

Supporting Information

Well-Dispersed Te-Doped Mesoporous Carbons as Pt-Free Counter Electrode for High-Performance Dye-Sensitized Solar Cells

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Characterization

NMR spectra were recorded on a Varian Mercury 300 spectrometer at the Department of Advanced Materials Chemistry in Korea University using tetramethylsilane (TMS; $\delta = 0$ ppm) as the internal standard. Field emission scanning electron microscopy (FE-SEM) was measured by S-4700 (Hitachi, Japan) microscope to confirm the surface morphology of prepared materials and electrodes. Transmission electron microscopy (TEM) was performed on an EM 912 Omega microscope at 120 kV. X-ray photoelectron spectroscopy (XPS) was carried out with an AXIS-NOVA (Kratos) using an Al-K α X-ray source. X-ray diffraction was performed on a Rigaku Smart Lab diffractometer with CuK α radiation measured at 40 kV and 30 mA. The nitrogen sorption isotherms were measured by Micromeritics ASAP 2020 equipment. Thermal properties of polymers were analyzed using TGA N-1000. Specific surface areas of Te-MC(P) materials were calculated by the BET equation using the nitrogen adsorption data. Total pore volumes were determined by the amount of gas adsorbed at relative pressure of 0.99. Pore size distributions were calculated by Micromeritics software based on the density functional theory method.

Synthesis

1-Chloro-2-octanone: 10 g (72.7 mmol) of 2-chloro-N-methoxy-N-methylacetamide was dissolved in dry THF (240 mL). The solution was placed into an ice bath to maintain the temperature (0°C). After 20 min, 46 mL (92.0 mmol) of hexylmagnesium bromide (2 M in diethyl ether) was added to the solution. The mixture was warmed to room temperature (RT) and stirred for 3 hours. Subsequently, the mixture was quenched with HCl (5%) solution. The reaction product was diluted with 300 mL of diethyl ether and the organic layer washed with saturated sodium bicarbonate and brine two times. The obtained solution was dried over MgSO₄ and evaporated under reduced pressure. A yellow liquid product (11.5 g, yield: 97%) was obtained by no further purification. ¹H NMR (CDCl₃, 300 MHz): δ 4.08 (s, 2H), 2.58 (t, $J=7.4$ Hz, 2H), 1.61 (m, 2H), 1.29 (m, 6H), 0.88 (t,

$J=6.9$ Hz, 3H).

3-(Chloromethyl)-1-nonyn-3-ol: 11.5 g (70.7 mmol) of 1-chloro-2-octanone was dissolved in dry THF (35 mL). 240 mL of ethynylmagnesium bromide (0.5 M in THF) was injected into the solution at 0°C under argon. The mixed solution was stirred at 0°C for 18 hours. Products were then poured into 300 mL of hexanes and quenched with saturated ammonium chloride. The organic layer was washed with brine (three times) and dried over MgSO₄. A dark orange oil was evaporated under reduced pressure to give 10.5 g (yield: 79%) and used without further purification. ¹H NMR (CDCl₃, 300 MHz): δ 3.72 (d, $J=11$ Hz, 1H), 3.62 (d, $J=11$ Hz, 1H), 2.56 (s, 1H), 2.52 (s, 1H), 1.74 (m, 2H), 1.59 (m, 2H), 1.31 (m, 6H), 0.88 (t, $J=6.9$ Hz, 3H). ¹H NMR (CDCl₃, 300 MHz): δ 7.72 (s, 1H), 2.52 (t, $J=7.8$ Hz, 2H), 1.54 (m, 2H), 1.31 (b, 6H), 0.89 (t, $J=6.9$ Hz, 3H)

3-Hexyltellurophene: 5 g (39 mmol) of tellurium in degassed ethanol (120 mL) was treated with 1.5 g (39 mmol) of NaBH₄ under argon and heated to reflux. 1.5 g of additional NaBH₄ was added in three times for 45 minutes and stirred at reflux for 1 hour. 4.5 g (24 mmol) of 3-(chloromethyl)-1-nonyn-3-ol in degassed ethanol (20 mL) was injected into the above reaction flask at 0°C and stirred for 1 hour. The reaction mixture was warmed to RT and a solution of potassium hydroxide (2.1 g, 37 mmol) in an ethanol-water mixture (20 mL, 40:1 v/v) was added to the mixture. The mixture was then refluxed for 2 hours then diluted with dichloromethane, filtrated through celite and evaporated under reduced pressure. The reaction mixture was dissolved in dichloromethane and washed with water and brine three times. Then, it was dried over MgSO₄ and concentrated under reduced pressure. Dark orange oil was dissolved in hexanes (25 ml) and treated with *p*-toluenesulfonic acid monohydrate (0.4 g, 2.2 mmol) and refluxed for 1 hour. The reaction mixture was cooled down to RT and diluted with hexanes (200 mL). The mixture was then quenched with saturated sodium bicarbonate solution. The organic layer was washed with brine three times and dried over MgSO₄ and evaporated under vacuum. Dark orange oil was purified by column chromatography (hexanes),

affording 1.6 g (yield: 25%) of the title product (orange oil). ^1H NMR (CDCl_3 , 300 MHz): δ 8.78 (dd, $J_1=1.9$ Hz, $J_2=6.6$ Hz, 1H), 8.33 (s, 1H), 7.76 (dd, $J_1=1.48$ Hz, $J_2=6.6$ Hz, 1H), 2.64 (t, $J=7.7$ Hz, 2H), 1.61 (m, 2H), 1.30 (m, 6H), 0.88 (t, $J=6.9$ Hz, 3H).

2,5-Diiodo-3-hexyltellurophene: 3-hexyltellurophene (1.6g, 6mmol) was dissolved in dimethylformamide (17 mL) under argon. 2.7 g (12 mmol) of *N*-iodosuccinimide was added in a Schlenk flask (amber glass) and stirred at 40°C for 12 hours, then cooled down to RT and quenched with deionized water. The aqueous layer was poured to 10% sodium thiosulfate solution (100 mL) and extracted with diethyl ether (120 mL). The organic layer was washed with water and brine two times, dried over MgSO_4 and evaporated under reduced pressure. Brownish oil was purified by column chromatography (hexanes) affording bright yellow oil (1.9 g, yield: 62%). ^1H NMR (CDCl_3 , 300 MHz): δ 7.72 (s, 1H), 2.52 (t, $J=7.8$ Hz, 2H), 1.54 (m, 2H), 1.31 (b, 6H), 0.89 (t, $J=6.9$ Hz, 3H).

