Electronic Supplementary Information

Imidazolium Functionalized Cobalt Tris(bipyridyl) Complex Redox Shuttles for High Efficient Ionic Liquid Electrolyte Dye-Sensitized Solar Cells

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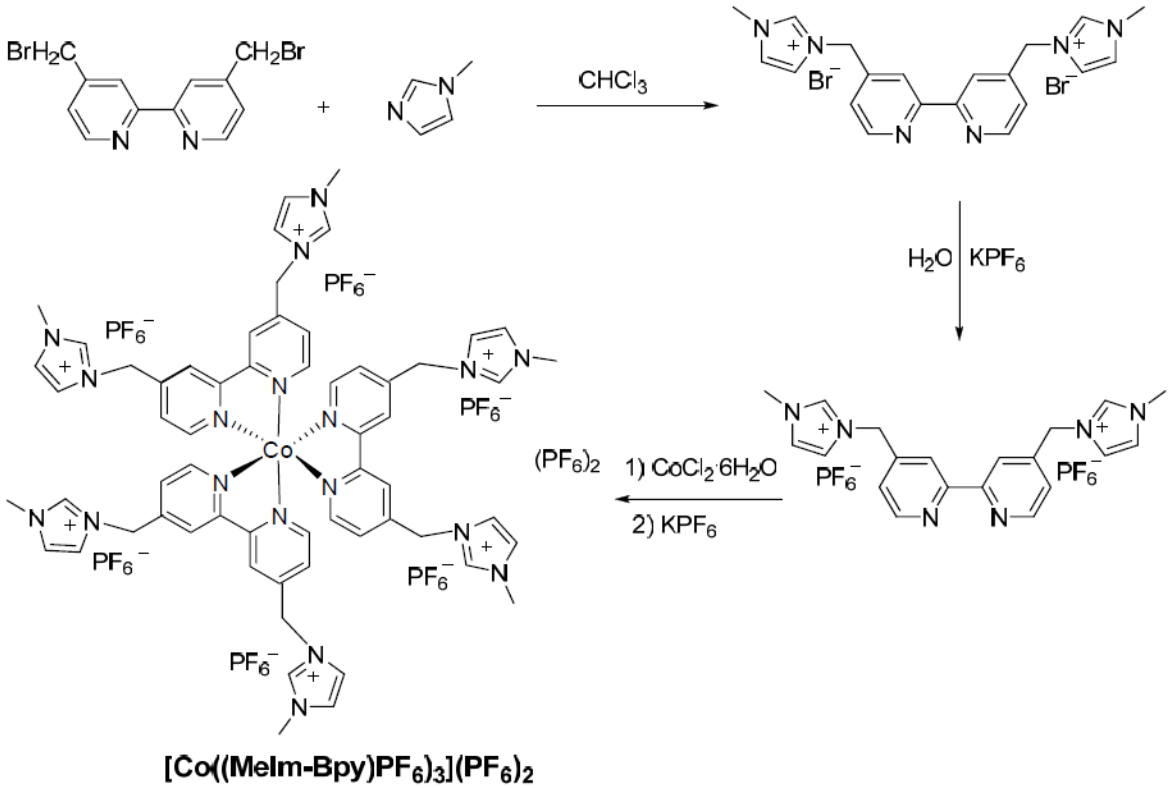
Chemicals

