Electronic supporting information to accompany:

The influence of phosphonic acid protonation state on the efficiency of bis(diimine)copper(I) dye-sensitized solar cells

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(1) DSCs constructed from electrodes treated with H_4**1** + ^{n}Bu$_4$NOH

Table S1. Performance parameters for duplicate DSCs containing the dye [Cu(H$_n$**1**)(**2**)]$^{n-3}$ where H$_4$**1** was treated with 0–4 equivalents of ^{n}Bu$_4$NOH prior to electrode functionalization. Values of relative photoconversion efficiency (Rel. η) are with respect to that of N719 set to 100%.

Dye	Eq. ^{n}Bu$_4$NOH	J_{SC} [mA cm^{-2}]	V_{OC} [mV]	FF [%]	η [%]	Rel. η [%]
On the day of sealing						
[Cu(H$_4$**1**)(**2**)]$^+$	0	4.61	521	72	1.72	27.5
[Cu(H$_4$**1**)(**2**)]$^+$	0	4.54	546	68	1.68	26.9
[Cu(H$_n$**1**)(**2**)]$^{n-3}$	1.0	5.11	535	72	1.97	31.5
[Cu(H$_n$**1**)(**2**)]$^{n-3}$	1.0	5.20	535	65	1.80	28.8
[Cu(H$_n$**1**)(**2**)]$^{n-3}$	2.0	4.59	512	70	1.65	26.4
[Cu(H$_n$**1**)(**2**)]$^{n-3}$	2.0	4.62	509	68	1.59	25.4
[Cu(H$_n$**1**)(**2**)]$^{n-3}$	3.0	1.04	404	68	0.29	4.6
[Cu(H$_n$**1**)(**2**)]$^{n-3}$	3.0	2.11	434	69	0.63	10.1
[Cu(H$_n$**1**)(**2**)]$^{n-3}$	4.0	0.75	404	70	0.21	3.4
[Cu(H$_n$**1**)(**2**)]$^{n-3}$	4.0	0.59	377	69	0.15	2.4
N719	–	14.3	635	70	6.25	100
3 days after sealing						
[Cu(H$_4$**1**)(**2**)]$^+$	0	3.48	548	72	1.38	22.1
[Cu(H$_4$**1**)(**2**)]$^+$	0	3.30	569	67	1.26	20.2
[Cu(H$_n$**1**)(**2**)]$^{n-3}$	1.0	3.59	551	72	1.43	22.9
[Cu(H$_n$**1**)(**2**)]$^{n-3}$	1.0	3.58	543	69	1.34	21.4
[Cu(H$_n$**1**)(**2**)]$^{n-3}$	2.0	3.43	526	70	1.25	20.0
[Cu(H$_n$**1**)(**2**)]$^{n-3}$	2.0	3.28	524	67	1.15	18.4
[Cu(H$_n$**1**)(**2**)]$^{n-3}$	3.0	0.92	414	69	0.26	4.2
[Cu(H$_n$**1**)(**2**)]$^{n-3}$	3.0	1.79	454	70	0.57	9.1
[Cu(H$_n$**1**)(**2**)]$^{n-3}$	4.0	0.76	410	71	0.22	3.5
[Cu(H$_n$**1**)(**2**)]$^{n-3}$	4.0	0.55	376	68	0.14	2.2
7 days after sealing						
[Cu(H$_4$**1**)(**2**)]$^+$	0	3.60	558	72	1.44	23.0
[Cu(H$_4$**1**)(**2**)]$^+$	0	3.31	579	68	1.31	21.0
[Cu(H$_n$**1**)(**2**)]$^{n-3}$	1.0	3.62	551	70	1.39	22.2
[Cu(H$_n$**1**)(**2**)]$^{n-3}$	1.0	3.61	544	57	1.13	18.1
[Cu(H$_n$**1**)(**2**)]$^{n-3}$	2.0	3.47	528	69	1.26	20.2
[Cu(H$_n$**1**)(**2**)]$^{n-3}$	2.0	3.53	530	65	1.22	19.5
[Cu(H$_n$**1**)(**2**)]$^{n-3}$	3.0	1.10	420	67	0.31	5.0
[Cu(H$_n$**1**)(**2**)]$^{n-3}$	3.0	2.11	468	68	0.67	10.7
[Cu(H$_n$**1**)(**2**)]$^{n-3}$	4.0	0.92	411	70	0.26	4.2
[Cu(H$_n$**1**)(**2**)]$^{n-3}$	4.0	0.71	385	67	0.19	3.0

