

Fig. S1 The J - V characteristics of fresh DSSCs containing different electrolytes (A1~A4) varying in cobalt redox complex concentrations.

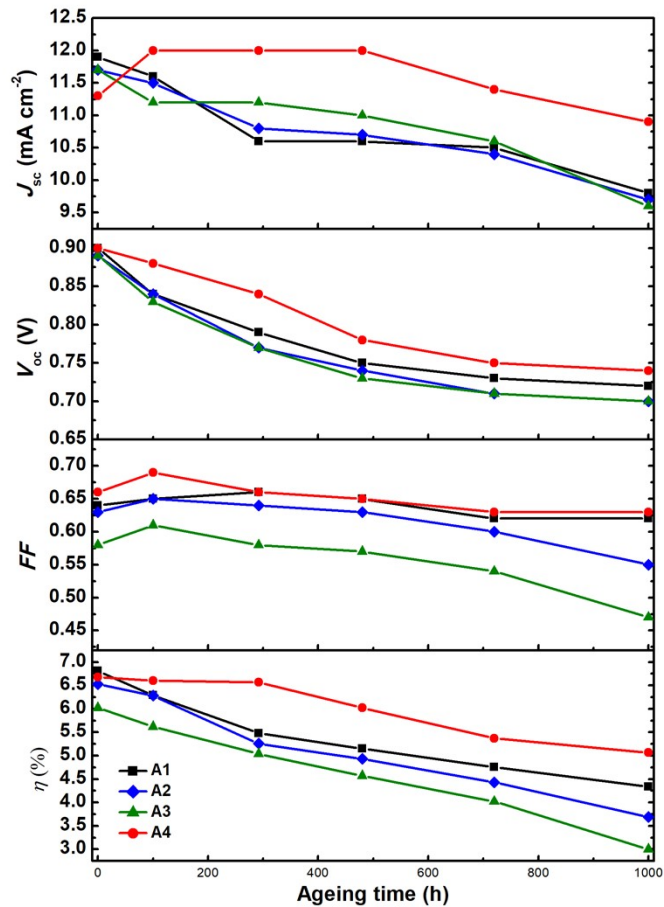


Fig. S2 The photovoltaic parameters for DSSCs containing different electrolytes (A1~A4) varying in cobalt redox complex concentrations and their evolutions with ageing time.

