Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

ESI to accompany:

Exploring simple ancillary ligands in copper-based dye-sensitized solar cells: effects of a heteroatom switch and of co-sensitization

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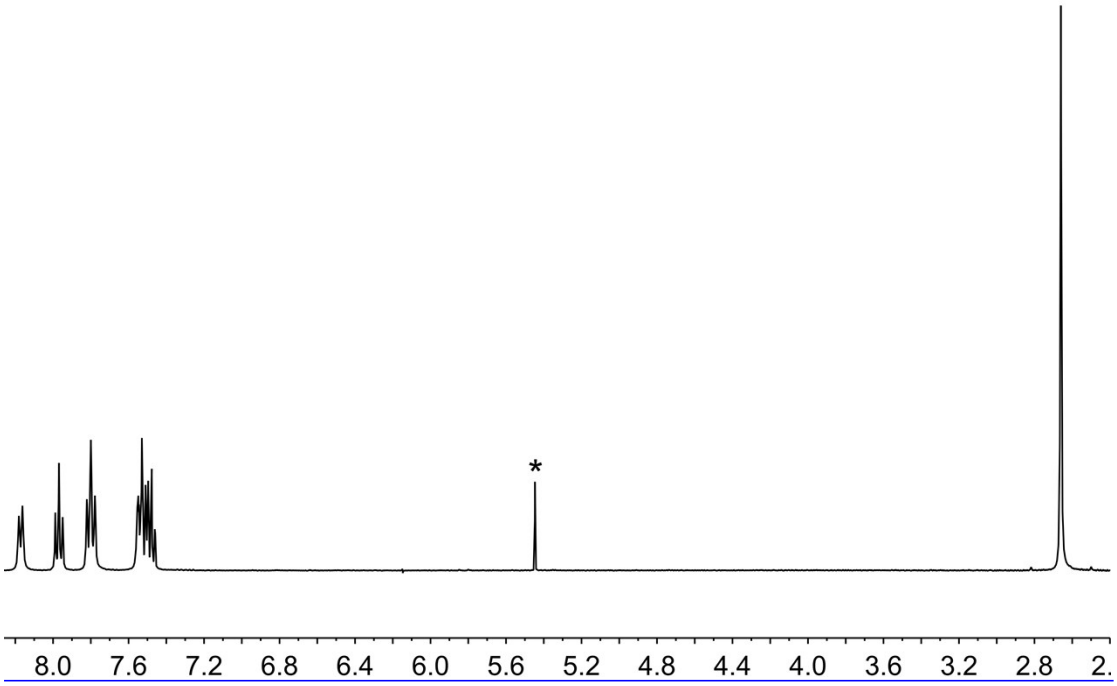

Fig. S1. 500 MHz ^{1}H NMR spectrum of [Cu(**2**)$_2$][PF$_6$] in CD_3CN at 295K. See Scheme 1 for proton labels. * = residual CH_2Cl_2. See Fig. 1 for expansion of the aromatic region.

