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Electronic Supporting Infromation

Well-defined triblock copolymer/TiO2 composite gel electrolytes for high-performance dye-sensitized solar cells

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Materials

Acrylonitrile (AN, CAS: 107-13-1), N-isobutoxymethylacrylamide (BMAAm, CAS: 16669-59-3), N,N-dimethylacrylamide (DMAAm, CAS: 2680-03-7), 4,4’-azobis(4-cyanovaleric acid, CAS: 2638-94-0) (ACVA), poly(ethylene glycol) (PEG, M_n=2050 g mol^{-1}, CAS: 25322-68-3), carbon disulfide (CS_2, CAS: 75-15-0), 1-dodecanethiol (CAS: 112-55-0), dimethylformamide (DMF, CAS: 68-12-2), lithium iodide (LiI, CAS: 10377-51-2), iodine (I_2, CAS: 7553-56-2), 4-(dimethylamino)pyridine (DMAP, CAS: 1122-58-3), tert-butylpyridine (TBP, CAS: 3978-81-2), acetonitrile(ACN, CAS: 75-05-8), and TiO_2 nanofiller (Aeroxide® P25, CAS: 13463-67-7) were obtained from Sigma-Aldrich. Dichloromethane (DCM, 75-09-2), methanol (CAS: 67-56-1), ethanol (CAS: 64-17-5), hexane (Hx, CAS: 110-54-3), potassium tertiary butoxide (t-BuOK, CAS: 865-47-4), anhydrous sodium sulfate (Na_2SO_4, CAS: 7757-82-6), sodium thiosulfate ($Na_2S_2O_3$, CAS: 7772-98-7), sodium bicarbonate ($NaHCO_3$, CAS: 144-55-8), ethyl acetate (EA, CAS: 141-78-6), tetrahydrofuran (THF, CAS: 109-99-9), N,N’-dicyclohexylcarbodiimide (DCC, CAS: 538-75-0), dimethyl sulfoxide (DMSO, CAS: 67-68-5) were purchased from Samchun-Chemical Co. ACVA is used as reactant of RAFT agent synthesis as well as an initiator of polymerization. 1,2-dimethyl-3-propylimidazolium iodide (DMPII, CAS: 218151-78-1) was acquired from Solaronix Co. All reactions were carried out under an argon atmosphere. Solvents were distilled with appropriate reagents.

Measurement

^{1}H-NMR spectra were recorded by using a Varian Oxford 300 MHz spectrometer; chemical shifts were reported in ppm units with tetramethylsilane (TMS) as an internal standard. Gas chromatography high resolution mass spectrometer (GC-HRMS) was measured by JMS-700 (JEOL) for checking exact mass of the RAFT agent. Gel permeation chromatography (GPC) of polymers was carried out in dimethylformamide (DMF) (flow rate : 1.0 mL min^{-1}) at 50˚C with e2695(WATERS) equipped with a 2414 RI detector and styragel HR columns (molecular weight range of three columns : $5 \times 10^2 \sim 3 \times 10^4$, $5 \times 10^3 \sim 6 \times 10^5$ and $5 \times 10^4 \sim 4 \times 10^6$ g mol^{-1}). Electrochemical impedance spectra of DSSCs were performed by connecting the VersaSTAT3 (AMETEK) to a potentiometer under dark condition at room temperature. EIS spectra were obtained in a frequency range of 10^6 to 0.1 Hz and with an AC modulation amplitude of 10 mV. EIS data analysis was fitted using Zplot / Zview software. Linear scan voltammetry was measured in a potential range of -0.7 V to 0.7 V and scan rate was 0.05V s^{-1}. Long-term stability of the DSSCs were evaluated with Suntest CPS plus (ATLAS) under 100 mW cm^{-2} (AM 1.5G) illumination at 50˚C.

Synthesis of Bis-(dodecylsulfanylthiocarbonyl) disulfide (BDSTDS) intermediate

BDSTDS intermediate, which can be isolated during RAFT agent synthesis, was acquired as follows. A 500 mL 1-neck Schlenk round bottom flask with magnetic bar was charged with t-BuOK (3.88 g, 35 mmol) and dried under a vacuum atmosphere. Distilled THF (20.0 mL) was injected into the flask in order to dissolve t-BuOK. After 1h of stirring, distilled Hx (150 mL) was injected and the flask was cooled down to 0˚C. n-Dodecylthiol (7g, 35mmol) was dropped into the flask slowly and the mixture was stirred to give a white slurry. The resulting white slurry was stirred at 0˚C for 30 minutes and then reacted with CS_2 (2.63 g, 0.35 mmol). The mixture was stirred at 0˚C for 1 hour, warmed to room temperature, and stirred for 4 hours to form a yellow slurry. The resulting yellow slurry was cooled to 0˚C and reacted with I_2 (4.39 g, 0.5 mmol) over 1 hour. The mixture was warmed to room temperature and stirred for 15 h. After the reaction was finished, the reaction solution was washed with saturated $Na_2S_2O_3$ aqueous solution in order to remove remaining I_2 molecules. Subsequently, the organic phase was washed with DI water and dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The resulting product was recrystallized in ethanol at -4˚C. The recrystallized product was filtered under reduced pressure and dried in a vacuum oven. The product was 6.86 g (89%) of yellow solid. ^{1}H NMR (300MHz, $CDCl_3$): δ 3.29 (t, J =6Hz, 4H), 1.69 (q, J = 6Hz, 4H), 1.45−1.19 (m, 36H), 0.88 (t, J = 6 Hz, 6H).

Synthesis of *S*-Dodecyl-*S′*-(α-cyano-α′-methyl-α″-butanoic acid)trithiocarbonate (DCMBAT) RAFT agent

DCMBAT RAFT agent was synthesized as follows. ACVA (6.74 g, 12 mmol) was charged with BDSTDS (3.40 g, 12 mmol) in a 250 mL 1-neck round bottom Schlenk flask fitted with a reflux condenser. The reactants were dried under vacuum atmosphere and distilled ethyl acetate (95.0mL) was injected into the flask. The resulting solution was heated to 70˚C and allowed to gently reflux for 16 h. After the reaction was finished, the reaction solution was washed with DI water and the organic phase was separated. The solution was dried with anhydrous $NaSO_4$ and the ethyl acetate was removed under reduced pressure. The product was allowed to be recrystallized from Hx at -4˚C to provide a pale yellow solid (6.30 g, 64%). ^{1}H NMR (300MHz, $CDCl_3$): δ 3.33 (t, J =6 Hz, 2H), 2.68 (t, J = 6 Hz, 2H), 2.54 (m, 1H), 2.39 (m, 1H), 1.88 (s, 3H), 1.69 (q, J = 6 Hz, 2H), 1.45−1.19 (m, 18H), 0.88 (t, J = 6 Hz, 3H). The mass of the RAFT agent was checked by gas chromatography high resolution mass spectrometer (GC-HRMS). MS (HR-GCMS) m/z calculated for $C_{19}H_{33}NO_2S_3$: 404.1752; found: 404.1746

Synthesis of Macro-RAFT agent

A 100 mL 1-neck round bottom Schlenk flask was charged with a solution of DCMBAT (0.86g, 2.14 mmol), PEG (M_n=2050 g mol^{-1}, 2.2 g, 1.07 mmol) and DMAP (0.026 g, 0.21

mmol) in dry DCM (30.0 mL), and cooled to 0˚C using an ice bath. Solution of DCC (0.44 g, 2.14 mmol) in dry DCM (10.0 mL) was added dropwise to the flask. After completion, the solution was stirred at 0˚C for 6h and at room temperature for 24h in sequence. The mixture was then filtered to remove N,N'-dicyclohexylurea (white solid). The filtrate was washed with 2M HCl aqueous solution in order to remove remaining DMAP and the organic phase was separated from the acidic aqueous solution. The organic solution was washed with saturated $NaHCO_3$ aqueous solution and DI water. The solution was dried with anhydrous Na_2SO_4 and filtered under reduced pressure. The obtained solution was then concentrated under vacuum and product was precipitated in diethyl ether/n-hexane solution(1:1 volume ratio). The precipitate was filtered and dried under vacuum to give a yellow solid (2.34 g, 77%). ^{1}H NMR (300MHz, $CDCl_3$): δ 4.25 (t, J =6 Hz, 4H), 3.37-3.90 (m, 180H), 3.33 (t, J = 6 Hz, 4H), 2.68 (t, J = 6 Hz, 4H), 2.54 (m, 1H), 2.39 (m, 1H), 1.88 (s, 3H), 1.69 (q, J = 6 Hz, 2H), 1.45−1.19 (m, 18H), 0.88 (t, J = 6 Hz, 3H).

