

Electronic Supplementary Information

Economical, Green and Dual-Function Pyridyl Iodides as Electrolyte Components for High-Efficiency Dye-Sensitized Solar Cells

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1. Experimental

Materials and Reagents: Lithium iodide (LiI), 4-*tert*-butylpyridine (TBP), iodine (I₂), ether, 4-Dimethylaminopyridine, iodoethane, 1-iodopropane, 1-iodohexane, 1-iodooctane and γ -butyrolactone were purchased from Aladdin Chemistry Co., Ltd. without purified. Acetonitrile was purchased from J&K Chemical Ltd.

Synthesis of pyridyl quaternary ammonium iodides: Briefly, 4-dimethylaminopyridine (2.44 g, 0.02mol) and iodoalkane (0.024mol) were dissolved in 20 ml acetonitrile in a Schlenk tube. The reaction mixture was stirred under nitrogen atmosphere at 80 °C for 24 h. After completion of reaction, the solvent was evaporated and the product was washed with ether to remove excess of iodoalkane. The resulting solid was dried under vacuum at 40 °C for 24h.

Ethyl-dimethyl-pyridin-4-yl-ammoniumiodide (**A**): ¹H NMR (400MHz, CDCl₃, δ ppm): 8.48 (2H, d), 7.02 (2H, d), 4.44-4.45 (2H, m), 3.29 (6H, s), 1.56 (3H, t). ¹³C NMR (400MHz, CDCl₃, δ ppm): 156.2, 142.2, 108.6, 77.5, 77.2, 76.9, 53.4, 40.8, 16.7. MS (API-ES): positive ion: m/z=151.0 [C₉H₁₅N₂]⁺, calculated 151.2; negative ion: m/z=126.7 [I]⁻, calculated 126.9. Elemental analysis (%) calcd for C₉H₁₅N₂I: C 38.86, H 5.44, N 10.07; found: C 38.86, H 5.24, N 10.02.

Propyl-dimethyl-pyridin-4-yl-ammoniumiodide (**B**): ¹H NMR (400MHz, CDCl₃, δ ppm): 8.44 (2H, d), 7.03 (2H, d), 4.32 (2H, t), 3.30 (6H, s), 1.92-1.98 (2H, d), 0.98 (3H, t). ¹³C NMR (400MHz, CDCl₃, δ ppm): 156.2, 142.5, 108.5, 77.5, 77.1, 76.8, 59.6, 40.8, 24.5, 10.6. MS (API-ES): positive ion: m/z=165.4 [C₁₀H₁₇N₂]⁺, calculated 165.3; negative ion: m/z=126.8 [I]⁻, calculated 126.9. Elemental analysis (%) calcd for C₁₀H₁₇N₂I: C 41.11, H 5.86, N 9.59; found: C 41.06, H 5.74, N 9.55.

Hexyl-dimethyl-pyridin-4-yl-ammoniumiodide (**C**): ¹H NMR (400MHz, CDCl₃, δ ppm): 8.50 (2H, d), 7.06 (2H, d), 4.34 (2H, t), 3.29 (6H, s), 1.88 (2H, m), 1.30 (6H, m), 0.87 (3H, t). ¹³C NMR (400MHz, CDCl₃, δ ppm): 156.3, 142.4, 108.6, 77.5, 77.2, 76.9, 58.4, 40.9, 31.2, 31.3, 25.8, 22.5, 14.0. MS (API-ES): positive ion: m/z=207.0 [C₁₃H₂₃N₂]⁺, calculated 207.3; negative ion: m/z=126.7 [I]⁻, calculated 126.9. Elemental analysis (%) calcd for C₁₃H₂₃N₂I: C 46.71, H 6.94, N 8.38; found: C 47.43, H 6.91, N 8.43.

