Supplementary Information

Fine-tuning the coordination atoms of copper redox mediators: an effective strategy in boosting the photovoltage of dye-sensitized solar cells

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Supplementary Figures and Tables

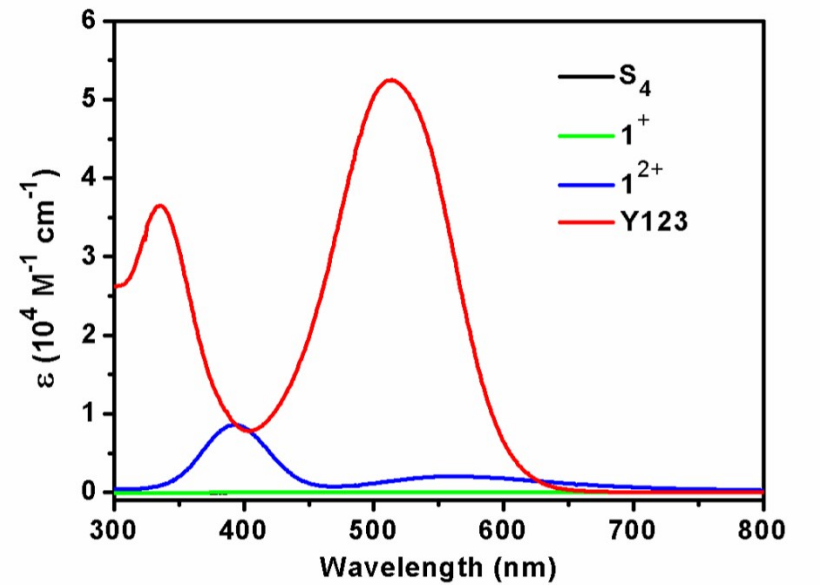


Fig. S1 UV−vis absorption spectra of S_4, $\mathbf{1}^{+}$, $\mathbf{1}^{2+}$, and dye Y123 in acetonitrile solutions. Concentrations: 0.1 mM for the ligand and the copper complexes, and 0.02 mM for dye Y123.

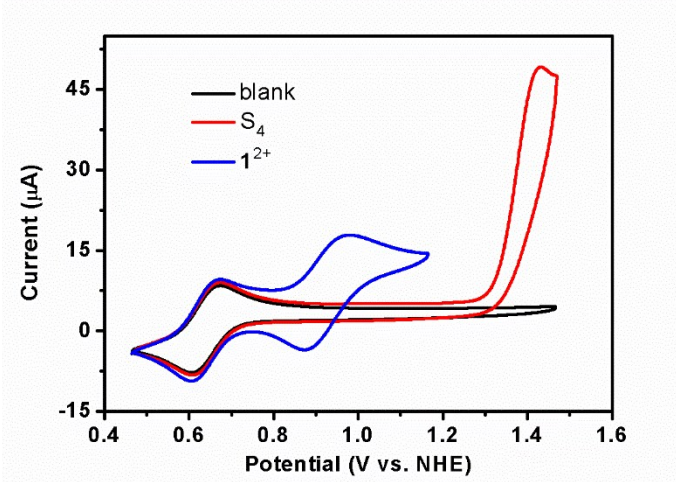


Fig. S2 Cyclic voltammograms of $\mathbf{1}^{2+}$, and S_4, as well as the blank CV with 1 mM concentration in acetonitrile containing 0.1 M nBu$_4$NPF$_6$ at a scan rate of 50 mV s^{-1}.

