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Electronic Supporting Information
for

Molecular organic conductors with triiodide/hole dual channels as efficient electrolytes for solid-state dye sensitized solar cells

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1. Experimental details

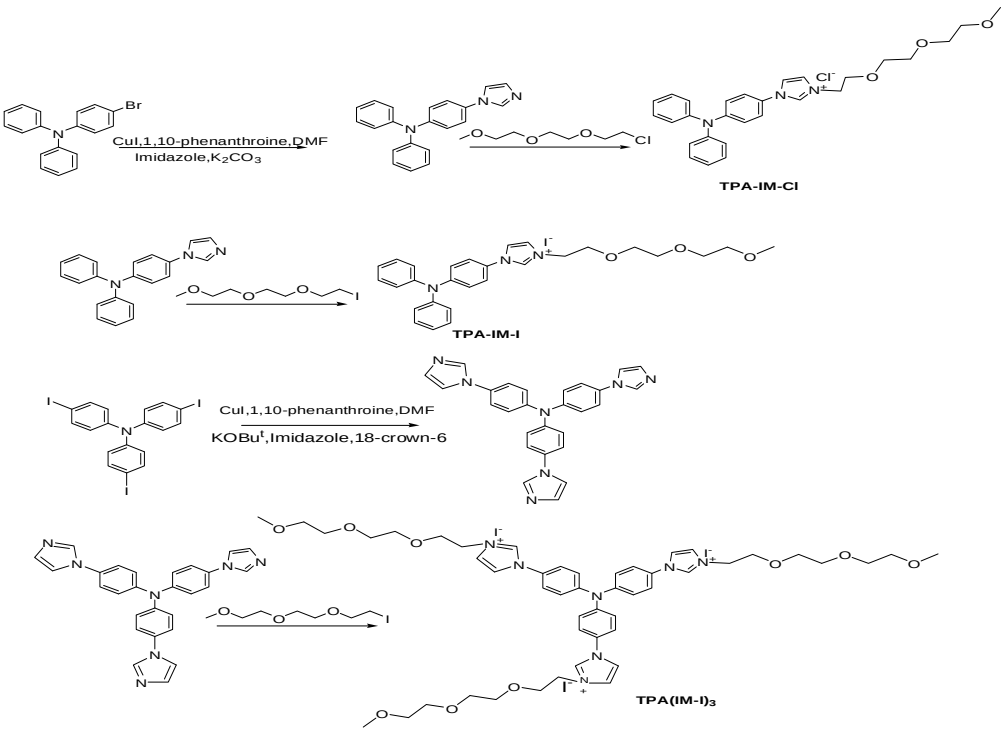


Fig .S1 Synthesis and molecular structures of solid-state molecular conductors

Synthesis. All reactions were performed under N_2 atmosphere unless otherwise stated. Compounds were synthesized referring published paper.[1]

1. (4-Imidazol-1-yl-phenyl)-diphenyl-amine

A mixture of CuI (0.38g, 0.02 mol), 1,10-phenanthroline (0.76g, 0.04mol), (4-Bromo-phenyl)-diphenyl-amine (32.42g, 0.10mol), imidazole (8.16g, 0.12mol) and K_2CO_3 (27.60g, 0.20mol) in DMF (100 mL) was degassed and heated at 120℃ for 24 hours. Then the solvent was removed under reduced pressure and the residue was dissolved in dichloromethane (200 mL). The resulting mixture was washed with water several times, dried over anhydrous $MgSO_4$ and was purified by column chromatography and concentrated in vacuo to give the target product as a white solid. (87% in yield)

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) =9.07 (s, 1H), 7.54 (d, 1H), 7.38 (d, 1H), 7.35-7.29 (d, 6H), 7.15-7.10 (d, 8H). MS *m/z*: 312 $[M + H]^+$

2. TPA-IM-Cl

1-{2-[2-(2-Chloro-ethoxy)-ethoxy]-ethoxy}-2-methoxy-ethane (0.15mol) was added to a round-bottom flask containing (4-Imidazol-1-yl-phenyl)-diphenyl-amine (0.10mol) dissolved in DMF (10 mL). The solution was then heated to 80 ºC and maintained for 48 hours. The reaction mixture was cooled to room temperature and then was added slowly to cold (~ 0℃) Et_2O with vigororous stirring, which resulted in phase separation of the product. The Et_2O layer was decanted off and the product was repeatedly washed with fresh Et_2O. The solid product was dried in vacuo to give TPA-IM-Cl as a red solid. (75% in yield)