Synthesis of Triblock Copolymers Using Macro-RAFT agent

Synthesis of PEG_{46}-b-$(P(AN\text{-}co\text{-}BMAAm))_2$ Triblock Copolymer (SGT-602)

To remove polymerization inhibitor from the materials, AN and BMAAm were passed through a basic alumina column prior to use. 0.5 g of the macro-RAFT agent (1.78×10^{-4} mol), 1mL of DMF, 0.01 g of ACVA (3.57×10^{-5} mol) and 45 mL of DMSO were mixed in a 250 mL Schlenk flask equipped with a magnetic stirring bar. Subsequently, 20.4 g of AN (0.39 mol) and 2.0 g of BMAAm (0.013 mol) were added to the Schlenk flask and Ar purging was carried out for 30 minutes. Then, the Schlenk flask was placed in an oil bath at a set temperature of 75˚C for 20 hour. At the end of the polymerization, the polymer was precipitated by dropping the polymerization solution to 50% aqueous methanol and dried in a vacuum oven for 12h to provide a white solid. (10.5 g, conv.=62.7%, $M_{n,th}\approx42300$ g mol^{-1}).

^{1}H NMR (300MHz, DMSO-d$_6$): δ 8.94-9.22 (m, 20H), 4.30-4.80 (m, 40H), 3.51 (s, 184H), 2.84-3.26 (m, 745H), 1.68-2.30 (m, 1438H), 1.24 (s, 18H), 0.85 (d, J = 6 Hz, 126H)

Synthesis of PEG$_{46}$-b-(P(AN-co-DMAAm))$_2$ Triblock Copolymer (SGT-604)

To remove polymerization inhibitor from the materials, AN and DMAAm were passed through a basic alumina column prior to use. 0.5 g of the macro-RAFT agent (1.78×10^{-4} mol), 1mL of DMF, 0.01 g of ACVA (3.57×10^{-5} mol) and 45mL of DMSO were mixed in a 250 mL Schlenk flask equipped with a magnetic stirring bar. Subsequently, 22.1 g of AN (0.42 mol) and 1.4 g of DMAAm (0.014 mol) were added to the Schlenk flask and Ar purging was carried out for 30 minutes. Then, the Schlenk flask was placed in an oil bath at a set temperature of 75˚C for 20 hour. At the end of the polymerization, the polymer was precipitated by dropping the polymerization solution to 50% aqueous methanol and dried in a vacuum oven for 12h to provide a white solid. (10.7 g, conv.=64.8%, $M_{n,th}\approx45500$ g mol^{-1}). ^{1}H NMR (300MHz, DMSO-d$_6$): δ 3.51 (s, 184H), 2.95-3.26 (m, 805H), 2.88 (t, J = 6 Hz, 117H), 1.55-2.30 (m, 1576H), 1.24 (s, 18H)

Fabrication of a Symmetrical Dummy Cell

Symmetrical dummy cells were fabricated with two identical Pt covered FTO glasses separated with a thermal adhesive film (Surlyn, DuPont 60 μm thick) as a sealant and a spacer, leaving a 0.6 × 0.7 cm^2 active area. An ultrasonic soldering system (USS-9200, MBR Electronics) was covered at the sheet edge for the purpose of improving electrical contact. Liquid electrolyte was composed of 0.1 M LiI, 0.05 M I_2, 0.6M DMPII, and 0.8 M TBP in acetonitrile. Polymer gel electrolytes were prepared by simply dissolving the polymers to the liquid electrolyte. Polymer compositions were chosen as 10 wt%, 13 wt%, and 15 wt% for **SGT-602** and 13 wt%, 15 wt%, and 17 wt% for **SGT-604**. To optimize the composition of the TiO_2 nanofiller, the amount of TiO_2 nanofillers was changed to 5 wt%, 10 wt% and 15 wt%, respectively, fixing the composition of **SGT-602** to 13 wt% and **SGT-604** to 15 wt%. One of the two Pt-FTO sheets was drilled to make holes for introducing each electrolyte via vacuum backfilling. In the case of the gel electrolytes, we used in-situ gelation in order to attain fine contact with electrodes. The in-situ gelation allows the gel electrolytes to be introduced to symmetrical cells in their liquid state and then gelated inside of the cells. We were also able to employ the gel electrolytes through vacuum backfilling due to in-situ gelation. The holes were overlaid with a glass cover employing a Surlyn seal. The structure of the symmetrical cell is illustrated in Fig. S6 (a).

Fabrication and Characterization of DSSC

An FTO plate was rinsed with detergent solution, water, and ethanol using an ultrasonic cleaner. The FTO substrate was plunged in a 40 mM aqueous solution of $TiCl_4$ at 70˚C for 30 minutes and washed with water and ethanol. Screen printing was used to spread TiO_2 colloidal paste (Dyesol, 18NR-T) on the FTO glass as a transparent active layer and the screen printed FTO plate was sintered in air at 500˚C for 30 minutes. Subsequently, a paste for an opaque scattering layer including 500 nm anatase particles (ENB Korea, STP-500N) was also deposited by screen printing and sintered at 500˚C. The thickness of the photoanode was measured to 10 μm for the active layer and 14 μm for both the active and scattering layers, using an Alpha-step 250 surface profilometer (Tencor Instruments, San Jose, California). The resulting TiO_2 photonanode was dipped in an absolute ethanol solution containing 0.3 mM of N-719 dye and kept at room temperature for 18 hours. The dye-adsorbed TiO_2 photoelectrodes were assembled with Pt counter electrodes using a 60 μm thick Surlyn tape as spacers to produce sandwich cells. As mentioned before, various electrolyte solutions ware introduced through the pierced CE by vacuum backfilling. In the case of gel electrolytes, in-situ gelation was used in order to allow the gel electrolytes to be applied to DSSCs in their liquid state and then gelated inside of the cells. The in-situ gelation leads to good contact between electrodes and electrolyte. We also employed vacuum backfilling as an introduction method of gel electrolytes because of the same reasons we mentioned in the fabrication section of symmetrical cell. The hole was sealed with a glass cover using adhesive Surlyn film. Photo-electrochemical data were measured employing a 1000 W xenon light source (Oriel, 91193) which was directed to give 100 mW cm^{-2} (1 sun at AM 1.5G). Under these conditions, J-V characteristics of the cells were determined by externally biasing the DSSCs and measuring a generated photocurrent. The power of solar simulator was adjusted by NREL-calibrated Si solar cells (PV Measurement Inc.). Applied potential and resulting photo-current were measured using a Keithley Model 2400 digital source meter. This process was fully automated using Wavemetrics software. Measurement settling time between applied voltage and resulting current was fixed at 80 ms.