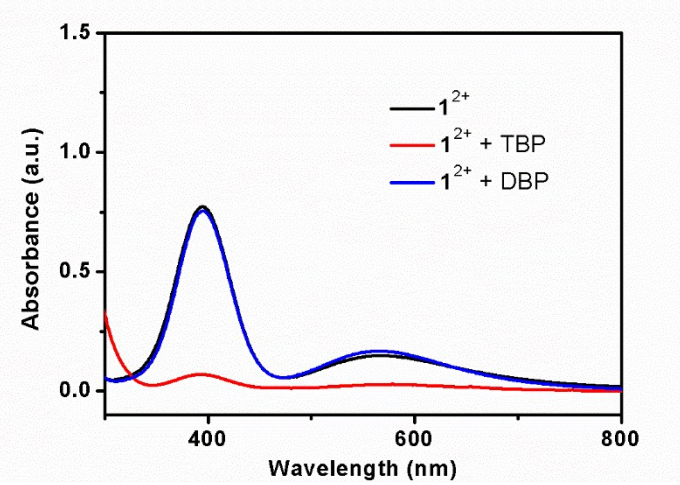


Fig. S3 UV−vis absorption spectra of $\mathbf{1}^{2+}$ (0.1 mM) with excess TBP or DBP (10 equivalent) in acetonitrile.

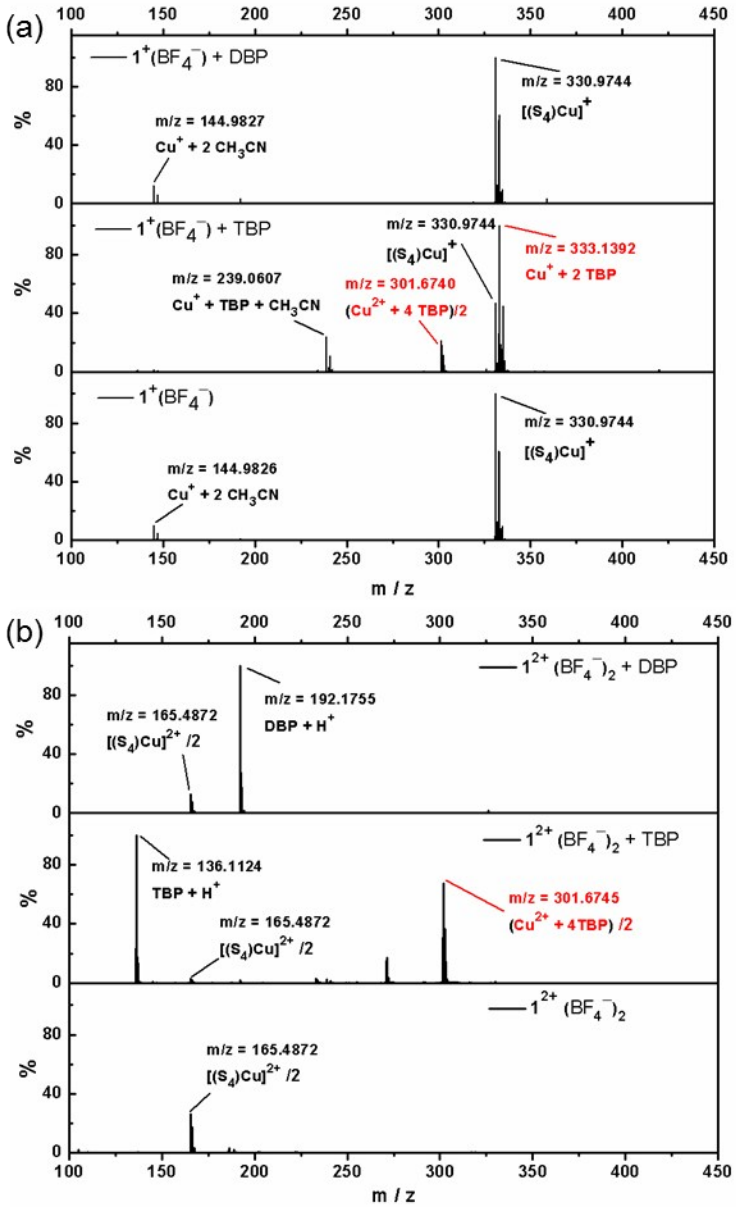


Fig. S4 The high-resolution mass spectra of (a) $\mathbf{1}^{+}$ and (b) $\mathbf{1}^{2+}$ with 5 equivalent TBP and DBP in acetonitrile.