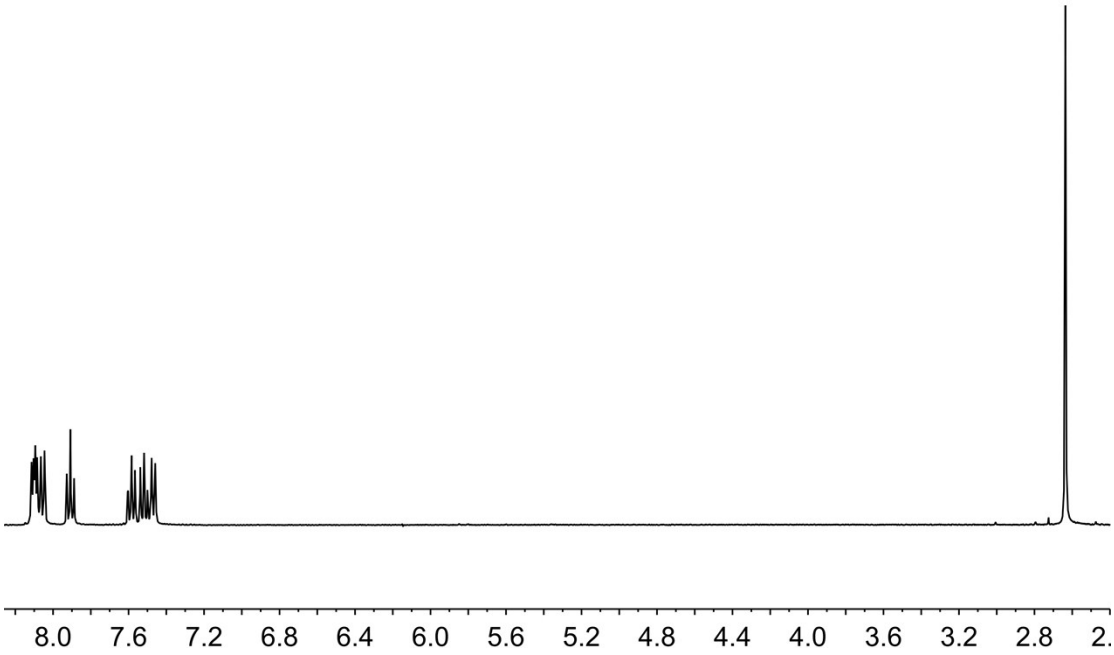

Fig. S2. 500 MHz ^{1}H NMR spectrum of [Cu(**3**)$_2$][PF_6] in CD_3CN at 295K. See Scheme 1 for proton labels. See Fig. 1 for expansion of the aromatic region.

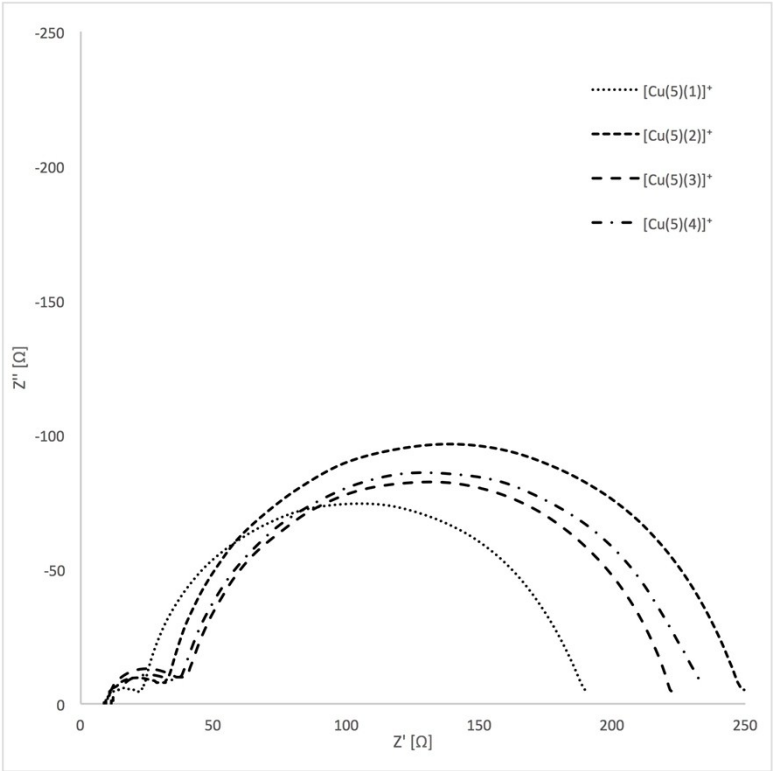

Fig. S3. Nyquist plots of DSCs containing the dyes [Cu(**5**)(L)]$^+$ (L = **1**, **2**, **3** or **4**) at a light intensity of 22 mW cm^{-2}. The Z' and Z'' axes are plotted on the same scale.