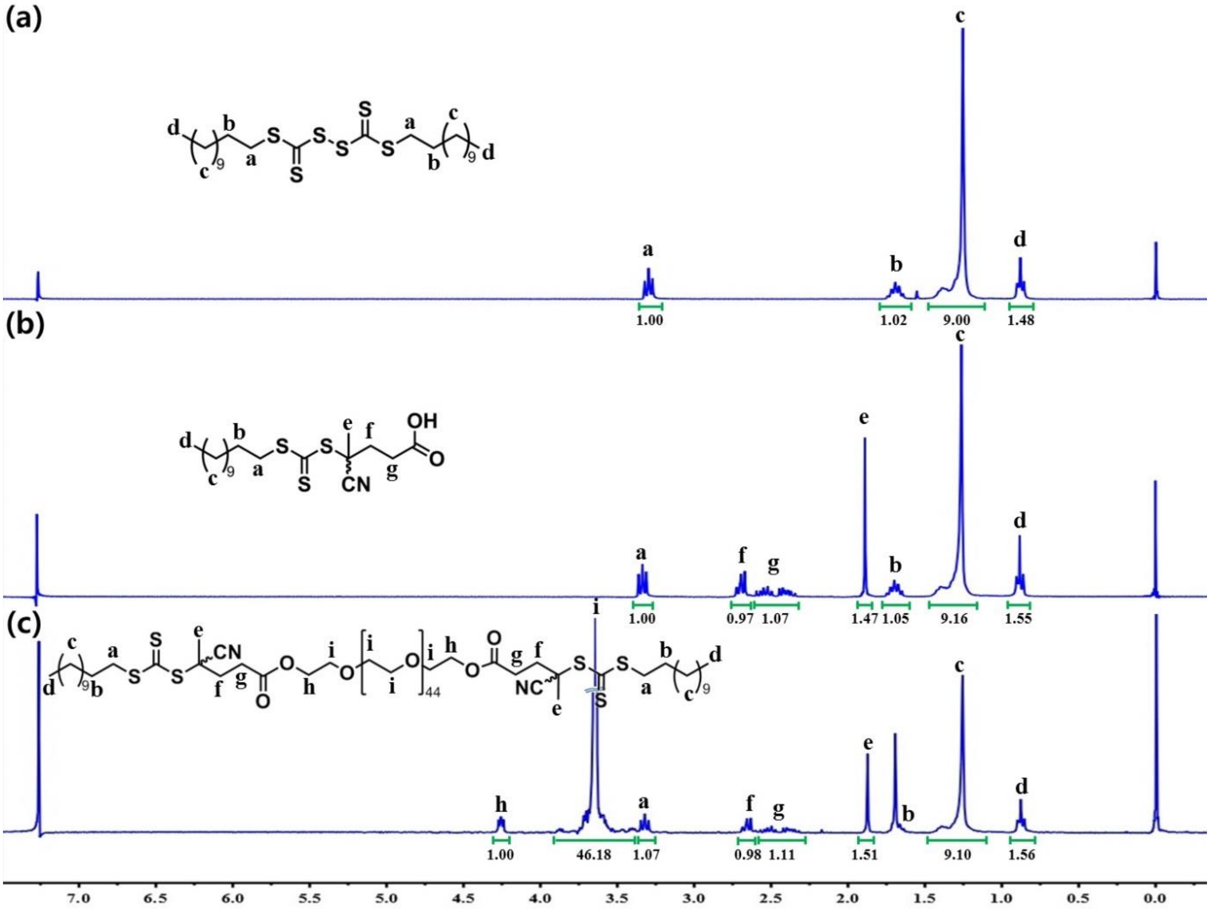
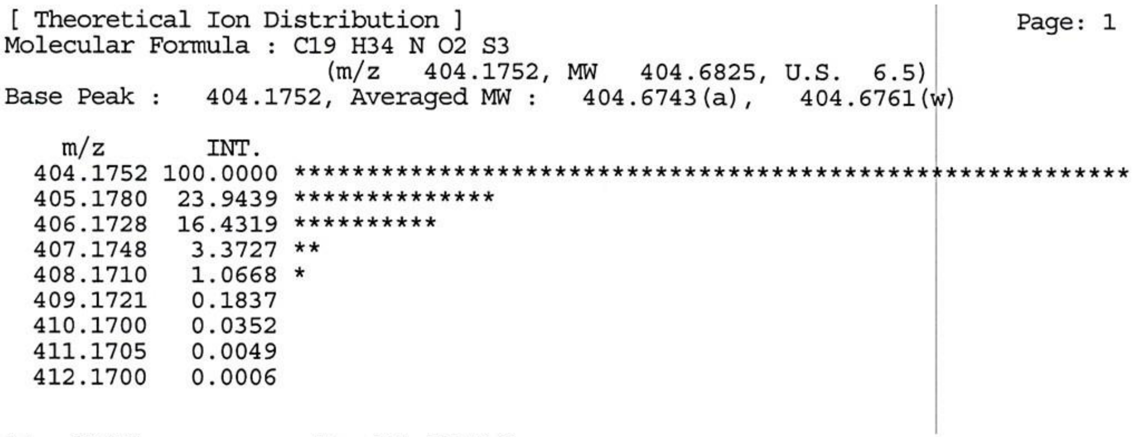


Fig. S1 1H NMR spectra of (a) BDSTDS, (b) DCMBAT, and (c) Macro-RAFT agent in $CDCl_3$.

(a)



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[ Theoretical Ion Distribution ]                                    Page: 1
Molecular Formula : C19 H34 N O2 S3
                         (m/z   404.1752, MW   404.6825, U.S.  6.5)
Base Peak :    404.1752, Averaged MW :    404.6743(a),    404.6761(w)

    m/z        INT.
  404.1752 100.0000 ******************************************************
  405.1780  23.9439 **************
  406.1728  16.4319 **********
  407.1748   3.3727 **
  408.1710   1.0668 *
  409.1721   0.1837
  410.1700   0.0352
  411.1705   0.0049
  412.1700   0.0006
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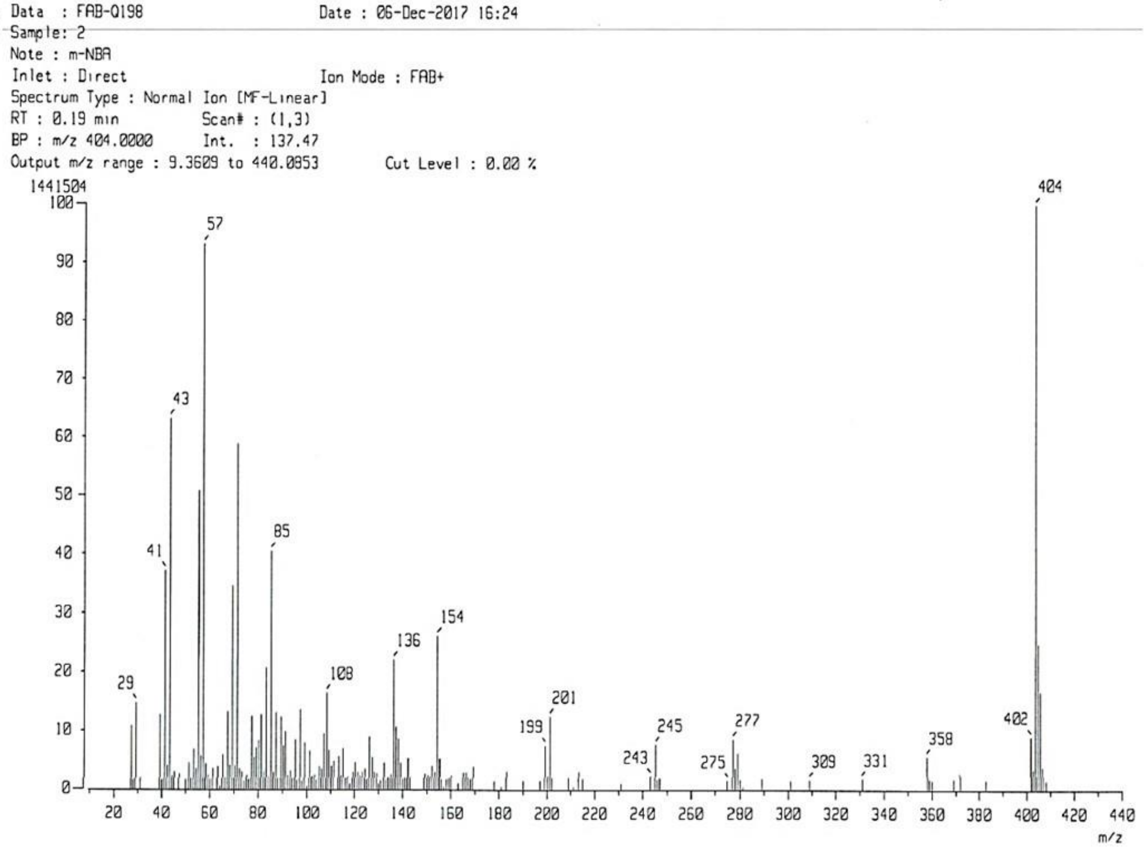
(b)