4,4'-Dimethyl-2,2'-dipyridyl, potassium dichromate ($K_2Cr_2O_7$), sodium borohydride ($NaBH_4$), hydrobromic acid (48 wt.% solution), 1-methylimidazole, potassium hexafluorophosphate (KPF_6), cobalt chloride, lithium perchlorate ($LiClO_4$) were purchased from Alfa Aesar. 4,4'-Bis(bromomethyl)-2,2'-bipyridine was prepared according to the literature procedure.[1] $[Co(dmp)_3](PF_6)_2$ (dmp = 4,4'-dimethyl-2,2'-bipyridine) was synthesized follow the literature method.[2] 1-Ethyl-3-methylimidazolium thiocyanate (EMINCS), nitrosonium tetrafluoroborate ($NOBF_4$) and 1-propyl-3-methylimidazolium iodine (PMII) were purchased from Merck. H_2PtCl_6 was purchased from Aldrich. *Cis*-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid) ruthenium(II) bis(tetrabutylammonium) (N719) was purchased from Solaronix SA (Switzerland). 20-nm-sized TiO_2 particles was prepared according to the literature procedure by modifying the porosity to improve the mass transport of the $[Co((MeIm\text{-}Bpy)PF_6)_3]^{2+/3+}$ redox couple.[3] Fluorine-doped tin oxide overlayer (FTO) glass electrodes (7 Ω/Sq), 200 nm-diameter light-scattering TiO_2 colloidal were purchased from Dalian Hepat Chroma Solar Tech. Co., Ltd (China). All general reagents and solvents were obtained from commercial sources.

Synthesis of the imidazolium functionalized cobalt tris(bipyridyl) complex ([Co((MeIm-Bpy)PF_6)$_3$](PF_6)$_2$)



Scheme S1. General synthetic procedure for [Co((MeIm-Bpy)PF_6)$_3$](PF_6)$_2$.

Synthesis of 3,3'-(2,2'-bipyridine-4,4'-diylbis(methylene))bis(1-methyl-1*H*-imidaz-ol-3-ium) bromide ([MeIm-Bpy]Br)

A mixture containing 4,4'-bis(bromomethyl)-2,2'-bipyridine (2.0 g, 5.88 mmol) and 1-methylimidazole (0.97 g, 11.8 mmol) in chloroform was refluxed for 6 h and then allowed to cool down to RT. The resulting precipitate was filtered, washed with diethyl ether and dried. ^{1}H NMR (400 MHz, D_2O): δ 8.71 (s, 2H, H_{py}), 8.33 (s, 2H, H_{py}), 7.75 (s, 2H, H_{im}), 7.68 (s, 2H, H_{im}), 7.47 (s, 2H, H_{py}), 5.65 (s, 4H, CH_2), 3.99 (s, 6H, N-CH_3).

Synthesis of 3,3'-(2,2'-bipyridine-4,4'-diylbis(methylene))bis(1-methyl-1*H*-imidaz-ol-3-ium)hexa fluorophosphate ([MeIm-Bpy]PF_6)

A solution of [MeIm-Bpy]Br (2.0 g, 3.96 mmol) and KPF_6 (1.46 g, 7.93 mmol) in water was stirred at RT for 2 h. The resulting precipitate was filtered, washed with water, and vacuum dried at 80 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.23 (s, 2H, NCHN), 8.71 (s, 2H, H_{py}), 8.38 (s, 2H, H_{py}), 7.83 (s, 2H, H_{im}), 7.75 (s, 2H, H_{im}), 7.41 (s, 2H, H_{py}). 5.58 (s, 4H, CH_2), 3.86 (s, 6H, N-CH_3).

Synthesis of Co((MeIm-Bpy)PF_6)$_3$](PF_6)$_2$

$CoCl_2 \cdot 6H_2O$ (0.22 g, 0.94 mmol) was added to the methanolic solution of [MeIm-Bpy]PF_6 (1.8 g, 2.83 mmol). After stirring at reflux for 2 h, excess KPF_6 (0.8 g) was added to form a precipitate. The precipitated complex was filtered, washed with methanol, and dried under vacuum to give a yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.20 (s, 6H, NCHN), 8.67-8.68 (d, 6H, H_{py}), 8.34 (s, 6H, H_{py}), 7.79 (s, 6H, H_{im}), 7.71 (s, 6H, H_{im}), 7.37-7.38 (d, 6H, H_{py}). 5.54 (s, 12H, CH_2), 3.82 (s, 18H, N-CH_3).