Octyl-dimethyl-pyridin-4-yl-ammonium iodide (**D**): ¹H NMR (400MHz, CDCl₃, δ ppm): 8.42 (2H, d), 6.99 (2H, d), 4.26 (2H, t), 3.20 (6H, s), 1.79 (2H, m), 1.15-1.22 (10H, m), 0.78 (3H, t). ¹³C NMR (400MHz, CDCl₃, δ ppm): 156.3, 142.4, 108.7, 77.5, 77.2, 76.9, 58.5, 40.9, 31.8, 31.3, 29.1, 26.2, 22.7, 14.2. MS (API-ES): positive ion: m/z

= 235.1 [C₁₅H₂₇N₂]⁺, calculated 235.4; negative ion: m/z = 126.8 [I]⁻, calculated 126.9. Elemental analysis (%) calcd for C₁₅H₂₇N₂I: C 49.73, H 7.51, N 7.73; found: C 49.82, H 7.36, N 7.59.

2. Device fabrication

The paste of TiO₂ were prepared using a commercially available 25nm-sized TiO₂ (Degussa, Germany) according to the procedure developed by our group.¹⁻³ The prepared TiO₂ paste was printed on an ultrasonically cleaned FTO glass (Asahi Glass, type-U, 7 Ω/□, Japan) by the screen-printing technique. The active area of TiO₂ film was set at 0.16 cm². The TiO₂ (P25) film with a thickness of 14 μm, and coated by a layer (4 μm) of TiO₂ (400nm) paste was finally sintered at 500 °C for 30 min. The sintered films were then treated with 40 mM TiCl₄ aqueous solution at 70 °C for 30 min followed by calcinations at 500 °C for 30 min. Then the TiO₂ film was cooled to 90 °C and subsequently immersed in a 5×10⁻⁴ M solution of N719 dye (Opvtech New Energy Co., Ltd., China) in acetonitrile/*tert*-butyl alcohol (1:1, v/v) for 20 h to obtain the sensitized-photoanode. Afterwards, the dye-sensitized TiO₂ electrode was washed with anhydrous ethanol and dried with cooled air. The counter electrodes of Pt were prepared by screen print Pt paste (Opvtech New Energy Co., Ltd., China). The fabrication of DSCs was assembled in our previous report.⁴

3. Characterization

NMR spectra were taken with VARIAN INOVA 400 MHz (USA) using TMS as standard. MS data were obtained with GC-Tof MS (UK), HP1100 LC/MSD (USA), and LC/Q-TOF MS (UK). Differential scanning calorimetry was studied on a DSC910S (USA) at a heating rate of 5 °C min⁻¹ in a temperature range of 40 °C to 500 °C under nitrogen atmosphere. The thermal analysis was performed through TGA (TGA/SDT851, Switzerland) at a heating rate of 5 °C min⁻¹ in a temperature range of 25 °C to 500 °C under nitrogen atmosphere. The *J-V* characteristics of the DSCs were measured under simulated AM 1.5 illumination (100 mWcm⁻², PEC-L15, Japan) with a Keithley digital source meter (Keithley 2601, USA). IPCE values were recorded using the monochromatic light from a system made of a xenon lamp, a monochromator, and appropriate filters. EIS measurements were carried out in the dark at room temperature with a computer-controlled potentiostat (Zennium Zahner, Germany) over a frequency range of 10⁻² Hz to 10⁶ Hz, which sets the AC amplitude at 10 mV and the bias at -0.75 V. The EIS spectra were fitted by Zview software. Charge-extraction measurements were performed using the SLIM-PCV (PSL-100, EKO) with a stepped laser beam. The Fermi level potential of TiO₂ films were analyzed using an impedance spectrum analyser (Zennium Zahner, Germany) along with the Mott-Schottky equation,⁵ i.e.

$$\frac{1}{C^2} = \left(\frac{2}{e\epsilon\epsilon_0 N_D} \right) \left(E - E_F - \frac{\kappa T}{e} \right) \quad (1)$$

Where *e* is the electron charge, ε₀ and ε are the vacuum permittivity and TiO₂ dielectric constants, N_D is the carrier density, E_F is the Fermi level, *k* is the Boltzmann constant. Generally, the temperature term is small and can be neglected. The Linear sweep voltammetry curve was derived from an electrochemical workstation system (CHI630, Chenhua, Shanghai) at a scan rate of 10 mVs⁻¹. Through linear sweep voltammetry, the mass transport limiting current (*J_{lim}*) resulted by ionic diffusion can be obtained at higher potential.

