SUPPORTING INFORMATION

EFFICIENT BINARY ORGANIC REDOX MEDIATORS IN DYE-SENSITIZED SOLAR CELLS BASED ON A CARBON BLACK COUNTER ELECTRODE

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EXPERIMENTAL SECTION

IN THIS STUDY, FLUORINE-DOPED TIN OXIDE (FTO) GLASS PLATES (PILKINGTON-TEC8) WERE CLEANED USING AN ULTRASONIC BATH WITH 2-PROPANOL (IPA), ACETONE, AND WATER. A DOCTOR BLADED LAYER OF 20 NM TIO_2 PARTICLES (18 NR-T, DYESOL) WAS USED AS THE PHOTO-ELECTRODE. A 6-MM-THICK FILM WAS FIRST COATED ON THE CONDUCTING GLASS ELECTRODE AND FURTHER COATED WITH A 5-MM-THICK SECOND LAYER OF ~200 NM LIGHT-SCATTERING PARTICLES (WER 2-O, DYESOL). THE TIO_2 ELECTRODES WERE HEATED AT 450 °C FOR 30 MINUTES. FOLLOWING HEAT TREATMENT, THESE ELECTRODES WERE IMMERSED IN A DYE SOLUTION (0.5 MM *CIS*-DIISOTHIOCYANATO-BIS (2,2’-BIPYRIDYL-4,4’-DICARBOXYLATO) RUTHENIUM (II) BIS(TETRABUTYLAMMONIUM) (N719, SOLARONIX) IN ACETONITRILE (ACN, WAKO)/TERT-BUTHYL ALCOHOL (T-BUOH, WAKO) (1/1, V/V) AND KEPT AT ROOM TEMPERATURE. THE TIO_2 ELECTRODE WAS RINSED WITH ACN AND DRIED. THE PT ELECTRODE WAS PREPARED BY SPIN-COATING 10 MM H_2PTCL_6 (SIGMA-ALDRICH) IN 2-PROPANOL (SIGMA-ALDRICH) AND THEN SINTERING AT 450 °C FOR 30 MINUTES. THE CB ELECTRODE WAS COATED WITH CB PASTE ON A FTO SUBSTRATE UTILIZING THE DOCTOR BLADE METHOD. THE CB PASTE WAS A MIXTURE OF CB (KETJEN BLACK EC-600JD, AKZO NOBEL)/POLYVINYLIDENE FLUORIDE (PVDF, SOLVAY SOLEXIS) (W/W, 1/1) IN N-METHYL-2-PYRROLIDONE (NMP, SIGMA-ALDRICH). AFTER COATING, THESE ELECTRODES WERE SINTERED AT 120 °C FOR 30 MINUTES. THE DYE-COATED TIO_2 ELECTRODE AND COUNTER ELECTRODE WERE ASSEMBLED WITH 25 MM SURLYN (DUPONT) FOR PT COUNTER ELECTRODE AND 60 MM SURLYN (DUPONT) FOR CB COUNTER ELECTRODE. THE DYE-SENSITIZED TIO_2 ACTIVE AREA WAS 0.25 CM^2. THE ELECTROLYTE SOLUTION WAS COMPOSED OF 0.4 M DISULFIDE, 0.4 M THIOLATE AND 0.5 M TERT-BUTHYL-PYRIDINE (TBP, ALDRICH) IN Γ-BUTYROLACTONE (GBL, WAKO). THE DISULFIDE DI-5-(1-METHYLTETRAZOLE) DISULFIDE (T_2) AND THIOLATE 5-MERCAPTO-1-METHYLTETRAZOLE N-TETRAMETHYLAMMONIUM SALT ($NME_4^+T^-$) WERE SYNTHESIZED AS DESCRIBED IN A PREVIOUS REPORT.[1] THE DISULFIDE, TETRAMETHYLTHIURAM DISULFIDE (M_2, SIGMA-ALDRICH), AND SODIUM DIMETHYLDITHIOCARBAMATE HYDRATE (NA^+M^-, SIGMA-ALDRICH) WERE PURCHASED FROM SIGMA-ALDRICH. I^-/I_3^- ELECTROLYTE WAS COMPOSED OF 0.4 M 1-METHYL-3-PROPYL IMIDAZOLIUM IODIDE (MPII, SIGMA-ALDRICH), 0.4 M IODINE (I_2, SIGMA-ALDRICH) AND 0.5 M TBP IN GBL.