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Data   : FAB-Q198                    Date : 06-Dec-2017 16:24
Sample: 2
Note : m-NBA
Inlet : Direct                       Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.19 min        Scan# : (1,3)
BP : m/z 404.0000    Int.   : 137.47
Output m/z range : 9.3609 to 440.0853        Cut Level : 0.00 %
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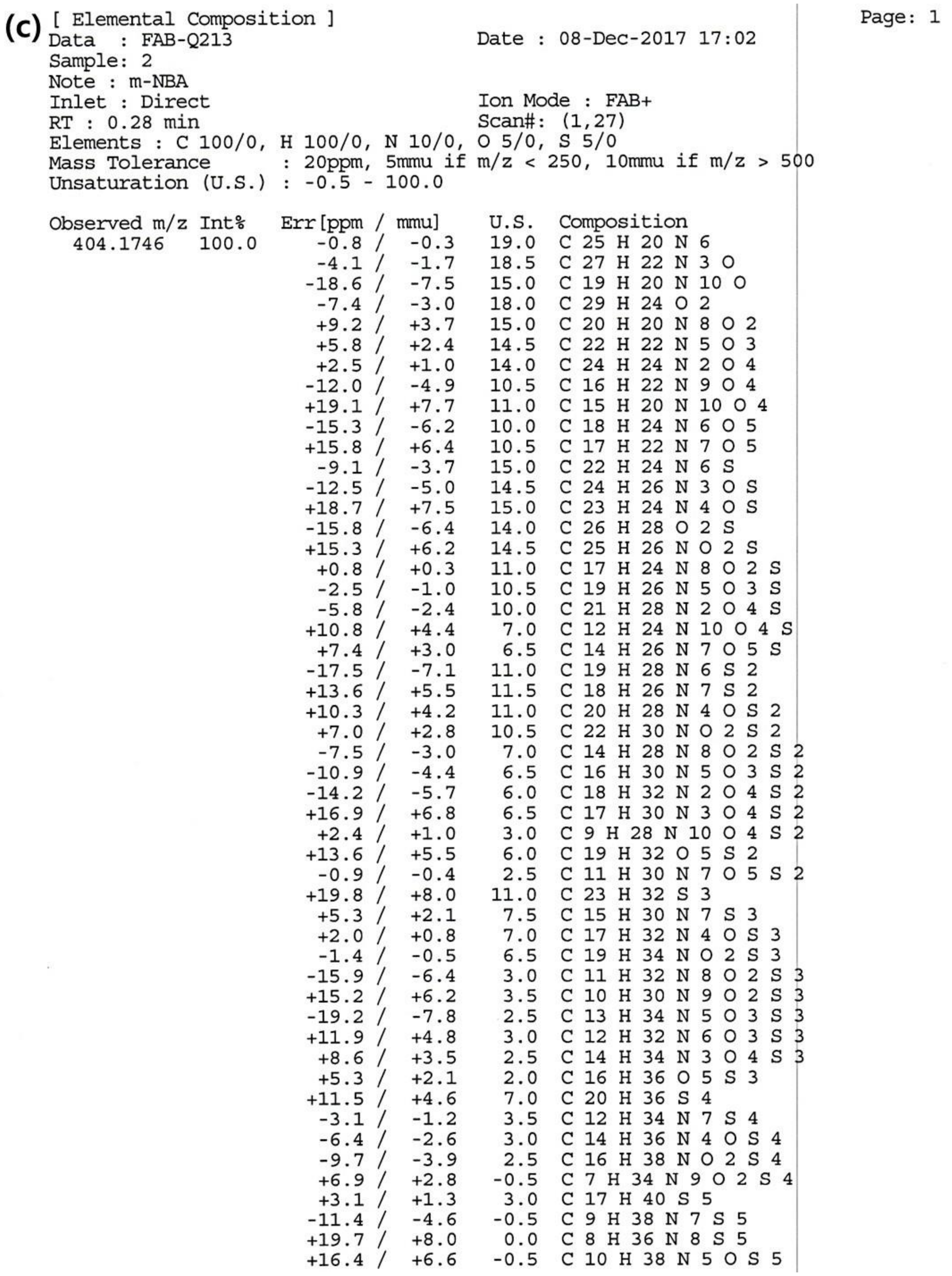

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[ Elemental Composition ]                                         Page: 1
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Sample: 2
Note : m-NBA
Inlet : Direct                         Ion Mode : FAB+
RT : 0.28 min                          Scan#: (1,27)
Elements : C 100/0, H 100/0, N 10/0, O 5/0, S 5/0
Mass Tolerance       : 20ppm, 5mmu if m/z < 250, 10mmu if m/z > 500
Unsaturation (U.S.) : -0.5 - 100.0

Observed m/z Int%   Err[ppm / mmu]    U.S.  Composition
  404.1746   100.0     -0.8 /  -0.3   19.0  C 25 H 20 N 6
                       -4.1 /  -1.7   18.5  C 27 H 22 N 3 O
                      -18.6 /  -7.5   15.0  C 19 H 20 N 10 O
                       -7.4 /  -3.0   18.0  C 29 H 24 O 2
                       +9.2 /  +3.7   15.0  C 20 H 20 N 8 O 2
                       +5.8 /  +2.4   14.5  C 22 H 22 N 5 O 3
                       +2.5 /  +1.0   14.0  C 24 H 24 N 2 O 4
                      -12.0 /  -4.9   10.5  C 16 H 22 N 9 O 4
                      +19.1 /  +7.7   11.0  C 15 H 20 N 10 O 4
                      -15.3 /  -6.2   10.0  C 18 H 24 N 6 O 5
                      +15.8 /  +6.4   10.5  C 17 H 22 N 7 O 5
                       -9.1 /  -3.7   15.0  C 22 H 24 N 6 S
                      -12.5 /  -5.0   14.5  C 24 H 26 N 3 O S
                      +18.7 /  +7.5   15.0  C 23 H 24 N 4 O S
                      -15.8 /  -6.4   14.0  C 26 H 28 O 2 S
                      +15.3 /  +6.2   14.5  C 25 H 26 N O 2 S
                       +0.8 /  +0.3   11.0  C 17 H 24 N 8 O 2 S
                       -2.5 /  -1.0   10.5  C 19 H 26 N 5 O 3 S
                       -5.8 /  -2.4   10.0  C 21 H 28 N 2 O 4 S
                      +10.8 /  +4.4    7.0  C 12 H 24 N 10 O 4 S
                       +7.4 /  +3.0    6.5  C 14 H 26 N 7 O 5 S
                      -17.5 /  -7.1   11.0  C 19 H 28 N 6 S 2
                      +13.6 /  +5.5   11.5  C 18 H 26 N 7 S 2
                      +10.3 /  +4.2   11.0  C 20 H 28 N 4 O S 2
                       +7.0 /  +2.8   10.5  C 22 H 30 N O 2 S 2
                       -7.5 /  -3.0    7.0  C 14 H 28 N 8 O 2 S 2
                      -10.9 /  -4.4    6.5  C 16 H 30 N 5 O 3 S 2
                      -14.2 /  -5.7    6.0  C 18 H 32 N 2 O 4 S 2
                      +16.9 /  +6.8    6.5  C 17 H 30 N 3 O 4 S 2
                       +2.4 /  +1.0    3.0  C 9 H 28 N 10 O 4 S 2
                      +13.6 /  +5.5    6.0  C 19 H 32 O 5 S 2
                       -0.9 /  -0.4    2.5  C 11 H 30 N 7 O 5 S 2
                      +19.8 /  +8.0   11.0  C 23 H 32 S 3
                       +5.3 /  +2.1    7.5  C 15 H 30 N 7 S 3
                       +2.0 /  +0.8    7.0  C 17 H 32 N 4 O S 3
                       -1.4 /  -0.5    6.5  C 19 H 34 N O 2 S 3
                      -15.9 /  -6.4    3.0  C 11 H 32 N 8 O 2 S 3
                      +15.2 /  +6.2    3.5  C 10 H 30 N 9 O 2 S 3
                      -19.2 /  -7.8    2.5  C 13 H 34 N 5 O 3 S 3
                      +11.9 /  +4.8    3.0  C 12 H 32 N 6 O 3 S 3
                       +8.6 /  +3.5    2.5  C 14 H 34 N 3 O 4 S 3
                       +5.3 /  +2.1    2.0  C 16 H 36 O 5 S 3
                      +11.5 /  +4.6    7.0  C 20 H 36 S 4
                       -3.1 /  -1.2    3.5  C 12 H 34 N 7 S 4
                       -6.4 /  -2.6    3.0  C 14 H 36 N 4 O S 4
                       -9.7 /  -3.9    2.5  C 16 H 38 N O 2 S 4
                       +6.9 /  +2.8   -0.5  C 7 H 34 N 9 O 2 S 4
                       +3.1 /  +1.3    3.0  C 17 H 40 S 5
                      -11.4 /  -4.6   -0.5  C 9 H 38 N 7 S 5
                      +19.7 /  +8.0    0.0  C 8 H 36 N 8 S 5
                      +16.4 /  +6.6   -0.5  C 10 H 38 N 5 O S 5
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Fig. S2 (a) Calculated ion distribution, (b) low resolution mass spectroscopy plot, and HR-GCMS elemental composition of DCMBAT.