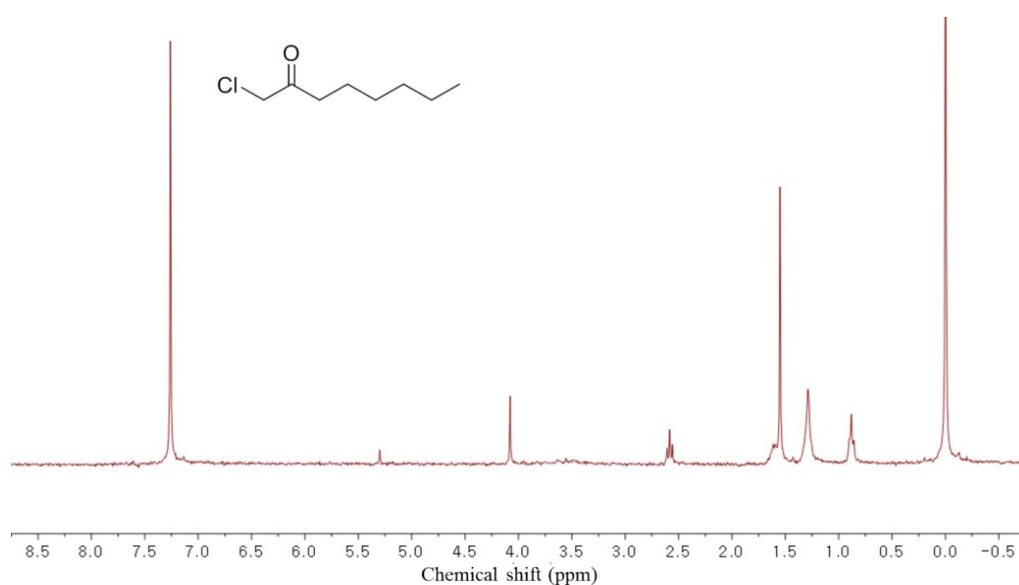


Figure S1. ^1H NMR spectrum of 1-chloro-2-octanone.

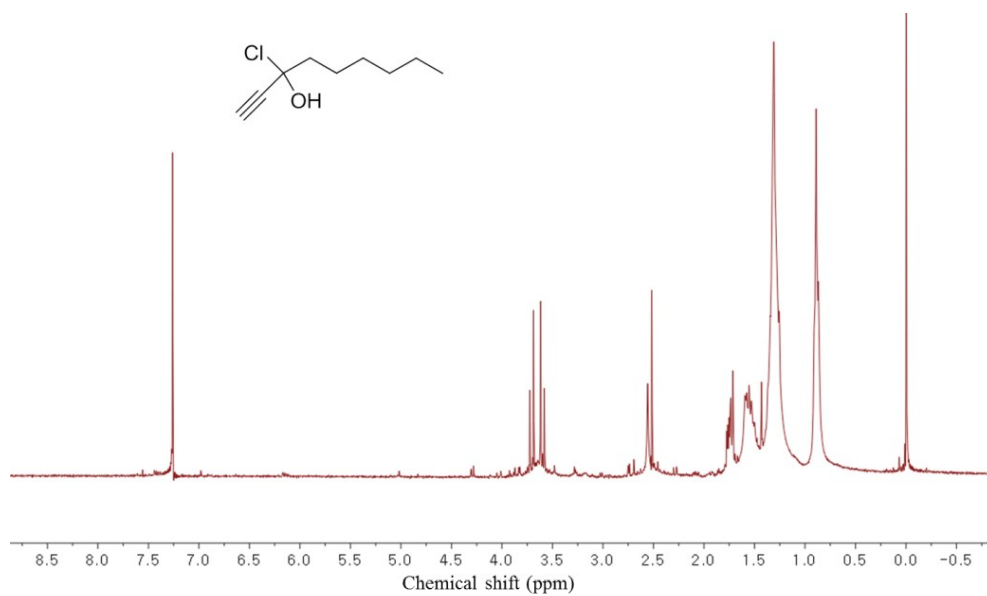


Figure S2. ^1H NMR spectrum of 3-(chloromethyl)-1-nonyn-3-ol.