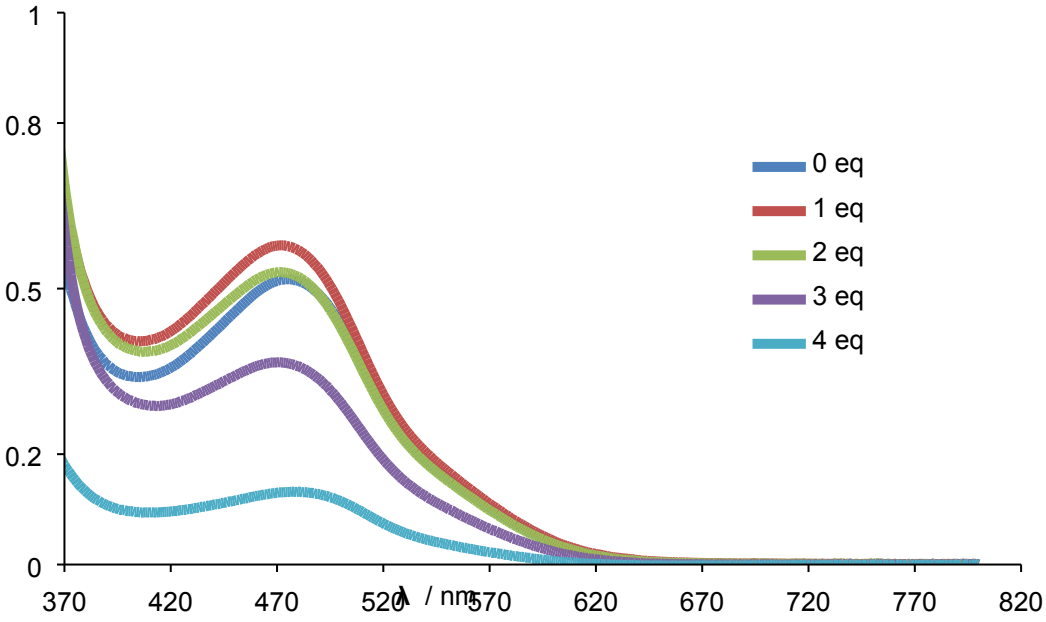

Fig. S1. Solid-state absorption spectra of dye-functionalized transparent TiO_2 electrodes treated with 0–4 eq of $^{n}Bu_4NOH$ added to the anchoring ligand H_4**1** solution (see Fig. 1 in the main paper).

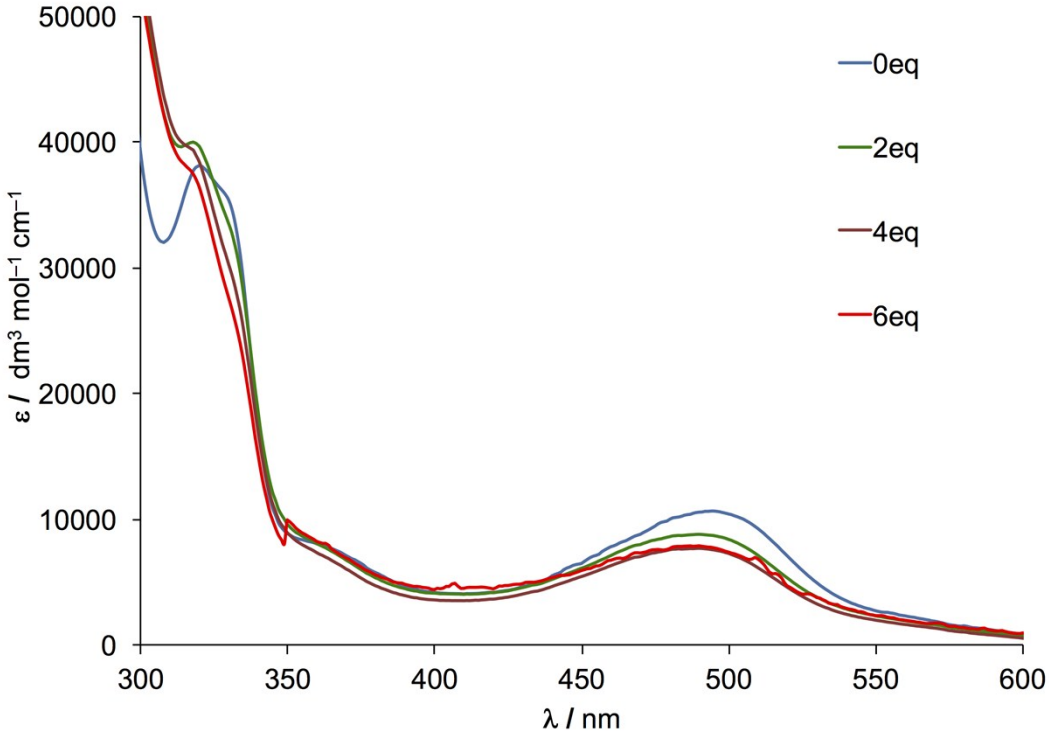

Fig. S2. Absorption spectra for a DMSO solution containing H_4**1** (2 equivalents) and $[Cu(MeCN)_4][PF_6]_2$ (1 equivalent) to which $^{n}Bu_4NOH$ was added. (Details: H_4**1** (4.96 mg, 10 μmol) and $[Cu(MeCN)_4][PF_6]_2$ (1.86 mg, 5 μmol) were combined in DMSO and stirred for 30 minutes. The reaction mixture was then diluted to give a final concentration of 10 μmol dm^{-3} (assuming full conversion to the homoleptic metal complex). The solution UV spectra were measured between the additions of a 0.1M solution (EtOH) of $^{n}Bu_4NOH$ in 10 μL aliquots.)

(2) DSCs constructed from electrodes treated with $H_4$1 + NaOH

Table S2. Performance parameters for duplicate DSCs containing the dye $[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$ where $H_4\mathbf{1}$ was treated with 0–4 equivalents of NaOH prior to electrode functionalization. Values of relative photoconversion efficiency (Rel. η) are with respect to that of N719 set to 100%.