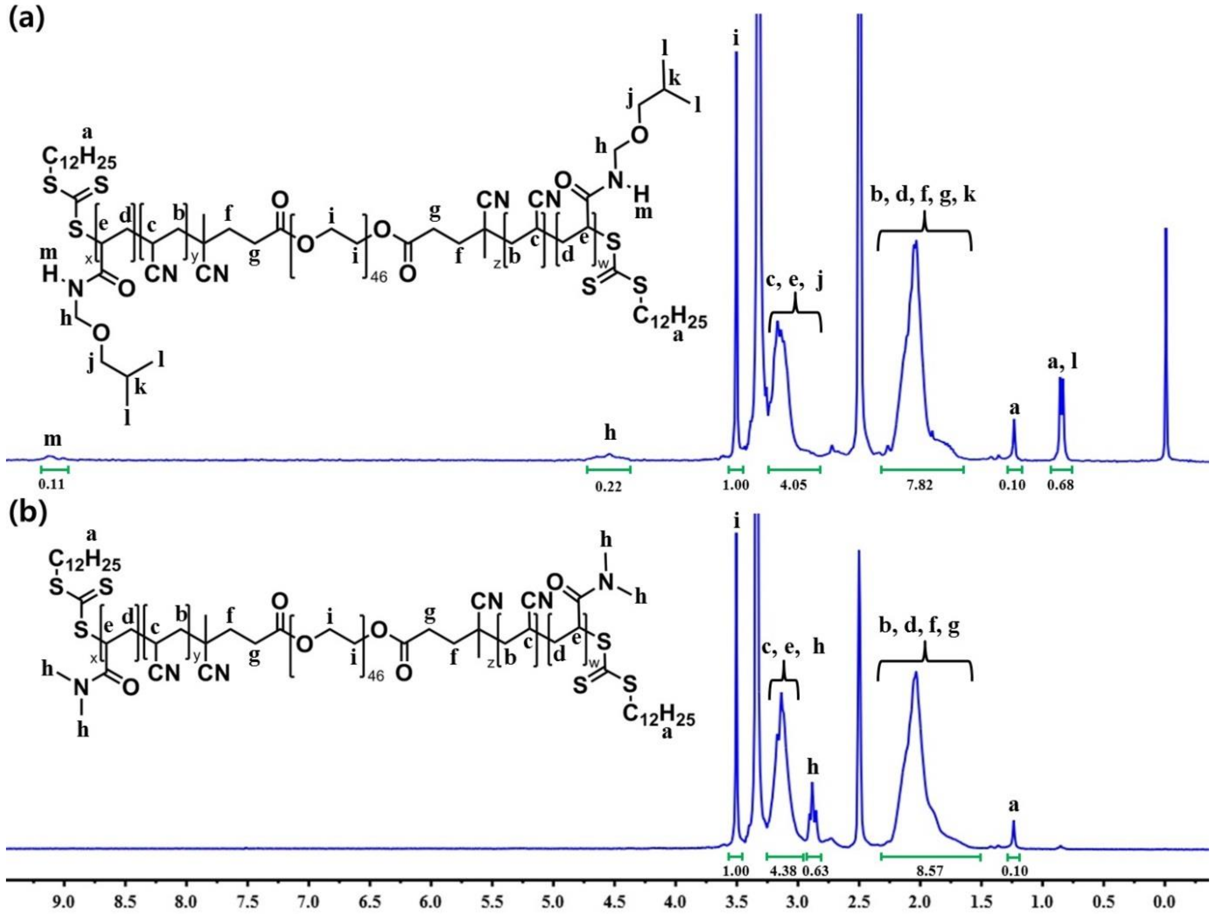

Fig. S3 1H NMR spectra of (a) **SGT-602** and (b) **SGT-604** in DMSO-d_6.

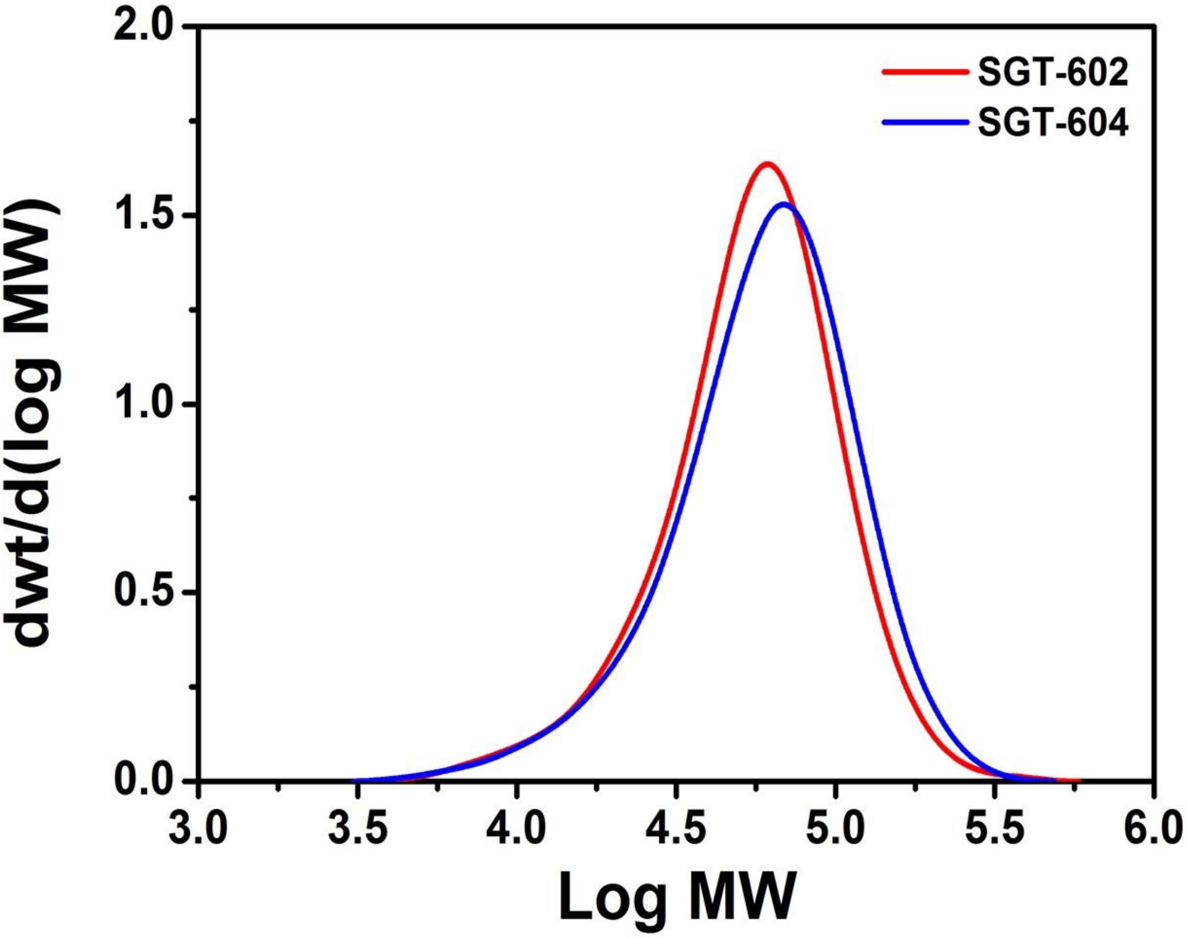

Fig. S4 GPC traces of (a) **SGT-602** and (b) **SGT-604**.