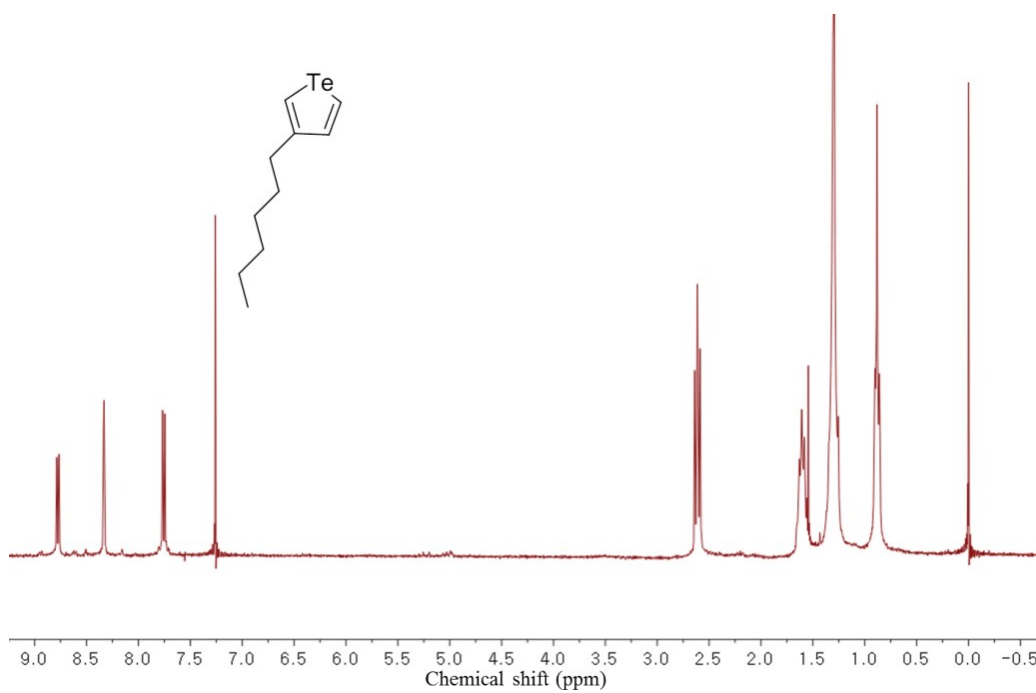


Figure S3. ^1H NMR spectrum of 3-hexyltellurophene

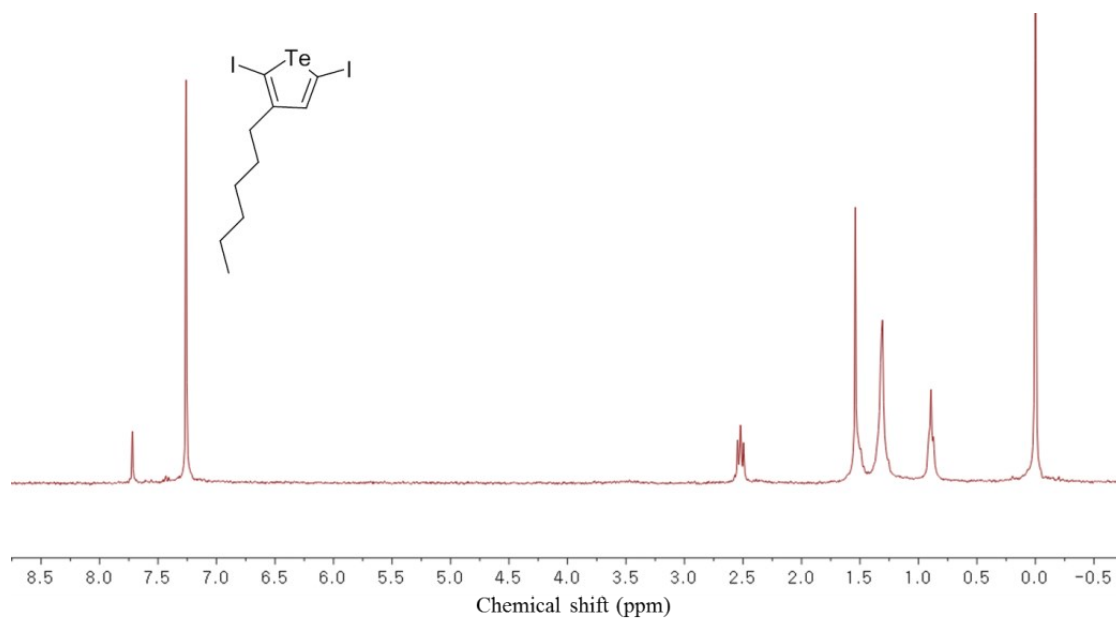


Figure S4. ^1H NMR spectrum of 2,5-diiodo-3-hexyltellurophene.

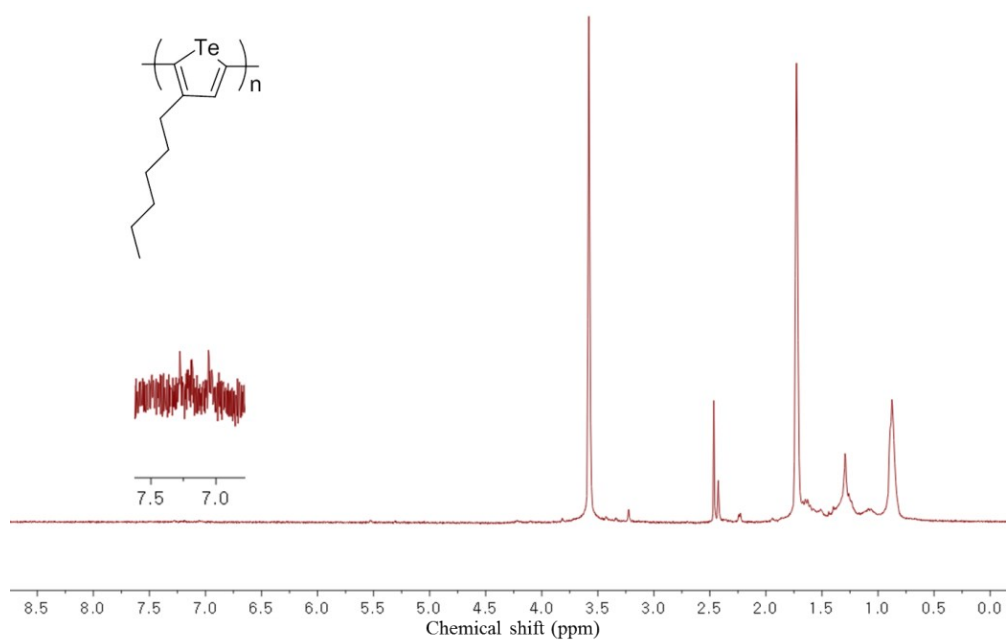


Figure S5. ^1H NMR spectrum of poly(3-hexyltellurophene) ^1H NMR (THF- d_8 , 300 MHz)

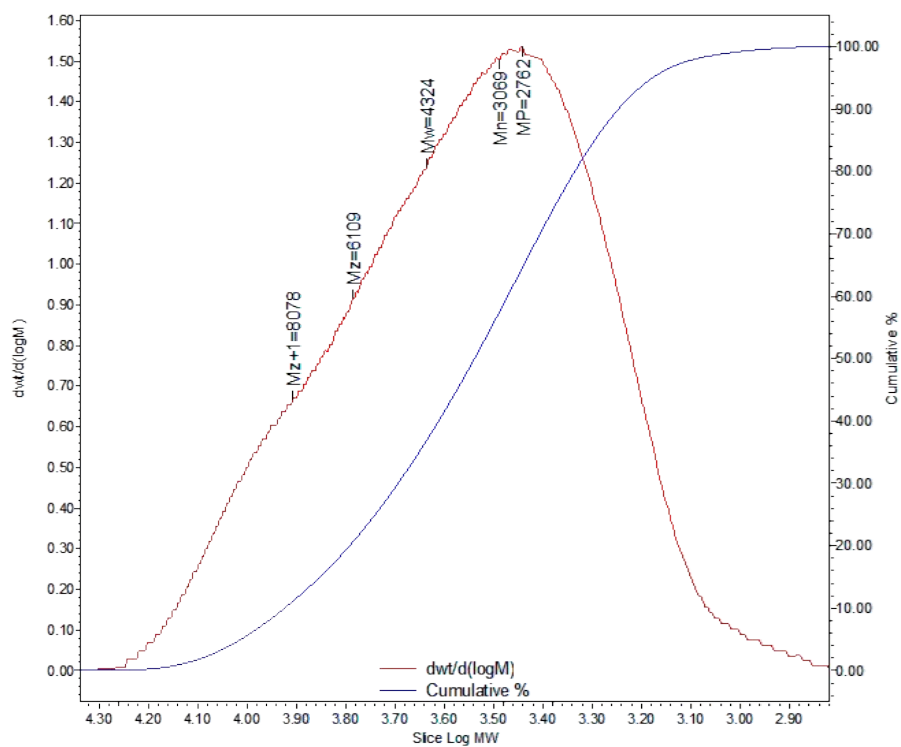


Figure S6. Gel Permeation Chromatography (GPC) result of poly(3-hexyltellurophene)

