ESI to accompany:

Exploring copper(I)–based dye–sensitized solar cells: a complementary experimental and TD–DFT investigation

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Table S1. Comparison of DFT and single crystal X–ray structural parameters for the coordaintion spheres in $[Cu(\mathbf{1})_2]^+$ and $[Cu(\mathbf{2})_2]^+$. Atom numbering corresponds to Fig. 3. Experimental data are from this work.

Parameter	$[Cu(\mathbf{1})_2]^+$ (DFT)	$[Cu(\mathbf{1})_2]^+$ (expt)	$[Cu(\mathbf{2})_2]^+$ (DFT)	$[Cu(\mathbf{2})_2]^+$ (expt)
Cu1–N1 / Å	2.004	2.0248(9)	2.020	2.038(2)
Cu1–N2 / Å	2.004	2.0472(9)	2.020	2.038(2)
Cu1–N3 / Å	2.004	2.0447(9	2.020	2.038(2)
Cu1–N4 / Å	2.004	2.0335(9)	2.020	2.038(2)
N1–Cu1–N2 / º	82.92	81.13(4)	83.06	80.48(6)
N1–Cu1–N3 / º	124.24	127.51(4)	131.56	125.64(6)
N2–Cu1– N3 / º	124.24	114.67(4)	131.56	125.64(6)
N1–Cu1– N4 / º	124.17	125.93(4	131.56	125.64(6)
N2–Cu1–N4 / º	124.11	132.08(4)	131.56	125.64(6)
N3–Cu1–N4 / º	82.92	81.59(3)	83.06	80.48(6)

Table S2. Orbital contributions to the electronic absorption transitions making up the band at 438 nm in the calculated electronic absorption spectrum of $[Cu(\mathbf{2})_2]^+$ using a 6–311++G** basis set on Cu and 6–31G* basis set on the ligand atoms; only transitions with oscillator strengths >0.03 have been taken into account.

Compound	Wavelength (nm)	*f*	Transition
$[Cu(\mathbf{2})_2]^+$	562	0.043	62% LUMO←(HOMO) 28% (LUMO)←HOMO–4 2% (LUMO+1)←(HOMO–4) 2% LUMO+1←HOMO
	499	0.035	16% LUMO←HOMO–5 21% LUMO←HOMO–3 20% LUMO+1←HOMO 17% LUMO+2←HOMO 5% LUMO+1←HOMO–4 7% LUMO+2←HOMO–4 2% LUMO+3←HOMO–4 5% LUMO+3←HOMO
	498	0.2653	88% LUMO←HOMO–1 4% LUMO+3←HOMO
	493	0.069	12% LUMO+1←HOMO–4 19% LUMO←HOMO–3 49% LUMO+1←HOMO 7% LUMO←HOMO–5 2% LUMO←HOMO–2 4% LUMO←HOMO
	491	0.2597	89% LUMO←HOMO–2 2% LUMO←HOMO–1
	477	0.1417	15% LUMO+3←HOMO–4 18% LUMO+2←HOMO 46% LUMO+3←HOMO 6% LUMO+2←HOMO–4 3% LUMO←HOMO–2 2% LUMO←HOMO–1 4% LUMO+4←HOMO
	472	0.0385	14% LUMO←HOMO–5 45% LUMO←HOMO–3 6% LUMO+2←HOMO–4 2% LUMO+4←HOMO–4 3% LUMO+1←HOMO 4% LUMO+2←HOMO 9% LUMO+4←HOMO
	470	0.1556	13% LUMO+4←HOMO–4 60% LUMO+4←HOMO 3% LUMO←HOMO–5 7% LUMO←HOMO–3 2% LUMO+1←HOMO–2 5% LUMO+3←HOMO
	463	0.2442	13% LUMO+2←HOMO–5 44% LUMO←HOMO–4 25% LUMO←HOMO 4% LUMO←HOMO–5 5% LUMO+3←HOMO–5 2% LUMO←HOMO–3
	456	0.2201	14% LUMO+2←HOMO–5 12% LUMO←HOMO–4 24% LUMO+2←HOMO–3 4% LUMO←HOMO–5 6% LUMO+3←HOMO–5 8% LUMO+1←HOMO–3 9% LUMO+3←HOMO–3 2% LUMO+4←HOMO–2 3% LUMO+4←HOMO–1 4% LUMO←HOMO 3% LUMO+2←HOMO
	454	0.36	47% LUMO+1←HOMO–2 13% LUMO+2←HOMO–1 8% LUMO+4←HOMO–3 4% LUMO+2←HOMO–2 3% LUMO+3←HOMO–2 8% LUMO+1←HOMO–1 5% LUMO+1←HOMO 3% LUMO+4←HOMO
	453	0.0557	68% LUMO+1←HOMO–3 5% LUMO+1←HOMO–4