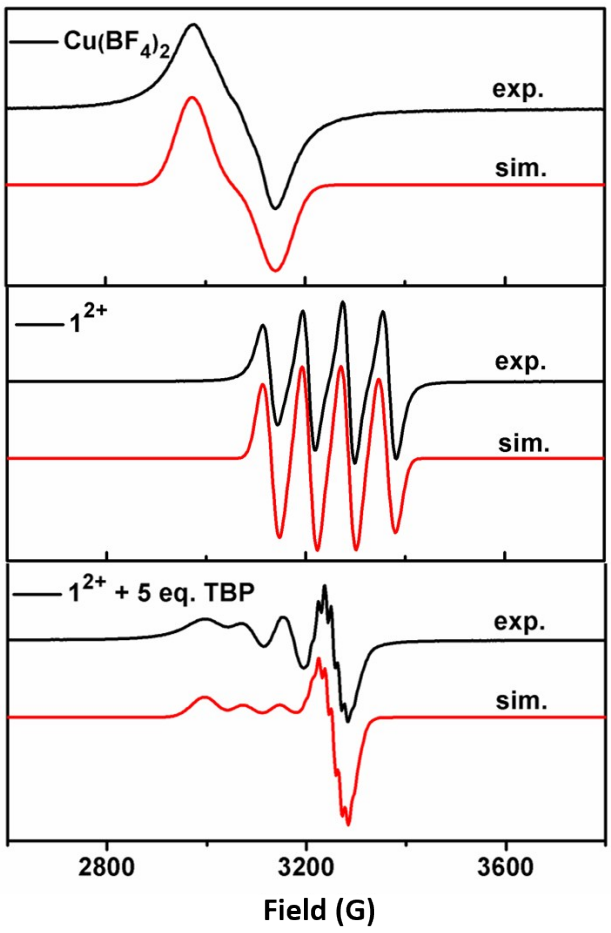


Fig. S5 Simulation of EPR spectra.

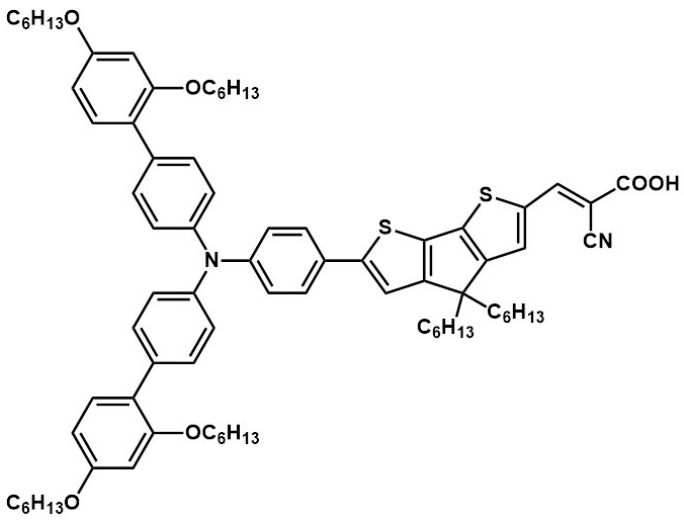


Fig. S6 Molecular structure of dye Y123.

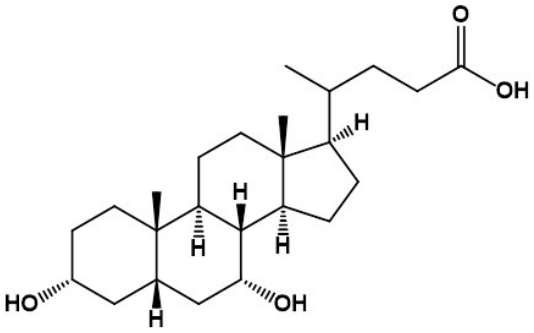


Fig. S7 Molecular structure of CDCA.

