Supporting Information

Alkynyl triphosphine copper complexes: synthesis and photophysical studies

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Synthesis of the ligands

1,3,5-(4-HC$_2$C$_6$H$_4$-4-C$_2$C$_6$H$_4$)$_3$C$_6$H$_3$ (L6). 1,3,5-(4-HC$_2$-C$_6$H$_4$)$_3$C$_6$H$_3$ (2.3 g, 6.08 mmol), 1,4-iodobromobenzene (5.2 g, 18.37 mmol), a catalyst Pd(PPh$_3$)$_2$Cl$_2$ (200 mg)/CuI (80 mg) were placed in a 100-mL Schlenk flask under a nitrogen atmosphere. Freshly distilled tetrahydrofurane (30 mL) and NEt$_3$ (20 mL) were added and the reaction mixture was stirred overnight at room temperature. The resulting thick yellow suspension was evaporated and the solid was washed with MeOH (2×30 mL). The crude 1,3,5-(4-BrC$_6$H$_4$-4-C$_2$-C$_6$H$_4$)$_3$C$_6$H$_3$ was dissolved in CHCl$_3$ (ca. 300 mL), passed through a layer of Silica (2.5×10 cm). The solvent was removed and the solid was washed again with CHCl$_3$/MeOH mixture (1:1 v/v, 3×40 mL) to give the product of a sufficient purity (4.87 g, 95 %). ^{1}H NMR (CDCl$_3$; 298 K; δ): 7.81 (s, 3H, C$_6$H$_3$), AB system 7.70 and 7.71 (12H, *J*(H–H) 7.7 Hz, C$_6$H$_4$), AB system 7.51 and 7.43 (12H, *J*(H–H) 7.5 Hz, C$_6$H$_4$). 1,3,5-(4-BrC$_6$H$_4$-4-C$_2$-C$_6$H$_4$)$_3$C$_6$H$_3$ (2.87 g, 3.40 mmol), a catalyst Pd(PPh$_3$)$_2$Cl$_2$ (250 mg)/CuI (90 mg) were placed in a 250-mL Schlenk flask under a nitrogen atmosphere. Freshly distilled tetrahydrofurane (50 mL) and NEt$_3$ (50 mL) were added, followed by trimethylsilylacetylene (1.7 g, 17.35 mmol). The reaction mixture was heated to 343 K and stirred for 2 days under an inert atmosphere. After cooling to room temperature the reaction was quenched with water (40 mL). The mixture was diluted with CH$_2$Cl$_2$ (50 mL), organic layer was separated, dried over

Na_2SO_4 and evaporated. The crude 1,3,5-(4-$Me_3SiC_6H_4$-4-C_2-C_6H_4)$_3C_6H_3$ was passed through a layer of Silica (2.5×15 cm, eluent CH_2Cl_2/hexane 3:5 v/v) to give a yellow solid after evaporation (2.90 g, 95 %). ^{1}H NMR ($CDCl_3$; 298 K; δ): 7.80 (s, 3H, C_6H_3), 7.67 (m, 12H, C_6H_4), 7.49 (m, 12H, C_6H_4), 0.29 (s, 27H, $SiMe_3$). 1,3,5-(4-$Me_3SiC_6H_4$-4-C_2-C_6H_4)$_3C_6H_3$ (2.90 g, 3.24 mmol) was dissolved in THF (50 mL), diluted with MeOH (50 mL) and K_2CO_3 (0.8 g) was added. The mixture was stirred overnight under a nitrogen atmosphere, then it was evaporated and the residue was washed with H_2O/MeOH (5:1 v/v, 2×30 mL), MeOH (2×30 mL) and dried. The solid was dissolved in $CHCl_3$ (50 mL), passed through a layer of Florisil (2.5×10 cm, 150 mesh) and evaporated The resulting product was additionally washed with CH_2Cl_2/MeOH mixture (1:3 v/v, 2×30 mL) and dried (1.86 g, 85 %). ^{1}H NMR ($CDCl_3$; 298 K; δ): 7.82 (s, 3H, C_6H_3), AB system 7.72 and 7.66 (12H, *J*(H–H) 7.7 Hz, C_6H_4), AB system 7.53 and 7.50 (12H, *J*(H–H) 7.5 Hz, C_6H_4), 3.20 (s, 3H, C_2H). Anal. Calcd. for $C_{54}H_{30}$: C, 95.55; H, 4.46; found: C, 95.93; H, 4.22.

