Electronic Supplementary Material (ESI) for Energy & Environmental Science

Efficient Dye-Sensitized Solar Cells Based on an Iodine-Free Electrolyte using *L*-Cysteine/ *L*-Cystine as redox couple

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Absorption spectra were recorded on HP8453 (USA), ^{1}HNMR 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). Electrochemical redox potentials were obtained by differential pulse voltammetry (DPV) using a three-electrode cell and an electrochemistry workstation (BAS100B, USA). The working electrode was a glass carbon disk electrode; the auxiliary electrode was a Pt wire; and Ag/Ag^+ was used as the reference electrode. $LiClO_4$ was used as supporting electrolyte in AN. The ferrocenium/ferrocene (Fc/Fc^+) redox couple was used as an internal potential reference. The potentials vs NHE were calibrated by addition of 440 mV to the potentials vs Fc/Fc^+. Electrochemical impedance spectroscopy (EIS) for DSSCs with forward bias -0.75V under dark was measured with an impedance/gain-phase analyzer (PARSTAT 2273, USA). The spectra were scanned in a frequency range of 10^{-2} -10^6Hz at room temperature. The alternate current (AC) amplitude was set at 10 mV.

A layer of 2 μm TiO_2 (13 nm paste, Heptachroma, China) was coated on the F-doped tin oxide conducting glass (TEC15, 15Ω/square, Pilkington, USA) by screen printing and then dried for 5 min at 125 °C. This procedure was repeated 6 times (12 μm) and finally coated by a layer (4 μm) of TiO_2 paste (DHS-SLP1, Heptachroma, China) as the scattering layer. The double-layer TiO_2 electrodes (area: 6 × 6 mm) were heated under an air flow at 520 °C for 30 min, and then cooled to room temperature. The sintered film was further treated with 40 mM $TiCl_4$ aqueous solution at 70 °C for 30 min, then washed with water, and annealed at 520 °C for 30 min. After the film was cooled to room temperature, it was immersed into a 2 × 10^{-4} M dye bath and maintained under dark for 24 h. The electrode was then rinsed with EtOH and dried. The hermetically sealed cells were fabricated by assembling the dye-loaded film as the working electrode and Pt-coated conducting glass as the counter electrode separated with a hot-melt Surlyn 1702 film (25 μm, Dupont). Light source for the photocurrent-voltage (J-V) measurement is an AM 1.5 solar simulator (16S-002, Solar Light Co. Ltd., USA). The incident light intensity was 100 mW/cm^{-2}

calibrated with a standard Si solar cell. The tested solar cells were masked to a working area of 0.159 cm^{-2}. The photocurrent-voltage curves were obtained by the linear sweep voltammetry (LSV) method using an electrochemical workstation (LK9805, Lanlike Co. Ltd., China). The measurement of the incident photon-to-current conversion efficiency (IPCE) was performed by a Hypermono-light (SM-25, Jasco Co. Ltd., Japan). The J_{sc} was calibrated by integrating the IPCE value tuned light density of AM 1.5 against wavelength.