TO DETERMINE THE PROPERTIES OF PHOTOVOLTAIC PERFORMANCE, THE CURRENT-VOLTAGE (J-V)

CHARACTERISTICS OF DSCS WERE MEASURED WITH A KEITHLEY MODEL 2400 SOURCE METER AND A SOLAR SIMULATOR, WITH A 300 W XENON ARC-LAMP (NEWPORT) UNDER 1 SUN ILLUMINATION (AM 1.5, 100 MW/CM^2). A LIGHT SHADING MASK, PLACED ON THE RESIDUAL AREA OF THE FRONT SIDE OF THE FTO SUBSTRATE (EXCEPT FOR THE 0.25 CM^2 TIO_2 ACTIVE AREA), WAS EMPLOYED TO PREVENT OVERESTIMATION OF THE POWER CONVERSION EFFICIENCY. IN ADDITION, THE QUANTUM EFFICIENCY OF DSCS WAS MEASURED BY AN IPCE DEVICE (PV MEASUREMENTS, INC.). THE INTERFACIAL PROPERTIES WERE CHARACTERIZED BY ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS) USING IM6 (ZAHNER) IN THE DARK. A BIAS POTENTIAL OF OPEN-CIRCUIT VOLTAGE (V_{OC}) WAS APPLIED BETWEEN THE TWO ELECTRODES, AND THE FREQUENCY RANGE VARIED FROM 1 M TO 500 MHZ, WITH FIXED AMPLITUDE OF 10 MV. SCANNING ELECTRON MICROSCOPY (SEM) WAS PERFORMED USING S-4700 (HITACHI). THE SAMPLES WERE COATED ON FTO GLASS. THE ELECTRON DIFFUSION COEFFICIENT AND ELECTRON LIFETIME WERE OBTAINED BY IMPS (INTENSITY MODULATED PHOTOCURRENT SPECTROSCOPY) UNDER SHORT CIRCUIT CONDITION AND IMVS (INTENSITY MODULATED PHOTOVOLTAGE SPECTROSCOPY) UNDER OPEN-CIRCUIT CONDITION AS A FUNCTION OF LIGHT INTENSITY USING A CIMPS (CONTROLLED INTENSITY MODULATED PHOTO SPECTROSCOPY) SYSTEM (ZAHNER).[2] TO CHARACTERIZE THE ELECTROCHEMICAL PROPERTIES OF THESE REDOX COUPLES, CYCLIC VOLTAMMETRY (CV) WAS MEASURED USING AN AUTOLAB INSTRUMENT (320N) WITH A THREE-ELECTRODE SYSTEM. THE THREE-ELECTRODE SYSTEM WAS COMPOSED OF 0.07 CM^2 GLASSY CARBON AS THE WORKING ELECTRODE, A GRAPHITE ROD COUNTER ELECTRODE (SIGMA-ALDRICH), AND AG/AGCL (3 M KCL, METROHM) AS THE REFERENCE ELECTRODE. THE ELECTROLYTE FOR CYCLIC VOLTAMMETRY WAS PREPARED USING 0.01 M THIOLATE, 0.01 M DISULFIDE AND 0.2 M LITHIUM PERCHLORATE ($LICLO_4$, SIGMA-ALDRICH) FOR THE SUPPORTING ELECTROLYTES IN GBL. CV EXPERIMENTS WERE CARRIED OUT AT 25 °C AT A SCAN RATE OF 50 MV/S. THE DIFFUSION COEFFICIENTS WERE DETERMINED BY MEASUREMENT OF A CYCLIC VOLTAMMOGRAM USING VARIOUS SCAN RATES (0.1 – 1 V/S) (FIG. S7). THE PEAK CURRENT (I_P) IS PROPORTIONAL TO THE DIFFUSION COEFFICIENT OF DISULFIDE (T_2, M_2), D:[3]

$$I_P=2.72 \text{ X } 10^5 N^{3/2} A D^{1/2} C V^{1/2}$$

WHERE N IS THE NUMBER OF EXCHANGED ELECTRONS, A IS AREA OF WORKING ELECTRODE, C IS THE DISULFIDE CONCENTRATION AND V IS SCAN RATE. FT-IR SPECTRA WERE RECORDED ON A JASCO

FT/IR-4200 SPECTROMETER.