Bis(2-diphenylphosphinophenyl)phenylphosphine (*P*^{3}). The ligand was obtained according to a modified procedure[1] to give a considerably higher yield. The synthesis was carried out under a nitrogen atmosphere. A solution of (2-bromophenyl)diphenylphosphine (1.2 g, 3.53 mmol) in THF (20 mL) was cooled to –78 ^{o}C and a 1.6 M solution of n-BuLi (2.2 mL, 3.52 mmol) was added dropwise within 10 minutes. The resulting orange solution was stirred for 1 h at this temperature and treated dropwise with $PPhCl_2$ (0.315 g, 1.76 mmol). The reaction mixture was stirred below –70 ^{o}C for 1 h, then allowed slowly (ca. 2 h) to reach room temperature and was additionally stirred for 3 h. The reaction was quenched with methanol (5 mL), the solvents were evaporated and yellow amorphous residue was washed with methanol (5 × 15 mL) to give white solid of sufficient purity (0.95 g, 86%). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K): δ = AB_2 system -15.2 (2P, PPh_2), -18.9 (1P, PPh) *J*(P–P) 153 Hz. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.26–7.10 (m, 31H, PPh_2), 6.86 (m, 2H, PPh).

1. J. G. Hartley, L. M. Venanzi, D. C. Goodall, *J. Chem. Soc.*, 1963, 3930-3936.

Table S1. Crystal data and structure refinement for **1**, **3** and **5**.

Identification code	**1**	**3**	**5**
Empirical formula	$C_{54}H_{46}CuOP_3$	$C_{107}H_{82}Cu_2N_2O_4P_6$	$C_{98}H_{76}Cu_2N_2OP_6$
Formula weight	867.36	1772.64	1610.50
Temperature	120(2) K	120(2) K	120(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P\,2_1/n$	$P\,2_1/n$	F d d 2
Unit cell dimensions	a = 22.6315(14) Å	a = 23.3830(10) Å	a = 24.0017(17) Å
	b = 16.7911(10) Å	b = 16.5769(6) Å	b = 40.189(3) Å
	c = 26.0313(17) Å	c = 24.6246(9) Å	c = 17.0010(13) Å
	α = 90°	α= 90°	α= 90°
	β = 91.691(3)°	β= 113.316(2)°	β= 90°
	γ = 90°	γ = 90°	γ = 90°
Volume	9887.8(11) Å^3	8765.4(6) Å^3	16399(2) Å^3
Z	8	4	8
Density (calculated)	1.165 Mg/m^3	1.343 Mg/m^3	1.305 Mg/m^3
Absorption coefficient	0.574 mm^{-1}	0.651 mm^{-1}	0.686 mm^{-1}
F(000)	3616	3672	6672
Crystal size	0.145 x 0.139 x 0.134 mm^3	0.140 x 0.108 x 0.098 mm^3	0.246 x 0.140 x 0.085 mm^3
θ range for data collection	1.689 to 25.997°	1.523 to 29.000°	1.977 to 26.995°
Index ranges	-27<=h<=27, -20<=k<=19, -31<=l<=32	-31<=h<=31, -22<=k<=17, -29<=l<=33	-30<=h<=30, -51<=k<=51, -18<=l<=21
Reflections collected	84838	93886	58655
Independent reflections	19377 [R(int) = 0.0316]	23300 [R(int) = 0.0405]	8563 [R(int) = 0.0479]
Completeness to θ= 25.242°	99.8 %	99.9 %	99.9 %
Absorption correction	Numerical	Numerical	Numerical
Max. and min. transmission	0.927 and 0.921	0.939 and 0.914	0.944 and 0.849
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	19377 / 78 / 1055	23300 / 0 / 1091	8563 / 1 / 497
Goodness-of-fit on F^2	1.029	1.045	1.054
Final R indices [I>2sigma(I)][a]	R1 = 0.0551, wR2 = 0.1506	R1 = 0.0445, wR2 = 0.1004	R1 = 0.0428, wR2 = 0.0950
R indices (all data)	R1 = 0.0819, wR2 = 0.1718	R1 = 0.0733, wR2 = 0.1120	R1 = 0.0691, wR2 = 0.1073
Largest diff. peak and hole	1.645 and -0.737 e.Å^{-3}	0.679 and -0.402 e.Å^{-3}	0.473 and -0.247 e.Å^{-3}