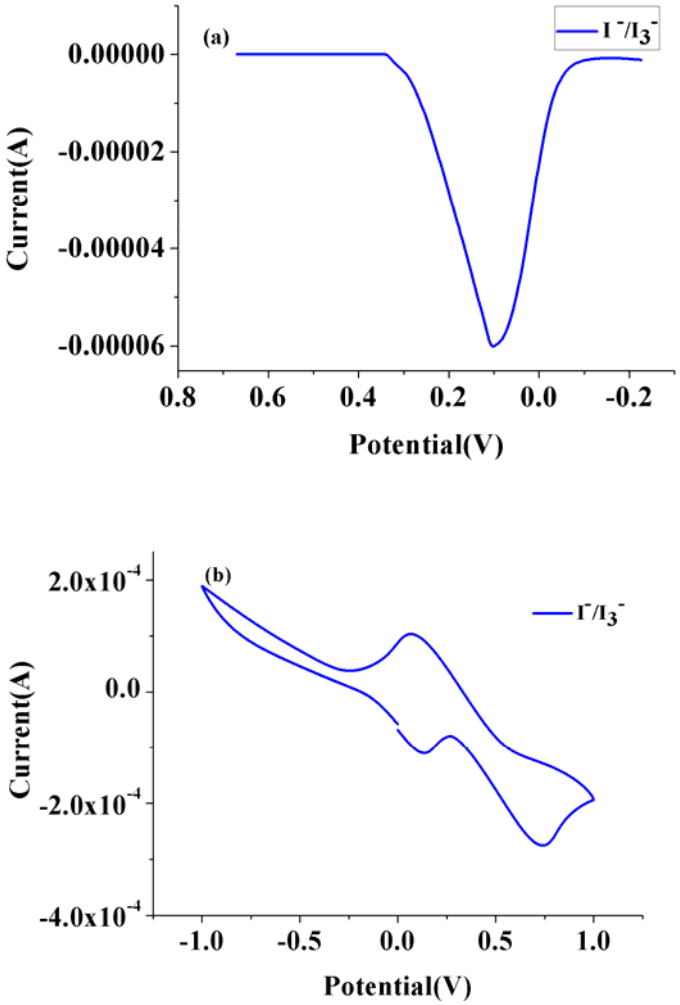


Fig. S1 DPV (a) and CV (b) curves of I_2/I_3^- redox couple

The electrolytes with different concentration of DMPIC and DMPIDC were prepared and applied to DSSCs sensitized by ruthenium dye N719 and metal–free dye TH202.

Electrolyte 1: 0.3 M DMPIC, 0.2 M DMPIDC, 0.1 M $LiClO_4$, 0.4 M TBP in AN

Electrolyte 2: 0.6 M DMPIC, 0.2 M DMPIDC, 0.1 M $LiClO_4$, 0.4 M TBP in AN

Electrolyte 3: 0.6 M DMPIC, 0.1 M DMPIDC, 0.1 M $LiClO_4$, 0.4 M TBP in AN

Electrolyte 4: 0.6 M DMPIC, 0.06 M DMPIDC, 0.1 M $LiClO_4$, 0.4 M TBP in AN

Electrolyte 5: 0.3 M DMPIC, 0.03 M DMPIDC, 0.1 M $LiClO_4$, 0.4 M TBP in AN

Electrolyte 6 (that is electrolyte A mention in paper): 0.6 M DMPIC, 0.02 M DMPIDC, 0.1 M $LiClO_4$, 0.4 M TBP in AN

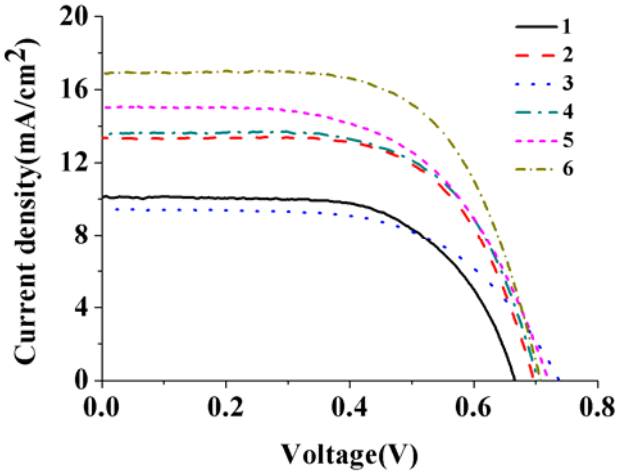


Fig. S2 Photovoltaic performances DSSCs sensitized by N719 with different electrolyte

Table S1 Photovoltaic performances of N719 based DSSCs with different electrolyte

Electrolyte	J_{sc} ($mA \cdot cm^{-2}$)	V_{oc} (V)	FF (%)	η (%)
1	10.1	0.67	62.7	4.2
2	13.3	0.70	64.1	6.0
3	9.5	0.74	59.2	4.1
4	13.6	0.70	63.6	6.1
5	15.0	0.72	58.2	5.3
6	16.9	0.71	64.2	7.7