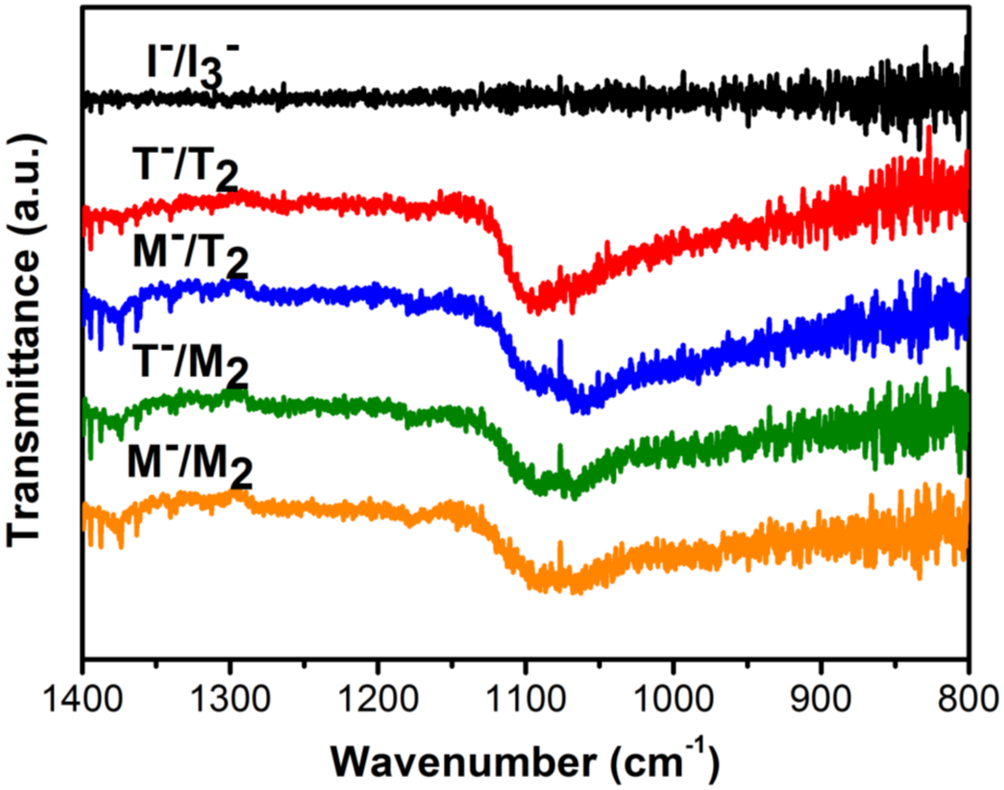

FIGURE S1. FT-IR SPECTRA OF THE PT ELECTRODE DIPPED FOR TWO DAYS IN I^-/I_3^- AND THIOLATE/DISULFIDE ELECTROLYTE. BASE LINE IS FTO GLASS THAT WAS DIPPED IN GBL FOR TWO DAYS.