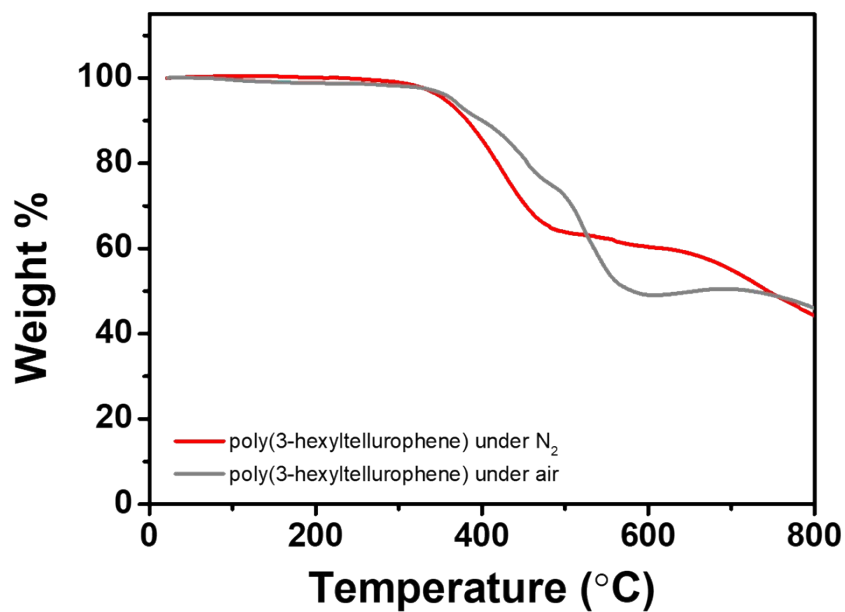
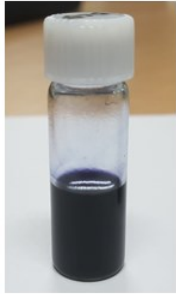





Figure S7. TGA results of poly(3-hexyltellurophene) under N₂ (red) and air (gray).

Table S1 The solubility test results of Poly(3-hexyltellurophene)

Sample	1,2-dichlorobenzene	Chlorobenzene	THF	DMF
Poly (3-hexyltellurophene)				
	Soluble (2 mg/mL)	Soluble (1 mg/mL)	Soluble (< 1 mg/mL)	Insoluble (N/A)

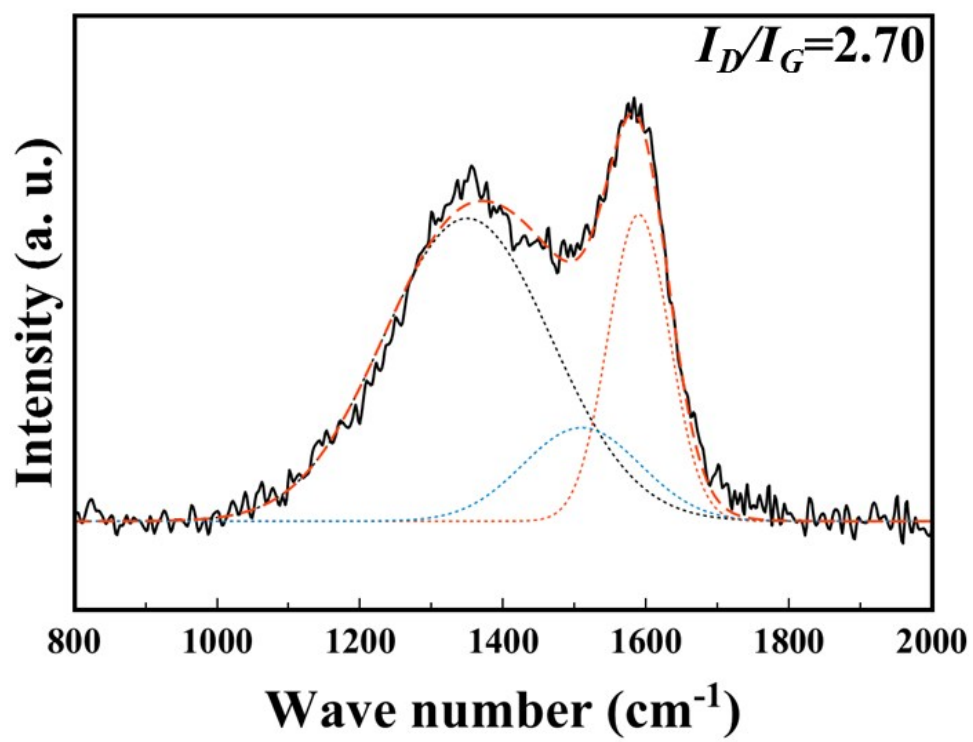


Figure S8. Raman spectra of Te-MC(P)

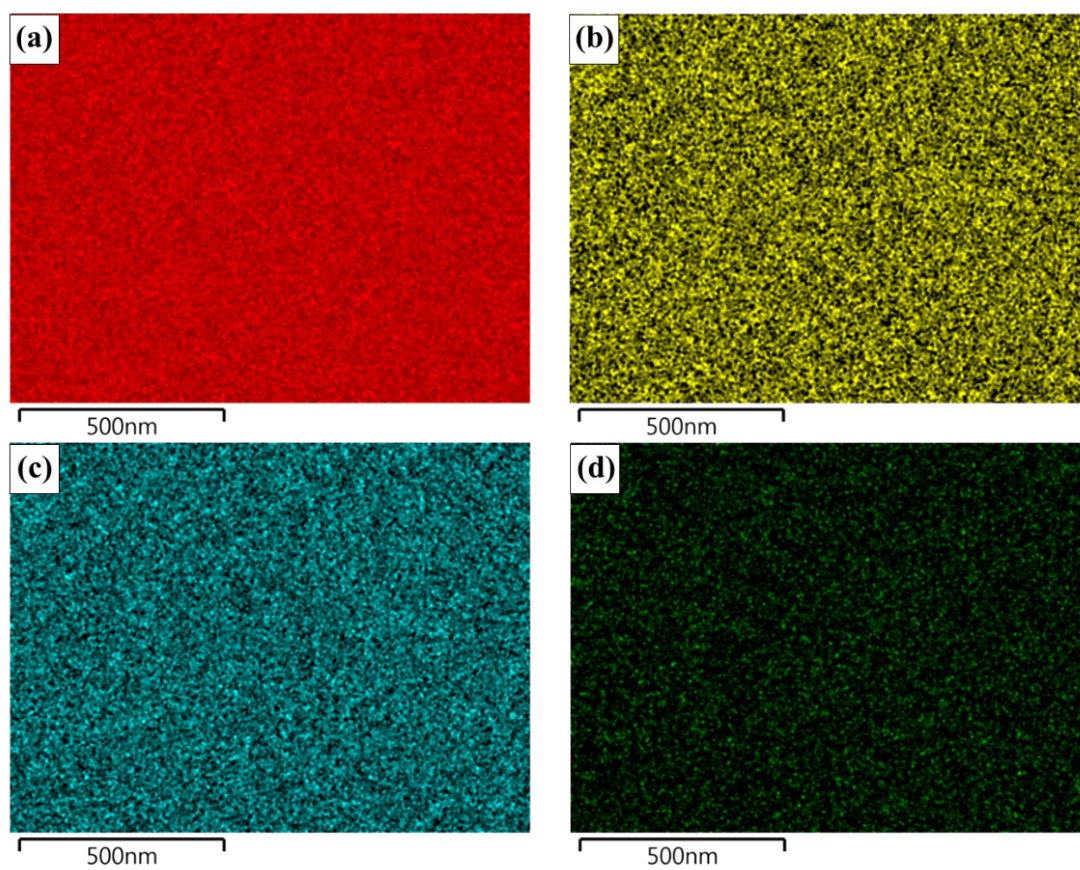


Figure S9. Elemental mapping images of Te-MC(P) material: **(a)** carbon, **(b)** nitrogen, **(c)** oxygen, **(d)** tellurium