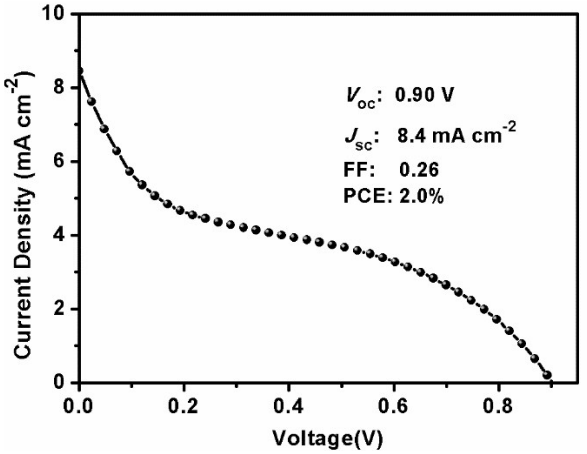


Fig. S8 *J*–*V* curve of the best DSC device containing the $\mathbf{1}^{2+/+}$-based electrolyte (0.1 M $\mathbf{1}^{+}$, 0.025 M $\mathbf{1}^{2+}$, 0.1 M Li-TFSI, 0.01 M CDCA, and 0.5 M TBP in acetonitrile) measured under one illumination (100 mW cm^{-2}, AM 1.5G).

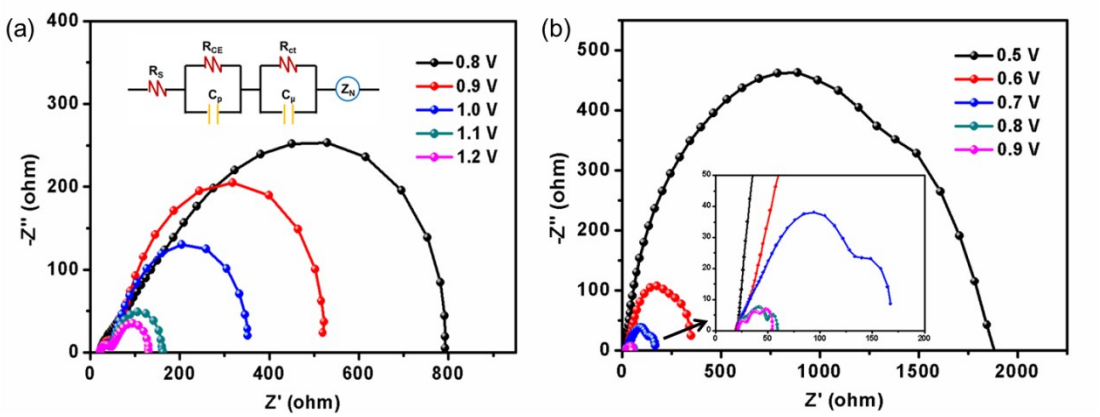


Fig. S9 Nyquist plots for DSC devices based on (a) **E1** and (b) **E3** electrolytes measured in the dark at varied bias potentials.

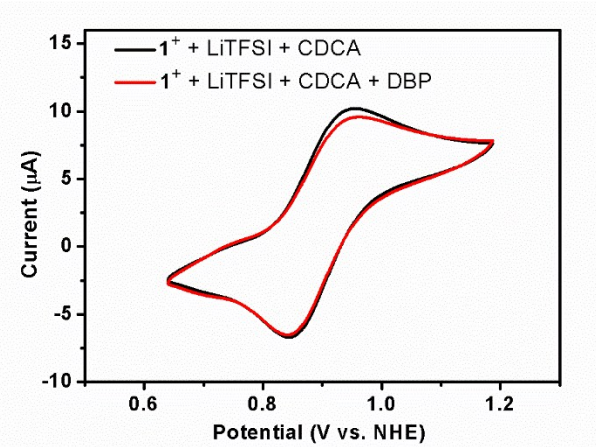


Fig. S10 Cyclic voltammograms of $\mathbf{1}^+$ with different additives. The concentration of $\mathbf{1}^+$ is 0.1 mM in acetonitrile, and the concentrations of other components are based on their relative proportion in the electrolyte. The solution contains 0.1 M $n\text{Bu}_4\text{NPF}_6$ as a supporting electrolyte, and the scan rate is 50 mV s^{-1}.