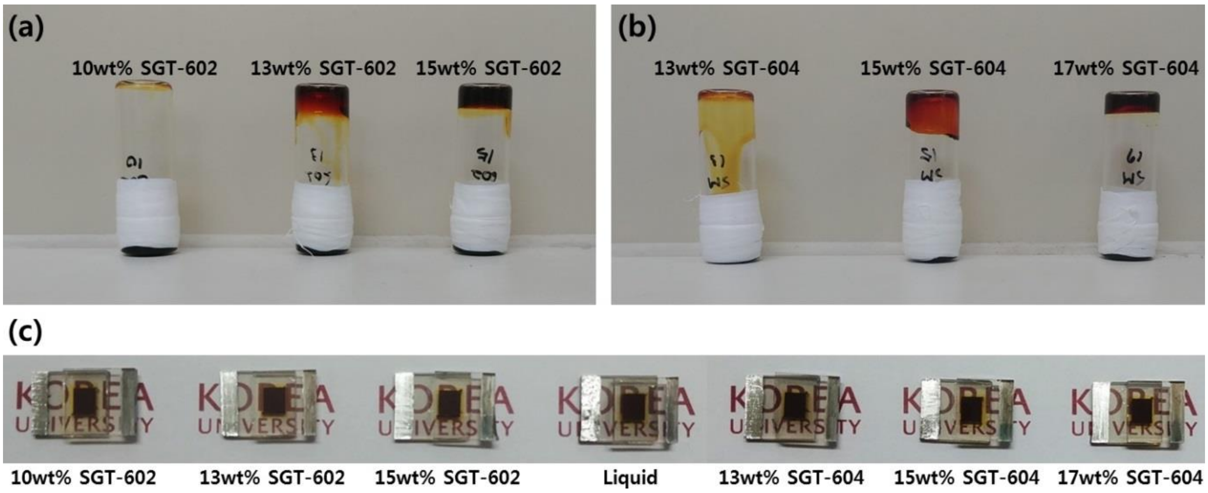

Fig. S5 Photographs of gel prepared with various polymer compositions of (a) **SGT-602** and (b) **SGT-604.** All vials were inverted after a day. (c) Pictures of fabricated devices with corresponding electrolytes.

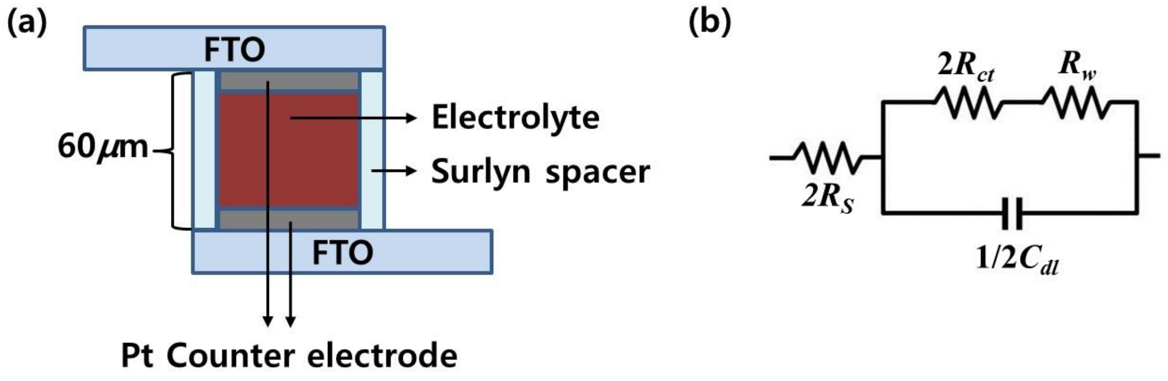

Fig. S6 (a) Illustrative model of symmetrical cell and (b) an equivalent circuit for fitting the electrochemical impedance spectra having two semicircles.

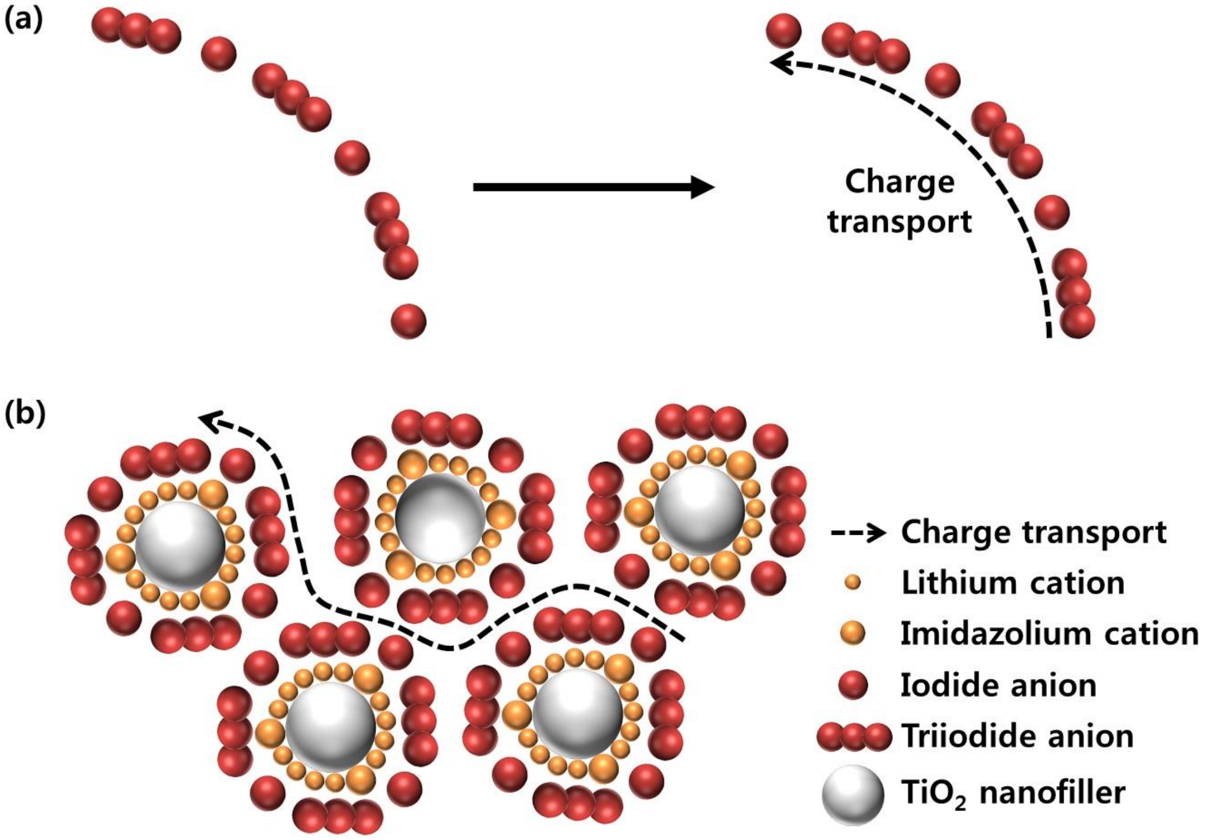

Fig. S7 (a) Charge transport through Grotthus mechanism and (b) facilitated Grotthus-type charge transport by the TiO_2 nanofillers.