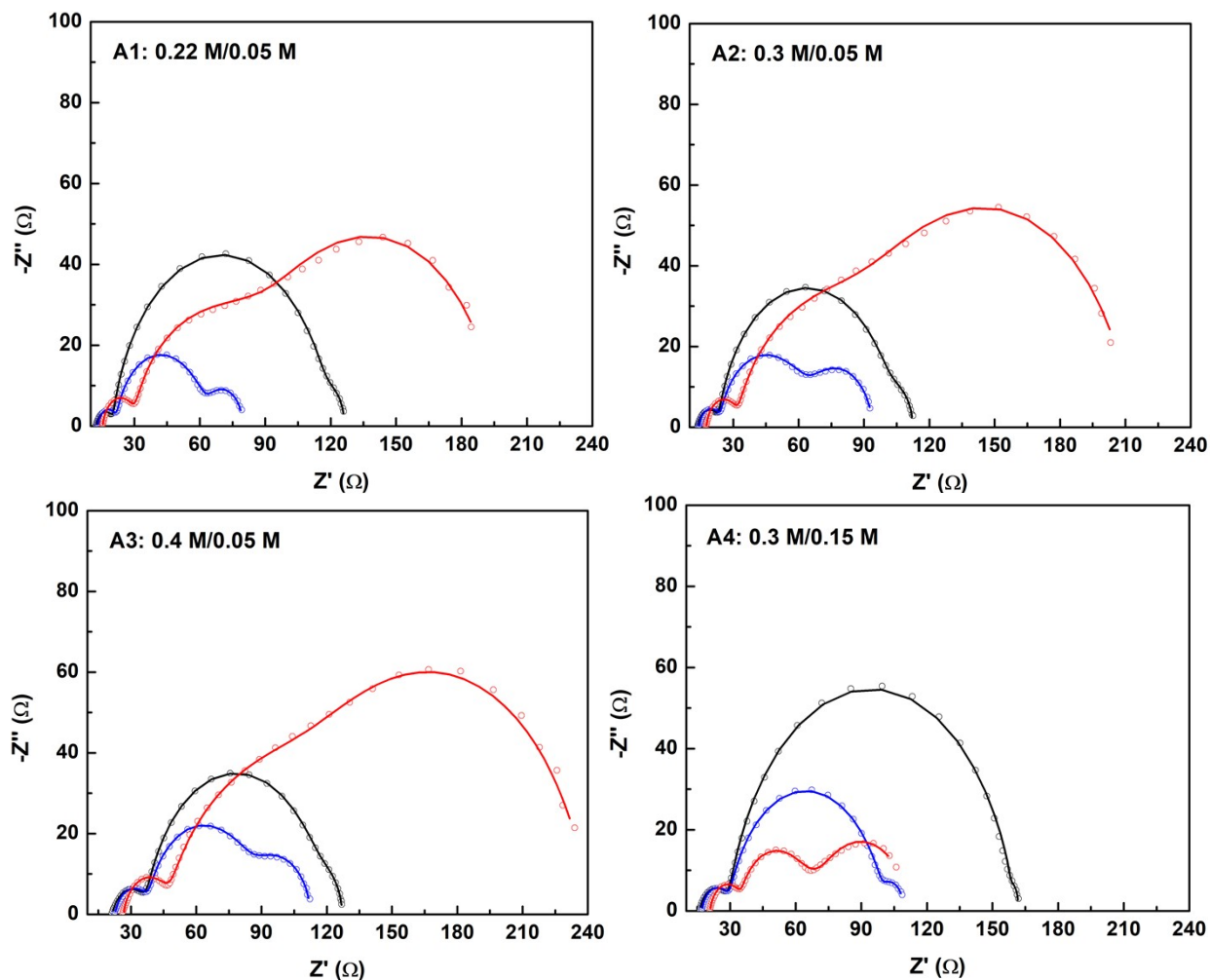


Fig. S3 The Nyquist plots of DSSCs containing different electrolytes (A1~A4) varying in cobalt redox complex concentrations after fabrication (black) and ageing for 300 h (blue), 1000 h (red); the data points were fitted by Z-View according to the equivalent circuit (Model 1).