Dye	Eq. NaOH	J_{SC} [mA cm^{-2}]	V_{OC} [mV]	FF [%]	η [%]	Rel. η [%]
On the day of sealing						
$[Cu(H_4\mathbf{1})(\mathbf{2})]^{+}$	0	4.61	521	72	1.72	27.5
$[Cu(H_4\mathbf{1})(\mathbf{2})]^{+}$	0	4.54	546	68	1.68	26.9
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	1.0	3.29	538	73	1.29	20.6
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	1.0	4.80	571	70	1.91	30.6
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	2.0	3.30	520	71	1.22	19.5
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	2.0	4.67	538	71	1.78	28.5
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	3.0	1.93	433	70	0.59	9.4
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	3.0	1.93	441	71	0.60	9.6
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	4.0	0.54	397	69	0.15	2.4
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	4.0	0.56	394	70	0.15	2.4
N719	–	14.3	635	70	6.25	100
3 days after sealing						
$[Cu(H_4\mathbf{1})(\mathbf{2})]^{+}$	0	3.48	548	72	1.38	22.1
$[Cu(H_4\mathbf{1})(\mathbf{2})]^{+}$	0	3.30	569	67	1.26	20.2
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	1.0	2.19	560	73	0.90	14.4
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	1.0	3.83	606	72	1.66	26.6
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	2.0	2.28	535	72	0.88	14.1
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	2.0	3.90	550	72	1.54	24.6
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	3.0	1.42	433	70	0.43	6.9
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	3.0	1.47	442	71	0.46	7.4
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	4.0	0.52	392	70	0.14	2.2
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	4.0	0.55	397	71	0.15	2.4
7 days after sealing						
$[Cu(H_4\mathbf{1})(\mathbf{2})]^{+}$	0	3.60	558	72	1.44	23.0
$[Cu(H_4\mathbf{1})(\mathbf{2})]^{+}$	0	3.31	579	68	1.31	21.0
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	1.0	2.16	570	74	0.92	14.7
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	1.0	3.79	604	73	1.66	26.6
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	2.0	2.27	538	73	0.90	14.4
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	2.0	3.86	552	73	1.55	24.8
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	3.0	1.46	435	70	0.44	7.0
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	3.0	1.66	458	72	0.55	8.8
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	4.0	0.58	392	68	0.16	2.6
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	4.0	0.61	396	71	0.17	2.7

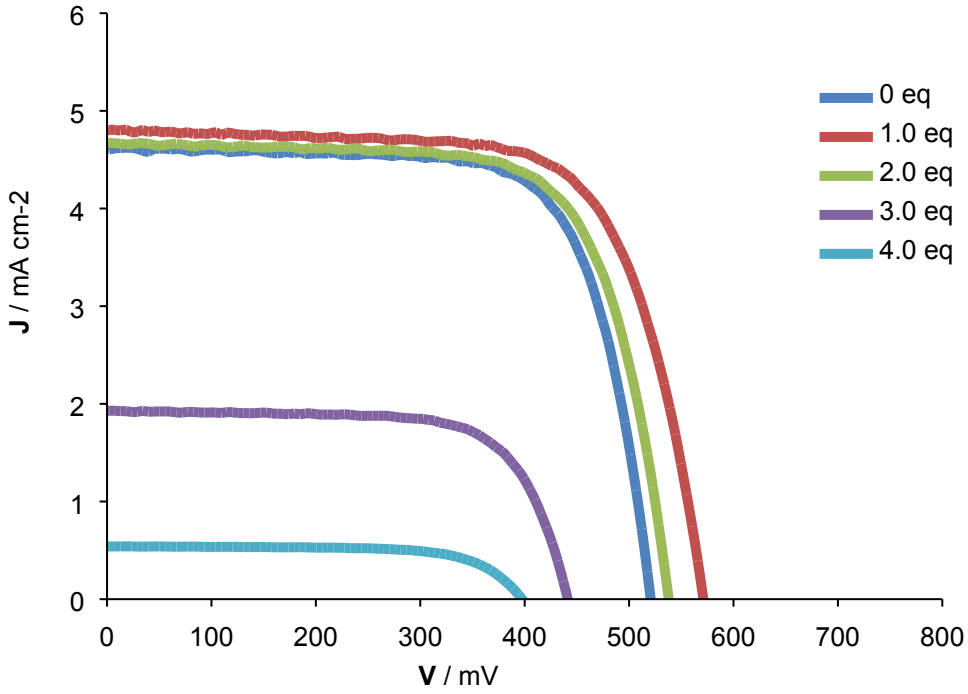

Fig. S3. *J*–*V* curves for DSCs constructed with 0–4 eq of NaOH added to H_4**1** (see Fig. 1 in the main paper). All spectra were measured on the day of DSC sealing (day 0).