			6% LUMO+2←HOMO–3 5% LUMO+1←HOMO–2 6% LUMO+2←HOMO–1 4% LUMO+5←HOMO
	451	0.1084	10% LUMO+1←HOMO–2 41% LUMO+2←HOMO–1 16% LUMO+3←HOMO–1 5% LUMO+1←HOMO–3 7% LUMO+3←HOMO–3 7% LUMO+2←HOMO–2 4% LUMO+3←HOMO–2 2% LUMO+1←HOMO–1
	444	0.0905	18% LUMO+1←HOMO–2 51% LUMO+2←HOMO–2 13% LUMO+3←HOMO–2 5% LUMO+4←HOMO–3 2% LUMO+1←HOMO–1 3% LUMO+2←HOMO
	436	0.0367	22% LUMO+2←HOMO–3 52% LUMO+3←HOMO–3 2% LUMO+3←HOMO–5 4% LUMO+1←HOMO–4 7% LUMO+4←HOMO–3 5% LUMO+3←HOMO–1
	434	0.5181	39% LUMO+1←HOMO–4 10% LUMO+4←HOMO–1 15% LUMO+1←HOMO 7% LUMO←HOMO–5 4% LUMO←HOMO–4 3% LUMO+3←HOMO–2 5% LUMO+3←HOMO–1 4% LUMO+2←HOMO
	432	0.0845	11% LUMO+2←HOMO–3 13% LUMO+4←HOMO–2 15% LUMO+2←HOMO–1 25% LUMO+3←HOMO–1 11% LUMO+4←HOMO–1 4% LUMO+1←HOMO–4 4% LUMO+2←HOMO 4% LUMO+3←HOMO
	430	0.0555	63% LUMO+4←HOMO–3 4% LUMO+2←HOMO–3 2% LUMO+3←HOMO–3 2% LUMO+1←HOMO–2 8% LUMO+2←HOMO–2 4% LUMO+4←HOMO–2
	427	0.0568	12% LUMO+2←HOMO–3 10% LUMO+3←HOMO–3 48% LUMO+4←HOMO–2 2% LUMO←HOMO–5 2% LUMO+2←HOMO–5 6% LUMO+4←HOMO–3 5% LUMO+3←HOMO–2 3% LUMO+4←HOMO–1
	420	0.8285	23% LUMO+2←HOMO–5 14% LUMO+2←HOMO–3 12% LUMO+4←HOMO–2 8% LUMO+3←HOMO–5 5% LUMO←HOMO–4 9% LUMO+1←HOMO–4 6% LUMO+3←HOMO–3 5% LUMO+3←HOMO–2 4% LUMO+4←HOMO–1
	415	0.1099	24% LUMO+2←HOMO–4 44% LUMO+3←HOMO–4 13% LUMO+3←HOMO 5% LUMO+5←HOMO–1 6% LUMO+2←HOMO
	411	0.1905	16% LUMO+4←HOMO–4 63% LUMO+5←HOMO–3 5% LUMO+1←HOMO–5 3% LUMO+5←HOMO–2 5% LUMO+5←HOMO
	410	0.0429	25% LUMO+5←HOMO–2 50% LUMO+5←HOMO–1

			7% LUMO+4←HOMO–4 7% LUMO+5←HOMO–3 3% LUMO+4←HOMO
	397	0.0402	19% LUMO←HOMO–5 31% LUMO+2←HOMO–4 15% LUMO+3←HOMO–4 4% LUMO←HOMO–8 3% LUMO←HOMO–6 6% LUMO+2←HOMO–5 4% LUMO+3←HOMO–5 2% LUMO+1←HOMO–4 5% LUMO+5←HOMO–4

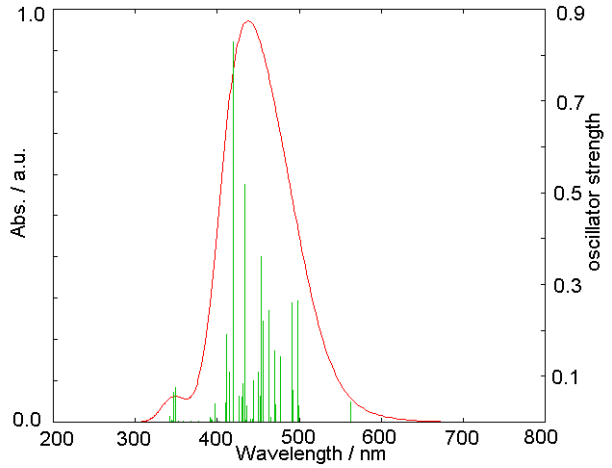


Fig. S1. Transitions making up the band at 438 nm in the calculated electronic absorption spectrum of $[Cu(\mathbf{2})_2]^+$ using a 6–311++G** basis set on Cu and 6–31G* basis set on the ligand atoms.