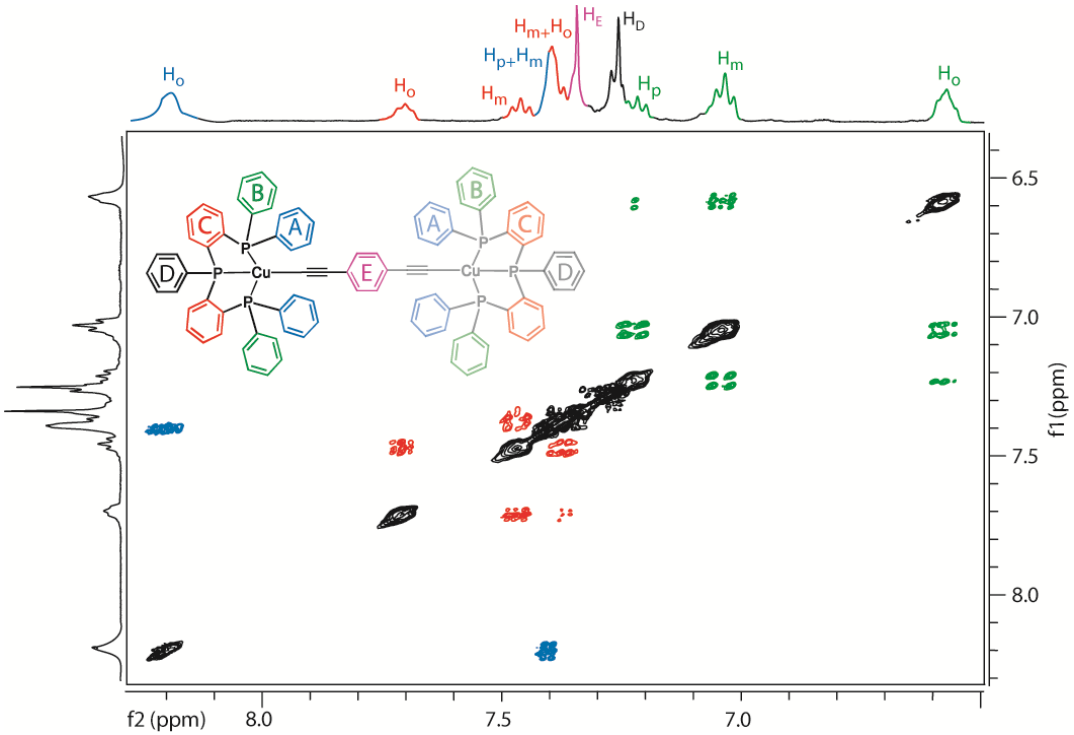

Figure S1. ^{1}H-^{1}H COSY NMR spectrum of the complex **6** (CD_2Cl_2, 298 K).

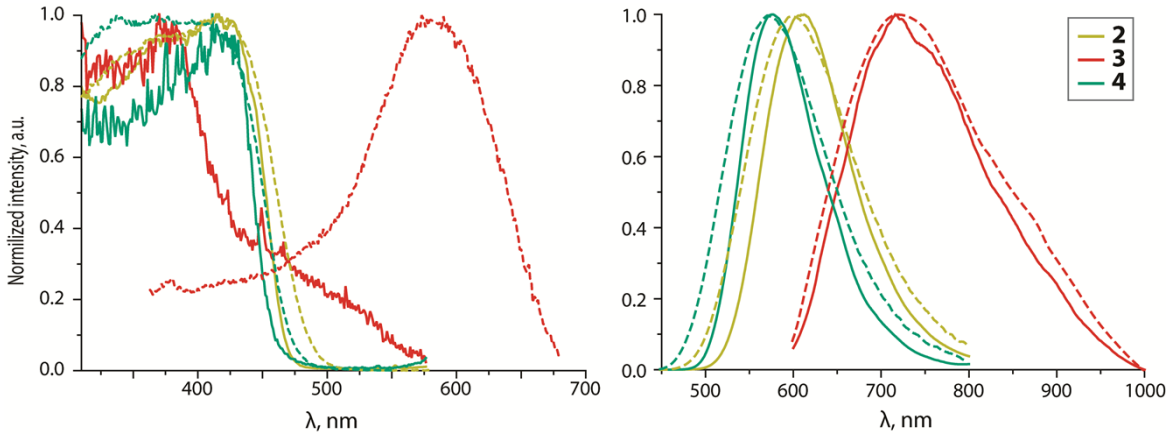

Figure S2. Normalized excitation (left) and emission (right) spectra of **2**–**4** in the solid state at 298 K (dashed lines) and 77 K (solid lines).