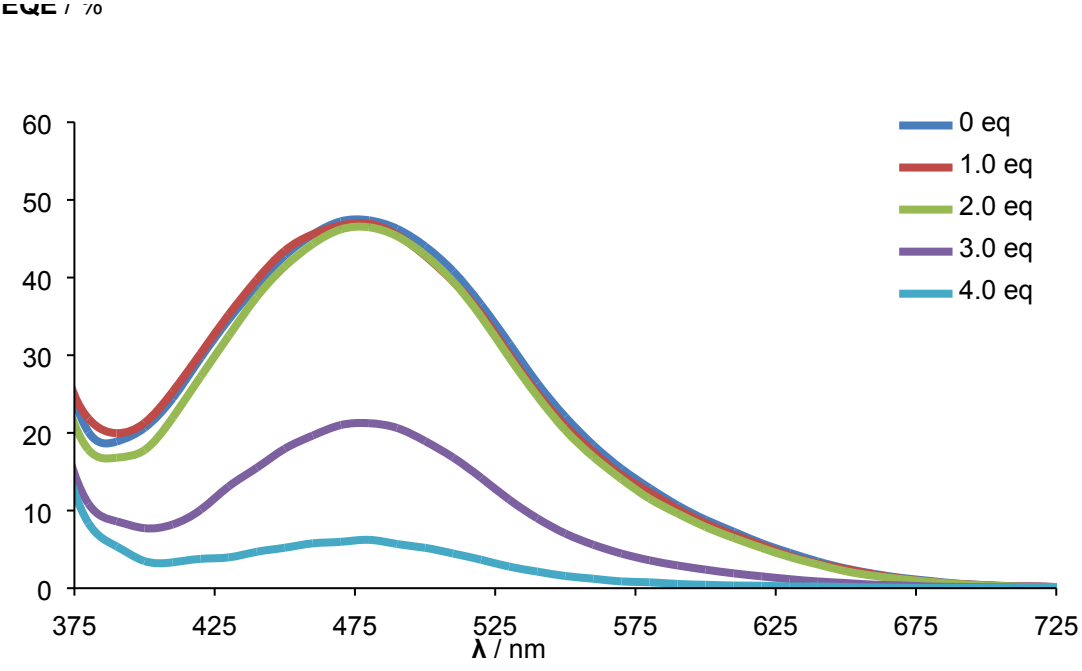

Fig. S4. EQE spectra of the DSCs in Fig. S1, constructed with 0–4 eq of NaOH added to H_4**1** (see Fig. 1 in the main paper). All spectra were measured on the day of DSC sealing (day 0).

(3) DSCs constructed from electrodes treated with H_4**1** + Cs_2CO_3

Table S3. Performance parameters for duplicate DSCs containing the dye $[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$ where H_4**1** is treated with 0–4 equivalents of Cs_2CO_3 prior to electrode functionalization. Values of relative photoconversion efficiency (Rel. η) are with respect to that of N719 set to 100%.

Dye	Eq. Cs_2CO_3	J_{SC} [mA cm^{-2}]	V_{OC} [mV]	FF [%]	η [%]	Rel. η [%]
On the day of sealing						
$[Cu(H_4\mathbf{1})(\mathbf{2})]^{+}$	0	4.61	521	72	1.72	27.5
$[Cu(H_4\mathbf{1})(\mathbf{2})]^{+}$	0	4.54	546	68	1.68	26.9
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	1.0	5.40	561	72	2.17	34.7
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	1.0	4.46	563	73	1.83	29.3
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	2.0	4.33	545	69	1.62	25.9
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	2.0	2.91	511	72	1.07	17.1
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	3.0	2.68	474	70	0.89	14.2
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	3.0	3.08	485	70	1.05	16.8
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	4.0	1.35	426	71	0.41	6.6
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	4.0	1.00	424	72	0.30	4.8
N719	–	14.3	635	70	6.25	100
3 days after sealing						
$[Cu(H_4\mathbf{1})(\mathbf{2})]^{+}$	0	3.48	548	72	1.38	22.1
$[Cu(H_4\mathbf{1})(\mathbf{2})]^{+}$	0	3.30	569	67	1.26	20.2
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	1.0	3.92	568	73	1.62	25.9
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	1.0	2.94	545	73	1.17	18.7
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	2.0	3.60	529	70	1.34	21.4
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	2.0	2.71	512	70	0.97	15.5
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	3.0	1.82	459	71	0.59	9.4
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	3.0	2.25	478	71	0.76	12.2
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	4.0	1.05	425	71	0.32	5.1
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	4.0	0.76	422	71	0.23	3.7
7 days after sealing						
$[Cu(H_4\mathbf{1})(\mathbf{2})]^{+}$	0	3.60	558	72	1.44	23.0
$[Cu(H_4\mathbf{1})(\mathbf{2})]^{+}$	0	3.31	579	68	1.31	21.0
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	1.0	3.97	577	73	1.67	26.7
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	1.0	2.90	554	73	1.17	18.7
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	2.0	3.64	527	71	0.98	15.7
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	2.0	2.72	507	69	0.61	9.8
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	3.0	1.90	466	71	0.62	9.9
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	3.0	2.43	486	70	0.83	13.3
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	4.0	1.23	431	71	0.37	5.9
$[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$	4.0	0.84	426	72	0.26	4.2