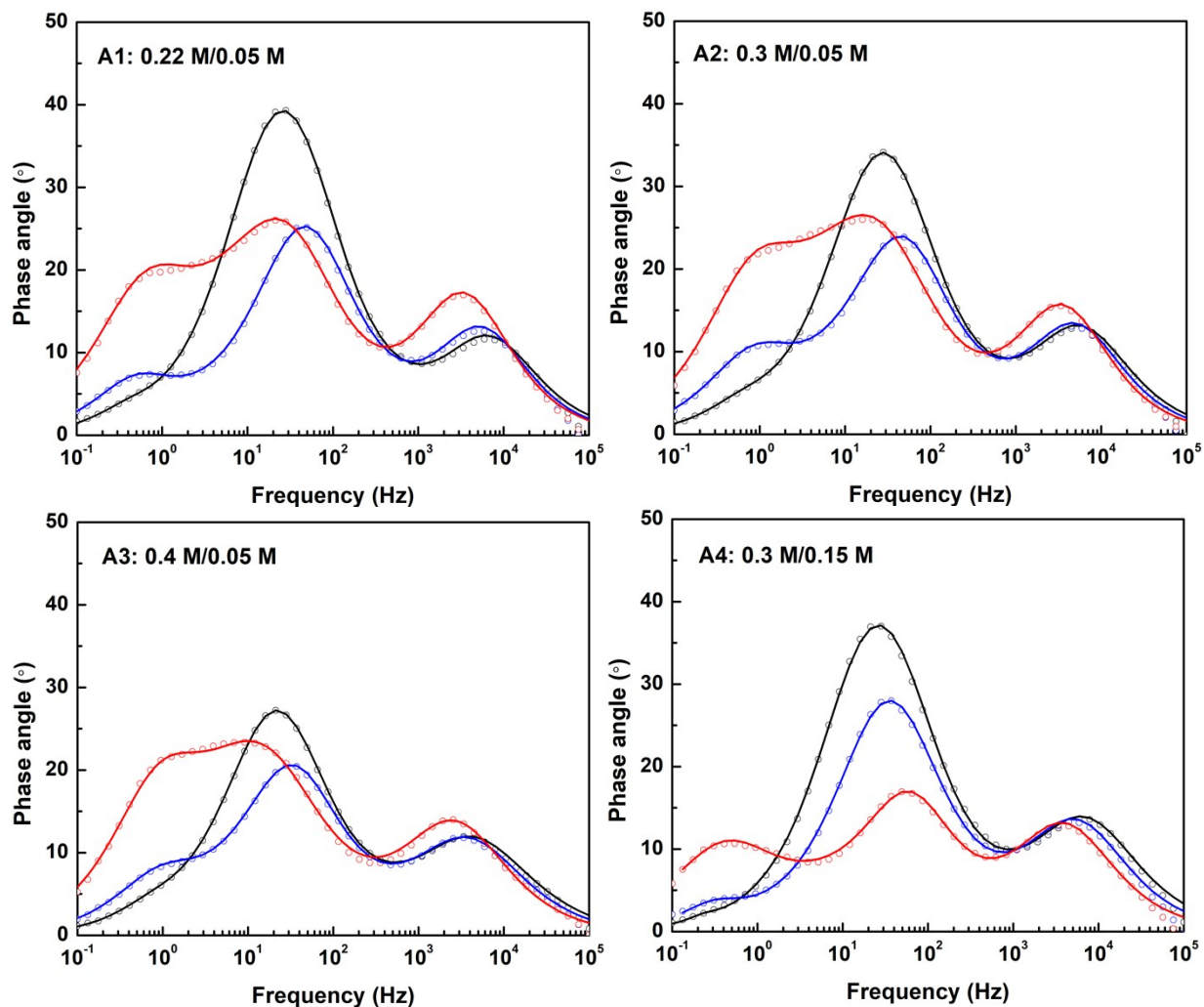


Fig. S4 Bode plots for DSSCs containing different electrolytes varying in cobalt redox complex concentrations (A1~A4) tested after fabrication (black) and ageing for 300h (blue), 1000 h (red); the data points were fitted by Z-View according to the equivalent circuit (Model 1).

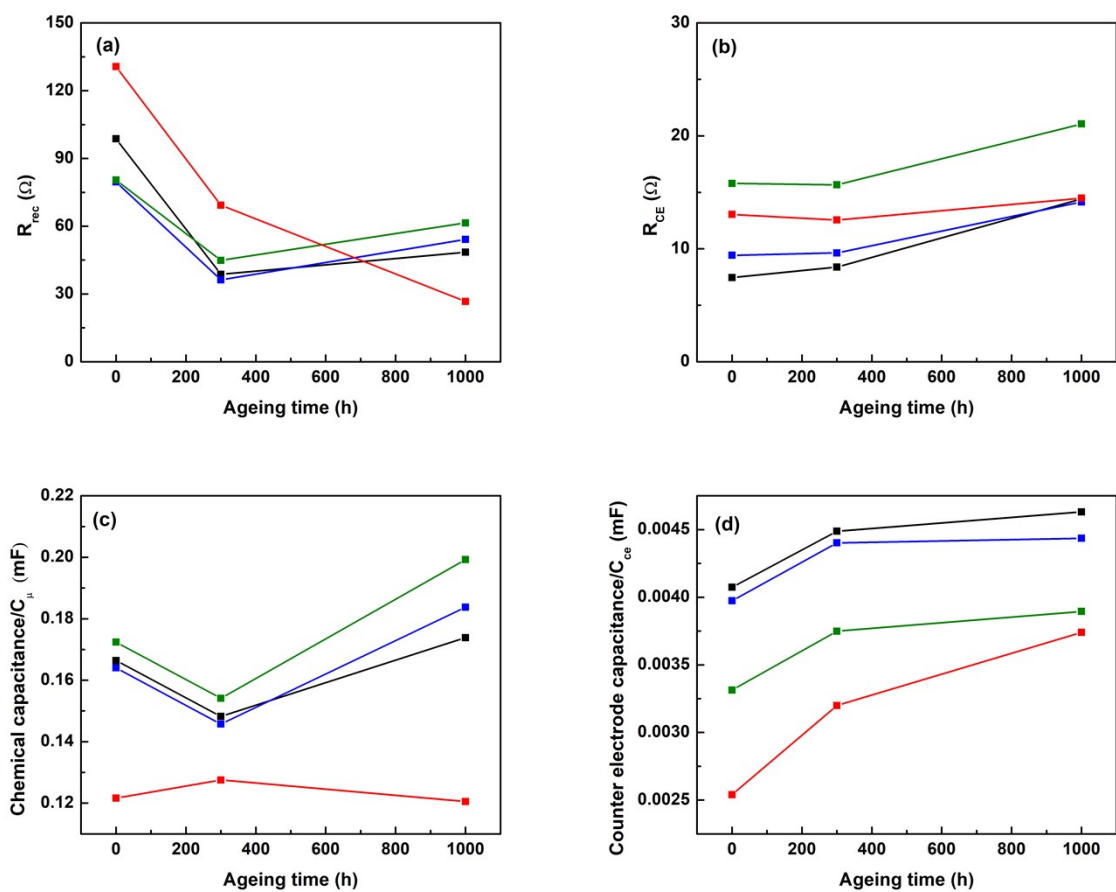


Fig. S5 The evolution of (a) R_{rec} , (b) R_{ct} , (c) C_{μ} and (d) C_{ce} with the ageing time for DSSCs varying in the electrolytes: A1, black; A2, blue; A3, green and A4, red. The data were extracted from EIS results.