Table S2 Photovoltaic performances of N719 based DSSCs with electrolyte A

Device	J_{sc} ($mA \cdot cm^{-2}$)	V_{oc} (V)	FF (%)	η (%)

A	17.1	0.71	62.7	7.5
B	16.7	0.73	64.1	7.8
C	16.9	0.71	65.4	7.8
D	17.0	0.70	64.6	7.6
E	17.3	0.69	65.1	7.7
Average	17.0	0.72	64.2	7.7

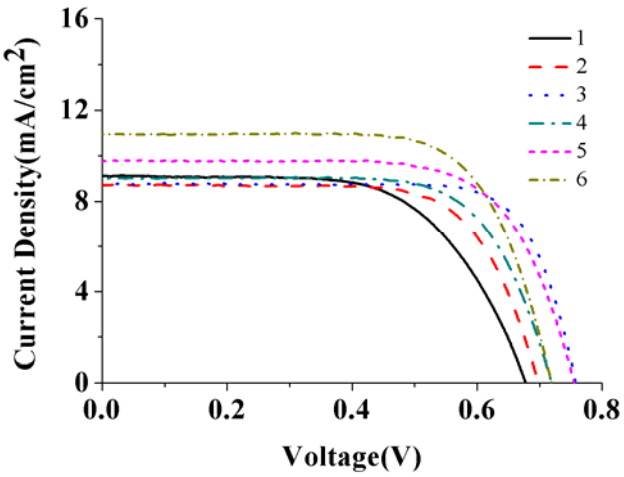


Fig. S3 Photovoltaic performances DSSCs sensitized by N719 with different electrolyte

Table S3 Photovoltaic performances of TH202 based DSSCs with different electrolyte

Electrolyte	J_{sc} ($mA \cdot cm^{-2}$)	V_{oc} (V)	FF (%)	η (%)
1	9.1	0.68	62.5	3.9
2	8.7	0.70	70.4	4.3
3	8.8	0.76	76.1	5.1
4	9.0	0.72	70.3	4.6
5	9.8	0.76	70.0	5.2
6	11.4	0.71	70.2	5.6

Table S4 Photovoltaic performances of TH202 based DSSCs with electrolyte A

Device	J_{sc} ($mA \cdot cm^{-2}$)	V_{oc} (V)	FF (%)	η (%)
A	10.8	0.73	70.1	5.4
B	11.7	0.73	70.2	5.8
C	11.2	0.71	69.4	5.4
D	12.0	0.70	68.6	5.7
E	10.7	0.74	72.1	5.6
Average	11.3	0.72	70.1	5.6

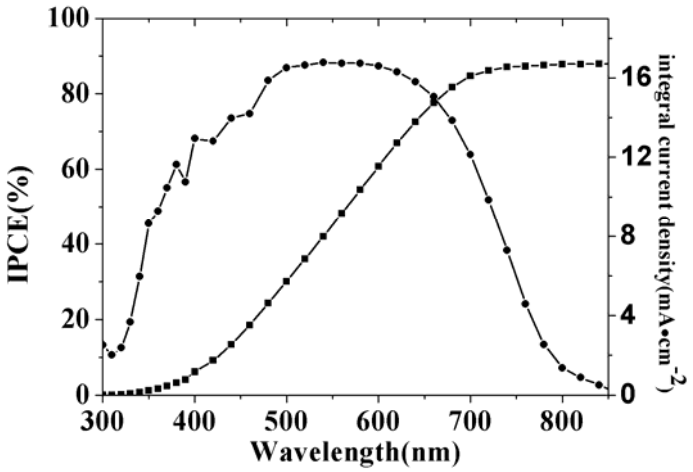


Fig. S4. IPCE spectrum of DSSC sensitized by N719 and integral current density with electrolyte A

