Electronic Supplementary Information (ESI)

for

Copper complexes of non-innocent β-diketiminate ligand containing phenol groups

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Fig. S1

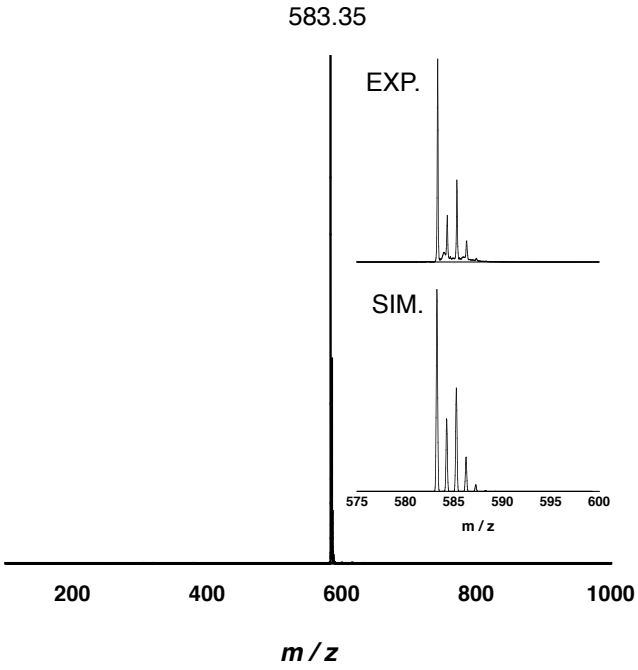
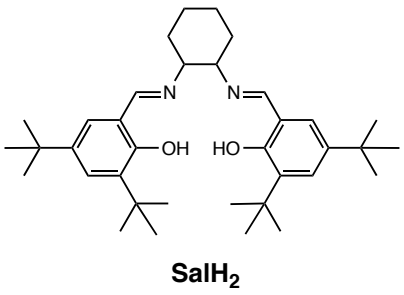


Fig. S1 ESI-MS (negative mode) of $[Cu^{II}(\mathbf{L}^{3-})]^{-}$ in CH_2Cl_2. Inset: Expanded spectrum (EXP) and its simulation spectrum (SIM)

Fig. S2



$SalH_2$

Fig. S2 Structure of ligand $SlaH_2$

Fig. S3

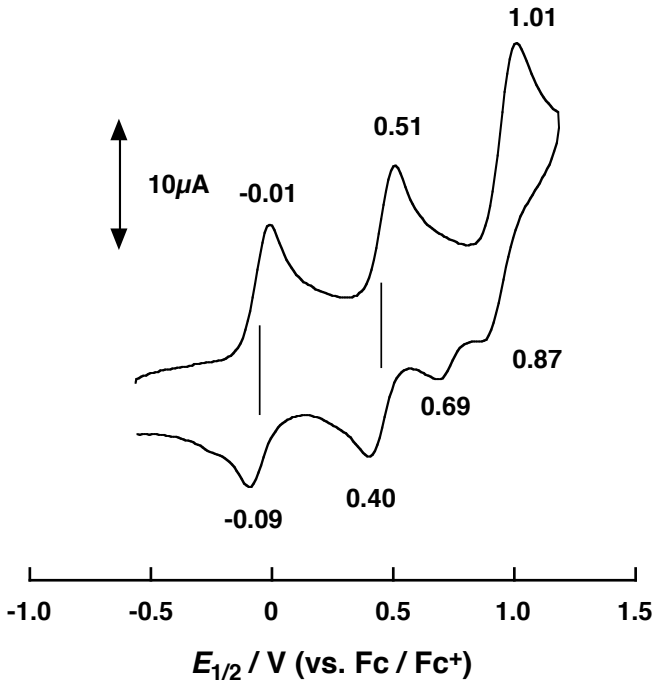


Fig. S3 Cyclic voltammogram of $(Et_4N)[Cu^{II}(\mathbf{L}^{3-})]$ (0.5 mM) in CH_2Cl_2 containing 0.1 M $TBAPF_6$; working electrode: grassy carbon, counter electrode: Pt, reference: ferrocene, scan rate 100 mV/s.