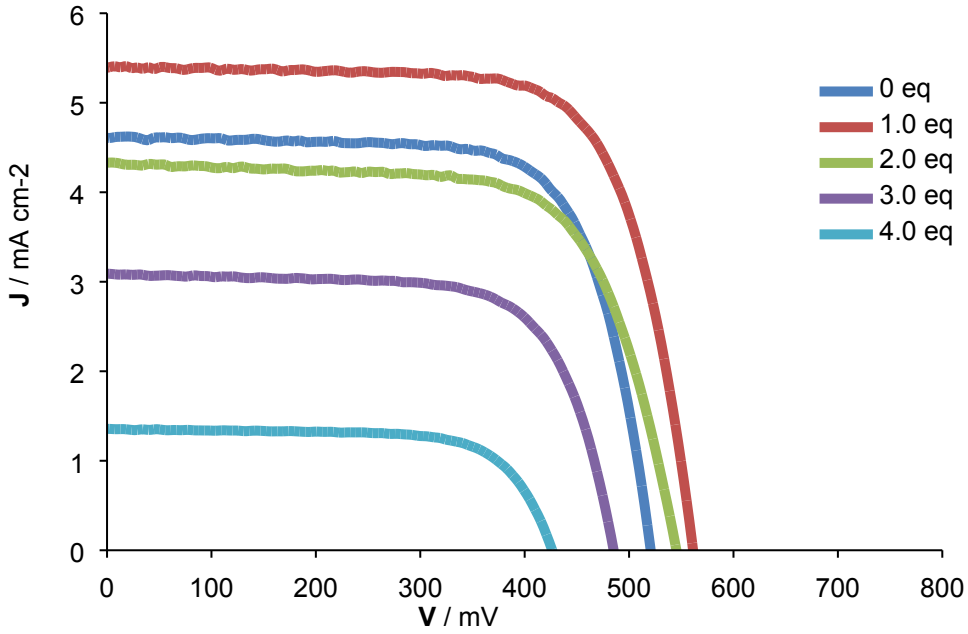

Fig. S5. *J*–*V* curves for DSCs constructed with 0–4 eq of Cs_2CO_3 added to H_4**1**. All spectra were measured on the day of DSC sealing (day 0).

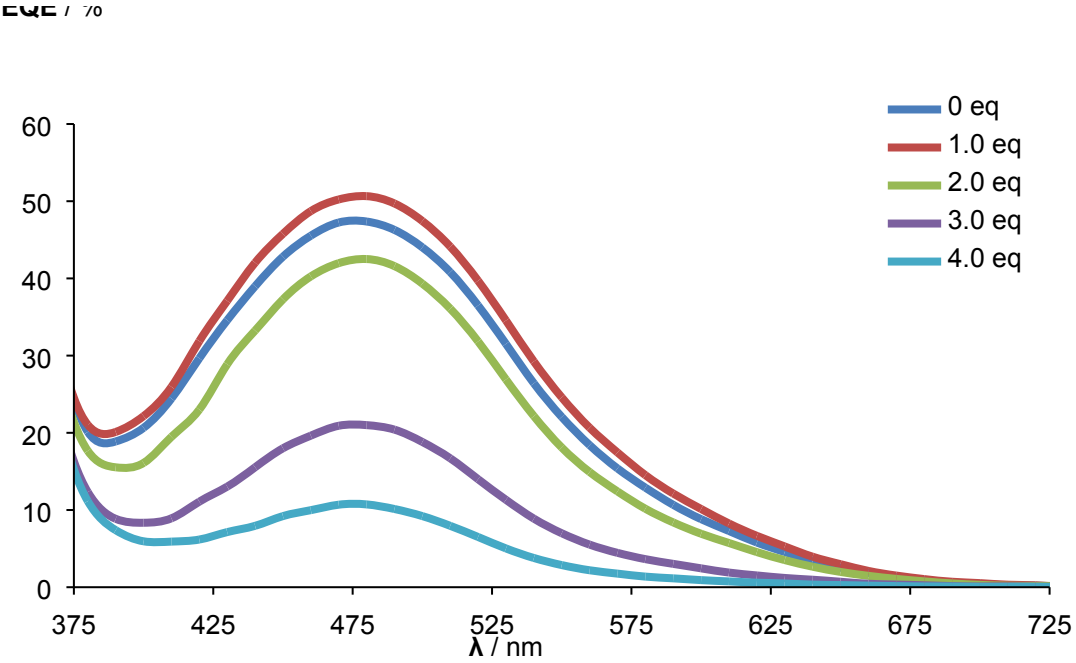

Fig. S6. EQE spectra of the DSCs in Fig. S4, constructed with 0–4 eq of Cs_2CO_3 added to H_4**1**. All spectra were measured on the day of DSC sealing (day 0).