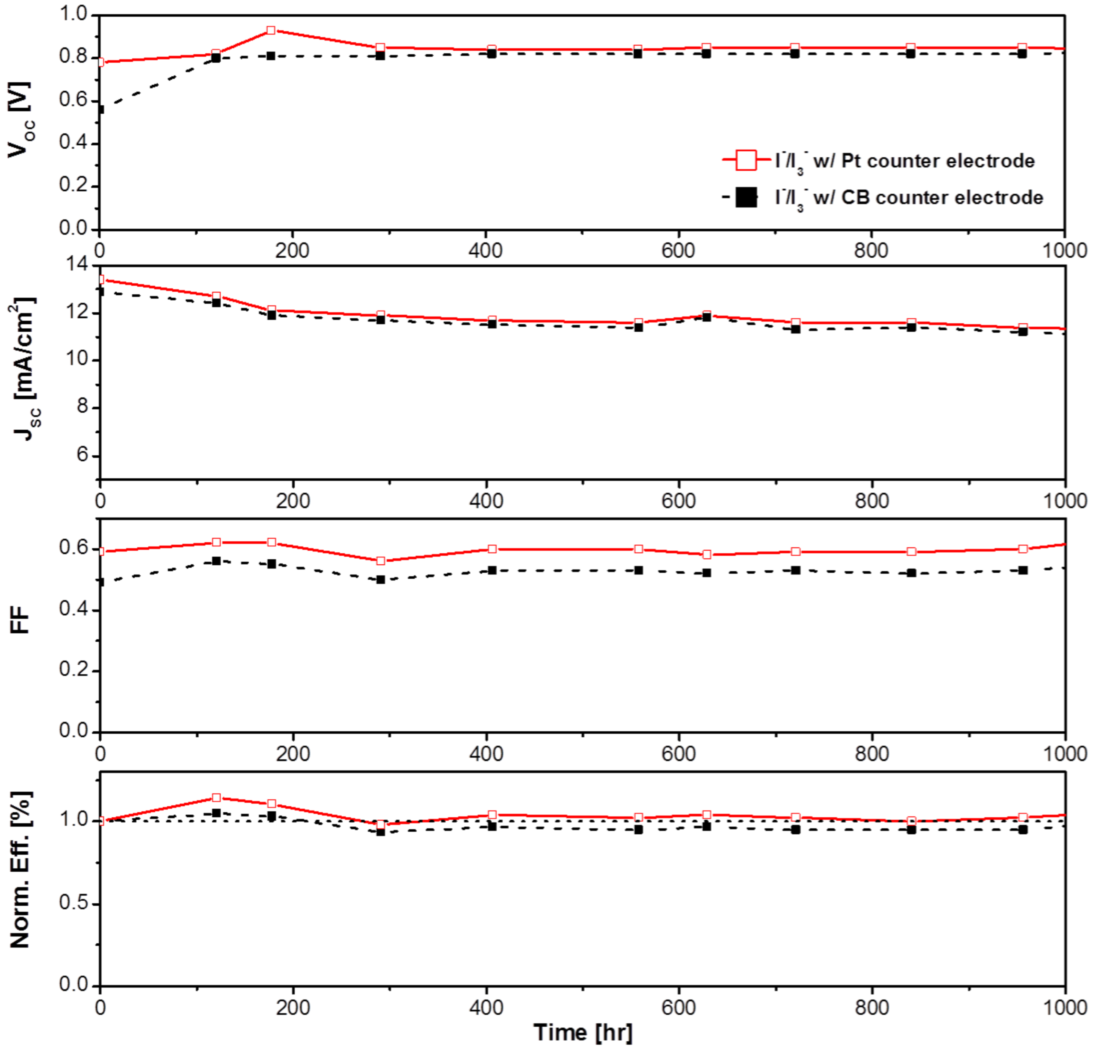

FIGURE S2. THE STABILITY TESTS OF DSCS BASED ON THE I^-/I_3^- ELECTROLYTE WITH PT (SOLID LINE) AND CB (DASHED LINE) COUNTER ELECTRODES OVER 1000 HOURS OF STORAGE IN THE DARK AT ROOM TEMPERATURE.

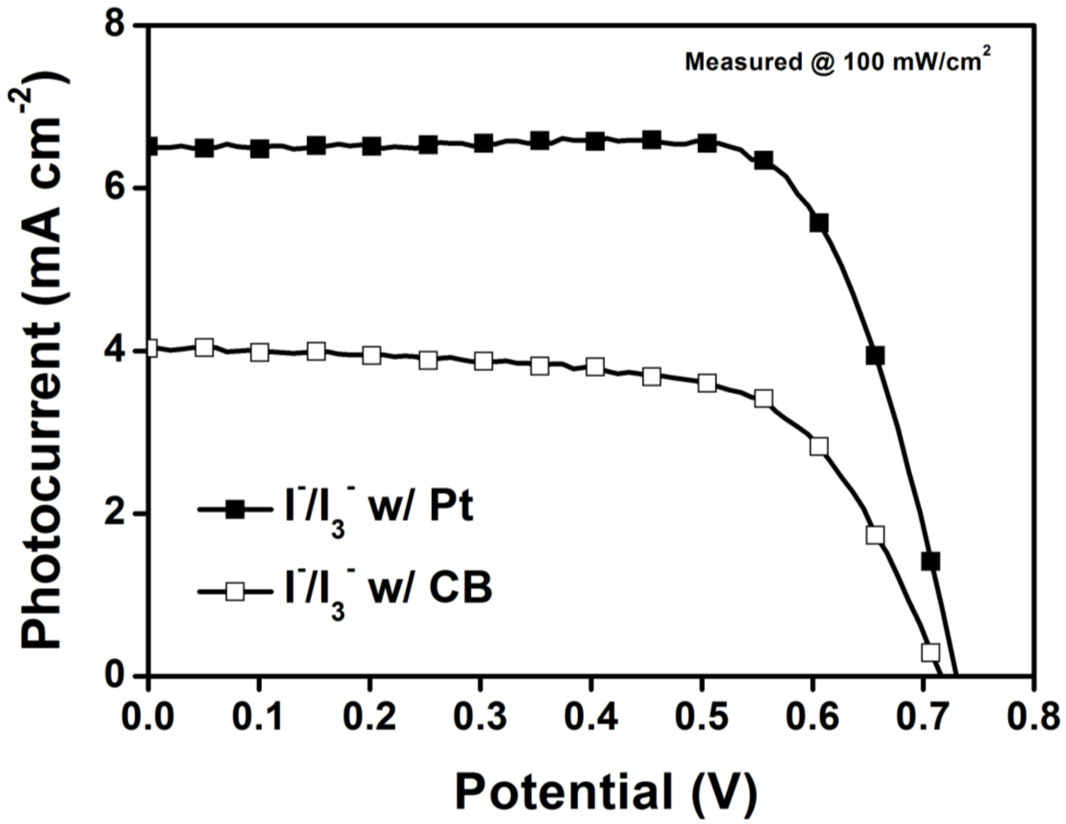

FIGURE S3. *J-V* CHARACTERISTICS OF THE DSCS BASED ON PT AND CB COUNTER ELECTRODES USING THE I^-/I_3^- REDOX COUPLES UNDER AM 1.5 IRRADIATION WITH 100 MW/CM^2. ACTIVE AREA OF THE DEVICES WHEN THE SHADING MASK WAS 0.25 CM^2.

