Electronic Supplementary Information for

Synthesis and structural characterisation of (aryl-BIAN)copper(I) complexes and their application as catalysts for the cycloaddition of azides and alkynes

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Table S1. Electrochemical data for the ligands **L1**-**L5**.[a]

Ligand	Anodic scan		Cathodic scan		Upon scan reversal after I^{ox}	
	$E_p^{ox}(I)^b$	$E_p^{ox}(II)^b$	$E_p^{red}(III)^c$	$E_p^{ox}(IV)^b$	$E_p^{red}(1)^b$	$E_{1/2}^{red}(2)^b$
L1	0.61	1.12	-2.00	-1.37		
L2	0.72	1.31	-2.08	-1.67	-0.57	-0.87
L3	0.86	1,39	-2.00	-1.40	-0.64	-0.83
L4	0.86	1,48	-2.00	-1.44	-0.55	-0.81
L5	0.90	1.48	-2.11	-1.64	-0.55	-0.78

[a] General conditions: $[NBu_4][BF_4]/CH_2Cl_2$ electrolyte solution, Pt-disk working electrode, scan rate: 200 mV/s. [b] E_p^{ox} and E_p^{red} stand for oxidation and reduction peak potentials, respectively. $E_{1/2}^{ox}$ and $E_{1/2}^{red}$ are the half-wave oxidation and reduction potentials respectively. All potentials are given in V *versus* Fc/Fc^+ redox couple.

Table S2. Energies of the HOMO and LUMO of ligands **L1**-**L5** calculated using the HF/DFT B3LYP/6-31G* model.

Ligands	HOMO/eV	LUMO/eV
L1	-5.78	-2.02
L2	-5.42	-1.99
L3	-5.61	-1.97
L4	-5.54	-2.07
L5	-5.60	-2.07

Computational Calculations. The calculations were performed using the Spartan'04 software (Wavefunction, Inc.). A hybrid HF/DFT B3LYP model with a 6-31G* basis set was used for all calculations and full geometry optimizations were performed.

Table S3. Crystal data and structure refinements for complexes **3**, **4**, **6** and **7**

Compounds	**3**	**4**·0.5(CH_2Cl_2)	**6**·0.3(CH_2Cl_2)	**7**·CH_2Cl_2
Empirical formula	$C_{60}H_{56}BCuF_4N_4$	$C_{60.5}H_{57}BClCuF_4N_4$	$C_{50.3}H_{50.6}B\ Cl_{0.6}CuF_4N_4$	$C_{67}H_{60}N_2CuBCl_2F_4P_2$
Formula weight	983.45	1025.90	882.77	1176.36
Temperature (K)	150(2)	150(2)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	*Fddd*	$P2_1/n$	*Pbca*
a (Å)	16.4565(5)	17.5980(13)	24.8522(14)	17.5292(7)
b (Å)	44.4015(13)	21.498(2)	11.9094(7)	24.6971(10)
c (Å)	29.1759(8)	27.979(2)	32.6051(19)	26.7660(11)
α (º)	90	90	90	90
β (º)	102.0550(10)	90	105.304(2)	90
γ (º)	90	90	90	90
V (Å^3)	20848.5(10)	10585.1(15)	9308.1(9)	11587.5(8)
Z	16	8	8	8
D_{calc} (mg Å^{-3})	1.253	1.287	1.260	1.349
μ (mm^{-1})	0.476	0.520	0.558	0.581
F(000)	8224	4280	3685	4880
Crystal size (mm)	0.20×0.18×0.10	0.25×0.15×0.10	0.32×0.26×0.24	0.40×0.34×0.26
θ (º)	0.92-25.67	3.33-25.67	0.92-25.72	2.53-25.70
Index ranges	-20≤h≤19,	-21≤h≤15,	-30≤h≤29,	-18≤h≤21,
	-48≤k≤54,	-26≤k≤25,	-14≤k≤14,	-26≤k≤30,
	-35≤l≤32	-31≤l≤33	-39≤l≤39	-32≤l≤32
Reflections collected	301428	13927	178251	166728
Independent reflections	39329	2500	17534	10983
Reflections observed [$I>2\sigma(I)$]	18846	1938	7059	7757
R_{int}	0.1300 [a]	0.0621	0.1835 [a]	0.0672
GOOF	0.995	1.089	1.000	1.070
R_1 [$I>2\sigma(I)$]	0.0755	0.0460	0.0589	0.0435
wR_2 [$I>2\sigma(I)$]	0.1879	0.1187	0.1385	0.1178
R_1, wR_2 all data	0.1852/0.2238 [a]	0.0618/0.1265	0.1502/0.1502 [a]	0.0795/0.1328

[a] These high values are due to the poor diffraction quality of the crystals.

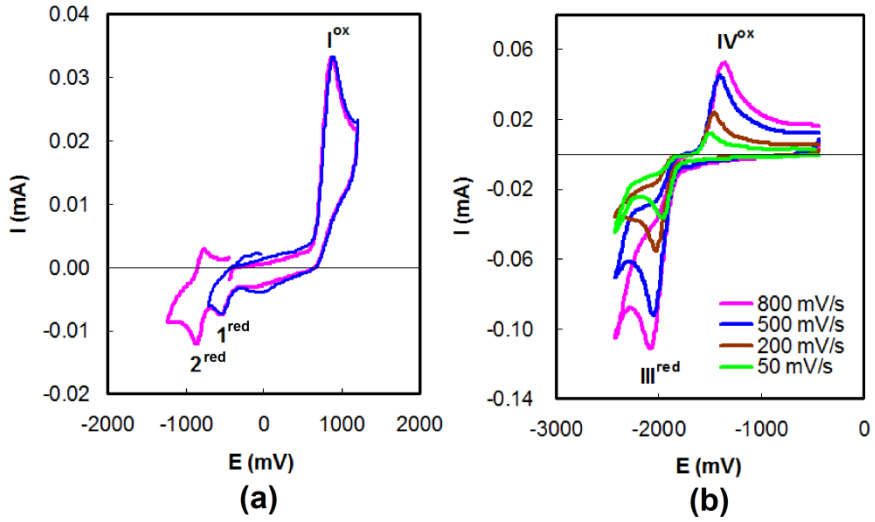

Figure S1. Cyclic voltammograms of **L4** obtained: (a) at scan rate of 200 mV/s for the anodic scan; (b) at varied scan rates for the cathodic scan.

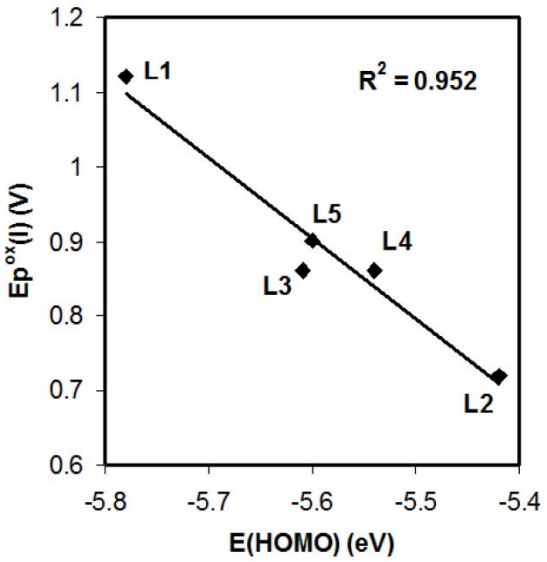

Figure S2. Plot of $E_p^{ox}(I)$ *versus* E(HOMO) of the ligands **L1**-**L5**.