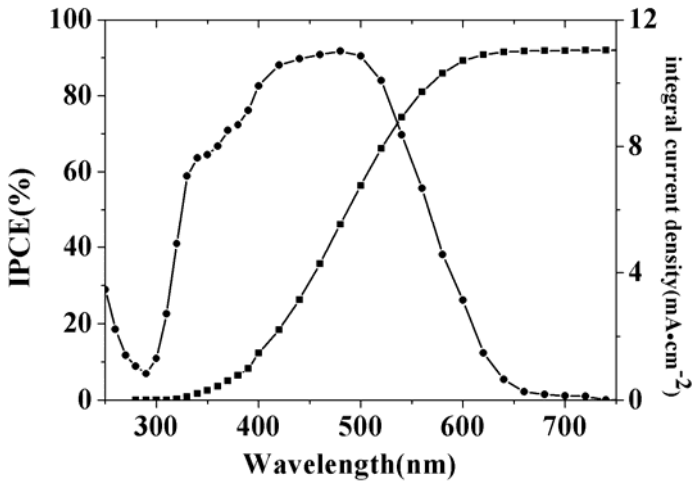


Fig. S5. IPCE spectrum of DSSC sensitized by TH202 and integral current density with electrolyte A

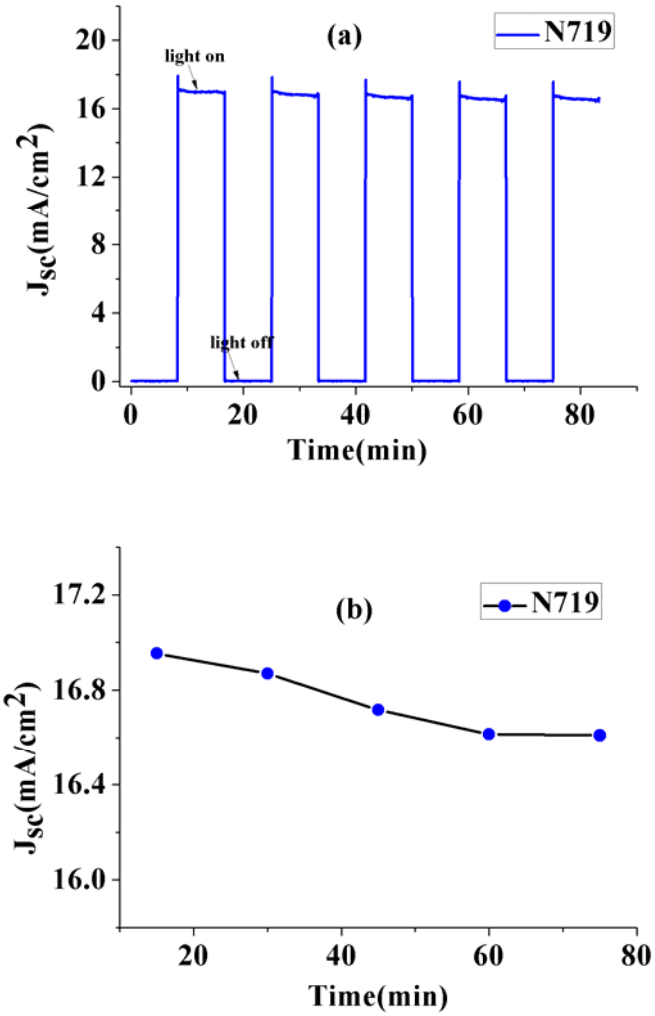
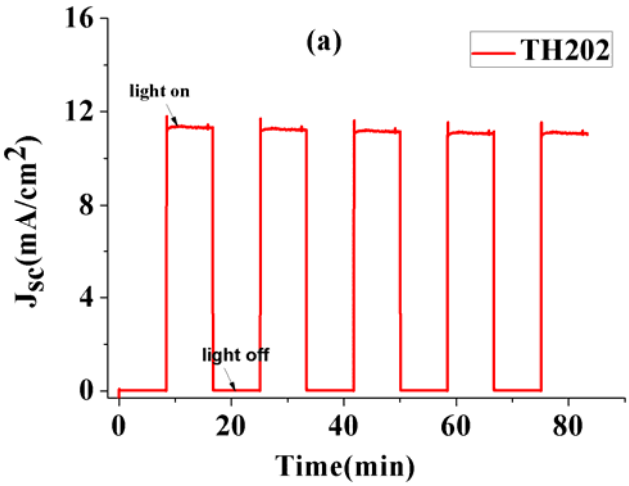