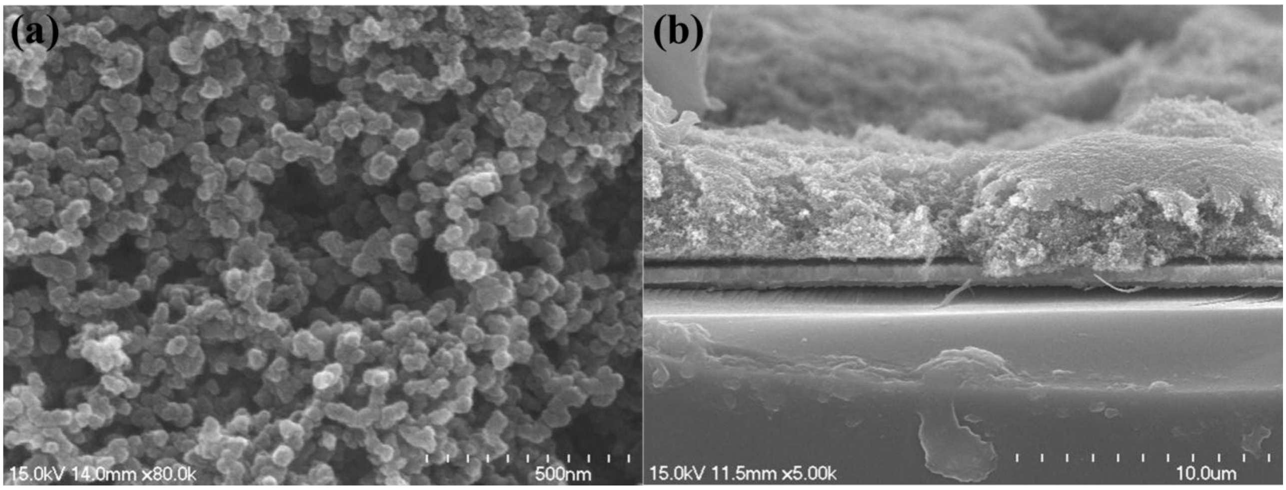

FIGURE S4. SCANNING ELECTRON MICROSCOPY (SEM) IMAGES OF THE CB COUNTER ELECTRODE: (A) TOP VIEW (B) CROSS-SECTIONAL VIEW.