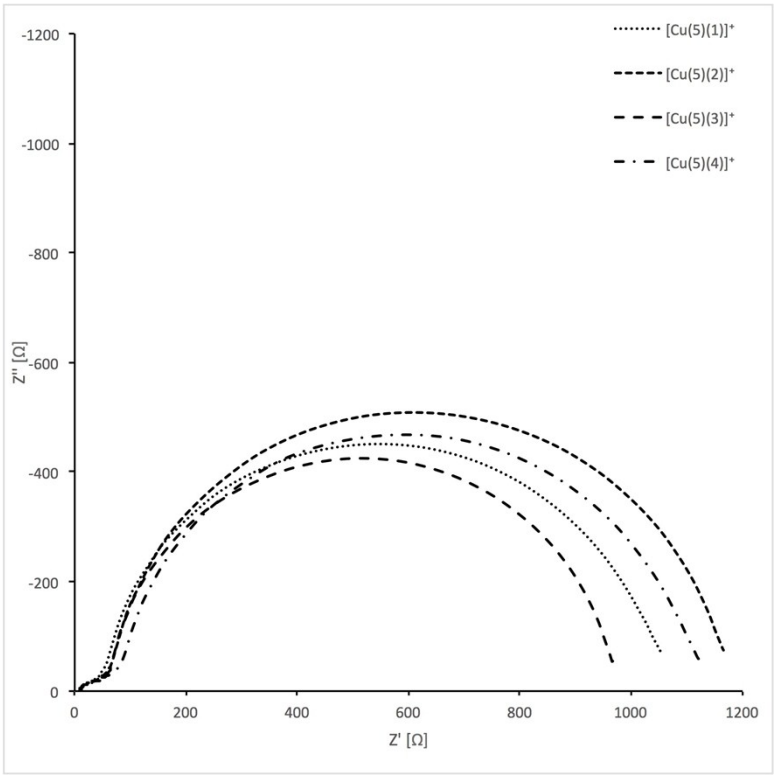

Fig. S4. Nyquist plots of DSCs containing the dyes [Cu(**5**)(L)]$^+$ (L = **1**, **2**, **3** or **4**) at a light intensity of 2.2 mW cm^{-2}. The Z' and Z'' axes are plotted on the same scale.

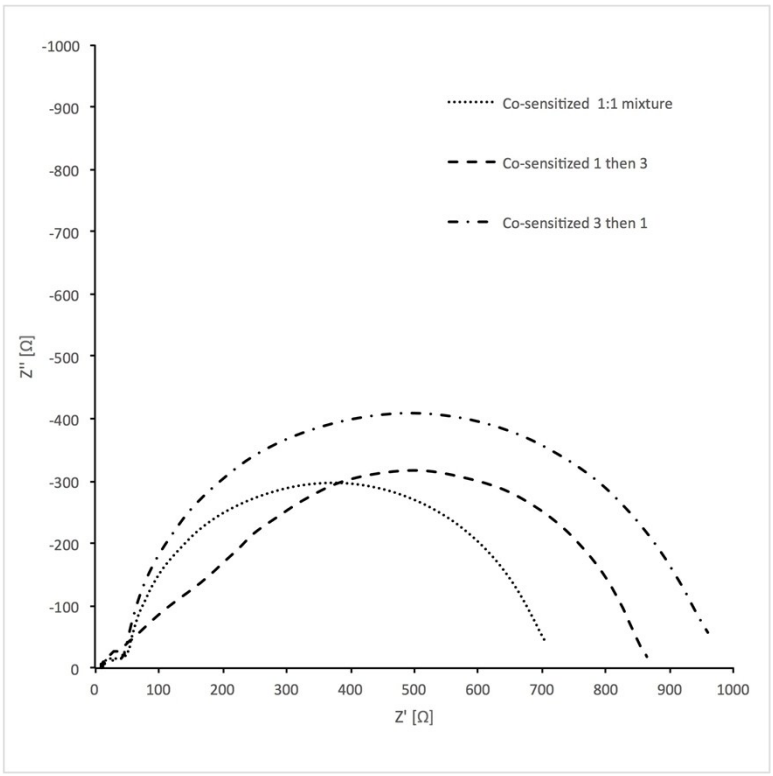

Fig S5. Nyquist plots of DSCs containing mixtures of the dyes [Cu(**5**)(**1**)]$^+$ and [Cu(**5**)(**3**)]$^+$ at a light intensity of 2.2 mW cm^{-2}. The Z' and Z'' axes are plotted on the same scale.