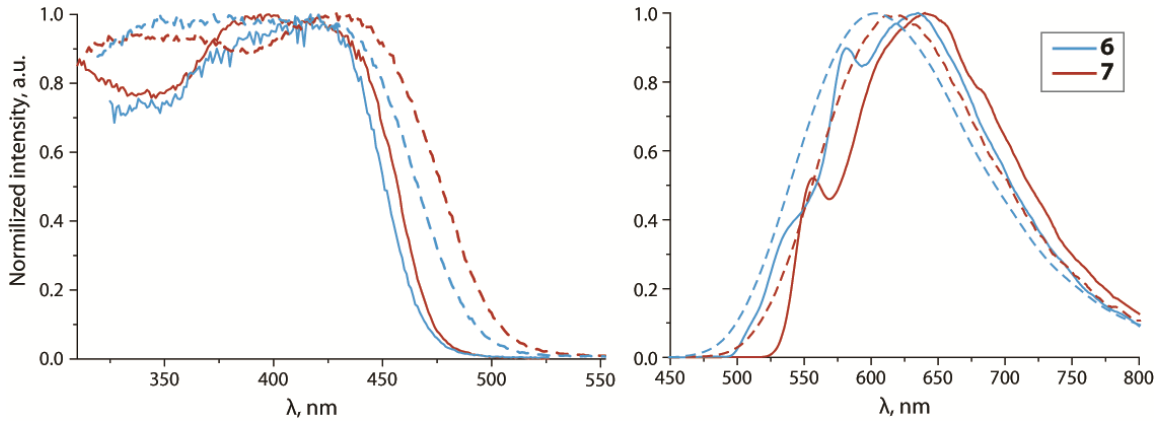

Figure S3. Normalized excitation (left) and emission (right) spectra of **6** and **7** in the solid state at 298 K (dashed lines) and 77 K (solid lines).

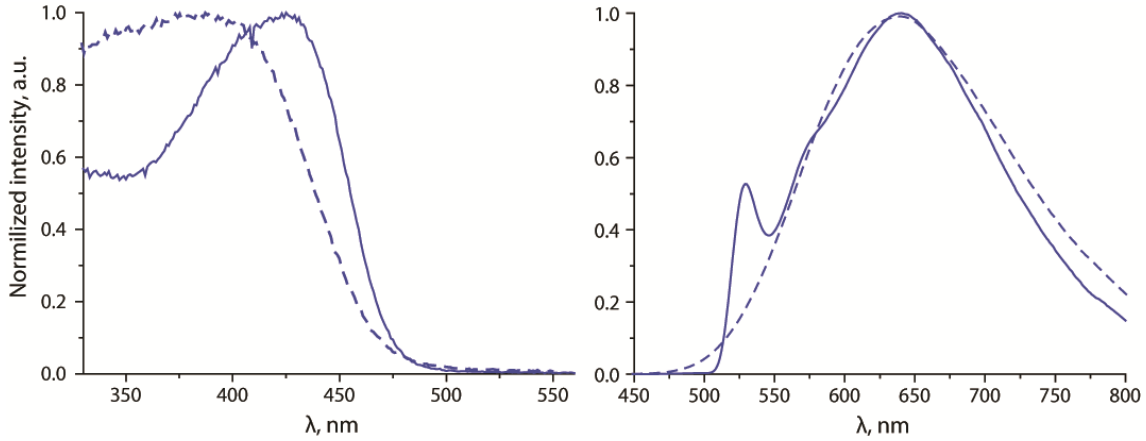

Figure S4. Normalized excitation (left) and emission (right) spectra of **9** in the solid state at 298 K (dashed lines) and 77 K (solid lines).