Fig. S6 Current density transient of DSSC sensitized by N719 employing electrolyte A under AM 1.5 illuminations



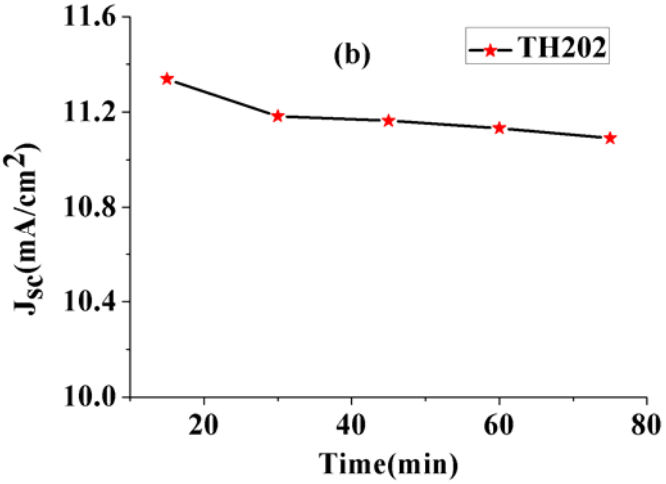


Fig. S7 Current density transient of DSSC sensitized by TH202 employing electrolyte A under AM 1.5 illuminations

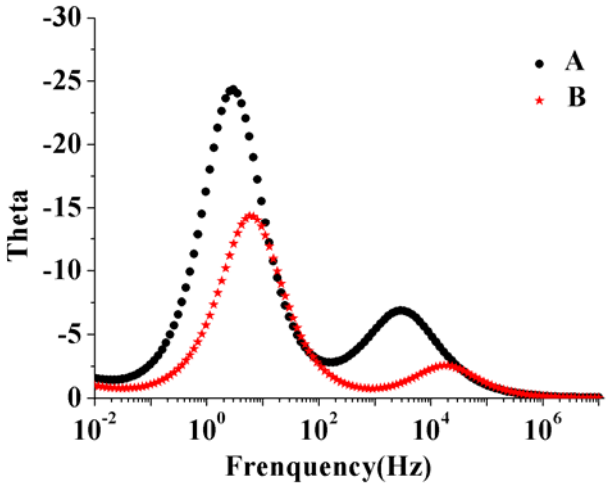


Figure S8 Bode phase plots of DSSCs sensitized by N719 with different electrolyte

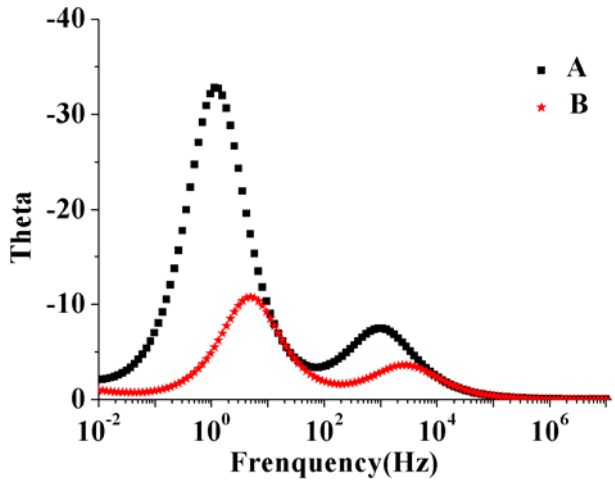


Figure S9 Bode phase plots of DSSCs sensitized by TH202 with different electrolyte