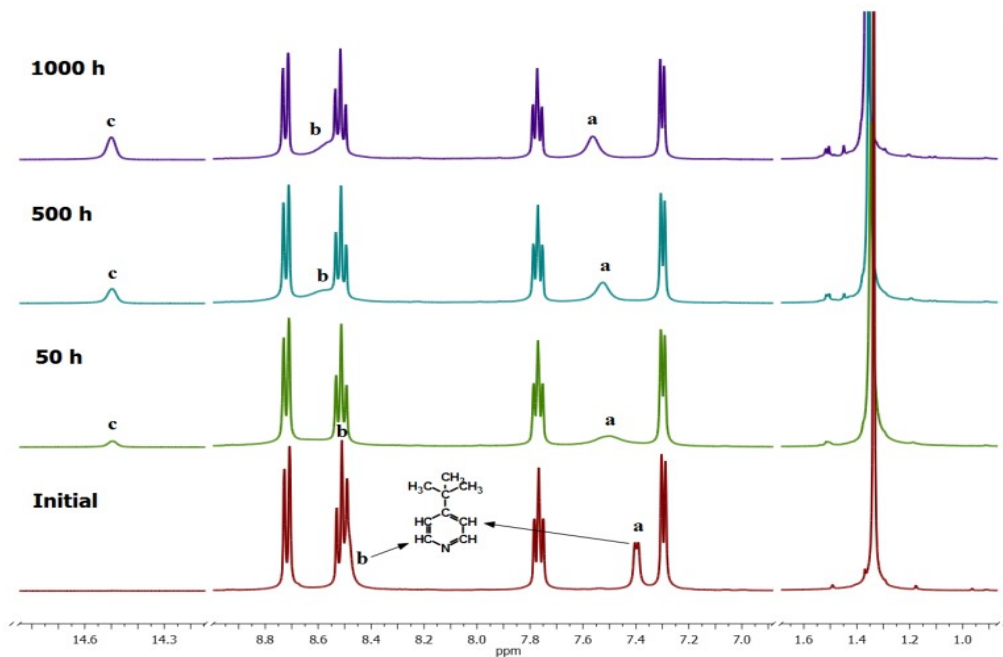


Fig. S6 $^1\text{H-NMR}$ spectra of the 0.05 M/0.06 M $\text{Co}(\text{bpy})_3^{3+}$ /TBP mixture in deuterated acetonitrile recorded during the ageing test. Characteristic peaks of the TBP-pyridine hydrogen atoms are labelled *a* and *b*. The new peak appearing is labelled *c*.

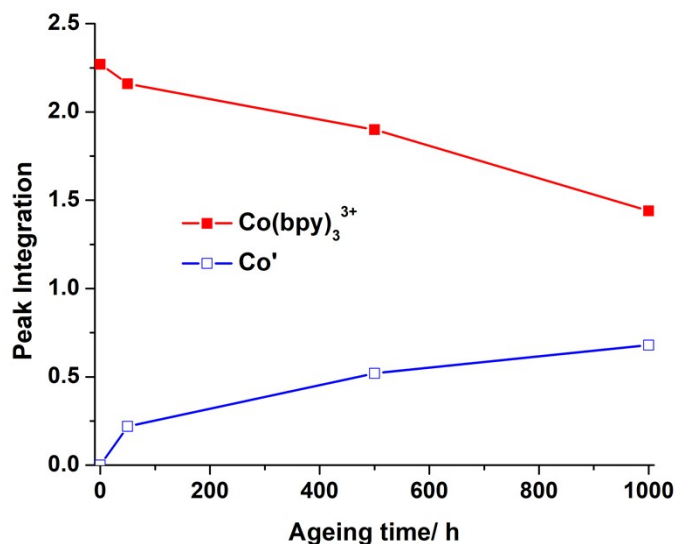


Fig. S7 Integration of characteristic H-peak of $\text{Co}(\text{bpy})_3^{3+}$ (7.75-7.78 ppm) and new cobalt complex (Co' , 14.5 ppm) as function of the ageing time. The peak of acetonitrile at 1.97 ppm was used as the reference.