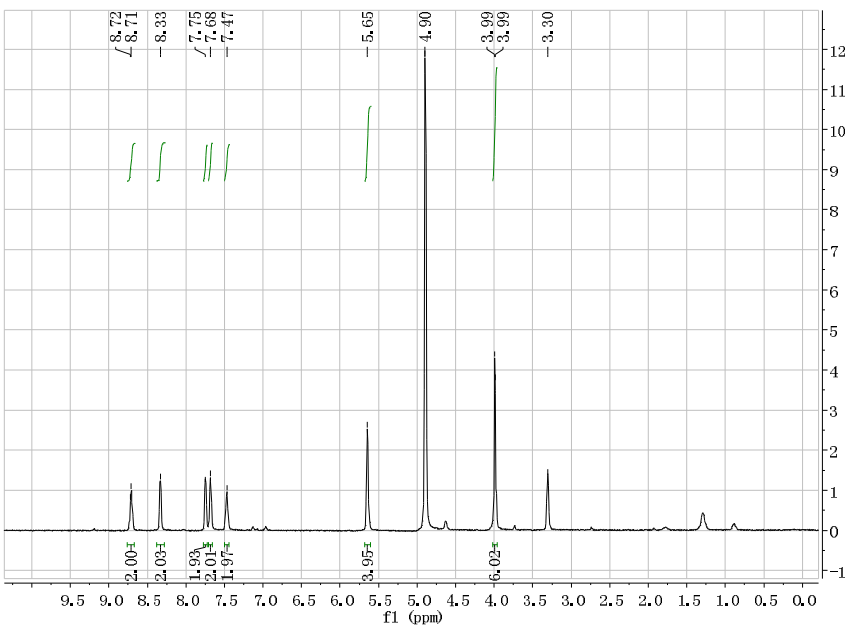


Fig. S1 ^{1}H NMR (D_2O) spectrum of [MeIm-Bpy]Br.

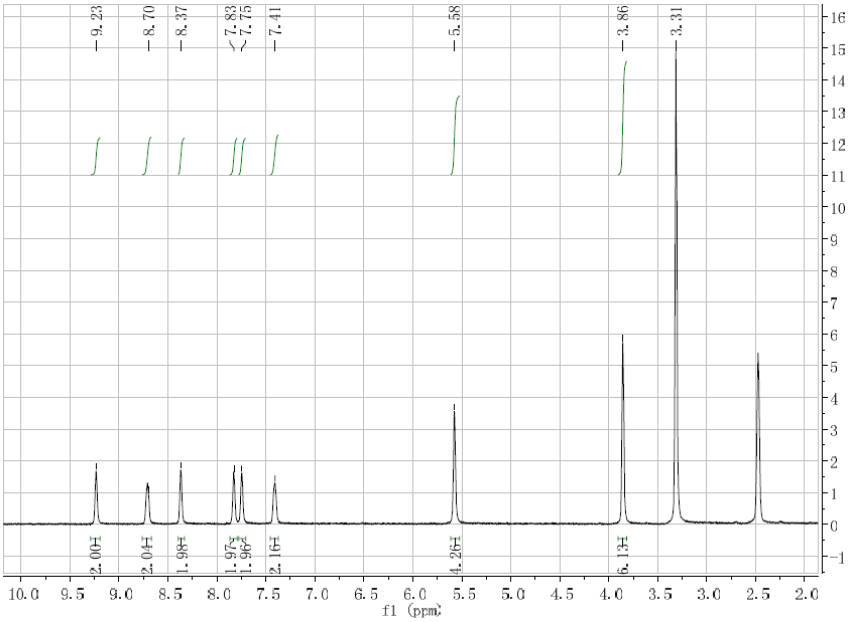


Fig. S2 ^{1}H NMR (DMSO-d_6) spectrum of [MeIm-Bpy]PF_6.