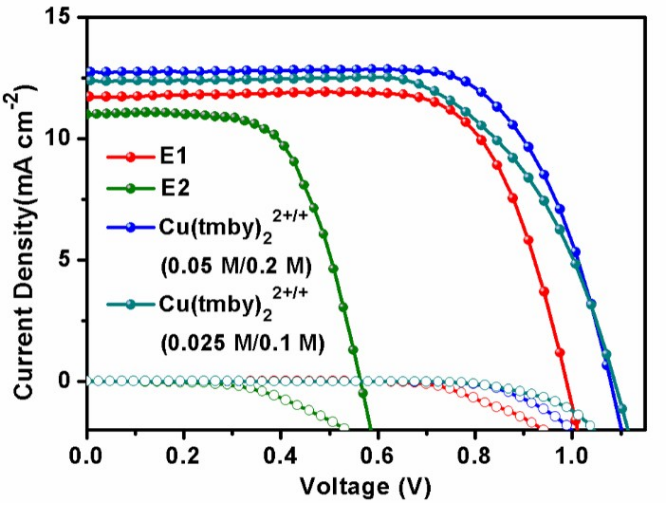


Fig. S11 *J*–*V* curves of DSC devices containing $\mathbf{1}^{2+/+}$-based electrolyte (**E1**, 0.1 M $\mathbf{1}^{+}$, 0.025 M $\mathbf{1}^{2+}$, 0.5 M DBP, 0.1 M Li-TFSI, and 0.01 M CDCA in acetonitrile), $\mathbf{2}^{2+/+}$-based electrolyte (**E2**, 0.2 M $\mathbf{2}^{+}$, 0.05 M $\mathbf{2}^{2+}$, 0.5 M DBP, 0.1 M Li-TFSI, and 0.01 M CDCA in acetonitrile), and $Cu(tmby)_2^{2+/+}$-based electrolytes (varied concentrations of the copper species with 0.1 M Li-TFSI and 0.5 M TBP in acetonitrile), measured under illumination (100 mW cm^{-2}, AM 1.5G, sphere mark) and in dark (open circle mark). CDCA (5 mM) was added in the dye Y123 solution used for all the devices.

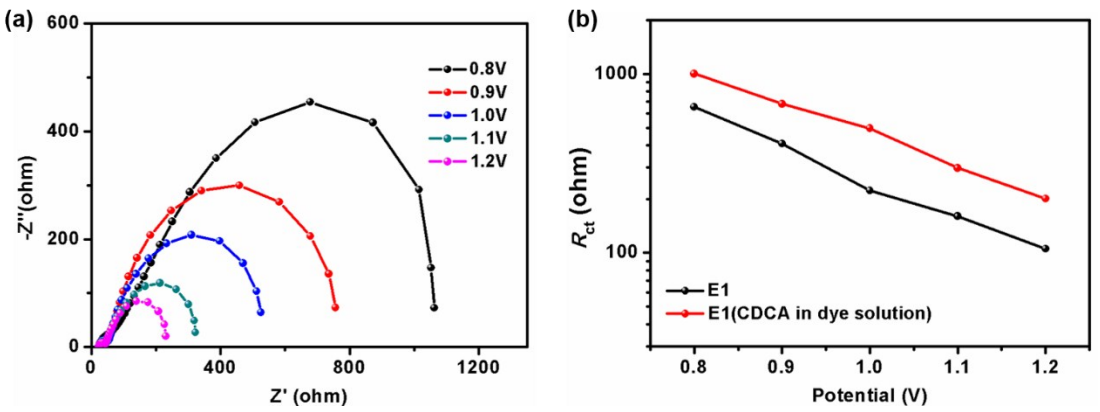


Fig. S12 (a) Nyquist plots of DSC devices based on **E1** measured in the dark under varied bias potentials. CDCA (5 mM) was added in the dye Y123 solution. (b) The charge recombination resistances extracted from the EIS measurements at varied bias potentials.