^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm)=7.90 (s, 1H) , 7.46 (d, 1H) , 7.44 (d, 1H), 7.33-7.29 (t, 6H) , 7.13-7.10 (d, 8H) , 3.98 (t, 2H) ,3.69 (t, 2H) , 3.65 (t, 4H) , 3.53 (t, 2H), 3.34 (s, 3H) , 2.65 (t, 2H). MS *m/z*: 458 $[M-Cl]^+$

3. TPA-IM-I

TPA-IM-I was synthesized from (4-Imidazol-1-yl-phenyl)-diphenyl-amine and 1-{2-[2-(2-Iodo-ethoxy)-ethoxy]-ethoxy}-2-methoxy-ethane as the same procedure for the synthesis of TPA-IM-Cl as a red solid with 73% in yield.

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm)=9.83 (s, 1H) , 9.34 (d, 1H) , 9.23 (d, 1H) , 8.57-8.42 (m, 7H) , 8.32 (d, 1H) , 8.25(d, 1H) , 8.33 (d, 1H) , 8.02 (d, 2H) , 7.91(m, 2H) , 4.32 (t, 2H) , 4.02 (t, 2H) , 3.77 (m, 2H) , 3.64-3.54 (m, 6H) , 3.40 (s, 3H). MS *m/z*: 458 $[M-I]^+$

4. Tris-(4-imidazol-1-yl-phenyl)-amine：

Cu1 (0.27g, 1.41mmo1), 1, 10-phenanthroline (0.60g, 3.00 mmo1), DMF (6mL) were placed in a round-bottomed flask. The mixture was stirred for 20 minutes at 120℃. After cooling to room temperature, potassium tert-butoxide (6.05 g, 54.0 mmo1), imidazole (3.65g, 54.0 mmo1), 4,4^{I},4^{II}-triiodotriphenylamine(4.90g, 8.0 mmo1), 18-crown-6 were added and heated at 160℃ for 24 hours. The mixture was cooled to room temperature, poured into dichloromethane and washed with water. The organic layer dried over $MgSO_4$, filtered and concentrated in vacuo to give the product as a gray solid**.** (56% in yield)

^{1}H NMR (DMSO-d_6, 300 MHz): δ(ppm)= 8.21 (s, 3H) , 7.70 (d, 3H) , 7.60 (d, 6H) , 7.17 (d, 6H) , 7.10 (d, 3H). MS *m/z*: 444 $[M + H]^+$

5. TPA(IM-I)$_3$

TPA(IM-I)$_3$ was synthesized from tris-(4-imidazol-1-yl-phenyl)-amine and 1-{2-[2-(2-iodo-ethoxy)-ethoxy]-ethoxy}-2-methoxy-ethane as the same procedure for the synthesis of TPA-IM-I as a golden yellow solid with 80% in yield.

^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm)=10.75 (s, 3H), 7.87-7.72 (m, 11H), 7.59 (d, 1H), 7.46 (d, 1H) , 7.24-7.19 (m, 5H) , 4.80-4.74 (m, 6H), 4.01-3.99 (t , 6H), 3.72-3.70 (m, 6H), 3.64 (m, 12H), 3.54 (m , 6H) , 3.35 (s, 9H). MS *m/z*: 295 $[M-3I/3]^+$