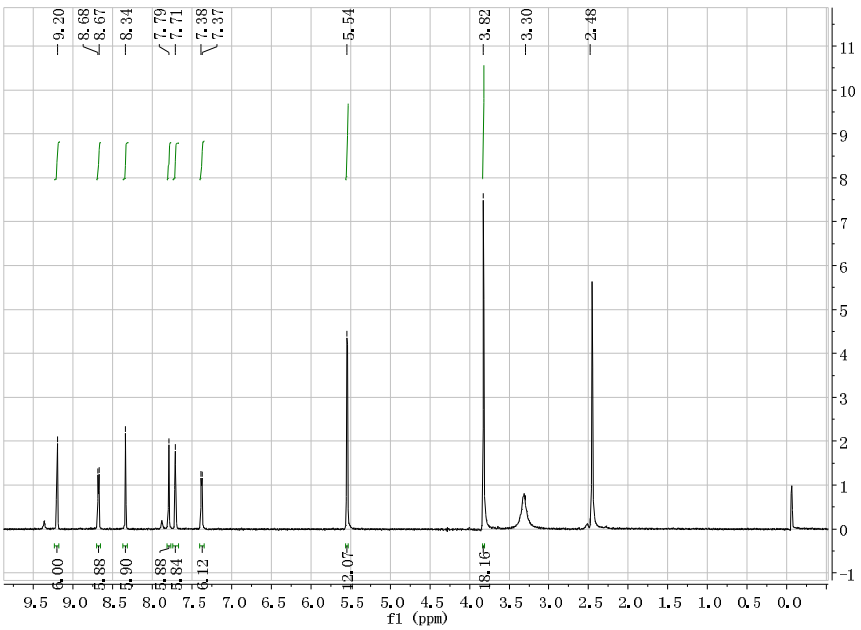


Fig. S3 ^{1}H NMR (DMSO-d_6) spectrum of [Co((MeIm-Bpy)PF_6)$_3$](PF_6)$_2$.

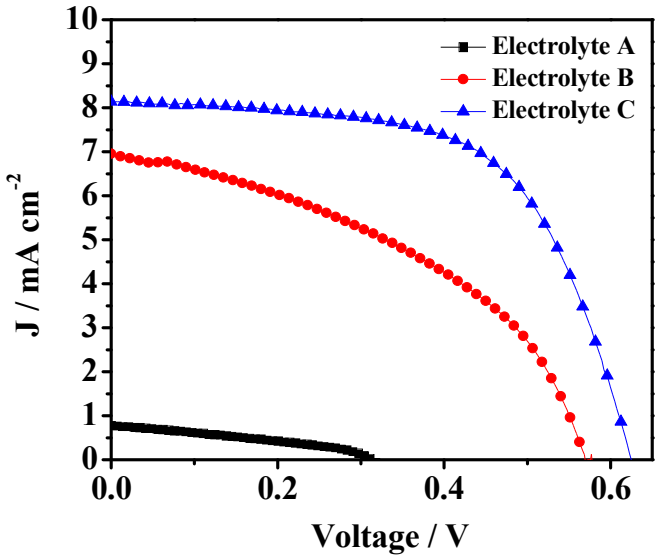


Fig. S4 The *J–V* curves of the DSSCs containing ionic liquid-based Electrolytes A, B and C under simulated AM 1.5 solar spectrum irradiation at 100 mW cm^{-2}.