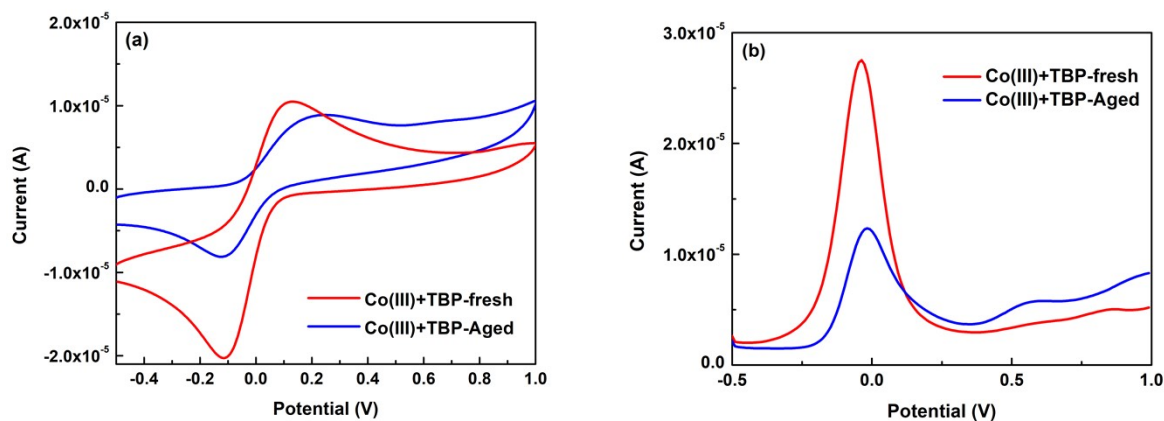


Fig. S8. (a) CV and (b) DPV curves measured in the fresh (red) and aged (blue) 3.5 mM/7 mM $\text{Co}(\text{bpy})_3^{3+}$ /TBP acetonitrile electrolyte under light/ 60°C exposure for 200 h with a scan rate of 50 mV/s.