(4) NMR titrations

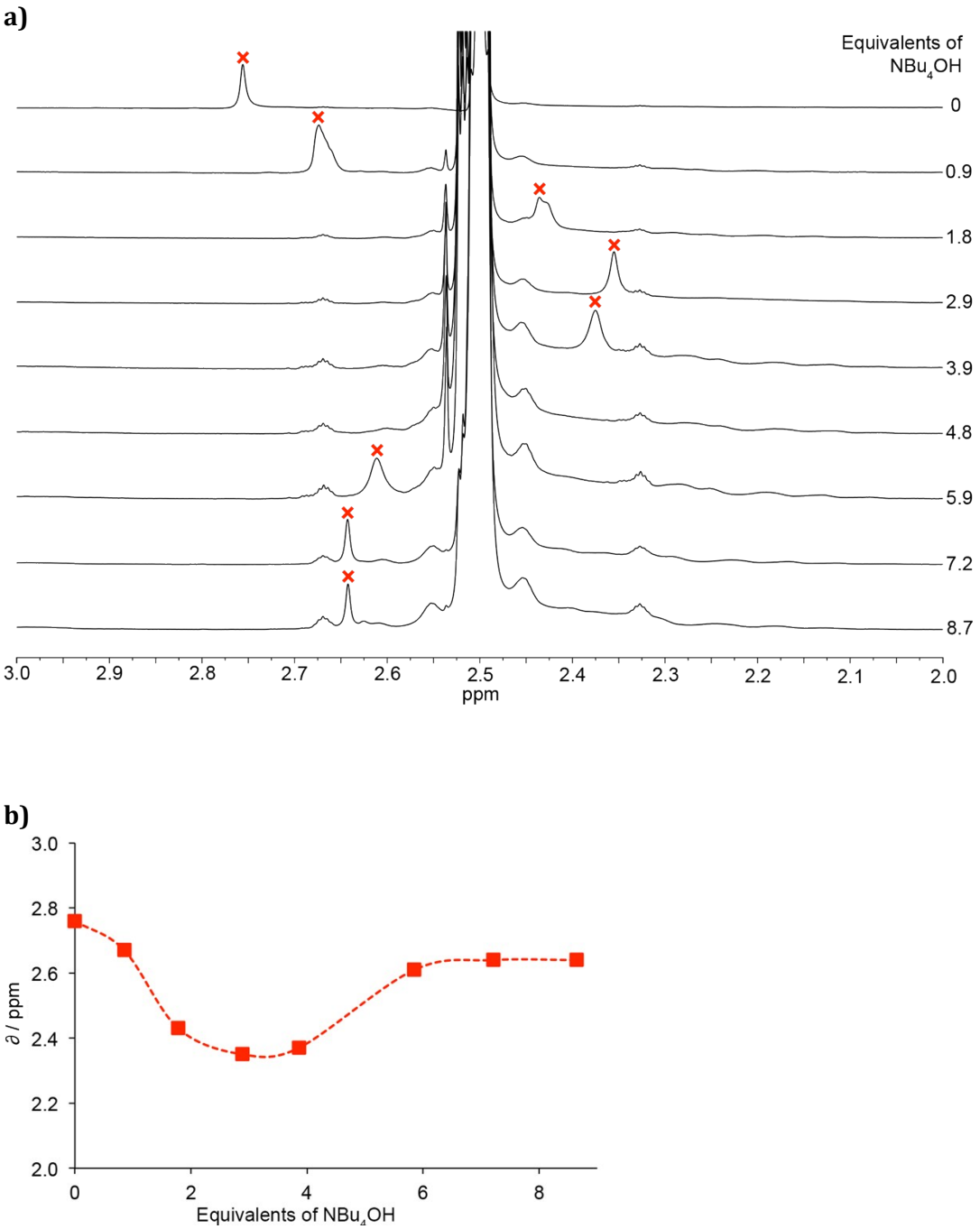

Fig. S7. NMR spectroscopic titration of $^{n}NBu_4OH$ into a solution of H_4**1** in DMSO-d_6, focused on the 6–methyl signal. *a)* stacked ^{1}H NMR spectra. *b)* Chemical shift of NMR signal vs. equivalents of $^{n}Bu_4NOH$.

***(5)* DSCs constructed from electrodes pre–treated or post–treated with $^{n}Bu_4NOH$.**

Table S4. Performance parameters for duplicate DSCs containing the dye $[Cu(H_n\mathbf{1})(\mathbf{2})]^{n-3}$ where electrodes are used with no base present in the dye baths (entries 1 and 2), or treated with $^{n}Bu_4NOH$ before (entries 3 and 4) or after (entries 5 and 6) exposure to a $H_4\mathbf{1}$ solution. Values of relative photoconversion efficiency (Rel. η) are with respect to that of N719 set to 100%.

Dip 1	Dip 2	Dip 3	J_{SC} [mA cm^{-2}]	V_{OC} [mV]	FF [%]	η [%]	Rel. η [%]
On the day of sealing							
$H_4\mathbf{1}$	$[Cu(\mathbf{2})_2][PF_6]$	–	4.48	522	70	1.64	26.2
$H_4\mathbf{1}$	$[Cu(\mathbf{2})_2][PF_6]$	–	4.23	531	72	1.61	25.8
$^{n}Bu_4NOH$	$H_4\mathbf{1}$	$[Cu(\mathbf{2})_2][PF_6]$	5.19	541	45	1.26	20.2
$^{n}Bu_4NOH$	$H_4\mathbf{1}$	$[Cu(\mathbf{2})_2][PF_6]$	4.49	534	56	1.34	21.4
$H_4\mathbf{1}$	$^{n}Bu_4NOH$	$[Cu(\mathbf{2})_2][PF_6]$	5.35	529	67	1.91	30.6
$H_4\mathbf{1}$	$^{n}Bu_4NOH$	$[Cu(\mathbf{2})_2][PF_6]$	5.07	521	68	1.80	28.8
N719	–	–	14.3	635	70	6.25	100