[Cu(1)(3)]$^+$

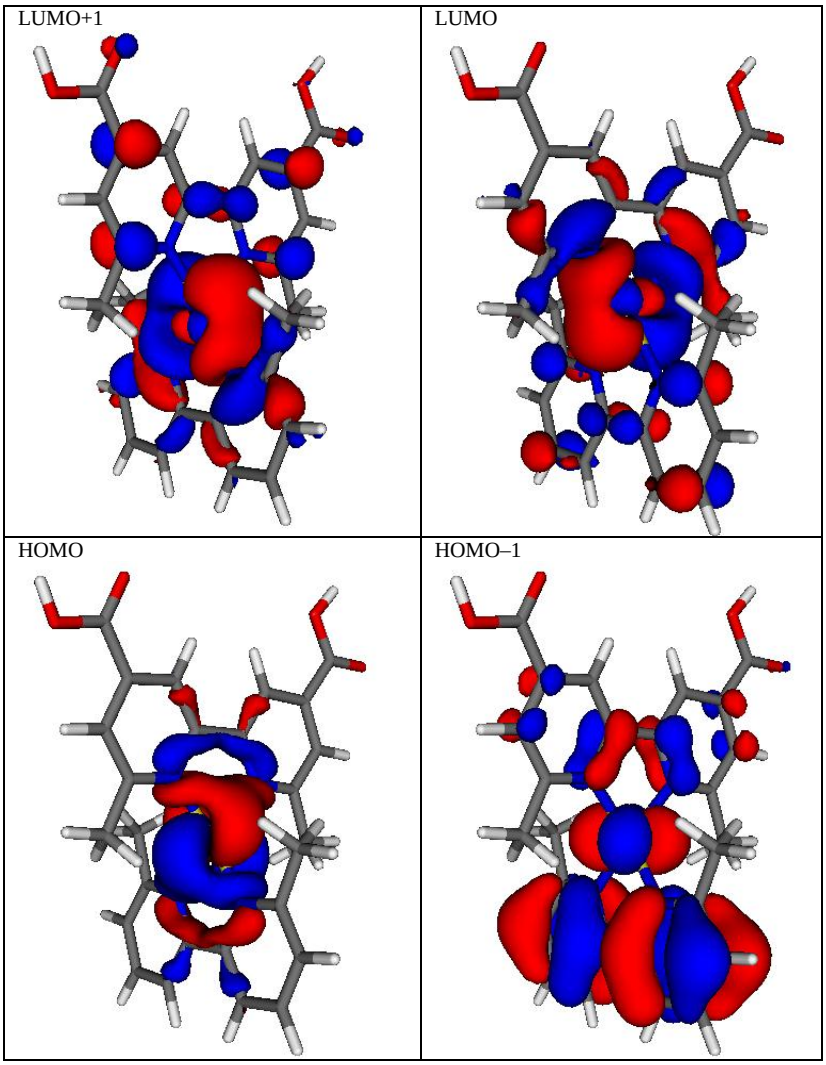


Fig. S2. Highest occupied and lowest unoccupied MOs involved in transitions which contribute to the calculated absorption spectrum of [Cu(**1**)(**3**)]$^+$. The anchoring ligand **3** is at the top of each graphic.

[Cu(1)(4)]$^+$

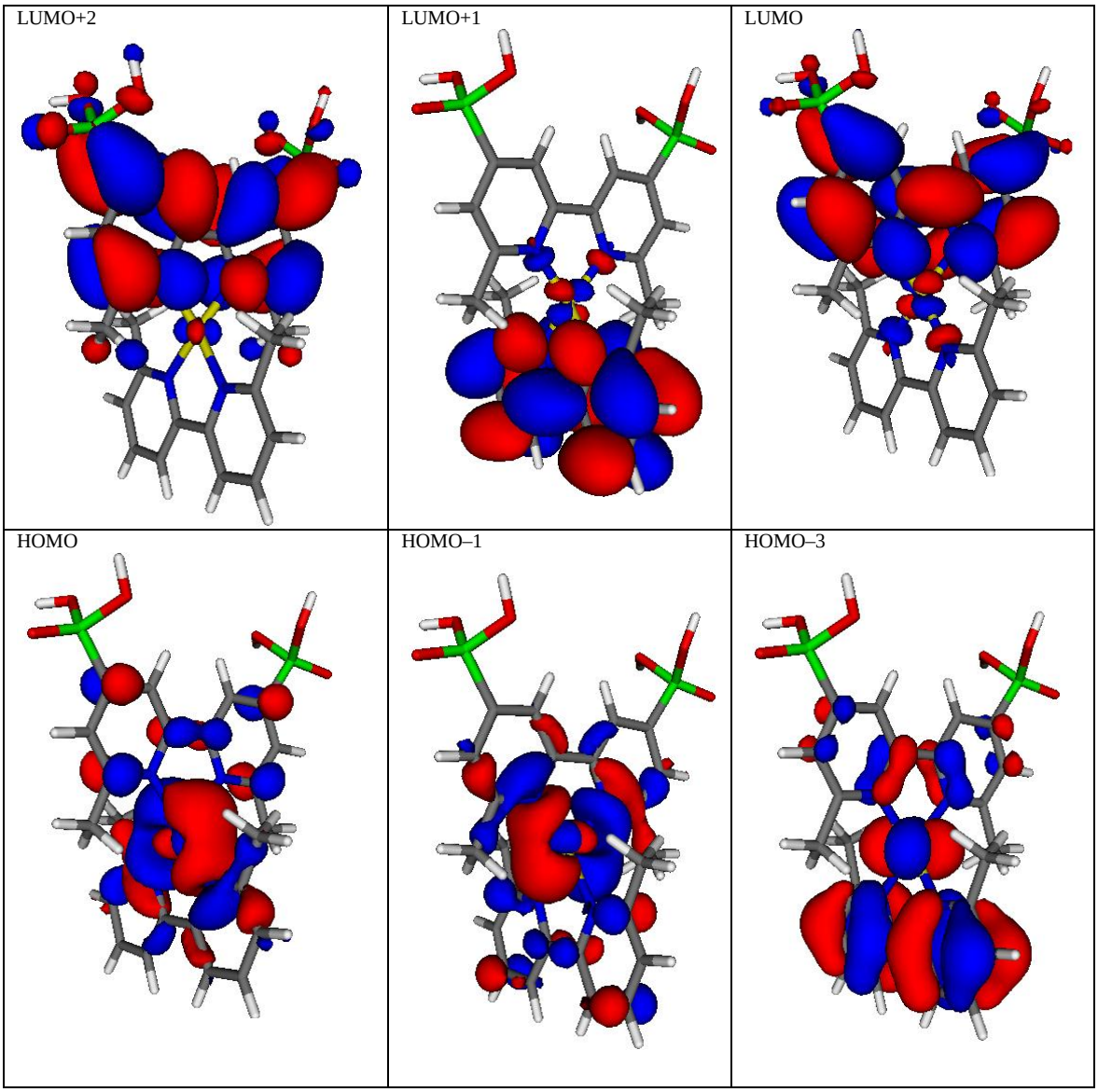


Fig. S3. Highest occupied and lowest unoccupied MOs involved in transitions which contribute to the calculated absorption spectrum of [Cu(**1**)(**4**)]$^+$. The anchoring ligand **4** is at the top of each graphic.