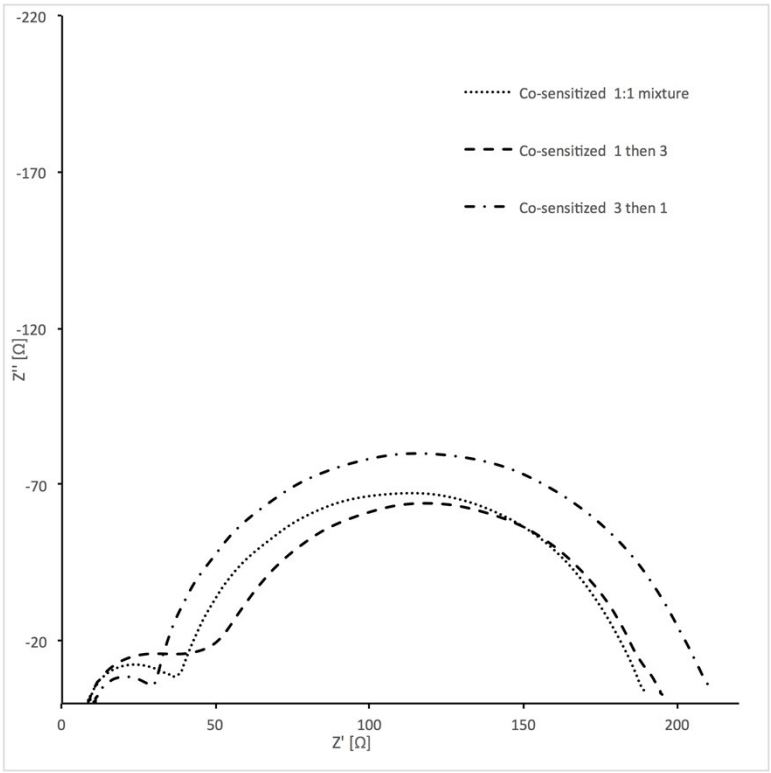

Fig S6. Nyquist plots of DSCs containing mixtures of the dyes [Cu(**5**)(**1**)]$^{+}$ and [Cu(**5**)(**3**)]$^{+}$ at a light intensity of 22 mW cm^{-2}. The Z' and Z'' axes are plotted on the same scale.

Table S1. Performance parameters for duplicate DSCs with dyes [Cu(**5**)(L)]$^+$ (L = **1**, **2**, **3** or **4**).

Dye	J_{SC} / mA cm^{-2}	V_{OC} / mV	*ff* / %	η / %	Relative η / %	IPCE max / nm, %
On the day of sealing the cell (Day 0)						
[Cu(**5**)(**1**)]$^+$	6.93	608	71.9	3.03	40.1	480, 53.0
[Cu(**5**)(**1**)]$^+$	6.16	594	72.4	2.65	35.1	480, 48.9
[Cu(**5**)(**2**)]$^+$	6.91	531	71.4	2.62	34.7	480, 54.1
[Cu(**5**)(**2**)]$^+$	7.14	541	70.3	2.72	36.0	480, 53.6
[Cu(**5**)(**3**)]$^+$	7.76	530	69.9	2.88	38.1	480, 53.8
[Cu(**5**)(**3**)]$^+$	7.16	522	71.8	2.68	35.5	480, 53.8
[Cu(**5**)(**4**)]$^+$	6.99	558	69.5	2.71	35.9	480, 55.3
[Cu(**5**)(**4**)]$^+$	6.76	549	68.9	2.56	33.9	480, 54.9
N719	16.57	630	72.4	7.55	100	540, 71.8
3 days after sealing the cell (Day 3)						
[Cu(**5**)(**1**)]$^+$	6.88	604	71.6	2.97	41.2	480, 53.1
[Cu(**5**)(**1**)]$^+$	5.77	591	70.7	2.41	33.4	480, 47.7
[Cu(**5**)(**2**)]$^+$	6.19	568	69.4	2.44	33.8	470, 50.5
[Cu(**5**)(**2**)]$^+$	6.20	573	68.3	2.42	33.6	470, 45.2
[Cu(**5**)(**3**)]$^+$	6.77	542	70.4	2.58	35.8	480, 50.8
[Cu(**5**)(**3**)]$^+$	6.52	553	71.6	2.59	35.9	470, 51.2
[Cu(**5**)(**4**)]$^+$	6.38	555	70.9	2.51	34.8	480, 53.4
[Cu(**5**)(**4**)]$^+$	6.02	542	69.7	2.28	31.6	480, 52.2
N719	15.03	660	72.6	7.21	100	520, 70.8
7 days after sealing the cell (Day 7)						
[Cu(**5**)(**1**)]$^+$	7.16	607	71.9	3.12	45.4	480, 54.7
[Cu(**5**)(**1**)]$^+$	6.05	603	71.3	2.60	37.8	480, 49.3
[Cu(**5**)(**2**)]$^+$	6.40	579	66.7	2.47	36.0	470, 50.5
[Cu(**5**)(**2**)]$^+$	6.61	584	65.9	2.54	37.0	470, 45.0
[Cu(**5**)(**3**)]$^+$	7.42	558	62.6	2.59	37.7	470, 46.2
[Cu(**5**)(**3**)]$^+$	6.67	547	70.7	2.58	37.6	470, 53.3
[Cu(**5**)(**4**)]$^+$	6.74	552	69.8	2.60	37.8	480, 54.0
[Cu(**5**)(**4**)]$^+$	6.37	546	68.7	2.39	34.8	480, 54.2
N719	14.47	650	73.0	6.87	100	540, 71.1