Fabrication of SDSCs. All solid state dye sensitized solar cells were fabricated as follows. Briefly, F-doped SnO_2 conductive glass (sheet resistance 10 per square) was pre-coated with a compact TiO_2 underlayer which made by a spray pyrolysis of $[(CH_3)_2CHO]_4Ti$ solution. Introducing polystyrene particles into TiO_2 colloidal paste can benefit the infiltration of the all-solid state electrolyte in a porous TiO_2 film.[2] TiO_2 paste containing 10 wt% polystyrene particles with 40 nm radii was then cast onto the FTO glass by the doctor-blade technique and sintered at 450 ℃ for 30 minutes. After cooling down, another TiO_2 colloidal paste containing 10 wt% polystyrene particles with 180 nm radii also deposited on and annealed again. The TiO_2 film layer was sensitized by a ruthenium dye (N3) solution overnight. Electrolytes contain 0.12 M solid state molecular conductor, 0.10 M *tert*-butylpyridine, 0.12 M Lithiumbis(trifluoro-methane sulfonyl)imide($Li[(CF_3SO_2)_2N]$) and 0.01 M methyl-3-methylimidazolium tetrafluoroborate in acetonitrile. For convenience, the electrolytes containing TPA-IM-I, TPA(IM-I)$_3$ and TPA-IM-Cl solid-state molecular conductors are simply denoted as TPA-IM-I, TPA(IM-I)$_3$ and TPA-IM-Cl, respectively. The coating solution used for performance improvement of TPA-IM-Cl contained 0.12 mM $N(p\text{-}C_6H_4Br)_3SbCl_6$. The electrolyte acetonitrile solution was drop casted onto the dye-sensitized TiO_2 electrode and evaporated slowly. The same process was repeated for several times to ensure the good pore filling of the TiO_2 film layer, and then covered by a counter electrode. The platinized FTO glass counter electrodes were prepared by thermal decomposition of H_2PtCl_6 in isopropanol at 390℃ for 15 minutes. The fabricated cells were kept in vacuum oven at 40℃ for 24 hours to completely remove the residual solvent.

2. ^{1}H-NMR spectra of TPA-IM-Cl before and after addition of $Li[(CF_3SO_2)_2N]$

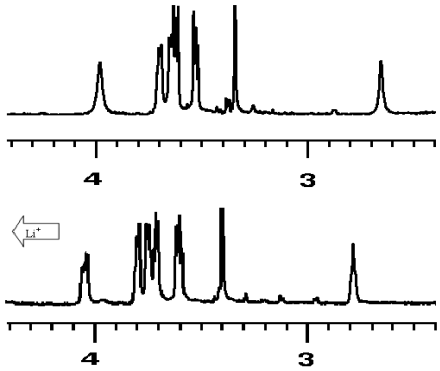
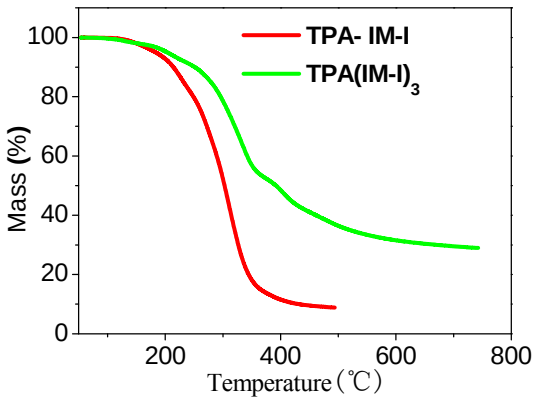


Fig .S2 ^{1}H-NMR spectra that before and after addition of $Li[(CF_3SO_2)_2N]$ (0.01 M) to the solution containing TPA-IM-Cl (0.01 M) in $CDCl_3$

We investigated interaction between alkoxy groups of TEG and Li^+ ions by measuring ^{1}H-NMR spectra of TPA-IM-Cl before and after addition of $Li[(CF_3SO_2)_2N]$. The concentrations of TPA-IM-Cl and $Li[(CF_3SO_2)_2N]$ were both 0.01 M in $CDCl_3$. The protons shown in Fig.S2 belong to TEG group. A mixture of $Li[(CF_3SO_2)_2N]$ and TPA-IM-Cl in $CDCl_3$ displayed peak shifts of the ethylene proton, which indicates a good association between TEG group and the lithium ions.

3. TGA curves of TPA-IM-I and TPA(IM-I)$_3$



Fi g. S3 TGA curves of TPA-IM-I and TPA (IM-I)$_3$

TGA analysis of molecular organic conductors was represented in Fig.S3. Obviously, it indicates high thermal stability, which is favorable for fabricating the durable DSCs.

4. References for supporting information

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2. M. Wang, X. Yin, X. R. Mao, X. W. Zhou, Z. Z. Yang, X. P. Li and Y. Lin, *J Photoch Photobio A*, 2008, **194**, 20-26.