[Cu(1)(5)]$^+$

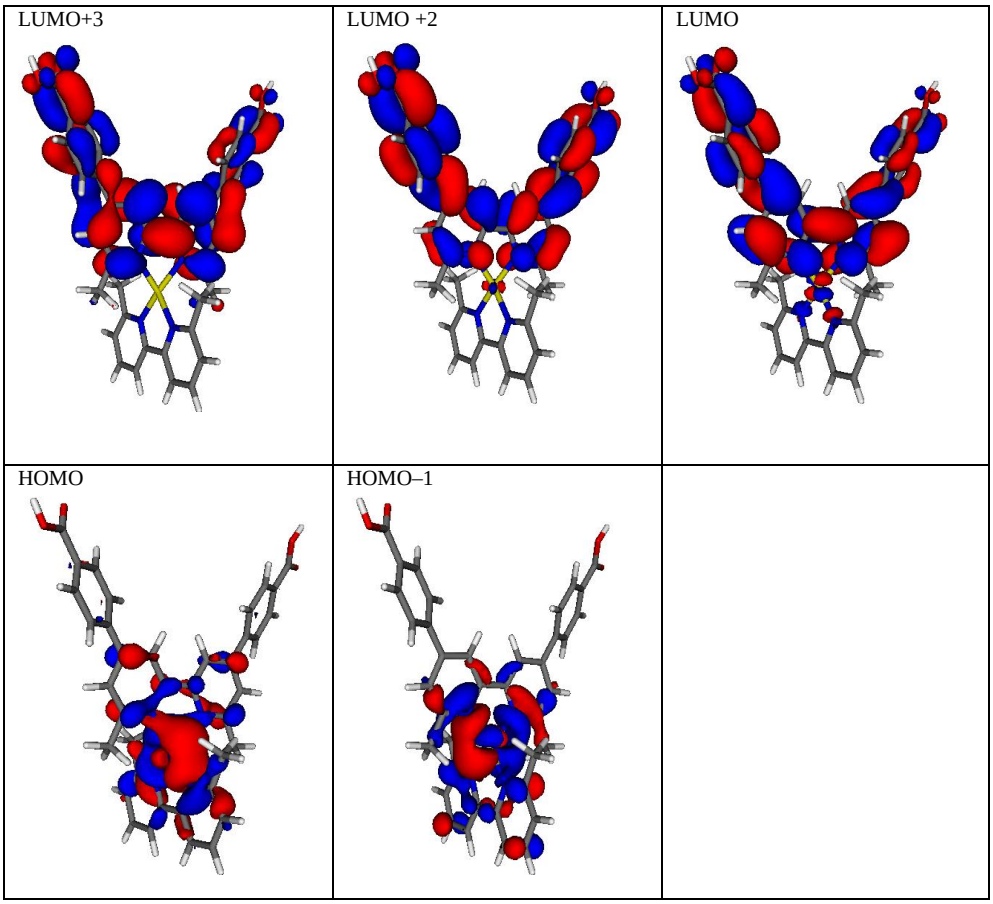
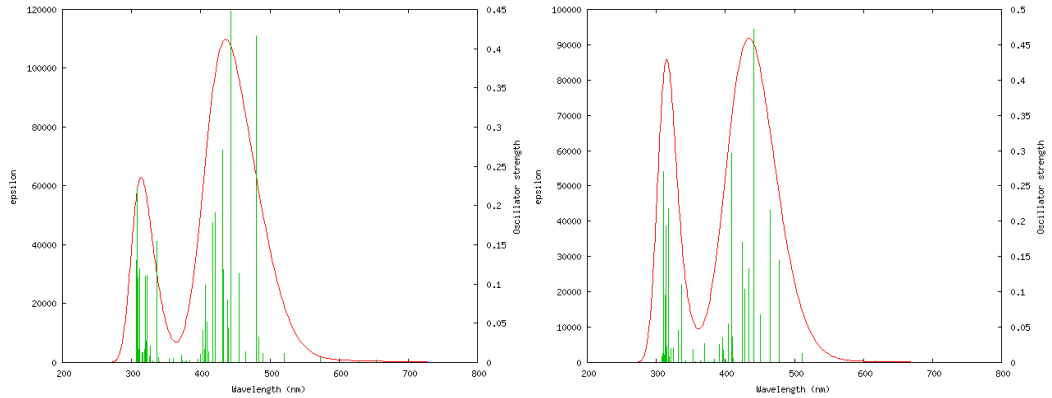
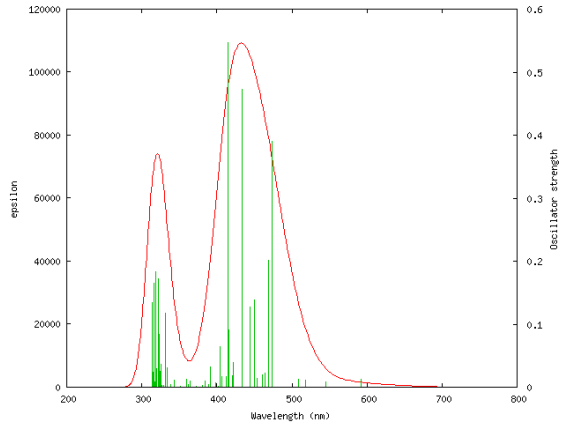


Fig. S4. Highest occupied and lowest unoccupied MOs involved in transitions which contribute to the calculated absorption spectrum of [Cu(**1**)(**5**)]$^+$. The anchoring ligand **5** is at the top of each graphic.