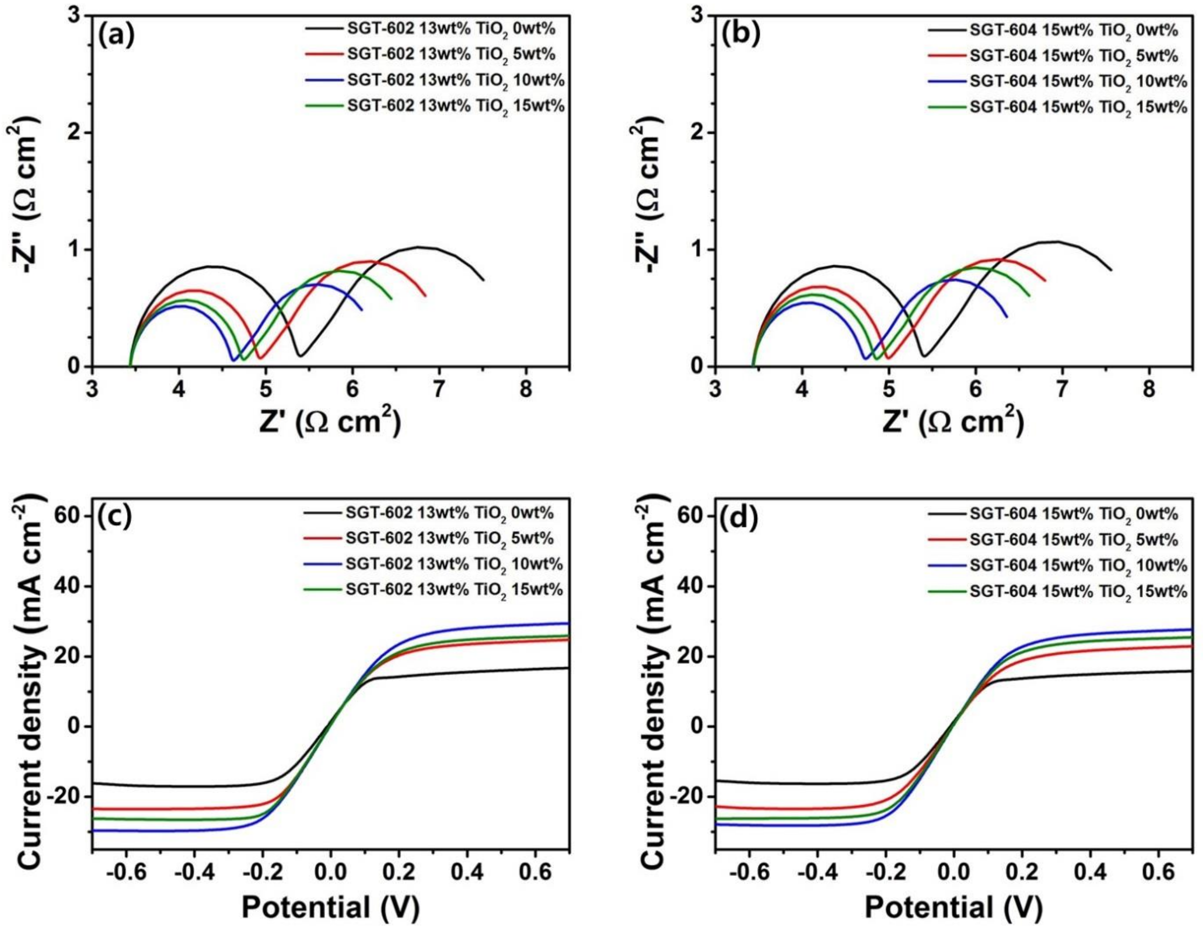

Fig. S8 Electrochemical impedance spectra of symmetrical cells using (a) **SGT-602** and (b) **SGT-604** with various TiO_2 compositions. Linear sweep voltammetry curves of symmetrical cells using (c) **SGT-602** and (b) **SGT-604** with various TiO_2 compositions. The polymer content was fixed to 13wt% for **SGT-602** and 15wt% for **SGT-604**.

Table S1. Electrochemical parameters obtained from EIS and LSV measurements.

		EIS			**LSV**	
Polymer	TiO_2 composition	R_{ct} (Ω cm^2)	R_w (Ω cm^2)	Σ (mS cm^{-1})	J_{lim} (mA cm^{-2})	D_{app} (cm^2 s^{-1})
SGT-602	0wt%	0.97	2.49	2.41	14.55	4.53e-6
	5wt%	0.74	2.19	2.74	23.56	7.32e-6
	10wt%	0.60	1.71	3.51	27.76	8.63e-6
	15wt%	0.66	1.98	3.03	24.08	7.49e-6
SGT-604	0wt%	0.98	2.61	2.30	14.34	4.46e-6
	5wt%	0.77	2.23	2.70	21.05	6.55e-6

	10wt%	0.65	1.81	3.32	25.80	8.02e-6
	15wt%	0.71	2.06	2.91	23.78	7.39e-6

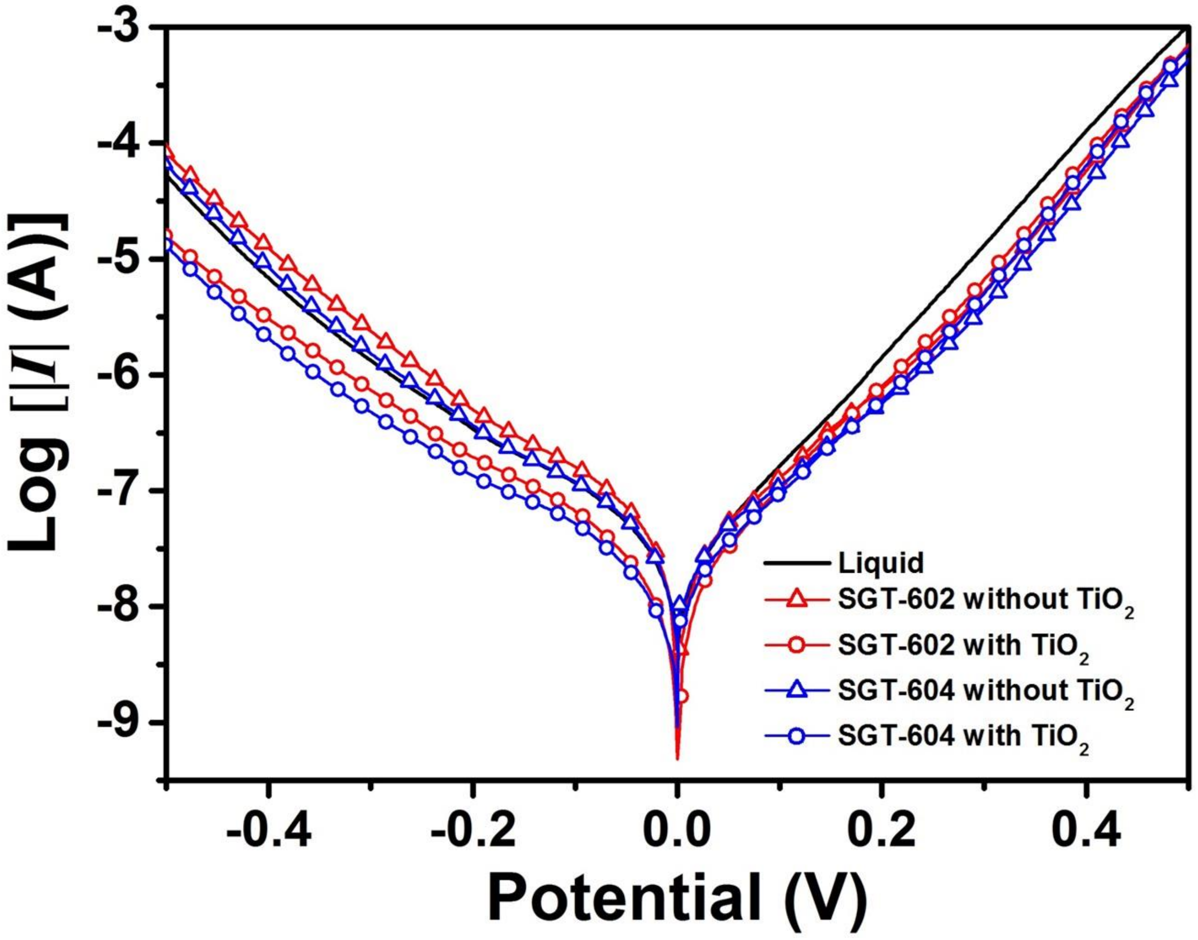

Fig. S9 Tafel polarization plots of DSSCs introducing **SGT**-gel electrolytes with or without TiO_2 nanofillers. Measurements were carried out under dark conditions.