Table S1. Crystallographic data and processing parameters for $[(S_4)Cu^{II}(OH_2)](BF_4)_2$ and $[(N_4)Cu^{II}(OH_2)](BF_4)_2$.

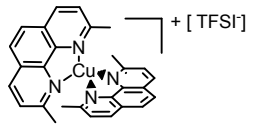
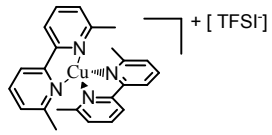
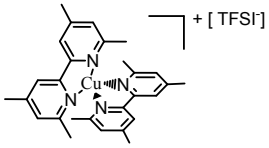
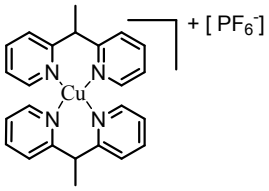
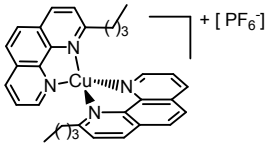
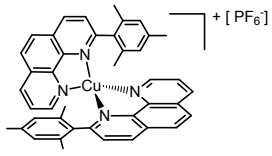
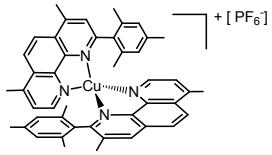
Complex	$[(S_4)Cu^{II}(OH_2)](BF_4)_2$	$[(N_4)Cu^{II}(OH_2)](BF_4)_2$
Formula	$C_{10}H_{22}S_4OB_2F_8Cu$	$C_{14}H_{34}N_4OB_2F_8Cu$
Formula weight	522.67	511.21
Crystal system	Orthorhombic	Triclinic
Space group	*A*ma2	*P*-1
Z	4	2
a / Å	12.8692(17)	9.4885(3)
b / Å	14.1500(18)	10.1789(3)
c / Å	10.8460(14)	11.6397(4)
α / deg	90.00	85.237(2)
β / deg	90.00	74.9220(10)
γ / deg	90.00	77.7440(10)
V / Å^3	1975.0(4)	1060.29(6)
D_{calcd} / g m^{-3}	1.758	1.504
□ / mm^{-1}	1.599	1.083
Crystal size / mm	0.21×0.20×0.11	0.14×0.12×0.11
Range / deg	2.37 / 30.77	2.27 / 27.45
Reflns collected/Indep.	1779 / 1751	3721 / 3520
Parameters refined	129	282
F(000)	1056	510
GOF on F^2	1.049	1.014
Final R_1 ($I > 2(I)$)	0.0430	0.0384
Final wR_2 ($I > 2(I)$)	0.1077	0.1001
max. peak/hole / e Å^{-3}	0.961 / -0.882	0.807 / -0.874

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(|F_o|^2 - |F_c|^2)^2/\Sigma(F_o^2)]^{1/2}$

Table S2. Selected bond lengths (Å) and angles (deg) for $[(S_4)Cu^{II}(OH_2)](BF_4)_2$ and $[(N_4)Cu^{II}(OH_2)](BF_4)_2$.