Fig. S4

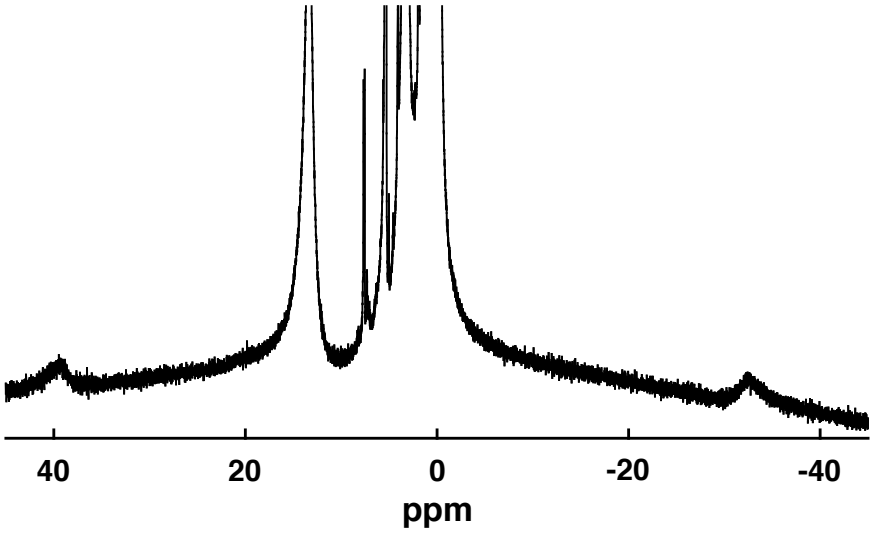


Fig. S4 ^1H NMR spectrum of $[Cu^{II}(\mathbf{L}^{\bullet 2-})]$ in CD_2Cl_2 at 193 K.

Table S1. TD-DFT calculated energies (λ), oscillator strengths for the major electronic transitions (f_{osc}) and the related molecular orbitals of triplet $Cu^{II}(\mathbf{L}^{\bullet 2-})$ using UCAM-B3LYP/DGTZVP//UCAM-B3LYP/6-311G(d) basis set

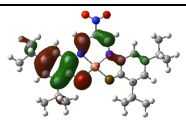
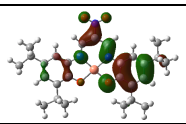
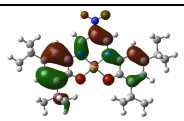
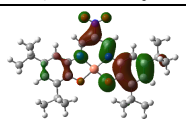
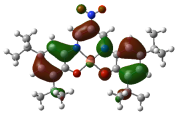
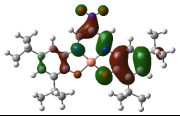
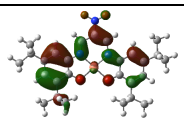
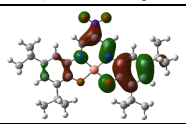
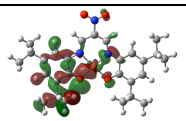
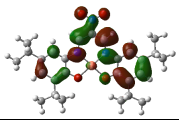
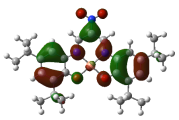
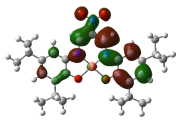
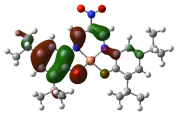
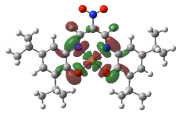
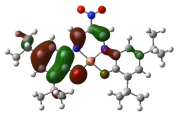
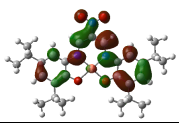
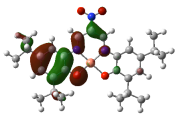
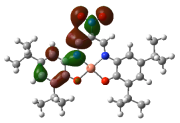
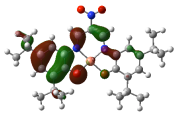
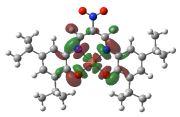
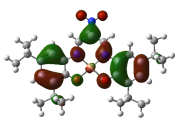
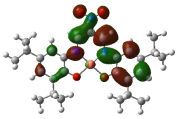
excited state	λ / nm	f_{osc}	transition	donor MO	acceptor MO	comment
1	1229	0.0597	154B → 155B			ligand
3	735	0.0348	153B → 155B			ligand
			152B → 155B			ligand
6	487	0.0368	153B → 155B			ligand
7	476	0.0325	151B → 156B			ligand
10	423	0.1231	155A → 157A			ligand
13	401	0.1167	154B → 157B			LMCT L→ Cu $d_{x^2-y^2}$
			154B → 156B			ligand
14	385	0.0449	156A → 158A			ligand
			154B → 157B			LMCT L→ Cu $d_{x^2-y^2}$
18	352	0.1445	155A → 157A			ligand