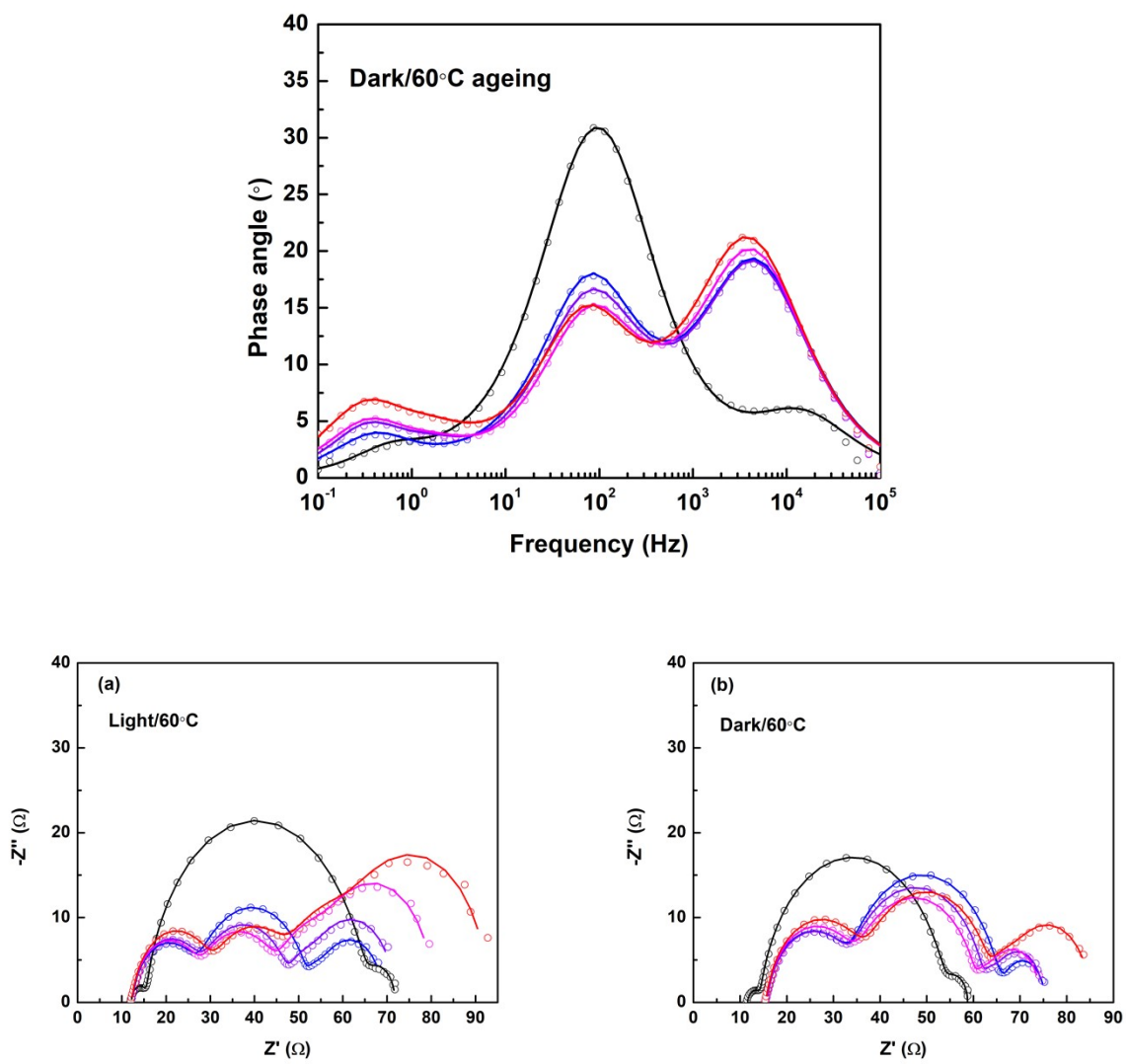


Fig. S9 Bode phase angle plots (above) and Nyquist plots (below) of DSSCs containing 0.1 M EIm⁺ aged under (a) light/60°C and (b) dark/60°C for 0 h, black; 274h, blue; 514h, purple; 730h, pink and 1000h, red. The data points were fitted by Z-View.

Table S1 The composition of the electrolyte and the photovoltaic characteristics of the corresponding DSSCs recorded under full sun irradiation (AM 1.5G, ~100 mW/cm²).

Electrolyte ^a	Cation, ionic radii/nm	[C ⁺] /M	J_{sc} /mA cm ⁻²	V_{oc} /V	FF	η /%	R_{dif} /Ω
A-Free	None	0	10.5	0.92	0.65	6.25	8.0
A-TEA	TEA ⁺ , 0.34 ^[S1]	0.1	10.7	0.93	0.66	6.57	9.7
A-TBA	TBA ⁺ , 0.41 ^[S1]	0.1	10.3	0.92	0.65	6.16	9.0
A-BIm	BIm ⁺ , 0.33 ^[S2]	0.1	10.6	0.93	0.65	6.41	9.6
[A-EIm]_{low}		0.1	10.5	0.93	0.68	6.60	9.0
[A-EIm]_{medi}	EIm ⁺ , 0.30 ^[S3]	0.8	10.8	0.93	0.67	6.70	13.0
[A-EIm]_{high}		1.5	10.0	0.94	0.66	6.24	28.5

^aAll electrolytes contained 0.3 M/0.15 M Co(bpy)₃^{2+/3+} and 0.2 M TBP in acetonitrile solvent.