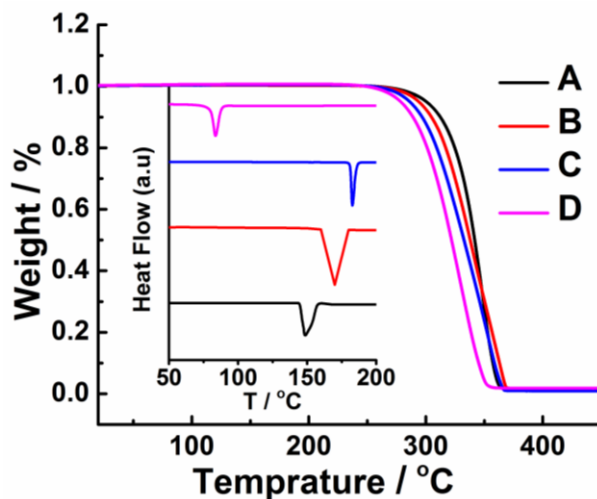


Fig. S1 Thermal gravimetric analysis (TGA) curves of our pyridyl iodides and their differential scanning calorimetry results.

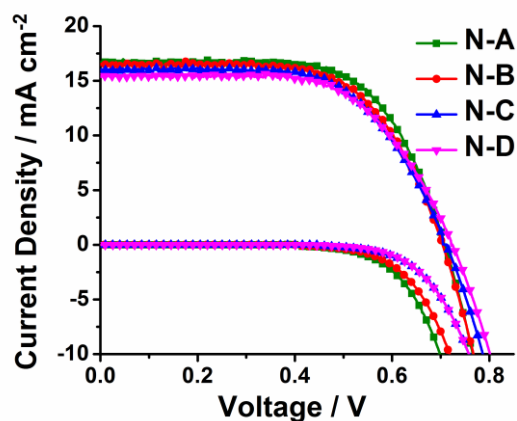


Fig. S2 *J-V* curves of DSCs based on four novel electrolytes under 100 mW cm⁻² illumination and dark-current curves.

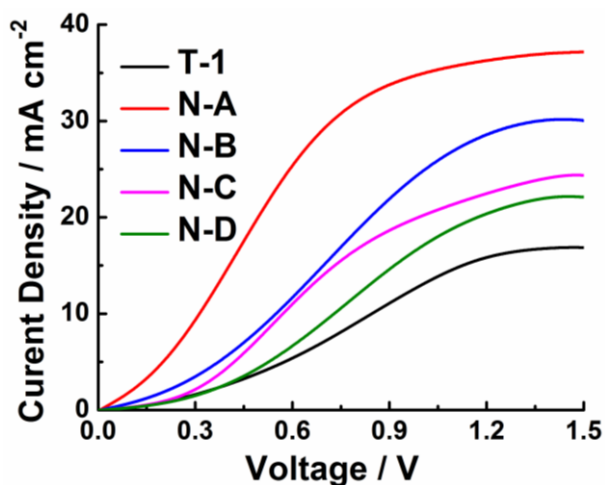


Fig. S3 Linear sweep voltammetry curves of the novel electrolytes, as well as the traditional electrolyte T-1, Scan rate: 10 mV s⁻¹.

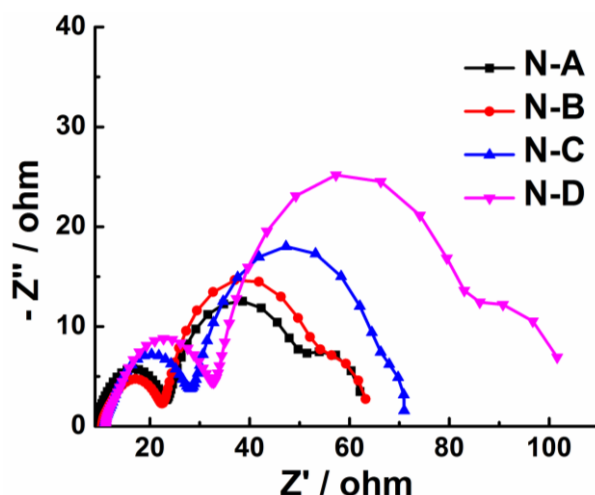


Fig. S4 Nyquist plots of the DSCs based on electrolytes from N-A to N-D, the EIS measurements were conducted in the dark with a bias of -0.75V.