$[(S_4)Cu^{II}(OH_2)](BF_4)_2$		$[(N_4)Cu^{II}(OH_2)](BF_4)_2$	
Bond lengths (Å)		Bond lengths (Å)	
Cu–S1	2.313(15)	Cu–N1	2.090(2)
Cu–S2	2.331(15)	Cu–N2	2.096(2)
Cu–S3	2.331(15)	Cu–N3	2.097(19)
Cu–S4	2.313(15)	Cu–N4	2.090(2)
Bond angles (deg)		Bond angles (deg)	
S1–Cu–S2	88.05(5)	N1–Cu–N2	93.36(8)
S1–Cu–S3	169.33(6)	N1–Cu–N3	152.88(8)
S1–Cu–S4	92.74(8)	N1–Cu–N4	85.72(8)
S2–Cu–S3	89.24(9)	N2–Cu–N3	86.07(8)
S2–Cu–S4	169.33(6)	N2–Cu–N4	176.79(7)
S3–Cu–S4	88.05(5)	N3–Cu–N4	93.34(8)

Table S3. Summary of some representative photovoltaic performance of DSCs based on different copper redox couples.

Redox Couples	$E_{1/2}$ (V vs. NHE)	λ_{max} (nm)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)	*Ref.*
	0.93	457	1.06	13.61	69.2	10.3	1
	0.97	455	1.07	14.15	68.7	10.0	1
	0.87	451	1.10	13.3	78	11.6	2
	0.59	—	0.895	14.1	71.3	9.0	3
	0.75	452	0.61	6.3	53	2.0	4
	0.70	451	0.81	5.9	77	3.7	5
	0.62	445	0.72	9.3	66	4.4	6

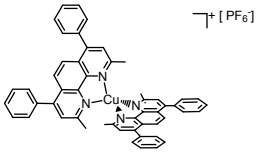
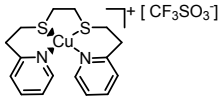
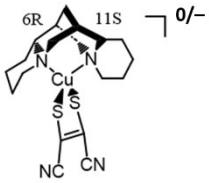
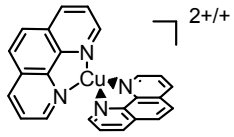
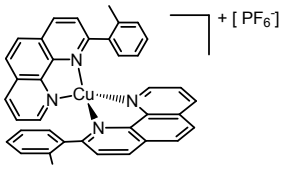
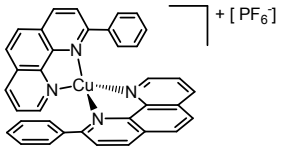
	0.93	—	0.71	1.1	49	0.4	7
	0.83	310	0.88	4	28	0.98	8
	0.53	—	0.66	4.4	44	1.3	9
	0.14	—	0.57	0.48	43	0.12	9
	0.65	455	0.87	11.1	62	6.0	10
	0.65	437	0.88	8.0	69	4.9	10
$[Cu(N_4)]^+$	0.31	293	0.57	11.0	60	3.7	This work
$[Cu(S_4)]^+$	0.91	217	0.99	11.7	72	8.4	This work

Table S4. The fitting results of EIS parameters for DSCs based on electrolytes **E1** and **E3**.

Electrolytes	Potential (V)	R_{ct} (Ohm)	C_{μ} (μF)	τ_e (ms)
E1	0.8	653.2	43.2	28.2
	0.9	408.0	49.1	20.0
	1.0	223.1	75.0	16.7
	1.1	160.0	99.7	15.9
	1.2	105.3	146.4	15.4
E3	0.5	1627	2.6	4.23
	0.6	380.6	4.0	1.52
	0.7	107.4	8.1	0.87
	0.8	23.4	51.7	1.21
	0.9	10.1	74.5	0.75

Table S5. Photovoltaic parameters of the best DSC devices based on different electrolytes measured under 100 mW cm^{-2} irradiation (AM 1.5G). CDCA (5 mM) was added in the dye Y123 solution

Electrolytes	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
$Cu(tmby)_2^{2+/+}$ (0.025 M/0.1 M)	1.09	12.4	0.65	8.7
$Cu(tmby)_2^{2+/+}$ (0.05 M/0.2 M)	1.08	12.7	0.71	9.7

References

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