Table S2. Performance parameters for duplicate DSCs with co-sensitization. The FTO/TiO_2 electrodes were functionalized with anchor **5** and then immersed in the dye baths containing $[PF_6]^-$ salts of the complex cations given in the left-hand column. The active dyes in every case are $[Cu(\mathbf{5})(\mathbf{1})]^+$ or $[Cu(\mathbf{5})(\mathbf{3})]^+$:

FTO/TiO_2/(**5**) + $[Cu(\mathbf{1})_2]^+$ ➔ FTO/TiO_2/$[(\mathbf{5})Cu(\mathbf{1})]^+$

FTO/TiO_2/(**5**) + $[Cu(\mathbf{3})_2]^+$ ➔ FTO/TiO_2/$[(\mathbf{5})Cu(\mathbf{3})]^+$

Dye-bath or baths	J_{SC} / mA cm^{-2}	V_{OC} / mV	*ff* / %	η / %	Relative η / %	IPCE max / nm, %
On the day of sealing the cell (Day 0)						
1:1 mixture of $[Cu(\mathbf{1})_2]^+$ and $[Cu(\mathbf{3})_2]^+$	7.20	592	70.9	3.02	40.0	480, 56.8
1:1 mixture of $[Cu(\mathbf{1})_2]^+$ and $[Cu(\mathbf{3})_2]^+$	7.30	578	71.0	2.99	39.6	480, 57.1
$[Cu(\mathbf{3})_2]^+$ followed by $[Cu(\mathbf{1})_2]^+$	6.91	588	72.8	2.96	39.2	480, 51.3
$[Cu(\mathbf{3})_2]^+$ followed by $[Cu(\mathbf{1})_2]^+$	7.09	561	73.0	2.90	38.4	480, 51.8
$[Cu(\mathbf{1})_2]^+$ followed by $[Cu(\mathbf{3})_2]^+$	6.35	528	72.8	2.44	32.3	460, 40.6
$[Cu(\mathbf{1})_2]^+$ followed by $[Cu(\mathbf{3})_2]^+$	6.26	531	71.5	2.38	31.5	470, 43.1
N719	16.57	630	72.4	7.55	100	540, 71.8
3 days after sealing the cell (Day 3)						
1:1 mixture of $[Cu(\mathbf{1})_2]^+$ and $[Cu(\mathbf{3})_2]^+$	7.34	593	70.5	3.07	42.6	470, 56.9
1:1 mixture of $[Cu(\mathbf{1})_2]^+$ and $[Cu(\mathbf{3})_2]^+$	7.04	579	70.4	2.87	39.8	470, 55.5
$[Cu(\mathbf{3})_2]^+$ followed by $[Cu(\mathbf{1})_2]^+$	6.18	583	72.4	2.61	36.2	470, 47.6
$[Cu(\mathbf{3})_2]^+$ followed by $[Cu(\mathbf{1})_2]^+$	5.99	560	72.4	2.43	33.7	470, 46.5
$[Cu(\mathbf{1})_2]^+$ followed by $[Cu(\mathbf{3})_2]^+$	5.93	519	71.6	2.20	30.5	470, 46.9
$[Cu(\mathbf{1})_2]^+$ followed by $[Cu(\mathbf{3})_2]^+$	5.82	532	70.7	2.19	30.4	470, 44.9
N719	15.03	660	72.6	7.21	100	520, 70.8
7 days after sealing the cell (Day 7)						
1:1 mixture of $[Cu(\mathbf{1})_2]^+$ and $[Cu(\mathbf{3})_2]^+$	7.30	600	70.7	3.10	45.1	470, 56.8
1:1 mixture of $[Cu(\mathbf{1})_2]^+$ and $[Cu(\mathbf{3})_2]^+$	7.11	590	70.3	2.95	42.9	470, 55.9
$[Cu(\mathbf{3})_2]^+$ followed by $[Cu(\mathbf{1})_2]^+$	6.24	586	71.9	2.63	38.3	480, 48.5
$[Cu(\mathbf{3})_2]^+$ followed by $[Cu(\mathbf{1})_2]^+$	5.99	568	72.3	2.46	35.8	480, 46.2
$[Cu(\mathbf{1})_2]^+$ followed by $[Cu(\mathbf{3})_2]^+$	5.95	521	71.7	2.22	32.3	480, 46.4
$[Cu(\mathbf{1})_2]^+$ followed by $[Cu(\mathbf{3})_2]^+$	5.99	525	70.4	2.21	32.2	470, 44.9
N719	14.47	650	73.0	6.87	100	540, 71.1