Preparation of Te-MC(P) electrodes. ^[1]

As-prepared Te-MC(P) (0.1 wt %) was dispersed in 2-propanol solution by ultrasonication for 30 minutes to produce a homogeneous solution. The homogeneous solution was spread directly onto FTO glass (TEC-8, Pilkington, 1.5 cm × 1.6 cm) with the copper tape mask with an aperture of 0.3 cm² (0.6 cm × 0.5 cm) using the electrospray method. First, the homogeneous solution was placed in a plastic syringe with a 30-gauge stainless steel needle. The needle was connected to a high-voltage power supply (ESN-HV30). A voltage of 3.3 kV was applied between the needle and the collector at a distance of 4 cm. The injection rate of the solution was 40 μL min⁻¹ controlled by syringe pump (KD Scientific Model 220). The electric fields overcame the surface tension of the droplets, resulting in minimization of numerous charged mist particles. The Te-MC(P) electrodes were sintered at 280°C for 15 minutes in air before device fabrication. Pt-FTO electrode (reference electrode, 1.5 cm × 1.6 cm) was prepared by deposition of approximately 30 μL cm⁻² of H₂PtCl₆ solution (2 mg of H₂PtCl₆ in 1 mL of ethanol) and sintered at 400°C for 15 minutes.

Fabrication of symmetrical dummy cell. ^[1]

Symmetrical dummy cells were fabricated with two identical Pt-, Te-MC(A)- and Te-MC(P)-FTO electrodes, which were separated by 25 and 60-μm thick Surlyn (Solaronix, Switzerland) tape as a spacer. The active area of the Pt based dummy cell was 0.42 cm² (0.7 cm × 0.6 cm) and those of two carbon based dummy cell were 0.3 cm² (0.6 cm × 0.5 cm). To improve the electrical contact, the FTO glass edges were coated with indium using the ultrasonic soldering system (USS-9200, MBR Electronics). Co(bpy)₃(BCN₄)₂ (0.22 M), Co(bpy)₃(BCN₄)₃ (0.05 M), LiClO₄ (0.1 M) and 4-*tert*-butylpyridine (0.8 M) were dissolved in acetonitrile to prepare the cobalt electrolyte (Co(bpy)₃^{3+/2+}). Cobalt complexes were synthesized by a previously reported method.^[1] Another iodide electrolyte solution was composed of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.1 M LiI, 0.05 M I₂ and 0.5 M TBP in acetonitrile. Electrolyte solutions were injected into the space between two electrodes through a hole in the CEs. The hole was covered by cover glass using a Surlyn seal.

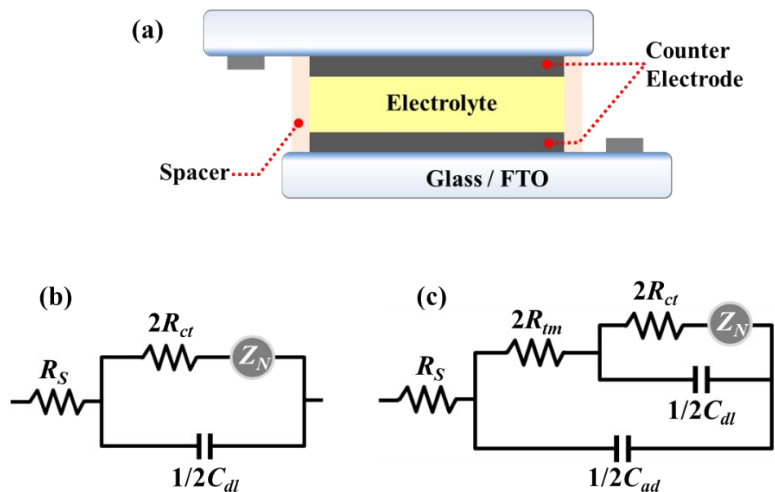


Figure S10 (a) A symmetrical dummy cell fabricated with two identical electrodes. An equivalent circuit for (b) cobalt and (c) iodide redox couples.

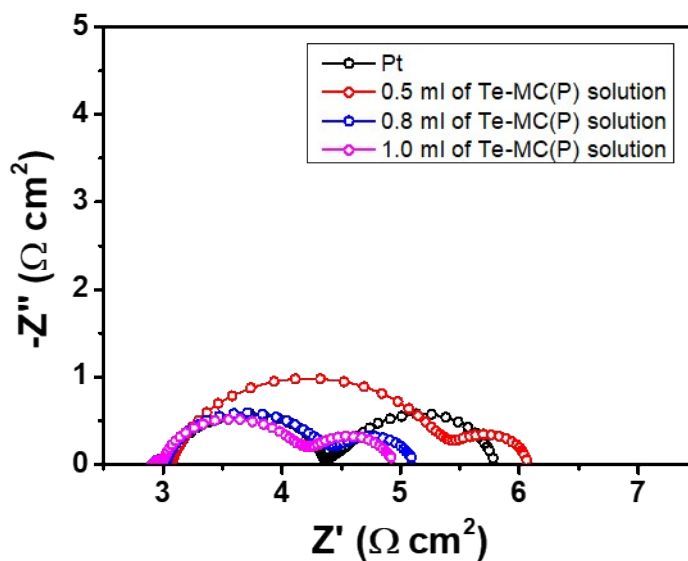


Figure S11 Nyquist plots of the Pt and Te-MC(P) with different amounts of loaded carbon on FTO glass: 0.5 mL (red), 0.8 mL (blue) and 1.0 mL (pink) with I^-/I_3^- electrolytes recorded at 0 V from 1×10^6 to 0.1 Hz.