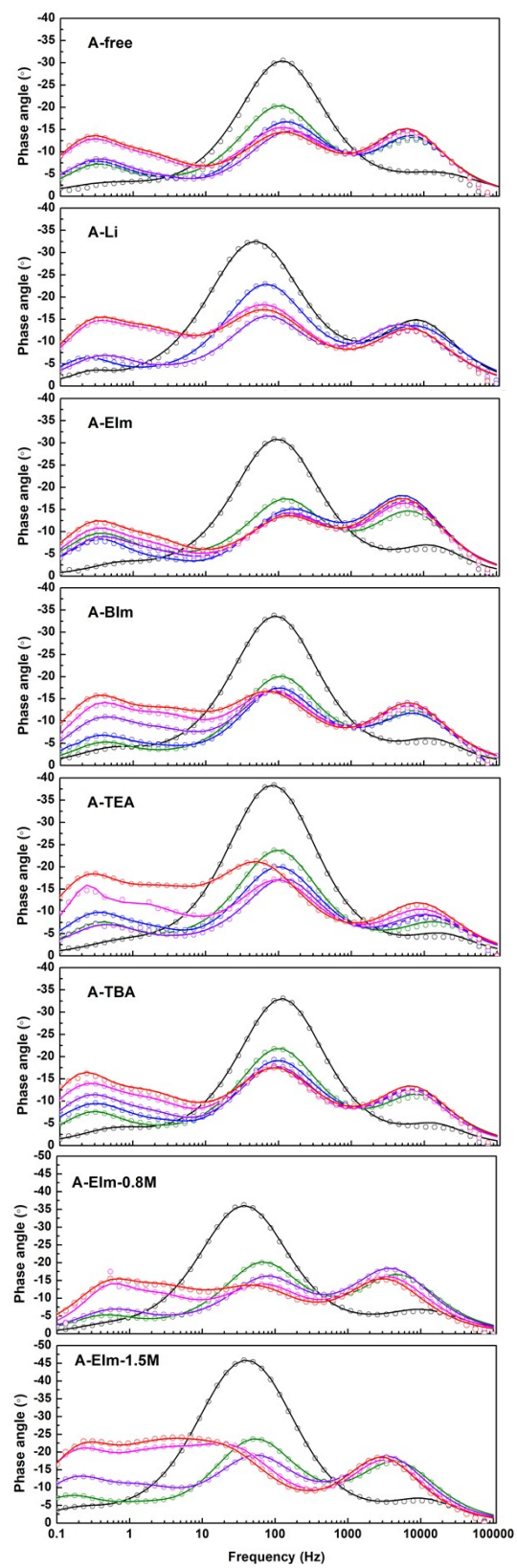


Fig. S10 Bode phase-angle plots for DSSCs containing no cation co-additives (A-Free), different cation co-additives of 0.1 M as labelled and EIm^+ of other two concentrations (0.8 M and 1.5 M). The plots were recorded during the ageing tests: Initial, black; 196h, green; 336h, blue; 576h, purple; 720h, pink; 1000h, red.

Table S2 Modelling data extracted from EIS results of DSSCs containing 1.5 M EIm^+ aged for 720 h.

Models	R_s/Ω	R_{ct}/Ω	Q_{ct}	n_{ct}	R_{rec}/Ω	Q_{μ}	n_{μ}	W_s/Ω	W_s-T	W_s-P	R_{new}/Ω	Q_{new}	n_{new}
Model 1	20.5	18.2	5.50E-06	0.96	68.0	4.30E-04	0.81	181.0	3.01	0.46	-	-	-
Model 2	20.5	18.8	6.03E-06	0.95	32.6	4.44E-04	0.88	135.4	2.35	0.51	82.28	1.51E-03	0.81

Table S3 Modelling parameters for the new EIS feature of DSSCs containing 0.1M EIm^+ varying in the ageing conditions and ageing time as listed.

Ageing conditions	Ageing time	R_{rec}/Ω	Q_{μ}	n_{μ}	R_{new}/Ω	Q_{new}	n_{new}
Light/60°C	274h	25.96	0.000203	0.88159	1.395	0.005326	1.352
	514h	20.30	0.000217	0.88455	6.309	0.006881	1.087
	730h	17.81	0.000265	0.87838	14.55	0.005206	0.9698
	1000h	17.28	0.000291	0.89202	16.42	0.003060	0.9715
Dark/60°C	514h	29.01	0.000144	0.92918	2.927	0.011353	1.224
	730h	25.94	0.000154	0.93124	3.079	0.010125	1.204
	1000h	26.81	0.000164	0.93496	6.241	0.008413	1.094

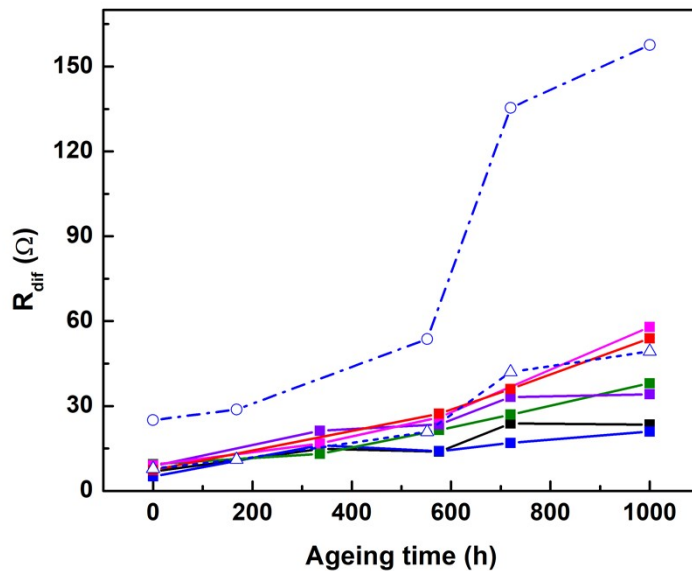


Fig. S11 The evolutions of R_{new} with the ageing time for DSSCs containing no (A-free, black) and various cation co-additives of 0.1 M: A- EIm^+ , blue solid lines; A- BIm^+ , green; A- TBA^+ , purple; A- TEA^+ , pink; A- Li^+ , red, and containing EIm^+ of higher concentrations: 0.8 M, blue, triangle, dash line; 1.5 M, blue, circle, dash dot line. The values were extracted from the corresponding EIS results.