(a) (b)



(c)

Fig. S5. Transitions making up the band at ≈430 nm in the calculated electronic absorption spectra of (a) [Cu(**2**)(**3**)]$^{+}$, (b) [Cu(**2**)(**4**)]$^{+}$ and (c) [Cu(**2**)(**5**)]$^{+}$ using a 6–311++G** basis set on Cu and 6–31G* basis set on the ligand atoms.

Table S3. Orbital contributions to the electronic absorption transitions making up the dominant band in each of the calculated electronic absorption spectra of $[Cu(\mathbf{2})(L)]^+$ (L = **3**, **4**, **5**) using a 6–311++G** basis set on Cu and 6–31G* basis set on the ligand atoms. Only transitions with oscillator strengths >0.03 have been taken into account.

Compound	Wavelength (nm)	*f*	Transition
$[Cu(\mathbf{2})(\mathbf{3})]^+$	484	0.0323	33% LUMO+1←HOMO–1 60% LUMO+1←HOMO 4% LUMO+2←HOMO–1
	481	0.4163	71% LUMO+2←HOMO 3% LUMO←HOMO–3 3% LUMO←HOMO–2 8% LUMO+2←HOMO–1 6% LUMO+3←HOMO–1 2% LUMO+4←HOMO–1
	456	0.113	20% LUMO+2←HOMO–3 22% LUMO+2←HOMO–2 29% LUMO+2←HOMO–1 4% LUMO+1←HOMO–3 6% LUMO+1←HOMO–2 6% LUMO+1←HOMO–1 3% LUMO+3←HOMO–1 5% LUMO+2←HOMO
	444	0.4481	10% LUMO+3←HOMO–2 62% LUMO+3←HOMO–1 2% LUMO+2←HOMO–1 6% LUMO+2←HOMO 6% LUMO+3←HOMO 5% LUMO+4←HOMO
	440	0.044	13% LUMO←HOMO–6 37% LUMO+1←HOMO–2 12% LUMO+2←HOMO–2 13% LUMO+3←HOMO 2% LUMO+4←HOMO–2 2% LUMO+1←HOMO–1 6% LUMO+4←HOMO–1 6% LUMO+4←HOMO
	439	0.0799	22% LUMO+1←HOMO–2 44% LUMO+3←HOMO 3% LUMO+3←HOMO–2 4% LUMO+4←HOMO–2 9% LUMO+4←HOMO–1 8% LUMO+4←HOMO
	433	0.1185	36% LUMO←HOMO–6 15% LUMO+1←HOMO–2 15% LUMO+3←HOMO 10% LUMO+4←HOMO 7% LUMO←HOMO–4 2% LUMO+4←HOMO–2 5% LUMO+3←HOMO–1 5% LUMO+4←HOMO–1
	431	0.2702	29% LUMO←HOMO–6 10% LUMO+3←HOMO–1 17% LUMO+4←HOMO–1 12% LUMO+3←HOMO 10% LUMO+4←HOMO 4% LUMO←HOMO–4 3% LUMO+2←HOMO–2 7% LUMO+4←HOMO–2
	421	0.1904	40% LUMO+4←HOMO–1 39% LUMO+4←HOMO 2% LUMO+3←HOMO–2 8% LUMO+5←HOMO
	417	0.1785	49% LUMO+5←HOMO–1 26% LUMO+5←HOMO 3% LUMO+2←HOMO–3 8% LUMO+5←HOMO–2 2% LUMO+4←HOMO–1 8% LUMO+4←HOMO
	409	0.0513	17% LUMO+1←HOMO–3 41% LUMO+3←HOMO–2 7% LUMO+2←HOMO–3 8% LUMO+2←HOMO–2 3% LUMO+2←HOMO–1 4% LUMO+5←HOMO–1

			6% LUMO+3←HOMO 6% LUMO+4←HOMO
	406	0.0991	43% LUMO+1←HOMO–3 28% LUMO+3←HOMO–2 9% LUMO+2←HOMO–2 5% LUMO+4←HOMO–2 3% LUMO+3←HOMO–1 3% LUMO+4←HOMO–1 2% LUMO+3←HOMO
	403	0.041	24% LUMO+1←HOMO–3 21% LUMO+2←HOMO–3 18% LUMO+4←HOMO–2 7% LUMO←HOMO–7 5% LUMO←HOMO–4 4% LUMO+1←HOMO–2 4% LUMO+2←HOMO–2 6% LUMO+4←HOMO–1
[Cu(**2**)(**4**)]$^{+}$	478	0.1443	21% LUMO+1←HOMO–3 10% LUMO←HOMO–2 14% LUMO+1←HOMO–2 30% LUMO+1←HOMO–1 9% LUMO←HOMO–3 3% LUMO+1←HOMO 7% LUMO+2←HOMO
	464	0.2154	15% LUMO+1←HOMO–3 13% LUMO+1←HOMO–2 47% LUMO+1←HOMO–1 4% LUMO+2←HOMO
	451	0.068	15% LUMO+1←HOMO–3 10% LUMO+1←HOMO–1 39% LUMO+1←HOMO 10% LUMO+2←HOMO 3% LUMO←HOMO–3 6% LUMO+1←HOMO–2 4% LUMO+2←HOMO–2 7% LUMO+2←HOMO–1
	442	0.4719	20% LUMO+1←HOMO–1 17% LUMO+2←HOMO–1 38% LUMO+2←HOMO 4% LUMO←HOMO–3 2% LUMO←HOMO–2 3% LUMO+1←HOMO–2 8% LUMO+2←HOMO–2
	434	0.1323	51% LUMO+2←HOMO–1 27% LUMO+2←HOMO 9% LUMO+2←HOMO–2 4% LUMO+3←HOMO–1 2% LUMO+1←HOMO
	428	0.1036	11% LUMO+1←HOMO–2 12% LUMO+3←HOMO–2 42% LUMO+3←HOMO–1 5% LUMO←HOMO–6 8% LUMO←HOMO–5 2% LUMO←HOMO–4 2% LUMO+1←HOMO–1 5% LUMO+2←HOMO 6% LUMO+3←HOMO
	424	0.1707	24% LUMO←HOMO–6 34% LUMO←HOMO–5 10% LUMO←HOMO–4 10% LUMO+3←HOMO–1 5% LUMO+3←HOMO–2 3% LUMO+2←HOMO 5% LUMO+3←HOMO
	411	0.0363	14% LUMO+4←HOMO–2 44% LUMO+4←HOMO–1 30% LUMO+4←HOMO
	410	0.2965	18% LUMO+1←HOMO–3 15% LUMO+1←HOMO–2 21% LUMO+3←HOMO–1 23% LUMO+3←HOMO 7% LUMO+2←HOMO–2 3% LUMO+2←HOMO–1
	405	0.0549	23% LUMO+2←HOMO–3