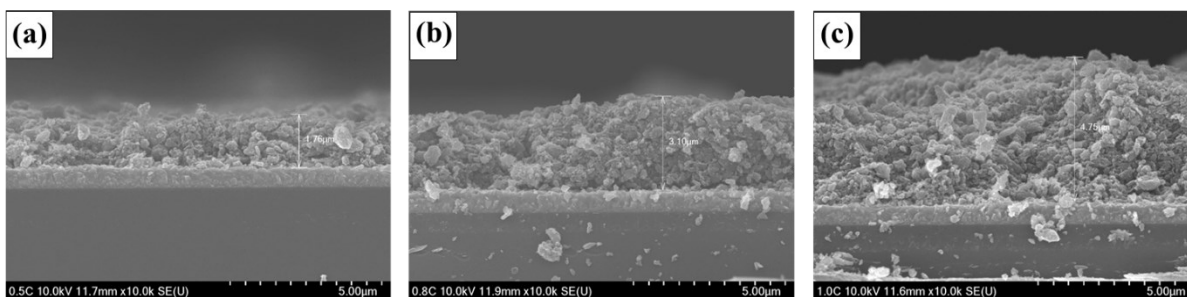


Figure S12 SEM cross-sectional images of Te-MC(P) CE with different amounts of loaded carbon on FTO glass: **(a)** 0.5 mL, **(b)** 0.8 mL and **(c)** 1.0 mL.

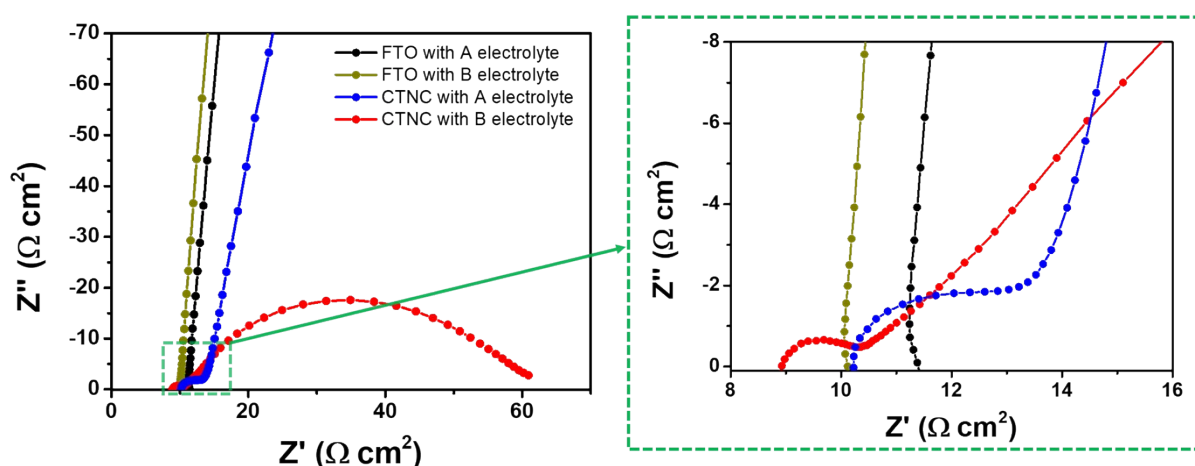


Figure S13 Nyquist plot of the FTO and CTNC dummy cells with A electrolytes (0.1 M LiClO₄ and 0.5 M TBP in acetonitrile) and B electrolytes (0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.1 M LiI, 0.05 M I₂ and 0.5 M TBP in acetonitrile).

Table S2. The corresponding parameters in **Figure S13**.

EIS						
CE	Electrolyte ^a	R_s ($\Omega \text{ cm}^2$)	R_{ct} ($\Omega \text{ cm}^2$)	C_{dl} ($\mu\text{F cm}^2$)	R_m ($\Omega \text{ cm}^2$)	C_{ad} ($\mu\text{F cm}^2$)
FTO	A electrolyte	11.41	$> 10^6$	0.15	-	-
CTNC		10.32	7180	4.15	1.69	$< 10^{-20}$
FTO	B electrolyte	10.16	$> 10^6$	0.16	-	-
CTNC		8.82	13.28	149.42	1.01	34.25

^a A electrolyte: 0.1 M LiClO₄ and 0.5 M TBP in acetonitrile, B electrolytes: 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.1 M LiI, 0.05 M I₂ and 0.5 M TBP in acetonitrile.