Table S2. TD-DFT calculated energies (λ), oscillator strengths for the major electronic transitions (f_{osc}) and the related molecular orbitals of $[Cu^{II}(\mathbf{L}^{-})]^{+}$ using UCAM-B3LYP/DGTZVP//UCAM-B3LYP/6-311G(d) basis set

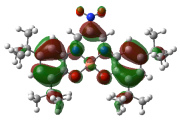
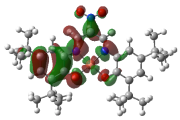
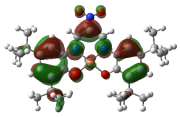
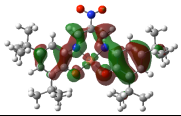
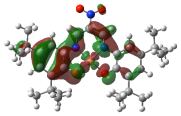
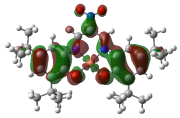
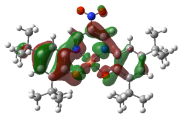
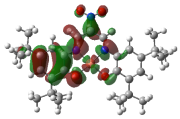
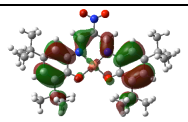
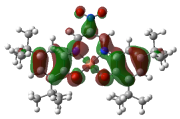
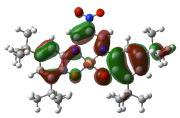
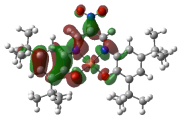
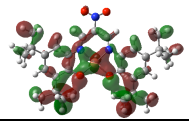
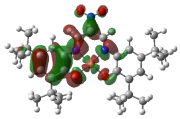
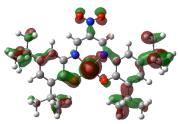
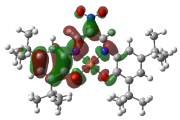
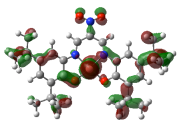
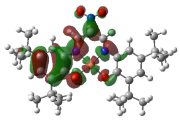
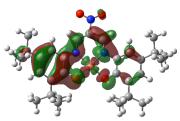
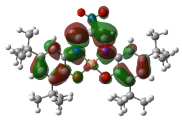
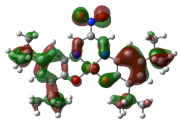
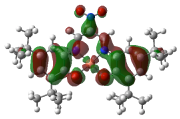
excited state	λ / nm	f_{osc}	transition	donor MO	acceptor MO	comment
2	1007	0.0001	153A → 156A			ligand
			153B → 155B			ligand
3	907	0.0067	154B → 156B			ligand
4	747	0.0742	155A → 156A			ligand
5	669	0.0306	152B → 156B			ligand
6	648	0.0505	154A → 156A			ligand
16	401	0.0150	128A → 156A			MLCT Cu d_{yz} → L
18	386	0.1454	136A → 156A			MLCT Cu d_z^2 → L
20	368	0.1936	136A → 156A			MLCT Cu d_z^2 → L
21	364	0.0410	154B → 157B			ligand
24	355	0.1412	147B → 156B			ligand