Table S1 Parameters obtained by fitting the EIS spectra to an electrochemical model.⁴

| Electrolyte | R_s [ohm] | R_{ct1} [ohm] | R_{ct2} [ohm] | Z_N [ohm] | τ_e [ms] |
|-------------|-------------|-----------------|-----------------|-------------|---------------|
| N-A | 9.24 | 13.27 | 32.91 | 22.90 | 14.3 |
| N-B | 10.41 | 14.32 | 34.39 | 25.35 | 16.8 |
| N-C | 10.95 | 19.21 | 43.02 | 39.43 | 19.8 |
| N-D | 11.29 | 24.19 | 57.66 | 53.53 | 23.3 |

In the Nyquist plots of DSCs, three semicircles observed in high, mid and low frequency were classified as the resistances of charge transfer resistance at counter electrode (R_{ct1}), charge transfer at the TiO_2 /electrolyte interface (R_{ct2}) and the Nernst diffusion within the electrolyte (Z_N), respectively. From the EIS measurements, the electron lifetime (τ_e) that represents the rate of electron recombination between the electrolyte and TiO_2 can be extracted from the angular frequency at the top of the second semicircle in Nyquist plot. The measurements were performed by scanning from 10^{-2} Hz to 10^6 Hz with a bias of -0.75 V in the dark.

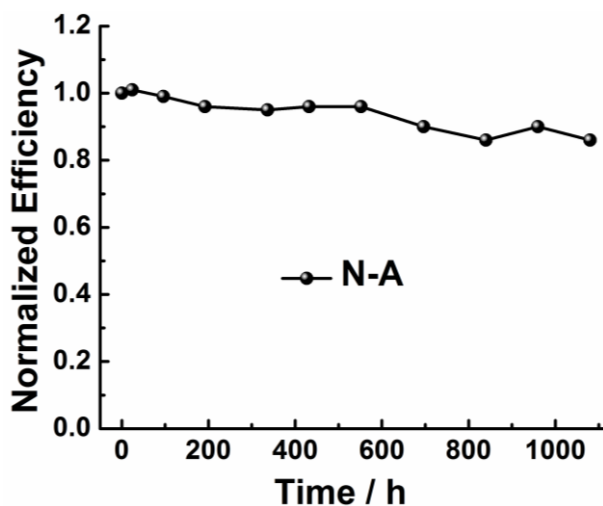


Fig. S5 Evolutions of the normalized photovoltaic parameter of DSCs fabricated with electrolyte N-A.

Table S2 Photovoltaic parameters of DSCs based on iodine-free electrolytes under 100 mWcm⁻².

| Electrolyte | V _{OC} [mV] | J _{SC} [mA cm ⁻²] | FF | PCEs [%] |
|-------------|----------------------|--|------|----------|
| 0.5 M LiI | 0.43 | 11.13 | 0.40 | 1.93 |
| 0.5 M A | 0.73 | 11.32 | 0.47 | 3.90 |
| 0.5 M B | 0.70 | 10.36 | 0.54 | 3.87 |
| 0.5 M C | 0.65 | 14.07 | 0.53 | 4.81 |
| 0.5 M D | 0.64 | 14.01 | 0.55 | 4.93 |

All the electrolytes consist of 0.5M pyridyl iodide salts dissolved in GBL.

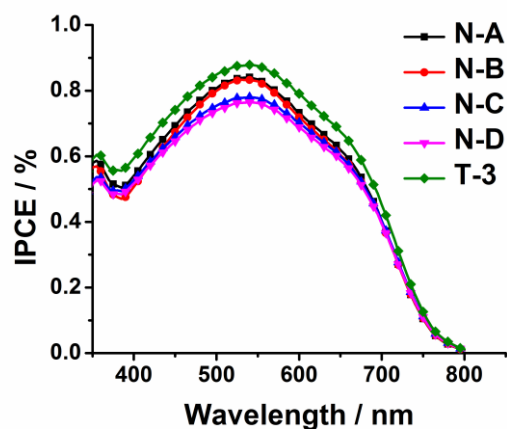


Fig. S6 The IPCE vs. wavelength profiles for devices based on different electrolytes.

Reference

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