			32% LUMO+2←HOMO–2 12% LUMO+4←HOMO 4% LUMO+1←HOMO–3 4% LUMO+1←HOMO–2 2% LUMO+5←HOMO–2 7% LUMO+2←HOMO–1 6% LUMO+5←HOMO–1 3% LUMO+5←HOMO
	396	0.0353	51% LUMO+2←HOMO–3 14% LUMO+2←HOMO–2 11% LUMO+3←HOMO–2 4% LUMO←HOMO–7 7% LUMO+3←HOMO–3 2% LUMO+2←HOMO–1 5% LUMO+2←HOMO–1 2% LUMO+3←HOMO
[Cu(**2**)(**5**)]$^{+}$	473	0.3897	11% LUMO←HOMO–3 15% LUMO+1←HOMO–3 21% LUMO+1←HOMO–1 13% LUMO+3←HOMO–1 13% LUMO+1←HOMO 6% LUMO←HOMO–2 3% LUMO+1←HOMO–2 3% LUMO+3←HOMO–2 9% LUMO+3←HOMO
	468	0.2013	39% LUMO+1←HOMO–3 16% LUMO+1←HOMO–2 16% LUMO+1←HOMO–1 14% LUMO+1←HOMO 3% LUMO←HOMO–2 3% LUMO+2←HOMO 2% LUMO+4←HOMO
	450	0.1386	16% LUMO+4←HOMO–2 15% LUMO+1←HOMO–1 13% LUMO+1←HOMO 16% LUMO+3←HOMO 18% LUMO+4←HOMO 6% LUMO←HOMO–3 2% LUMO←HOMO–2 7% LUMO+3←HOMO–2 3% LUMO+4←HOMO–1
	444	0.1268	11% LUMO+4←HOMO–2 22% LUMO+1←HOMO 31% LUMO+4←HOMO 6% LUMO←HOMO–3 3% LUMO←HOMO–2 9% LUMO+1←HOMO–2 6% LUMO+1←HOMO–1 3% LUMO+4←HOMO–1
	433	0.4728	73% LUMO+3←HOMO–1 10% LUMO+3←HOMO 2% LUMO←HOMO–3 3% LUMO+4←HOMO–2
	422	0.0391	72% LUMO+2←HOMO–2 4% LUMO+3←HOMO–2 4% LUMO+2←HOMO 5% LUMO+3←HOMO 4% LUMO+5←HOMO
	416	0.0912	34% LUMO+3←HOMO–2 13% LUMO+3←HOMO 23% LUMO+5←HOMO 2% LUMO+1←HOMO–3 8% LUMO+3←HOMO–3 3% LUMO+1←HOMO–2 4% LUMO+5←HOMO–2 4% LUMO+4←HOMO–1
	415	0.5465	55% LUMO+4←HOMO–1 22% LUMO+4←HOMO 8% LUMO+1←HOMO–3 7% LUMO+1←HOMO–2
	404	0.0641	29% LUMO+4←HOMO–2 13% LUMO+5←HOMO–1 10% LUMO+4←HOMO 12% LUMO+5←HOMO

			7% LUMO←HOMO–5 3% LUMO←HOMO–4 2% LUMO+1←HOMO–3 8% LUMO+3←HOMO–3 5% LUMO+4←HOMO–3 2% LUMO+4←HOMO–1
	391	0.0327	88% LUMO+2←HOMO–3 5% LUMO+3←HOMO–3 3% LUMO+7←HOMO–3