Fig. S5

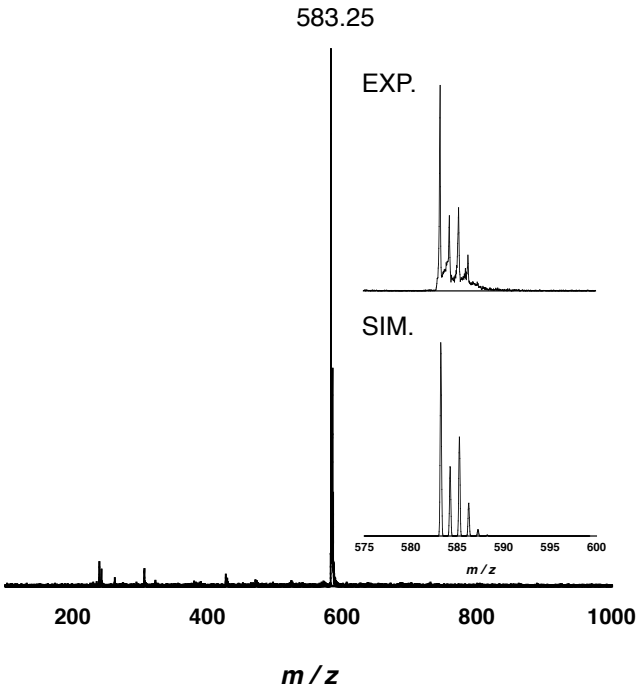


Fig. S5 ESI-MS (*positive* mode) of $[Cu^{II}(\mathbf{L}^{-})]^{+}$ in CH_2Cl_2. Inset: Expanded spectrum (EXP) and its simulation spectrum (SIM).