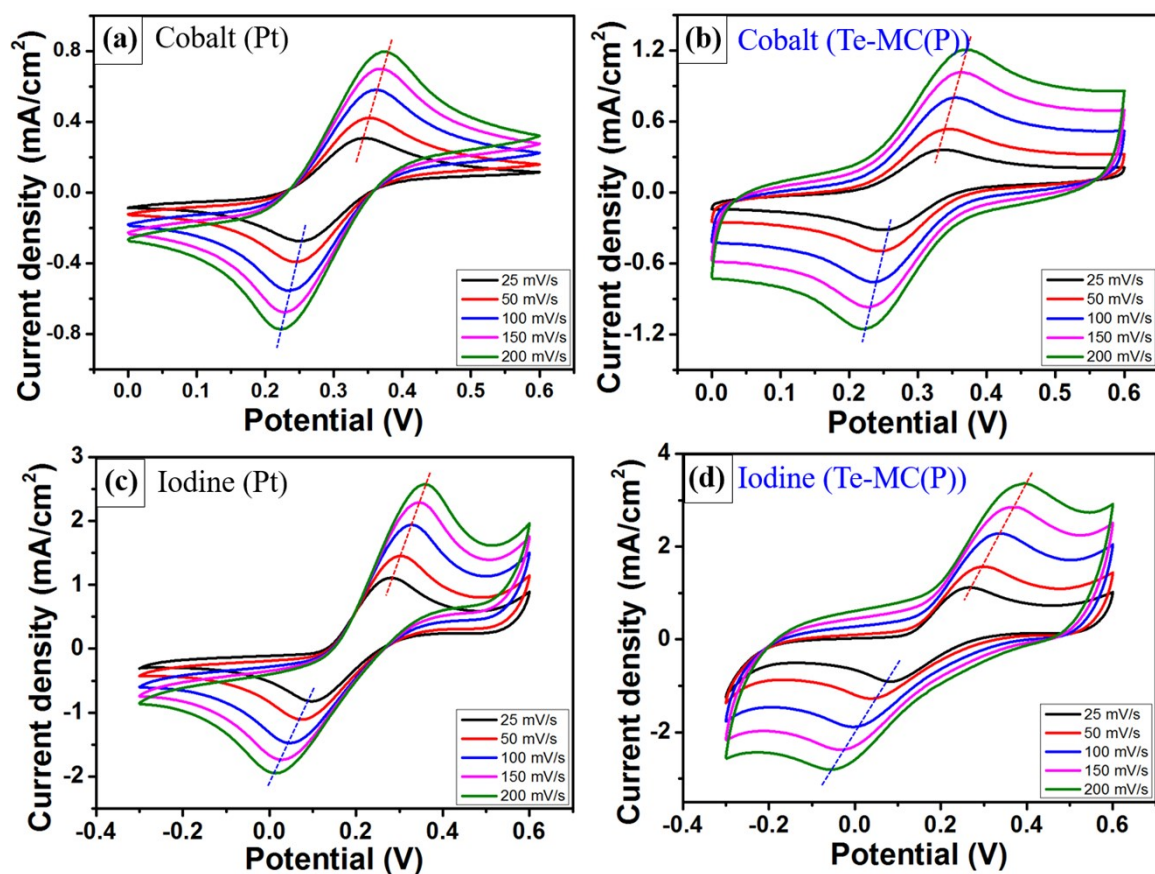


Figure S14 CV curves of CEs with different scan rates for cobalt (a), (b) and iodide redox couple (c), (d) for Pt and Te-MC(P) electrodes, respectively, as the working electrodes with Pt wire as the counter electrode, Ag/AgCl as the reference electrode and 0.1 M LiClO₄ as the supporting electrolyte.

Table S3. The corresponding parameters in **Figure S14**.

Electrode	Electrolyte	scan rate (mV/s)	E_{pa} (V)	Highest current (I_H) at E_{pa} (mA/cm ²)	E_{pc} (V)	Lowest current (I_L) at E_{pc} (mA/cm ²)	E_{pp} (V)	$I_H - I_L$ (mA/cm ²)
Pt	Co(bpy) ₃ ^{2+/3+}	25	0.346	0.309	0.250	-0.275	0.096	0.583
		50	0.352	0.422	0.244	-0.392	0.108	0.814
		100	0.362	0.581	0.234	-0.555	0.128	1.137
		150	0.370	0.699	0.228	-0.677	0.142	1.375
		200	0.374	0.796	0.222	-0.774	0.152	1.570
Te-MC(P)		25	0.336	0.361	0.252	-0.318	0.084	0.679
		50	0.346	0.536	0.242	-0.495	0.104	1.031
		100	0.354	0.799	0.236	-0.758	0.118	1.557

		150	0.362	1.015	0.226	-0.969	0.136	1.984
		200	0.370	1.207	0.220	-1.155	0.150	2.362
Pt	Γ/I_3^-	25	0.280	1.119	0.098	-0.823	0.182	1.942
		50	0.305	1.450	0.074	-1.108	0.231	2.558
		100	0.330	1.938	0.046	-1.476	0.284	3.414
		150	0.348	2.288	0.026	-1.738	0.322	4.027
		200	0.362	2.572	0.014	-1.949	0.348	4.521
Te-MC(P)	Γ/I_3^-	25	0.268	1.120	0.082	-0.907	0.186	2.027
		50	0.300	0.570	0.038	-1.273	0.262	1.843
		100	0.334	2.283	-0.002	-1.883	0.336	4.167
		150	0.368	2.850	-0.034	-2.377	0.402	5.227
		200	0.396	3.360	-0.056	-2.800	0.452	6.160

Electrochemical analysis.^[2]

To evaluate the electrocatalytic activity, electrochemical measurements were carried out using the VersaSTAT 3 (Version 1.31) AMETEK connected to a potentiostat under dark conditions at room temperature. EIS spectra were determined in the frequency range of 1×10^6 to 0.1 Hz, at 0 V open-circuit voltage, and AC modulation amplitude of 10 mV. EIS data analysis was fitted using the Zplot/Zview2 software.

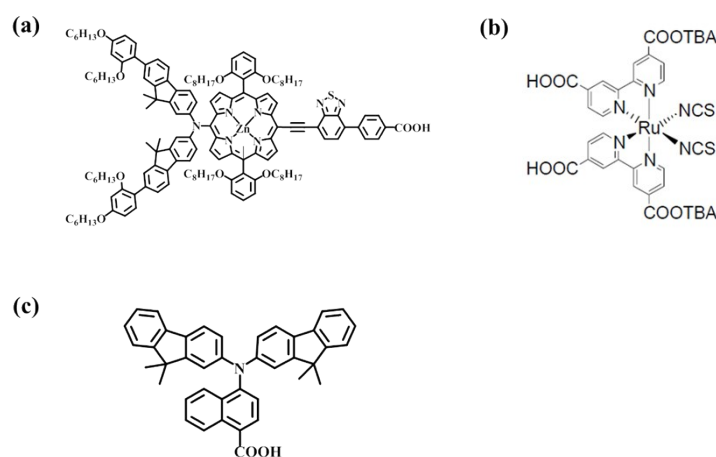


Figure S15 Chemical structures: (a) SGT-021 sensitizer; (b) N719 sensitizer; (c) HC-A4 coadsorbent.

Fabrication and characterization of DSSCs. ^[1]

First, FTO glasses were cut to the size 4.5×9.0 cm and cleaned in detergent solution (water/ethanol/acetone 1:1:1 volume ratio) using an ultrasonic bath. After washing, they were immersed in 40 mM aqueous TiCl_4 solution at 70°C for 30 minutes and washed with water and ethanol. TiO_2 paste (Dyesol, 18NR-T) was screen-printed onto the FTO glass and sintered at 500°C for 30 minutes in air. The thickness of the TiO_2 active layer was confirmed by an Alpha Step 250 surface profilometer (Tencor Instruments, San Jose, CA). The scattering layer (ENB Korea, STP-500 N) was deposited by screen-printing and then dried at 25°C for 2 hours. TiO_2 electrodes were sintered at 500°C for 30 minutes. The resulting layer was composed of a 3.2 cm transparent layer and a 4.0 cm scattering layer with a total area of 0.3 cm^2 ($0.6 \text{ cm} \times 0.5 \text{ cm}$). The resulting TiO_2 photoanode was immersed in THF/ethanol (v/v, 1:3) solution containing 0.2 mM of sensitizers (SGT-021 and N719) and 0.6 mM of HC-A4 coadsorbent, and then kept at room temperature for 3 (SGT-021) and 10 (N719) hours. The dye-adsorbed TiO_2 photoanodes were assembled with Pt, Te-MC(A) and Te-MC(P) CEs using a thermal adhesive film (25 μm and 60 μm thick Surlyn, DuPont) as a spacer to produce a sandwich-type cell. Electrolyte solutions were injected through a hole in the CE. The hole was covered by cover glass using Surlyn. The light intensity was adjusted with a Si solar cell that was double-checked with a NREL-calibrated Si solar cell (PV Measurement Inc.). The applied potential and measured cell current were measured by Keithley model 2400 digital source meter. Photoelectrochemical data were measured by 1000 W xenon light source (Oriel, 91193) that was focused to give 100 mW cm^{-2} (1 sun at AM 1.5 G). The J - V characteristics of the cell under these conditions were determined by biasing the cell externally and measuring the generated photocurrent. This process was fully automated using Wavemetrics software. The measurement settling time between applying the voltage and measuring the current for the J - V characterization of DSSCs was fixed at 80 ms.