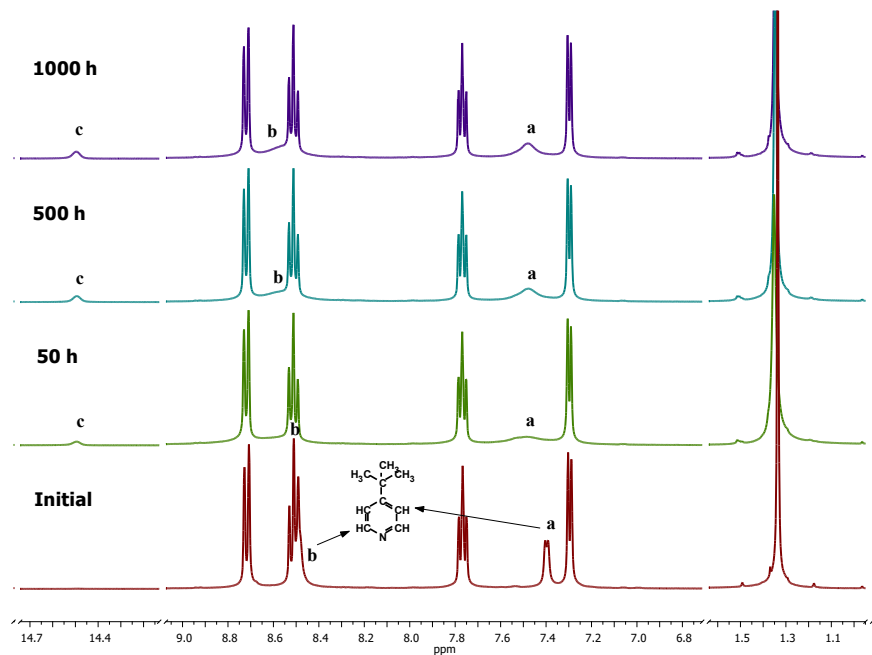


Fig. S12. ¹H NMR spectra of 0.05 M/0.06 M Co(bpy)₃³⁺/TBP in d³-acetonitrile recorded during the stability tests under exposure to darkness/60°C conditions. Characteristic peaks of TBP pyridine hydrogen are labelled a and b. The new peak is labelled c.

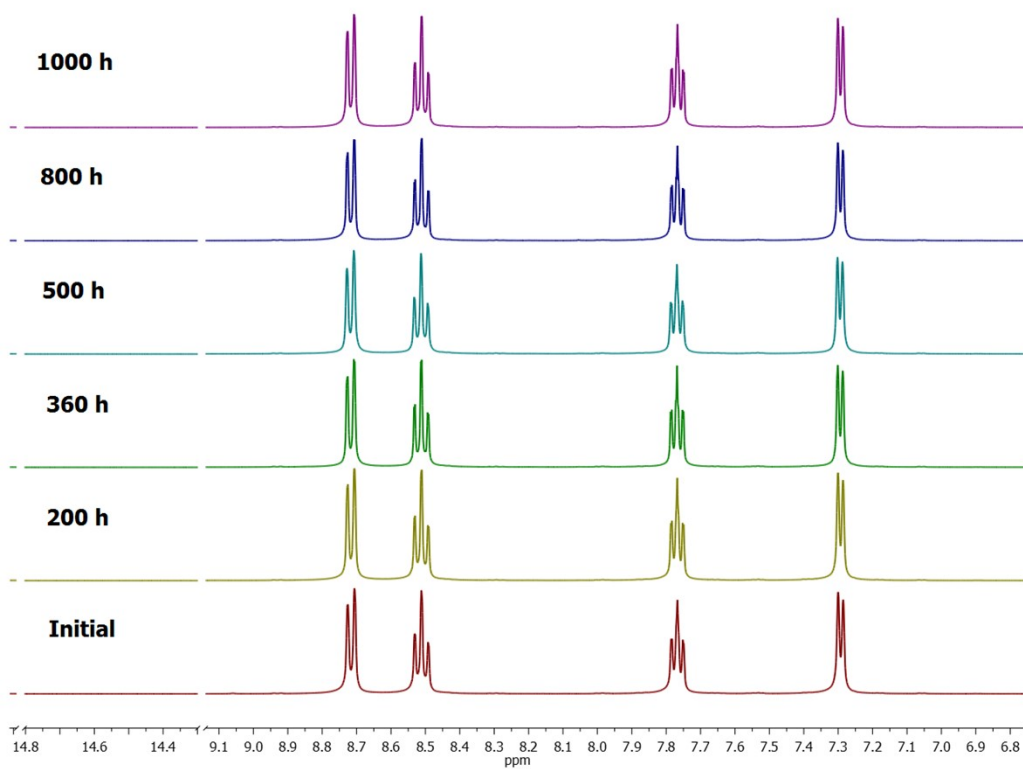


Fig. S13 ¹H NMR spectra of Co(bpy)₃³⁺ in d³-acetonitrile monitored during the ageing test.

References

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