Syntheses of DMPBrI

1 equivalent of 1, 2-dimethyl-1H-imidazole was added into autoclave. Under nitrogen protection conditions , 1 equivalent of 1-Bromopropane was added from injection port and reacted at 120 ^{o}C for 2h. After reaction, the product was transformed to flask，the excessive 1-Bromopropane was removed under dynamic vaccum at 75 ^{o}C for 5h and white solid was got as product. ^{1}H NMR (400 MHz, Acetone-d6) δ 7.77 (d, *J* = 2.0 Hz, 1H), 7.73 (d, *J* = 1.9 Hz, 1H), 4.35 – 4.28 (m, 2H), 4.00 (s, 3H), 2.61 (s, 3H)1.97 – 1.85 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H) MS (API-ES): negative ion: m/z=79.0 $[Br]^{-}$, calculated 78.9; positive ion: m/z=139.1 $[DMPI]^{+}$,calculated 139.1

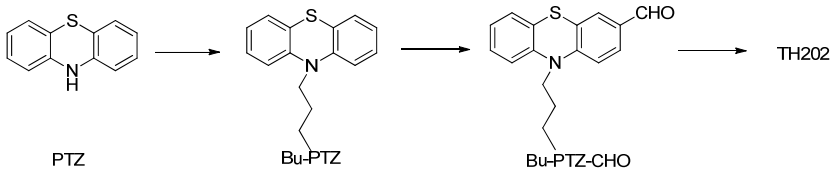
Syntheses of the DMPIC

A methanol solution of 1 equivalent of bromide ionic liquid (DMPBrI) and 1 equivalent of KOH was stirred at room temperature for 12 h to form the hydroxide ionic liquid solution. Then, 0.5 equivalent of *L*-cysteine was added into the solution. After stirring at room temperature for 12 h, the solvent was removed under dynamic vaccum. The remaining residue was dissolved in acetone and filtered. The organic solvent of the filtrate was again removed under vaccum to produce the crude ionic liquid, which was further purified through washing with ethyl acetate. The pure organic salt was obtained after removing the residual organic solvent and drying at 60 ^{o}C under vaccum. ^{1}H NMR (400 MHz, Acetone) ^{1}H NMR (400 MHz, Acetone-d6) δ 7.77 (d, *J* = 2.0 Hz, 2H), 7.73 (d, *J* = 1.9 Hz, 2H), 4.35 – 4.28 (m, 4H), 4.00 (s, 6H), δ 3.57 (dd, *J* = 7.6, 4.7 Hz, 1H), 3.11 (dd, *J* = 13.6, 4.7 Hz, 1H), 2.90 (dd, *J* = 13.6, 7.6 Hz, 1H), 2.61 (s, 6H)1.97 – 1.85 (m, 4H), 0.98 (t, *J* = 7.4 Hz, 6H) MS (API-ES): negative ion: m/z=119.0 $[L\text{-Cys}]^{2-}$, calculated 119.0; positive ion: m/z=139.1 $[DMPI]^{+}$, calculated 139.1 Elem. Anal. (%):found C 57.28, H 9.03, N 17.84, O 8.25, S 8.13; calculated C 57.40, H 8.87, N 17.62, O 8.05, S 8.07

Syntheses of the DMPIDC

A methanol solution of 1 equivalent of bromide ionic liquid (DMPBrI) and 1 equivalent of KOH was stirred at room temperature for 12 h to form the hydroxide ionic liquid solution. Then, 0.5 equivalent of *L*-cystine was added into the solution. After stirring at room temperature for 12 h, the solvent was removed under dynamic vaccum. The remaining residue was dissolved in acetone and filtered. The organic solvent of the filtrate was again removed under vaccum to produce the crude ionic liquid, which was further purified through washing with ethyl acetate. The pure organic salt was obtained after removing the residual organic solvent and drying at 60 ^{o}C under vaccum. ^{1}H NMR (400 MHz, Acetone) ^{1}H NMR (400 MHz, Acetone-d6) δ 7.77 (d, *J* = 2.0 Hz, 2H), 7.73 (d, *J* = 1.9 Hz, 2H), 4.35 – 4.28 (m, 4H), 4.00 (s, 6H), δ 3.57 (dd, *J* = 7.6, 4.7 Hz, 2H), 3.11 (dd, *J* = 13.6, 4.7 Hz, 2H), 2.90 (dd, *J* = 13.6, 7.6 Hz, 2H), 2.61 (s, 6H)1.97 – 1.85 (m, 4H), 0.98 (t, *J* = 7.4 Hz, 6H) MS (API-ES): negative

ion: m/z=238.0 [*L*-cystine]$^{2-}$, calculated 238.0; positive ion: m/z=139.1 [DMPI]$^{+}$, calculated 139.1 Elem. Anal. (%): found C 51.38, H 7.94, N 16.44, O 12.45, S 12.29; calculated C 51.14, H 7.80, N 16.26, O 12.39, S 12.41