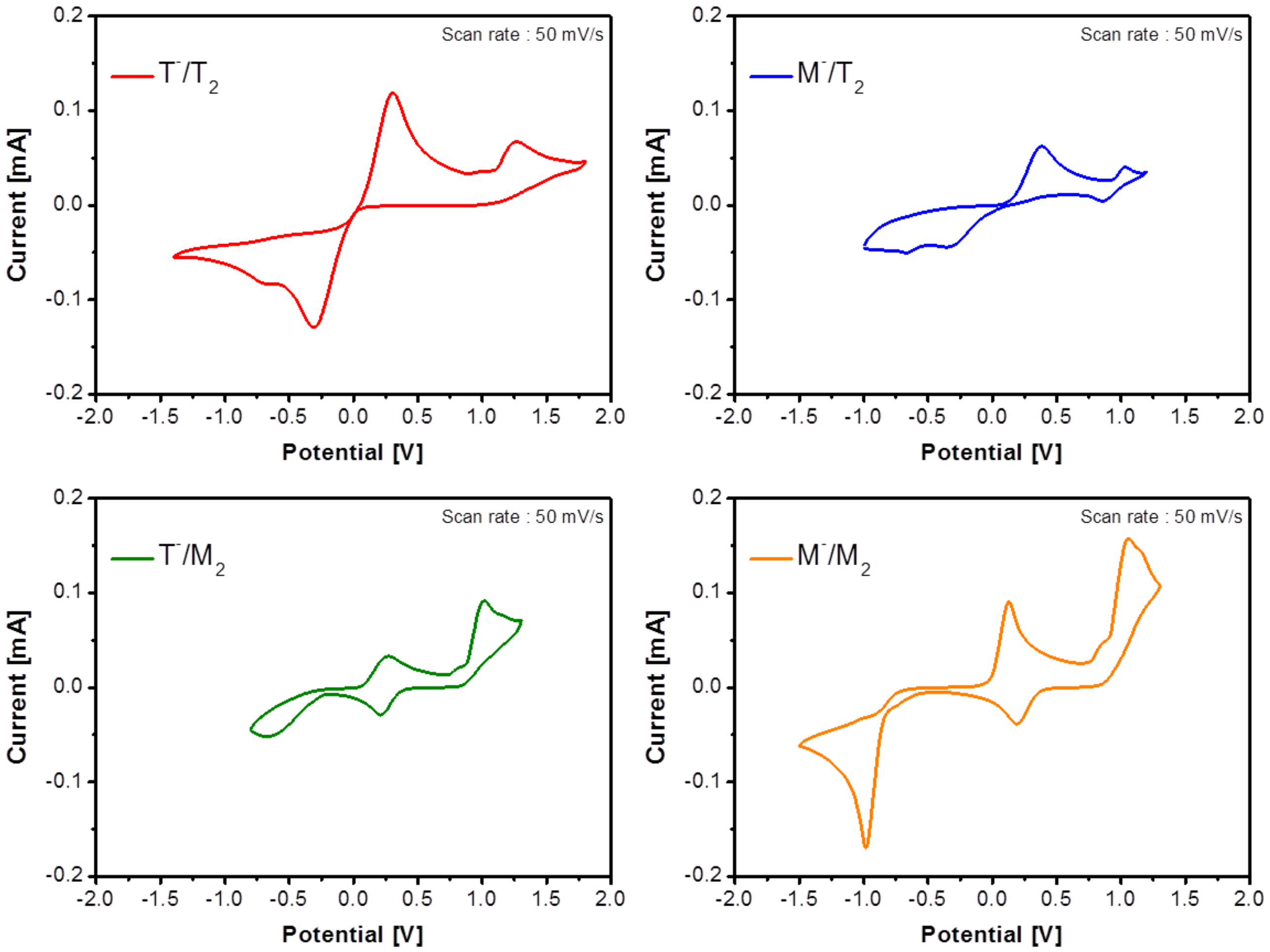

FIGURE S5. CYCLIC VOLTAMMETRY OF THIOLATE/DISULFIDE REDOX COUPLES IN A SOLUTION OF 0.01 M DISULFIDE, 0.01 M THIOLATE AND 0.2 M $LICLO_4$ IN GBL. THE EXPERIMENTS WERE PERFORMED WITH A GLASSY CARBON ELECTRODE AS THE WORKING AND COUNTER ELECTRODE, AND AG/AGCL IN SATURATED KCL AS THE REFERENCE ELECTRODE. THE SCAN RATE WAS 50 MV/S.

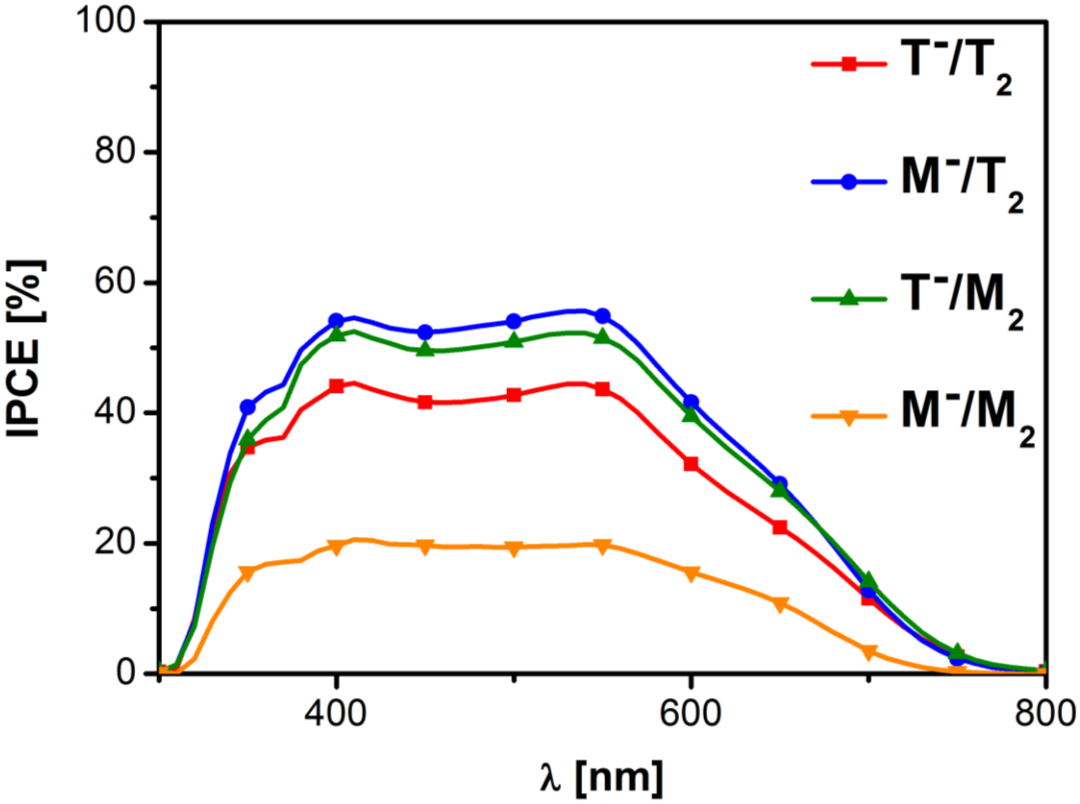

FIGURE S6. INCIDENT PHOTON-TO-CURRENT CONVERSION EFFICIENCY (IPCE) OF DSCS BASED ON CB COUNTER ELECTRODE WITH REDOX COUPLES.