[Cu(2)(3)]$^+$

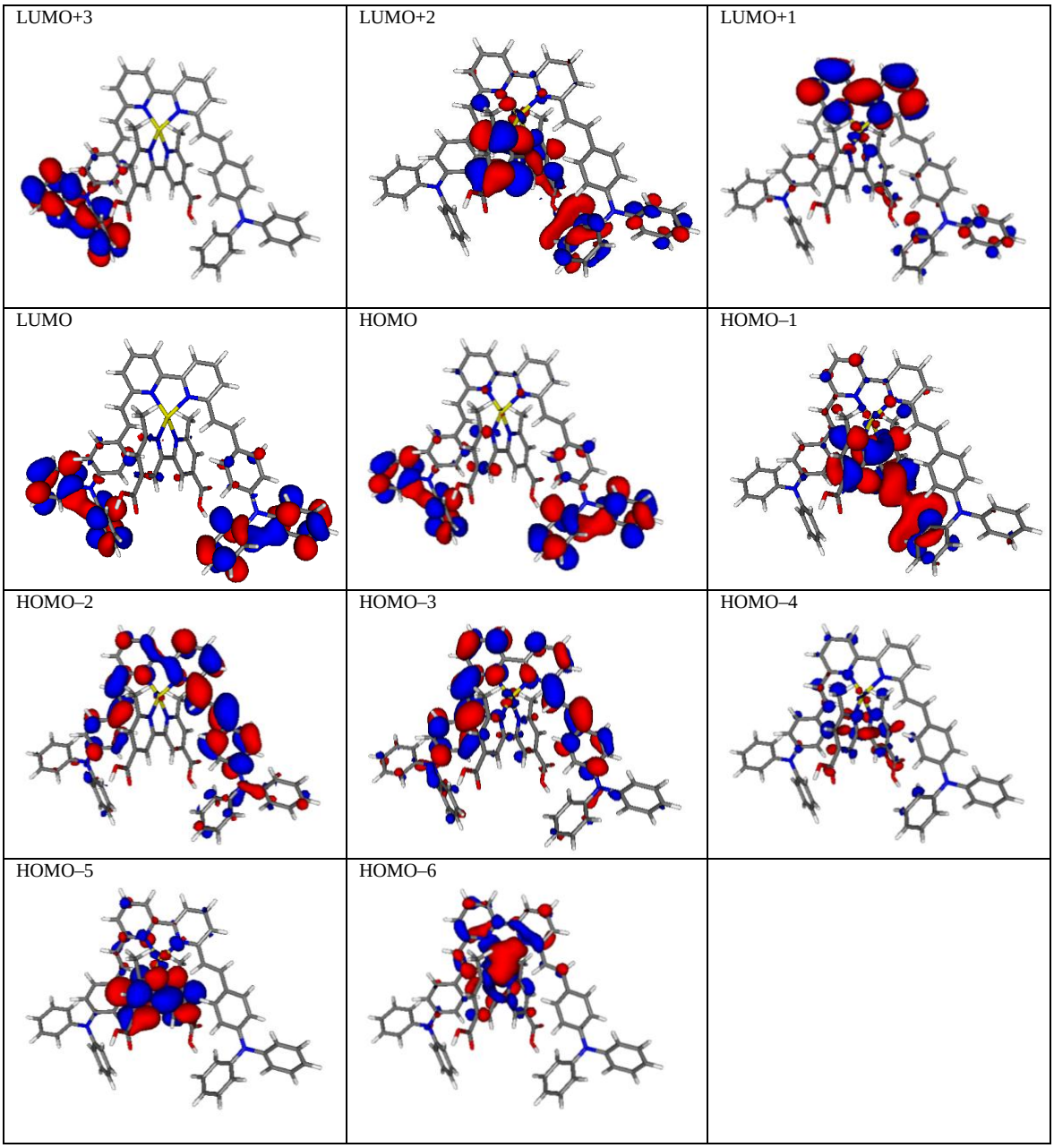


Fig. S6. Highest occupied and lowest unoccupied MOs in [Cu(**2**)(**3**)]$^+$. See Table S3 for their role in calculated transitions. The anchoring ligand **3** is at the bottom of each graphic.