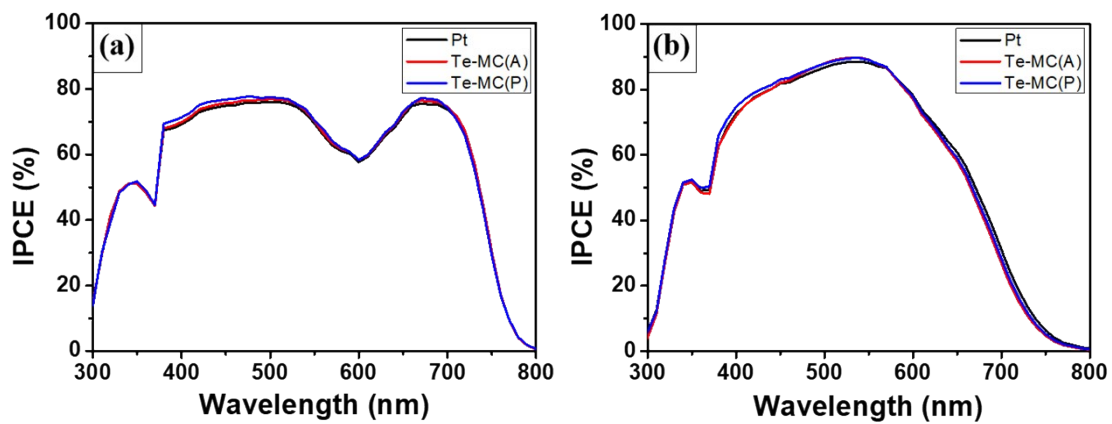


Figure S16 The corresponding incident photon-to-current conversion efficiency (IPCE) plots of **(a)** SGT-021 with cobalt electrolyte and **(b)** N719 with iodide electrolyte.

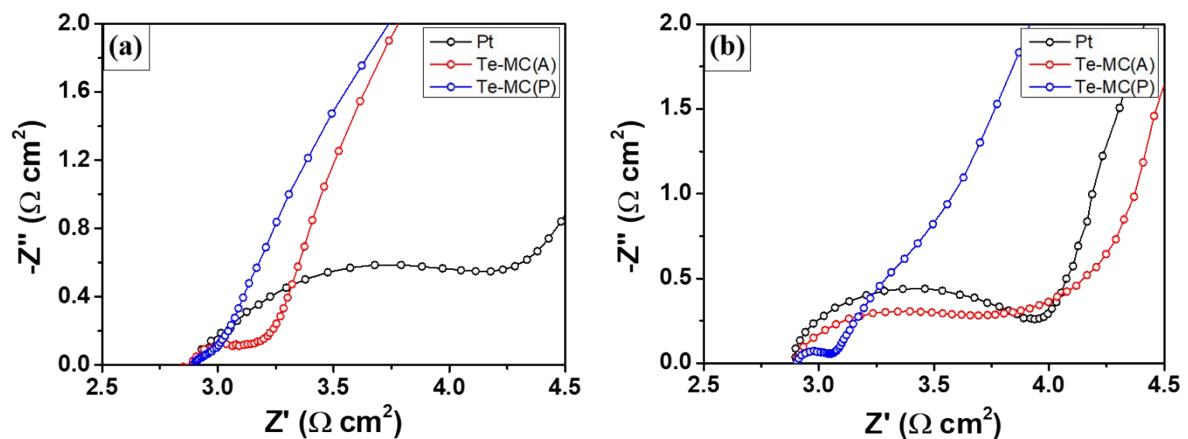


Figure S17 Nyquist spectra of the high-frequency region for **(a)** SGT021 with $\text{Co}(\text{bpy})_3^{2+/3+}$ and **(b)** N719 with I^-/I_3^- -based DSSC devices.

Table S4 Photovoltaic performance of DSSCs with Pt, Te-MC(A) and Te-MC(P) CEs.

Sample	Dye / Electrolyte	J_{SC} [mA cm ⁻²]	V_{oc} [mV]	FF [%]	PCE [%]
Pt-1		17.39	921.76	75.87	12.16
Pt-2		17.31	919.13	75.62	12.03
Pt-3		17.34	917.56	76.18	12.12
Pt-4		17.21	920.91	75.61	11.98
Pt-5		17.08	919.28	76.35	11.99
Te-MC(A)-1		17.16	923.88	78.30	12.41
Te-MC(A)-2	SGT-021 / Co(bpy) ₃ ^{2+/3+}	17.48	923.88	77.30	12.49
Te-MC(A)-3		17.29	922.80	77.81	12.41
Te-MC(A)-4		17.29	923.75	78.44	12.53
Te-MC(A)-5		17.40	923.53	77.15	12.40
Te-MC(P)-1		17.56	924.32	77.66	12.60
Te-MC(P)-2		17.29	923.88	79.03	12.62
Te-MC(P)-3		17.28	921.31	79.26	12.62
Te-MC(P)-4		17.71	921.48	78.01	12.73
Te-MC(P)-5		17.32	921.08	78.58	12.54
Pt-1		16.24	766.02	74.41	9.26
Pt-2		16.52	757.10	74.18	9.28
Pt-3		16.55	762.56	73.81	9.32
Pt-4		16.27	761.73	75.22	9.32
Pt-5		16.33	757.84	75.46	9.34
Te-MC(A)-1		16.32	762.38	75.15	9.35
Te-MC(A)-2	N-719 / I ⁻ /I ₃ ⁻	16.48	756.26	75.39	9.40
Te-MC(A)-3		16.45	759.51	75.5	9.43
Te-MC(A)-4		16.5	754.6	75.12	9.35
Te-MC(A)-5		16.23	755.73	76.32	9.36
Te-MC(P)-1		16.75	765.61	75.66	9.70
Te-MC(P)-2		16.66	764.49	76.18	9.70
Te-MC(P)-3		16.44	766.65	77.06	9.71
Te-MC(P)-4		16.11	769.73	76.87	9.53
Te-MC(P)-5		16.54	762.12	76.33	9.62

Supplementary References

- [1] C. K. Kim, H. Zhou, T. Kowalewski, K. Matyjaszewski, H. K. Kim, *ACS Appl. Mater. Interfaces* **2019**, 11, 2093.
- [2] I.-Y. Jeon, H. M. Kim, D. H. Kweon, S.-M. Jung, J.-M. Seo, S.-H. Shin, I. T. Choi, Y. K. Eom, S. H. Kang, H. K. Kim, M. J. Ju, J.-B. Baek, *Nano Energy* **2016**, 30, 867.