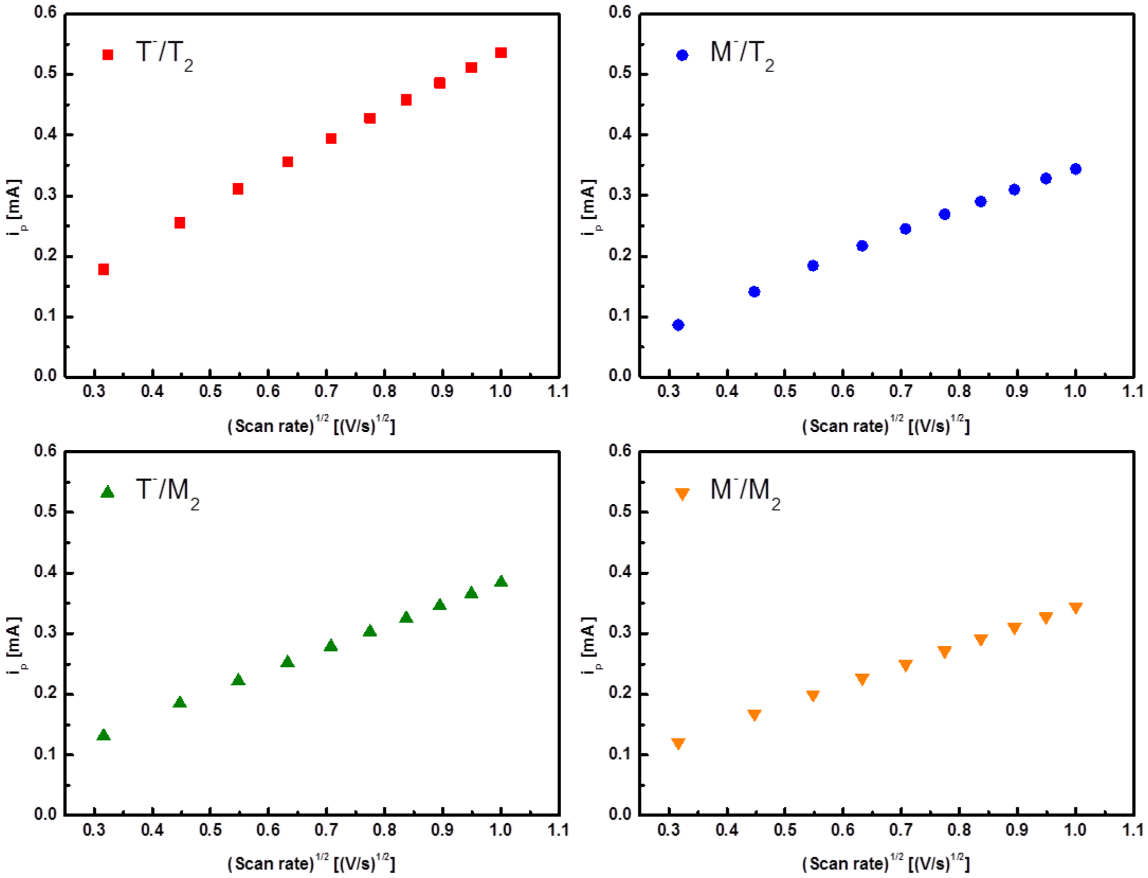

FIGURE S7. PEAK CURRENT WITH (SCAN RATE)$^{1/2}$ IN CYCLIC VOLTAMMETRY USING 0.01 M THIOLATE, 0.01 M DISULFIDE AND 0.2 M $LICLO_4$ IN GBL. THE EXPERIMENTS WERE PERFORMED WITH A GLASSY CARBON ELECTRODE AS THE WORKING AND COUNTER ELECTRODE, AND AG/AGCL IN SATURATED KCL AS THE REFERENCE ELECTRODE. THE SCAN RATE WAS 0.1 TO 1 V/S.

