LanL2Dz with Los Alamos ECP - RIGHT of the iodo and isothiocyanato copper(I) complexes with dmp and **1** or **2** in ground singlet and triplet states

	Cu: 6-311+G**; I: 6-311G** N, P, O and S: 6-31+G**; C, H: 6-31G*				C, H, N, P, O, S: 6-31G**; I: 6-311G**; Cu: LanL2Dz with Los Alamos ECP			
	1I	**2I**	**1T**	**2T**	**1I**[a]	**2I**	**1T**	**2T**
$^1A_1$								
Cu-P	2.3052	2.3018	2.2995	2.3012	2.3515	2.3498	2.3509	2.3461
Cu-I(N)	2.6736	2.6742	1.9622	1.9609	2.6775	2.6812	1.9918	1.9916
N-C			1.1855	1.1855			1.1870	1.1868
C-S			1.6343	1.6341			1.6334	1.6338
P-Cu-I(N)	110.48	110.27	113.75	116.48	110.76	110.16	112.02	114.93
Cu-N-C			177.45	177.32			175.50	172.78
N-C-S			179.32	179.45			179.06	179.19
S4	**57.55**	**57.21**	**56.53**	**57.07**	**56.49**	**56.06**	**54.48**	**54.36**
α	86.45	86.02	83.76	84.69	86.76	85.76	84.04	85.16
β	141.92	142.22	132.51	129.40	143.24	143.91	132.67	131.17
γ	107.58	107.51	113.77	114.13	106.02	105.93	115.31	113.90
β- *γ*	34.34	34.71	18.74	15.27	37.22	37.98	17.36	17.27
$^3A_1$								
Cu-P	2.5000	2.5185	2.5271	2.5491	2.5018	2.5136	2.6022	2.6213
Cu-I(N)	2.6271	2.6149	1.9074	1.9075	2.6658	2.6626	1.9253	1.9266
av.(P-Cx)*								
N-C			1.1892	1.1895			1.1912	1.1915
C-S			1.6169	1.6165			1.6161	1.6159
P-Cu-I(N)	99.16	99.13	92.05	91.69	97.64	97.72	90.47	90.46
Cu-N-C			165.59	165.50			162.04	161.38
N-C-S			179.03	179.01			178.97	179.01
S4	**52.23**	**53.75**	**49.77**	**51.11**	**49.85**	**50.86**	**49.29**	**50.93**
α	73.94	72.94	67.66	68.36	70.63	70.98	67.06	69.56
β	133.47	126.85	116.38	119.08	142.95	141.70	114.93	118.75
γ	127.34	134.01	151.56	149.24	119.44	120.59	154.61	150.83
β- *γ*	6.33	-7.16	-35.16	-30.16	23.25	21.11	-39.68	-32.08

[a] From ref. A32

Figure S5.

Molecular geometries in ground singlet and first triplet states determined with DFT methods (B3Lyp/Cu: 6-311+G*; I: 6-311G**; N, P, O and S: 6-31+G**;C, H: 6-31G**)