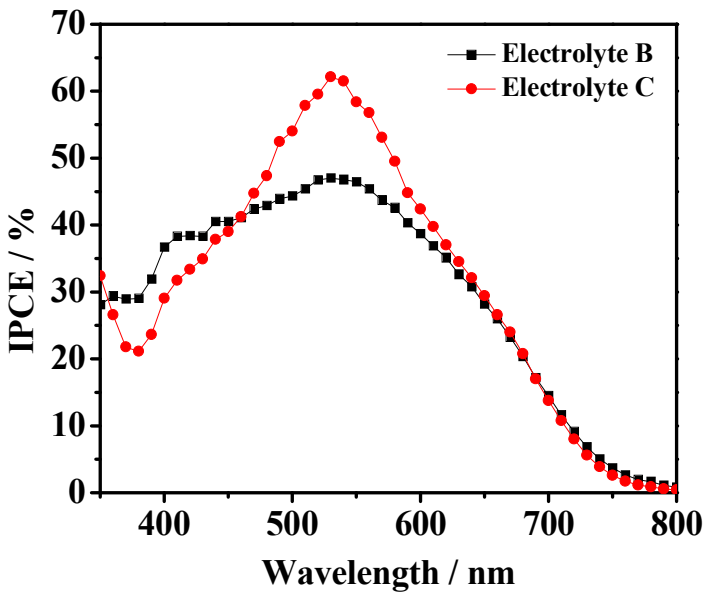


Fig. S5 The IPCE *vs.* wavelength profiles for the devices based on the ionic liquid Electrolytes B and C.

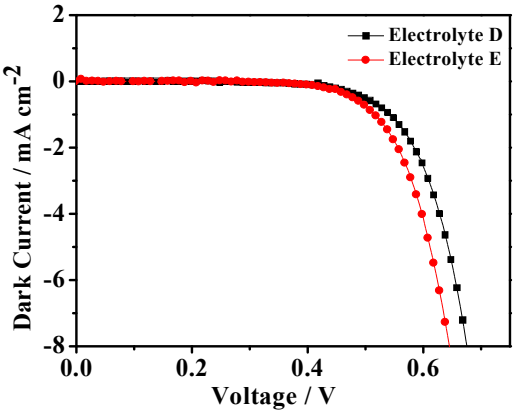


Fig. S6 Dark current-voltage characteristics of the DSSCs based on Electrolytes D and E were tested using an aluminium foil mask with an aperture area of 0.1 cm^2.

Table S1. The photovoltaic properties of the DSSCs based on binary ionic liquid electrolyte under simulated AM 1.5 solar spectrum illumination at 100 mW cm^{-2} (average of five cells).

Electrolyte	Composition	J_{sc} (mA cm^{-2})	V_{oc} (V)	*FF*	*PCE* (%)
E 1	0.03 M $[Co((MeIm\text{-}Bpy)PF_6)_3]^{2+}$, 0.02 M $NaOBF_4$, 0.14 M GuNCS, 0.5 M TBP in PMII:EMINCS = 13:7 (v:v)	14.8 ± 0.1	0.711 ± 0.002	0.679 ± 0.008	7.14 ± 0.10
E 2	0.05 M $[Co((MeIm\text{-}Bpy)PF_6)_3]^{2+}$, 0.02 M $NaOBF_4$, 0.14 M GuNCS, 0.5 M TBP in PMII:EMINCS = 13:7 (v:v)	15.1 ± 0.1	0.706 ± 0.002	0.691 ± 0.007	7.37 ± 0.05
E 3	0.08 M $[Co((MeIm\text{-}Bpy)PF_6)_3]^{2+}$, 0.02 M $NaOBF_4$, 0.14 M GuNCS, 0.5 M TBP in PMII:EMINCS = 13:7 (v:v)	14.9 ± 0.2	0.698 ± 0.003	0.672 ± 0.008	6.98 ± 0.08
E 4	0.12 M $[Co((MeIm\text{-}Bpy)PF_6)_3]^{2+}$, 0.02 M $NaOBF_4$, 0.14 M GuNCS, 0.5 M TBP in PMII:EMINCS = 13:7 (v:v)	13.1 ± 0.2	0.658 ± 0.003	0.671 ± 0.006	5.78 ± 0.08

References:

1 S. M. Feldt, E. A. Gibson, E. Gabrielsson, L. Sun, G. Boschloo and A. Hagfeldt, *J. Am. Chem. Soc.* 2010, **132**, 16714–16724.

2 I. Gillaizeau-Gauthier, F. Odobel, M. Alebbi, R. Argazzi, E. Costa, C. A. Bignozzi, P. Qu and G. J. Meyer, *Inorg. Chem.* 2001, **40**, 6073–6079.

3 H. Seon Kim, S. B. Ko, I. H. Jang and N. G. Park, *Chem. Commun.,* 2011, **47**, 12637–12639.