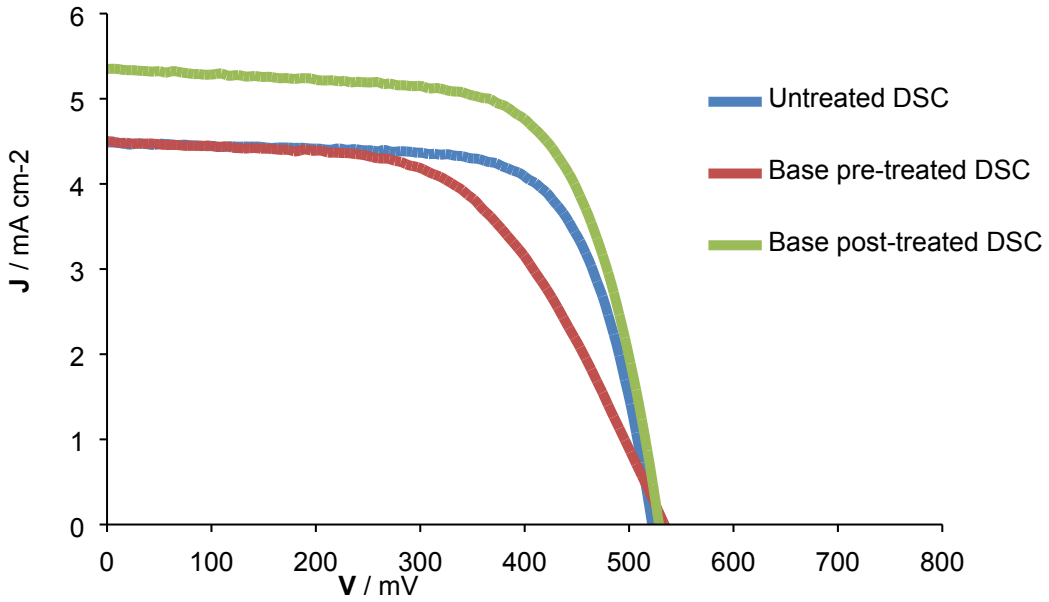

Fig. S8. *J–V* curves for DSCs listed in Table S4. Untreated DSC = entries 1 and 2 (Table S4), base pre-treated DSCs = entries 3 and 4 (Table S4), and base post-treated = entries 5 and 6 (Table S4).

***(6)* EIS measurements.**

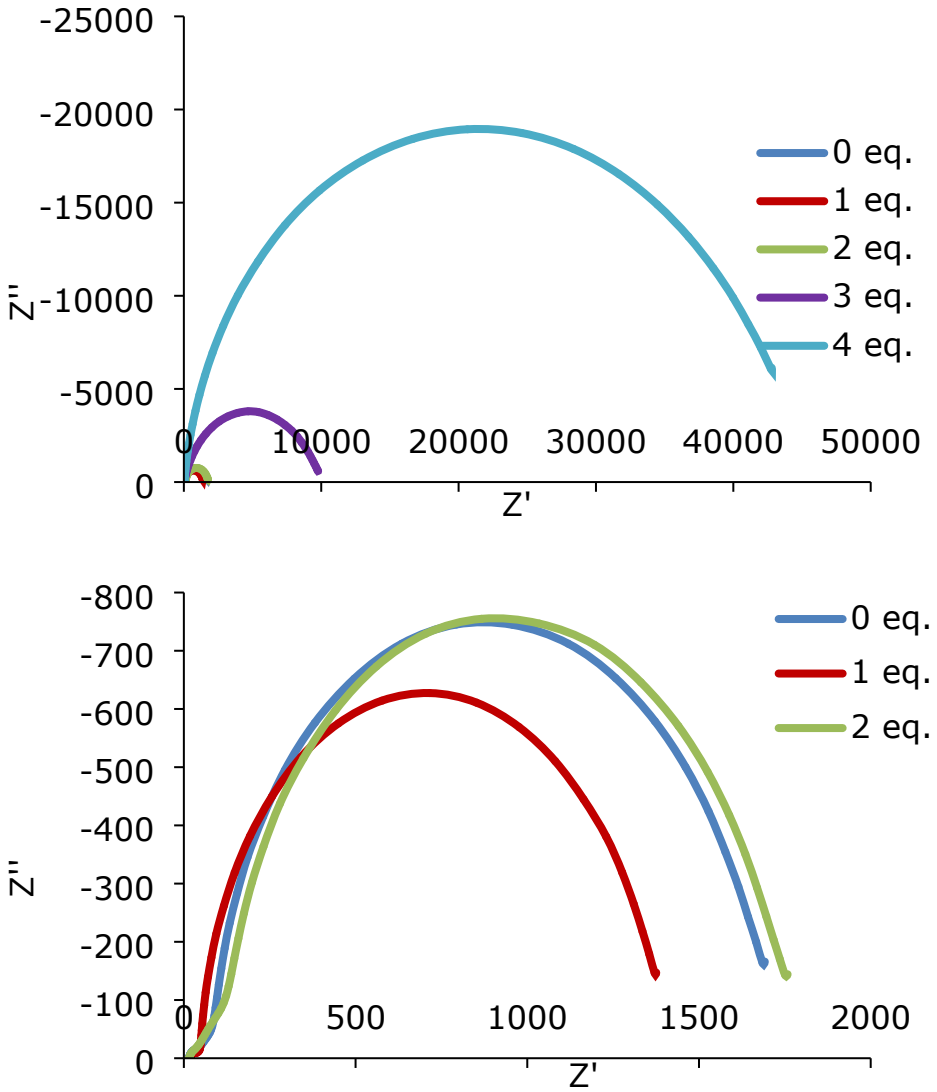

Fig. S9. Nyquist plots of EIS measurements at a light intensity of 2.2 mW cm^{-2}. The lower plot is an expansion from the upper plot.