Fig. S6

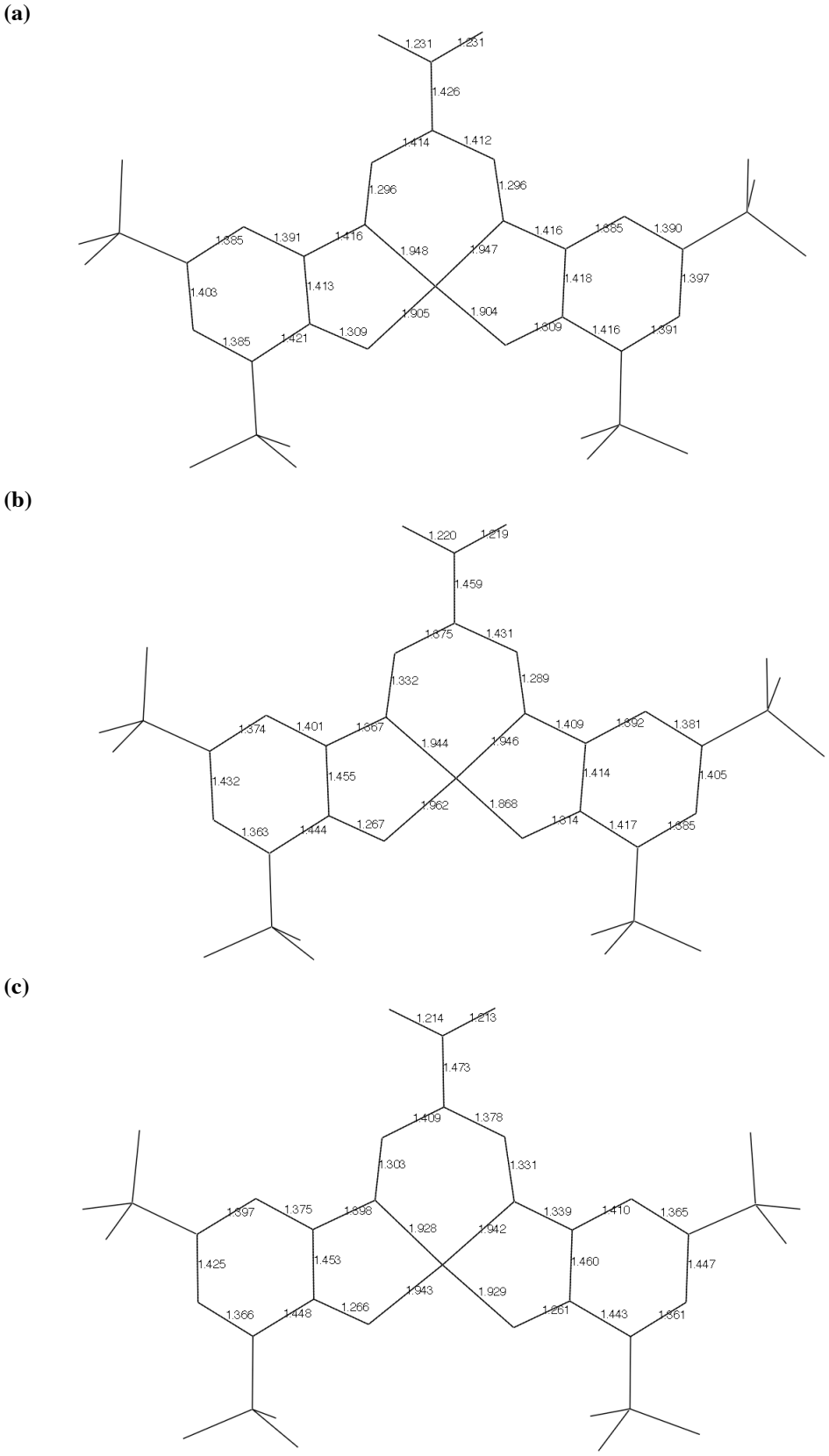


Fig. S6 The optimized structures and their selected bond lengths of (a) $[Cu^{II}(\mathbf{L}^{3-})]^{-}$, (b) $[Cu^{II}(\mathbf{L}^{\bullet 2-})]$ and (c) $[Cu^{II}(\mathbf{L}^{-})]^{+}$ calculated by DFT using UCAM-B3LYP/6-311G(d) basis set.

Fig. S7

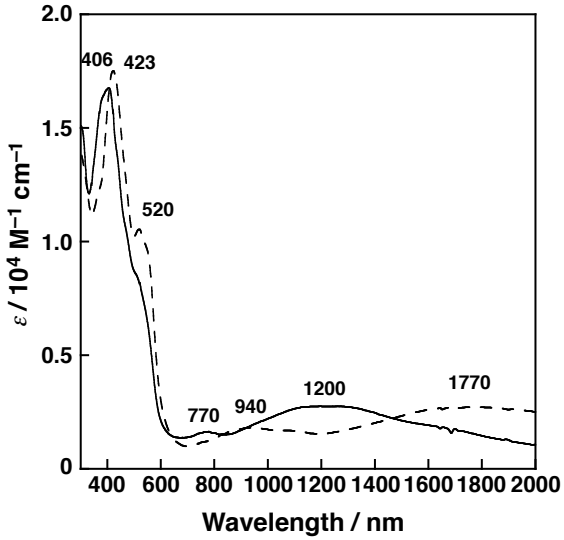


Fig. S7 UV-vis spectrum of the final reaction mixture of $[Cu^{II}(\mathbf{L}^{-})]^{+}$ (2.0×10^{-4} M) and 1,4-cyclohexadiene (1.2×10^{-2} M) in CH_2Cl_2 at 30 °C (solid line) and the spectrum generated by the addition of 1 equiv of triethylamine (dotted line). The dotted line spectrum is identical to the spectrum of $[Cu^{II}(\mathbf{L}^{\bullet 2-})]$ shown in Figure 3.

Fig. S8

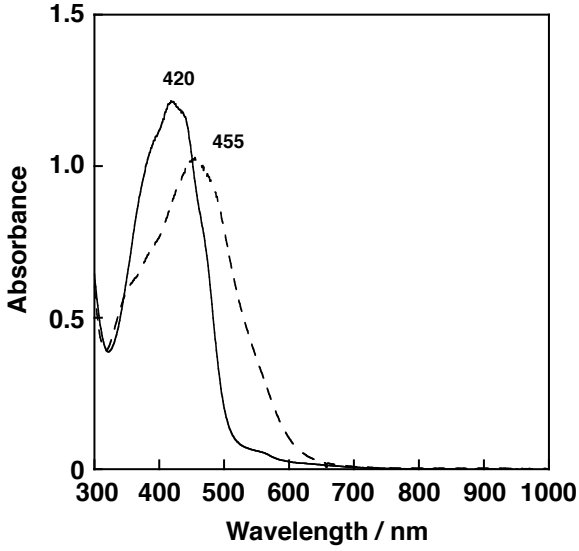


Fig. S8 UV-vis spectrum of the final reaction mixture of $[Cu^{II}(\mathbf{L}^{\bullet 2-})]$ (2.0×10^{-4} M) and 1,4-cyclohexadiene (0.30 M) in CH_2Cl_2 at 30 °C (solid line) and the spectrum generated by the addition of 1 equiv of triethylamine (dotted line). The dotted line spectrum is identical to the spectrum of $[Cu^{II}(\mathbf{L}^{3-})]$ shown in Figure 3.