Syntheses of Bu-PTZ:

To a PTZ (1.99 g, 10 mmol) solution in 10 ml dry acetone containing palmityl trimethyl ammonium bromide (100 mg) as catalyst, sodium hydroxide (600 mg, 15 mmol) was added at room temperature and refluxed for 2 h. Then 1-bromobutane (1.64 g, 12 mmol) was added to the refluxing mixture and which was kept refluxing overnight. After removing the solvent, the residue was purified by column chromatography using silica gel and dichloromethane-petroleum ether (1/1; v/v) as the eluent to give Bu-PTZ, colorless viscous liquid (2.00 g, 78.4 %). ^{1}H-NMR (400 MHz, Acetone-d6): δ (ppm): 0.86 (3H, t), 1.40-1.45 (2H, m), 1.69-1.76 (2H, m), 3.90 (2H, t), 6.90 (2H, t), 6.98 (2H, d, J = 8.1 Hz), 7.10 (2H, d, J = 7.6 Hz), 7.15 (2H, t). TOF MS ES^{+}: Found m/z 255.1079. Calc. for $C_{16}H_{17}NS$: 255.1082.

Syntheses of Bu-PTZ-CHO:

To a solution of Bu-PTZ and dry DMF (548 mg, 7.5 mmol) in CHCl3 (15 ml) in an ice water bath, phosphorus oxychloride (2.3 g, 15 mmol) was added slowly below 15 °C. Then the bath was heated to reflux and maintained for overnight. Dilute sodium hydroxide aqueous solution was added into and extracted by with dichloromethane (10 ml) for 3 times. The organic layer was dried with anhydrous sodium sulfate and then rotary evaporated. The residue was purified by column chromatography using silica gel and dichloromethane as the eluent to give Bu-PTZ-CHO, yellow viscous liquid (900 mg, 81.1 %). ^{1}H-NMR (400 MHz, Acetone-d6): δ (ppm): 0.87 (3H, t), 1.42-1.48 (2H, m), 1.73-1.80 (2H, m), 4.01 (2H, t), 6.90 (1H, t), 7.07 (1H, d, J = 8.0 Hz), 7.13 (2H, m), 7.21 (1H, t), 7.57 (1H, d, J = 1.9 Hz), 7.70 (1H, dd, J1 = 1.9 Hz, J2 = 1.9 Hz), 9.79 (1H, s). TOF MS ES: Found m/z 283.1024. Calc. for $C_{17}H_{17}NOS$: 283.1031.

Syntheses of TH202：

An acetonitrile solution of Bu-PTZ-CHO and cynaoacetic acid was refluxed in the presence of piperidine for 2 h. After removing the solvent, the residue was purified by column chromatography using silica gel and dichloromethane-methanol (10/1; v/v) as the eluent to give product. T2-1 (yield 81.4 %, dark-red solid), ^{1}H-NMR (400 MHz, Acetone-d6): δ (ppm): 0.91 (3H, t), 1.42-1.51 (2H, m), 1.75-1.86 (2H, m), 4.02 (2H, t), 6.98 (1H, t),

7.08 (1H, d, J = 8.2 Hz), 7.13 (1H, d, J = 7.8 Hz), 7.16 (1H, d, J = 8.4 Hz), 7.21 (1H, t), 7.85 (1H, d, J = 2.0 Hz), 7.94 (1H, dd, J = 2.0 Hz, J = 2.0 Hz), 8.13 (1H, s). TOF MS ES+: Found m/z 350.1085. Calc. for $C_{20}H_{18}N_2O_2S$: 350.1089.

References

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