Table S2. Results derived from the Tafel polarization curves of DSSCs under dark conditions.

	β_c (mV decade^{-1})	β_a (mV decade^{-1})	J_0 (μA cm^{-2})
Liquid	229.38	107.22	0.252
SGT-602 without TiO_2	212.44	141.01	0.279
SGT-602 with TiO_2	230.87	120.39	0.154
SGT-604 without TiO_2	244.67	153.00	0.253
SGT-604 with TiO_2	262.89	125.93	0.148

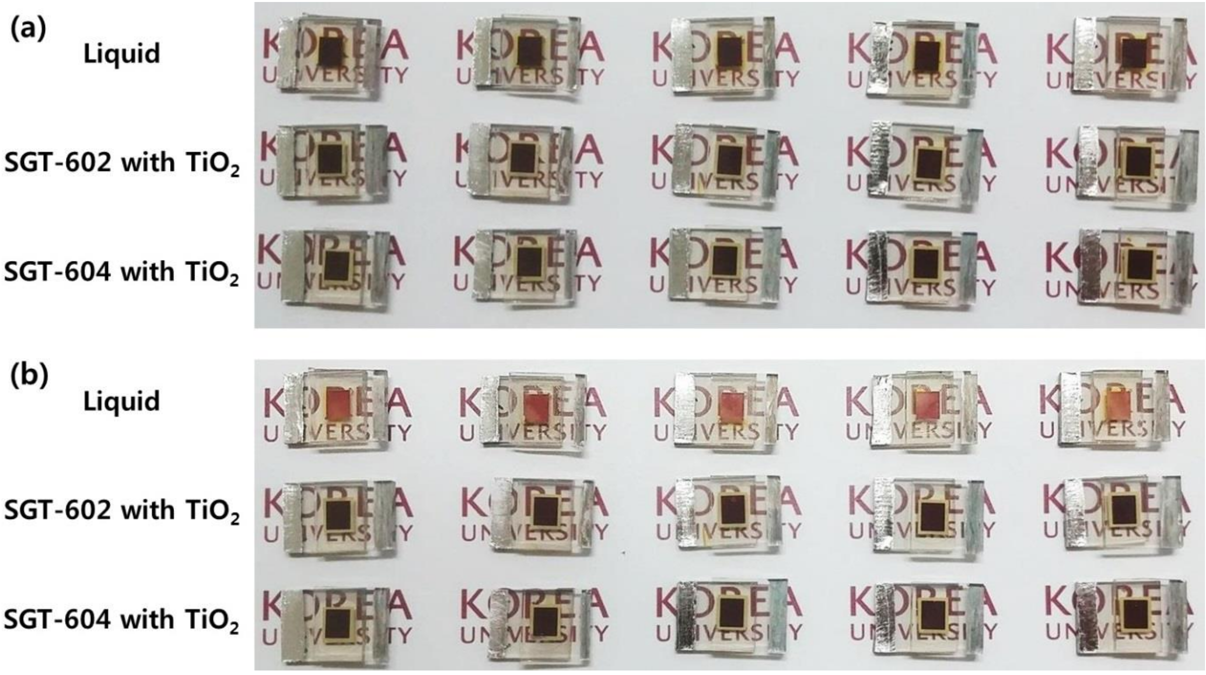

Fig. S10 Pictures of (a) fresh and (b) aged devices.

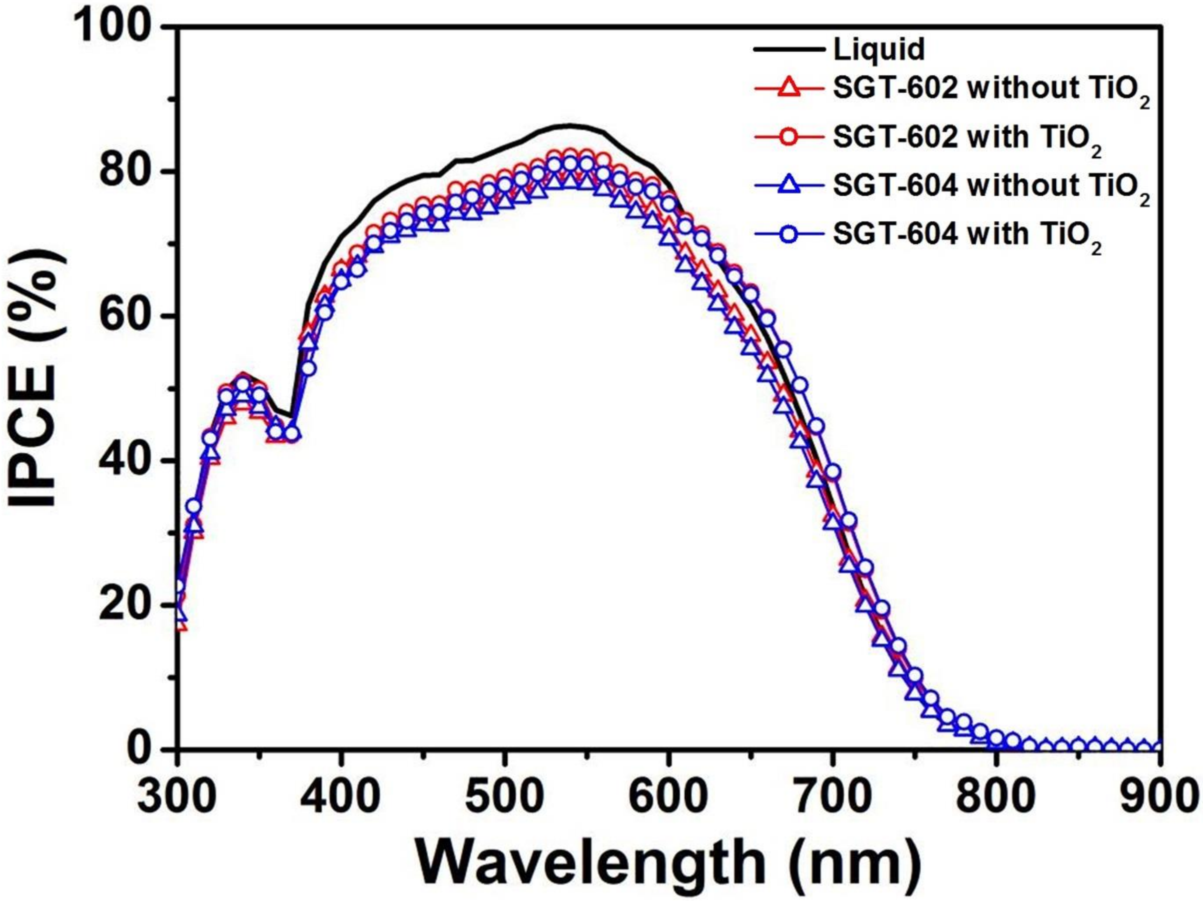

Fig. S11 IPCE spectra of the DSSCs introducing **SGT**-gel electrolytes with or without TiO_2 nanofiller.