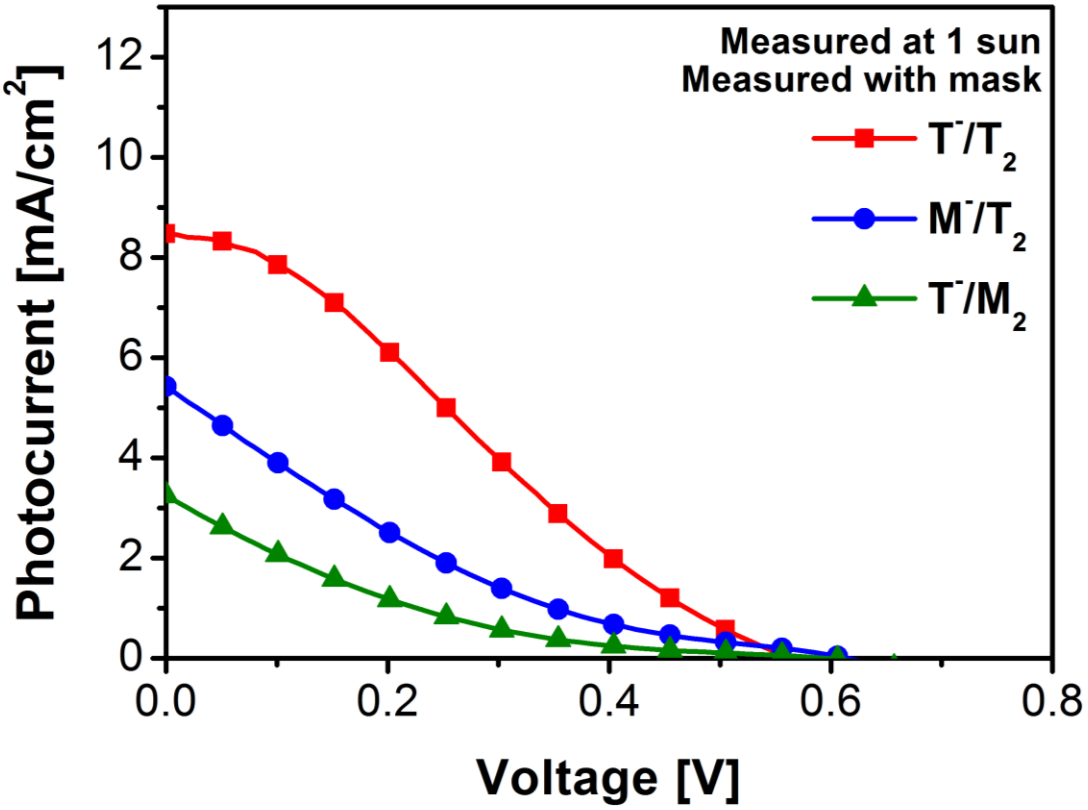

FIGURE S8. *J-V* CHARACTERISTICS OF THE DSCS BASED ON PT COUNTER ELECTRODES USING THE 60 MM SURLYN FOR SPACER UNDER AM 1.5 IRRADIATION WITH 100 MW/CM^2. ACTIVE AREA OF THE DEVICES WHEN THE SHADING MASK WAS 0.25 CM^2.

TABLE S1. ELECTROCHEMICAL PROPERTIES AND DIFFUSION COEFFICIENTS OF THIOLATE/DISULFIDE REDOX COUPLES IN A SOLUTION OF 0.01 M DISULFIDE, 0.01 M THIOLATE AND 0.2 M $LICLO_4$ IN GBL. THE EXPERIMENTS WERE PERFORMED WITH A GLASSY CARBON ELECTRODE AS THE WORKING AND COUNTER ELECTRODE, AND AG/AGCL IN SATURATED KCL AS THE REFERENCE ELECTRODE. THE SCAN RATE WAS 50 MV/S.

	E_{PC}	E_{PA}	E_{REDOX}	E_{REDOX}	DIFFUSION COEFFICIENT OF DISULFIDE
	[V VS. AG/AGCL]			[V VS. NHE]	[X 10^{-5} CM^2/S]
T^-/T_2	0.31	-0.31	0.00	0.20	9.53
M^-/T_2	0.38	-0.35	0.02	0.22	4.99
T^-/M_2	0.27	-0.67	-0.20	0.00	4.73
M^-/M_2	0.13	-0.98	-0.43	-0.23	3.71

*E_{PC}: CATHODIC PEAK POTENTIAL, E_{PA}: ANODIC PEAK POTENTIAL, E_{REDOX}: REDOX POTENTIAL

TABLE S2. PHOTOVOLTAIC PARAMETERS OF DSCS WITH THE COMBINATION OF I^-/I_3^- WITH COUNTER ELECTRODES AT 1 SUN ILLUMINATION

COUNTER ELECTRODE	J_{SC}/MACM^{-2}	V_{OC}/V	*FF*	*H* (%)
PT	6.5	0.73	0.75	3.5
CB	4.0	0.72	0.66	1.9

TABLE S3. PHOTOVOLTAIC PARAMETERS OF DSCS WITH THE COMBINATION OF THIOLATE/DISULFIDE USING PT COUNTER ELECTRODES WITH 60 MM SURLYN FOR SPACER AT 1 SUN ILLUMINATION

DEVICES	J_{SC}/MACM^{-2}	V_{OC}/V	*FF*	*H* (%)
T^-/T_2	8.5	0.57	0.27	1.3
M^-/T_2	5.4	0.62	0.15	0.5
T^-/M_2	3.2	0.60	0.13	0.2
M^-/M_2	-	-	-	-

REFERENCE

1. M. WANG, N. CHAMBERLAND, L. BREAU, J.-E. MOSER, R. HUMPHRY-BAKER, B. MARSAN, S. M. ZAKEERUDDIN AND M. GRÄTZEL, *NAT. CHEM.*, 2010, **2**, 385-389.
2. J. KRÜGER, R. PLASS, M. GRÄTZEL, P. J. CAMERON AND L. M. PETER, *THE JOURNAL OF PHYSICAL CHEMISTRY B*, 2003, **107**, 7536-7539.
3. L. R. F. ALLEN J. BARD, *ELECTROCHEMICAL METHODS, FUNDAMENTAL AND APPLICATIONS*, WILEY: NEW YORK, 2001.