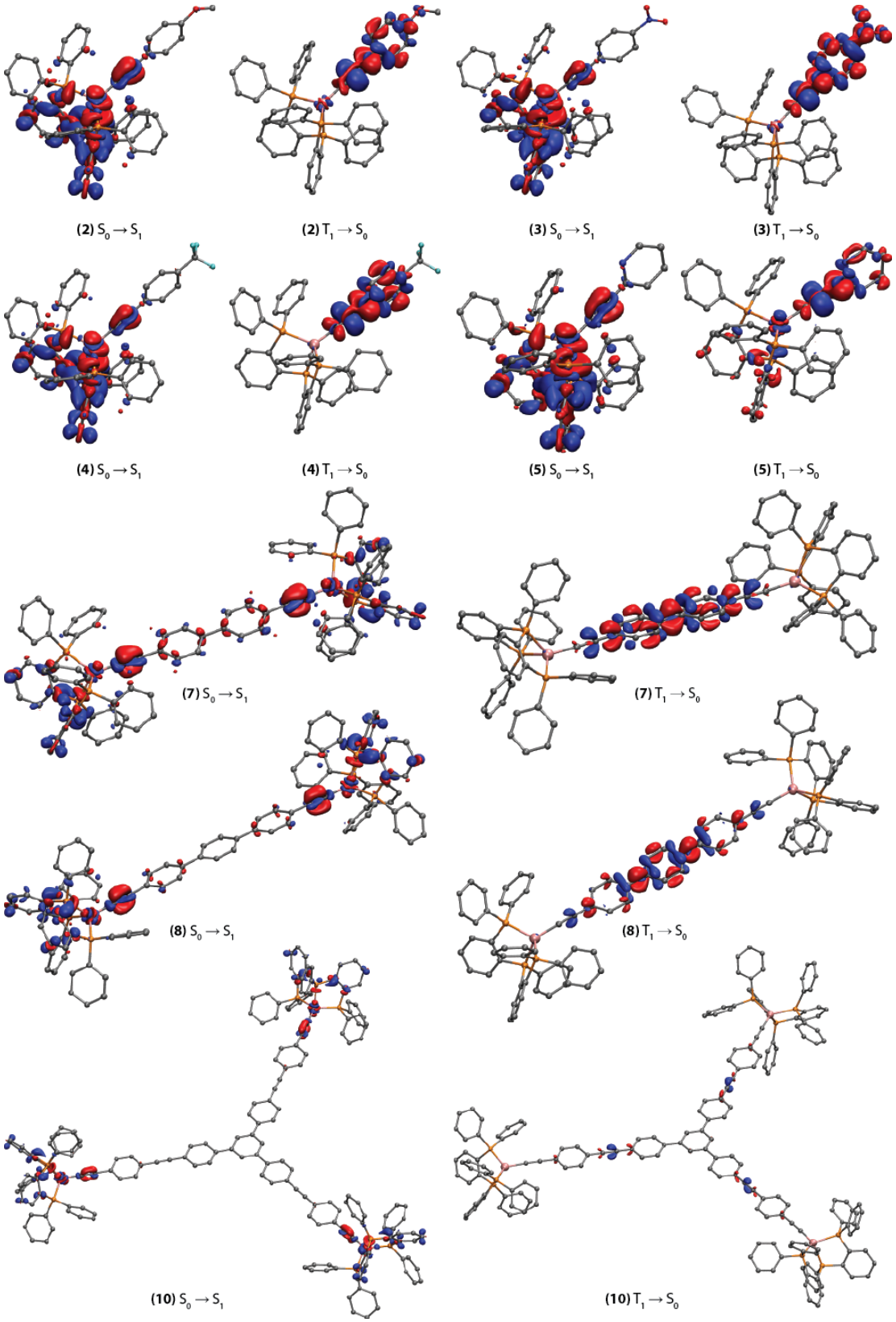

Figure S5. Electron density difference plots for the lowest energy singlet excitation ($S_0 \rightarrow S_1$) and the lowest energy triplet emission ($T_1 \rightarrow S_0$) of the Cu(I) complexes **2–5**, **7, 8**, and **10** (isovalue 0.002 a.u.). During the electronic transition, the electron density increases in the blue areas and decreases in the red areas. Hydrogen atoms omitted for clarity.