[Cu(2)(4)]$^+$

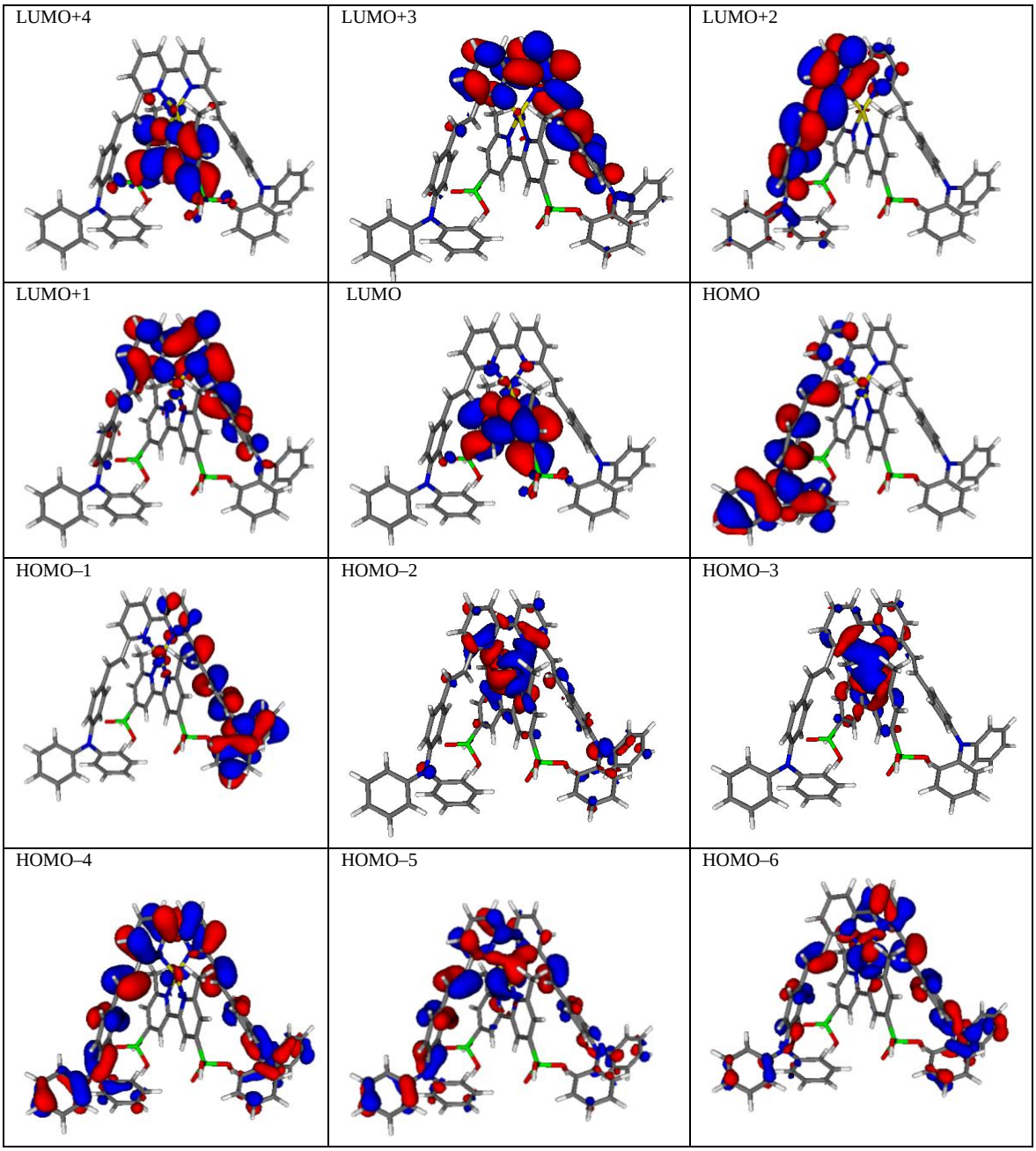


Fig. S7. Highest occupied and lowest unoccupied MOs in [Cu(**2**)(**4**)]$^+$. See Table S3 for their role in calculated transitions. The anchoring ligand **4** is at the bottom of each graphic.

[Cu(2)(5)]$^+$

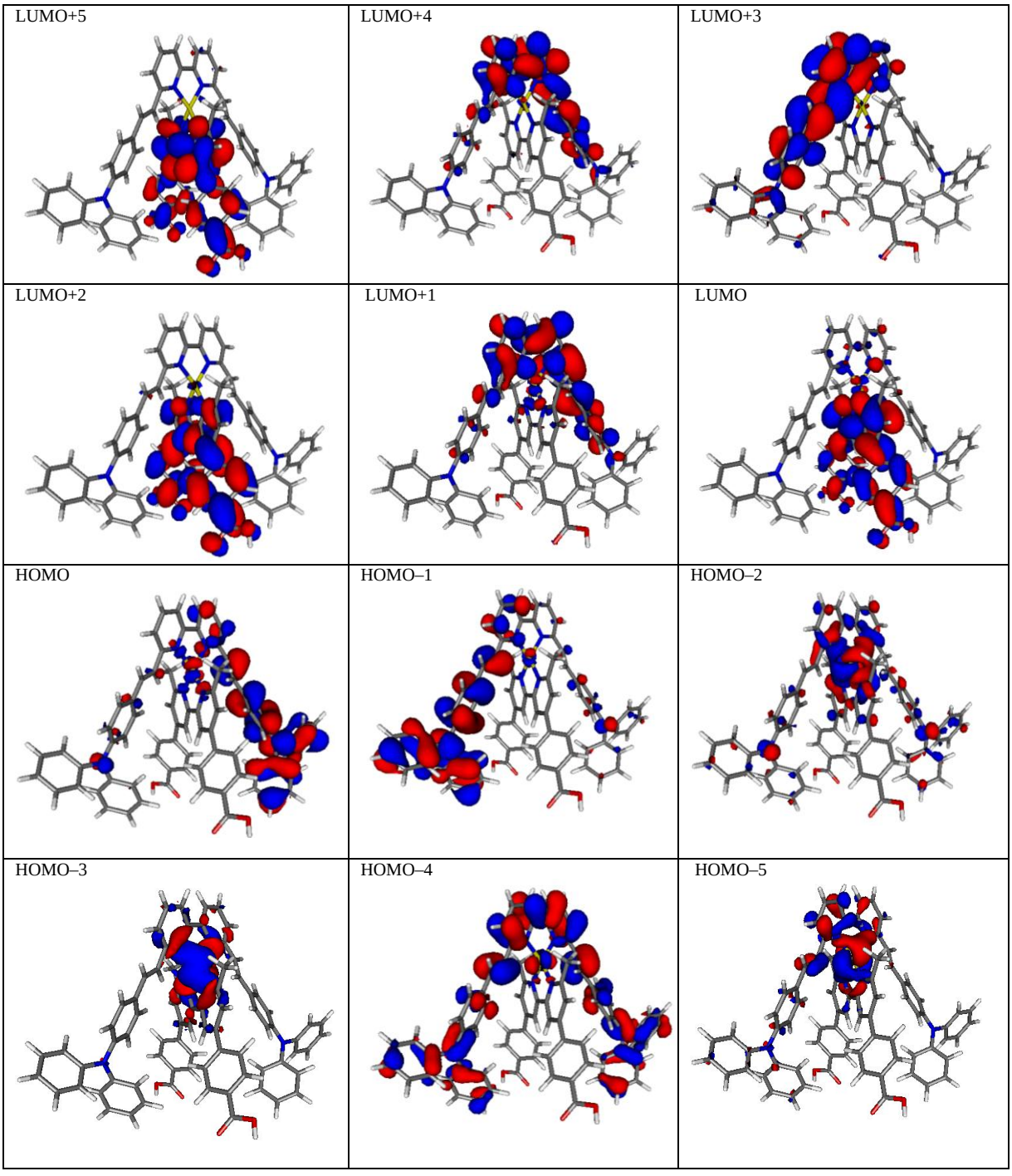


Fig. S8. Highest occupied and lowest unoccupied MOs in [Cu(**2**)(**5**)]$^+$. See Table S3 for their role in calculated transitions. The anchoring ligand **5** is at the bottom of each graphic.