(7) DSCs constructed using different solvents in the anchoring step with either H_4**1** or $[Bu_4N]_{4-n}[H_n$**1**$]$.

Table S5. Performance parameters for duplicate DSCs containing the dye $[Cu(H_n$**1**$)($**2**$)]^{n-3}$ constructed using different solvents in the initial electrode functionalization with H_4**1** or $[^nBu_4N]_{4-n}[H_n$**1**$]$.

Solvent	Anchoring Ligand	Equiv. Base	J_{SC} [mA cm^{-2}]	V_{OC} [mV]	FF [%]	η [%]	Rel. η [%]
On the day of sealing							
EtOH	H_4**1**	0	0.72	423	71	0.21	3.4
EtOH	H_4**1**	0	0.53	418	70	0.15	2.4
EtOH	$[^nBu_4N]_{4-n}[H_n$**1**$]$	1	5.27	549	62	1.80	28.8
EtOH	$[^nBu_4N]_{4-n}[H_n$**1**$]$	1	5.34	556	67	1.98	31.7
H_2O	H_4**1**	0	0.92	437	71	0.29	4.6
H_2O	H_4**1**	0	0.23	376	67	0.06	1.0
H_2O	$[^nBu_4N]_{4-n}[H_n$**1**$]$	1	5.17	554	66	1.90	30.4
H_2O	$[^nBu_4N]_{4-n}[H_n$**1**$]$	1	5.36	560	66	1.97	31.5
CH_2Cl_2	H_4**1**	0	0.12	367	68	0.03	0.5
CH_2Cl_2	H_4**1**	0	0.14	376	68	0.03	0.5
CH_2Cl_2	$[^nBu_4N]_{4-n}[H_n$**1**$]$	1	3.91	564	67	1.47	24.5
CH_2Cl_2	$[^nBu_4N]_{4-n}[H_n$**1**$]$	1	3.65	561	63	1.28	20.5
N719	–	–	14.3	635	70	6.25	100

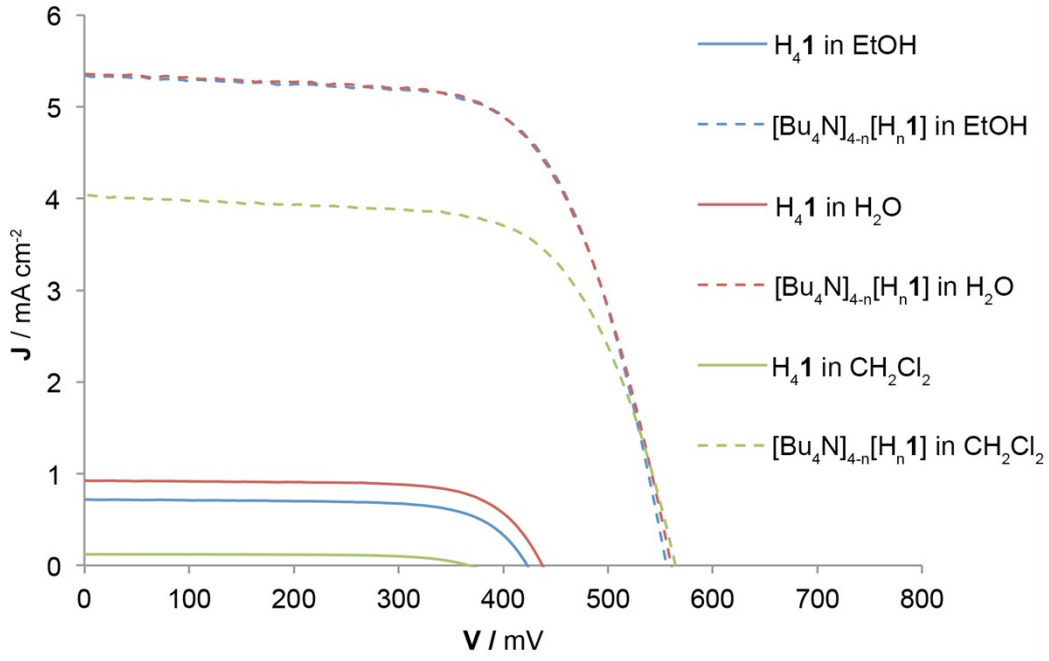

Fig. S10. *J*–*V* curves for DSCs listed in Table S5. The curves for $[^nBu_4N]_{4-n}[H_n$**1**$]$ in EtOH and $[^nBu_4N]_{4-n}[H_n$**1**$]$ in H_2O are strongly overlapping.