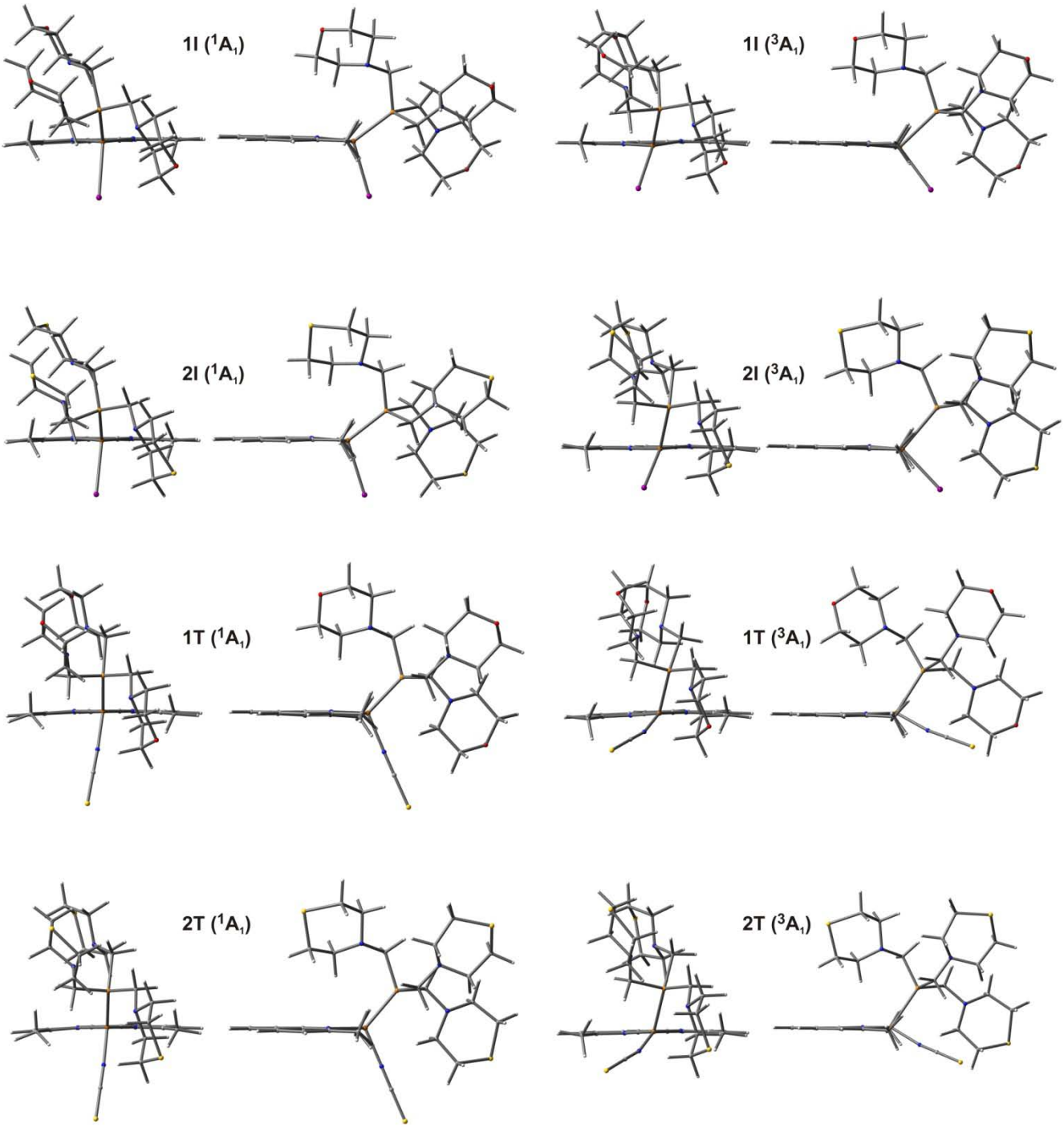

Table S4.

UV-Vis transitions (in nanometres) from TDDFT calculations obtained with a simple basis set (6-31G** except I: 6-311G(d,p) and Cu: LanL2Dz with Los Alamos ECP)

	1I[a]	**2I**	**1T**	**2T**
First triplet transition	T_1: 565.52	T_1: 562.86	T_1:674.68	T_1:666.24
transition type:	H→L (93%) H1→L (7%)	H→L (91%) H1→L (9%)	H→L (97%) H1→L (3%)	H→L (98%) H1→L (2%)
1st (edge) singlet trans.	S_1: 557.20	S_1: 554.45	S_1:670.46	S_1: 662.88
(oscillator strength)	(0.0021)	(0.0023)	(0.0020)	(0.0012)
transition type:	H→L (100%)	H→L (100%)	H→L (100%)	H→L (100%)
2nd triplet transition	T_2: 551.36	T_2: 549.40	T_2:656.54	T_2:649.67
transition type:	H2→L (11%) H1→L (79%)	H2→L (15%) H1→L (74%)	H→L (3%) H1→L (97%)	H→L (2%) H1→L (98%)
1st intense singlet trans.	S_4: 499.78	S_4: 498.43	S_5: 442.70	S_5: 439.14
(oscillator strength)	(0.0252)	(0.0321)	(0.0225)	(0.0195)
transition type:	H2→L (56%) H1→L1 (44%)	H2→L (67%) H1→L1 (33%)	H2→L (62%) H4→L (25%)	H3→L (63%) H5→L (14%)
2nd intense singlet trans.	S_5: 495.06	S_5: 493.36	S_6: 423.42	S_6: 416.02
(oscillator strength)	(0.0373)	(0.0310)	(0.0360)	(0.0338)
transition type:	H2→L (41%) H1→L1 (59%)	H2→L (30%) H2→L1 (70%)	H2→L (29%) H3→L (31%)	H3→L (27%) H5→L (53%)

[a] From ref. A32; [b] H - HOMO - highest occupied molecular orbital; L -LUMO - lowest unoccupied molecular orbital; H1, H2... - orbitals of lower energy than HOMO (in descending order); L1, L2... - orbitals of higher energy than LUMO (in ascending order); [c]- most calculated transitions are complex, the percentage is given for dominating participation.

Figure S6. Molecular orbitals for the optimized geometries (6-311+G except I: 6-311G**)**