Supporting Information

Highly Efficient Dye-Sensitized Solar Cell Based on a Ruthenium Sensitizer Bearing a Hexylthiophene Modified Terpyridine Ligand

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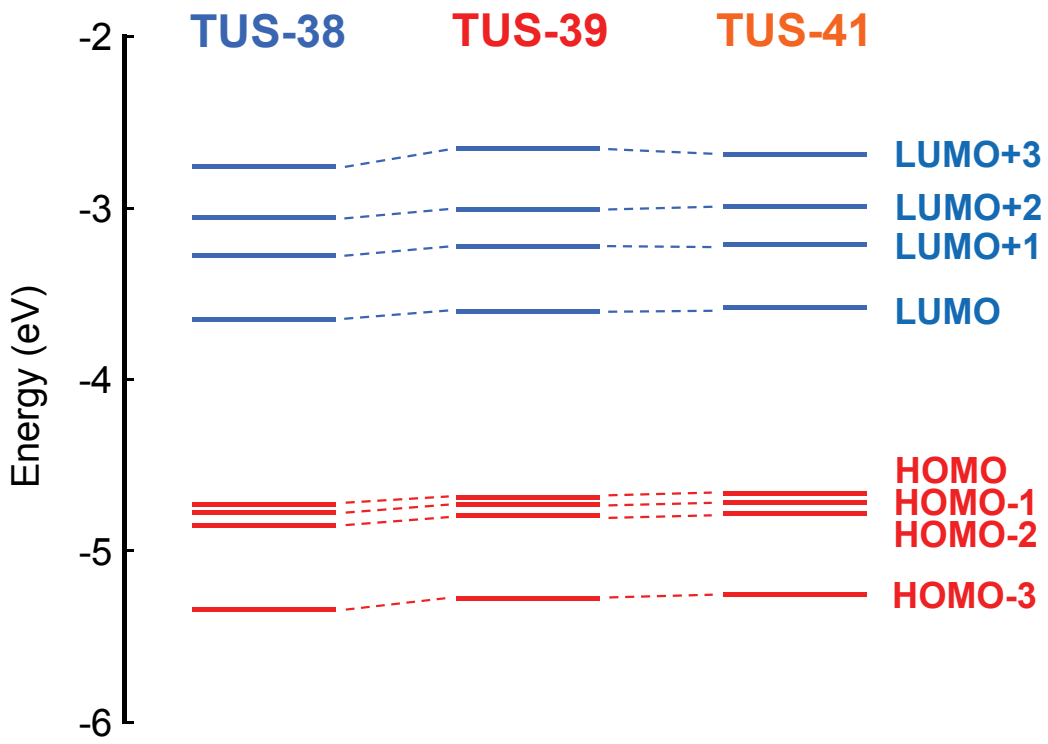

Figure S1. Energy diagrams of the frontier molecular orbitals of a fully optimized structure of **TUS-38**, **TUS-39**, and **TUS-41** in acetonitrile.

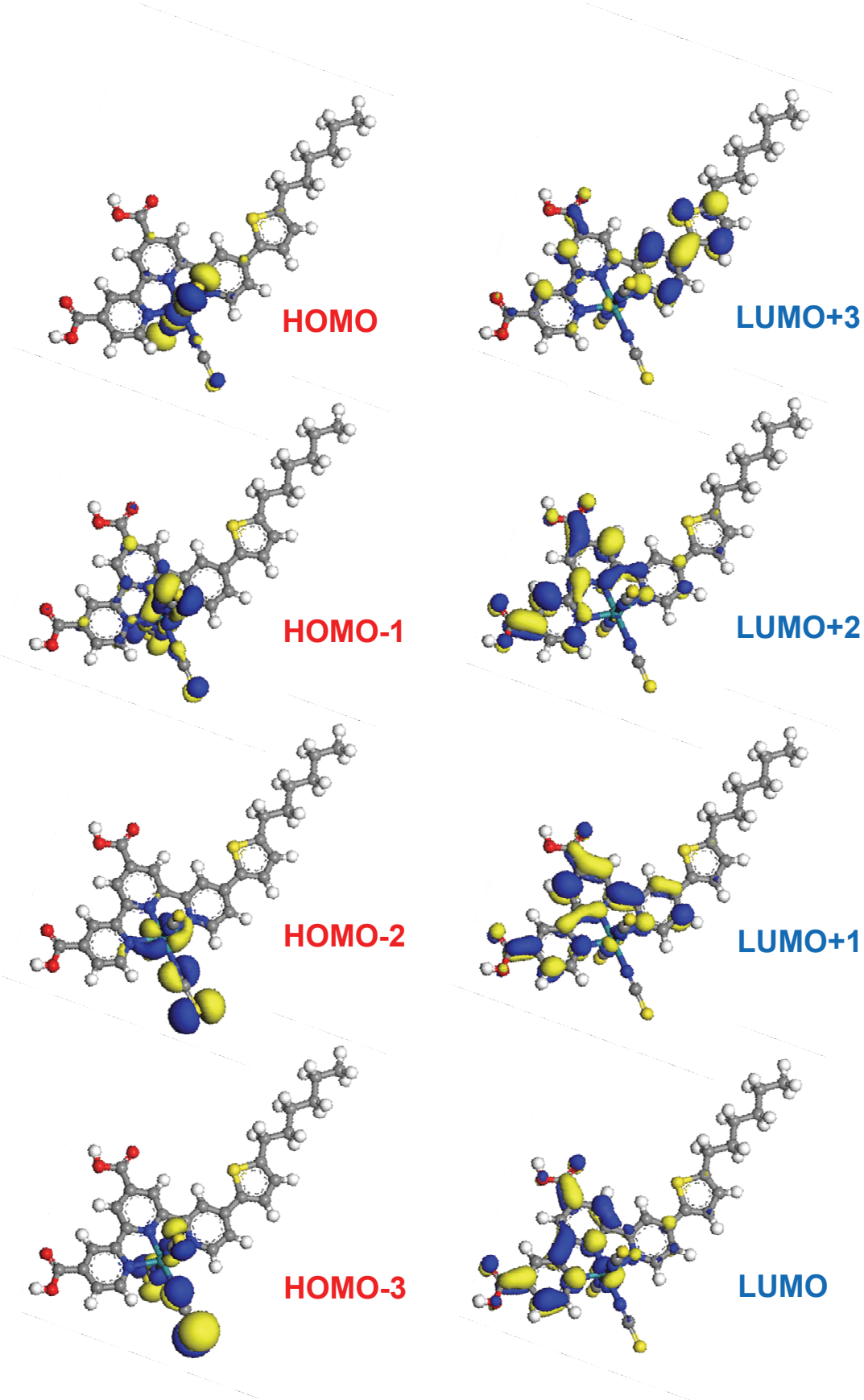

Figure S2. Frontier molecular orbitals (occupied and unoccupied MOs) of a fully optimized structure of **TUS-38** in acetonitrile.

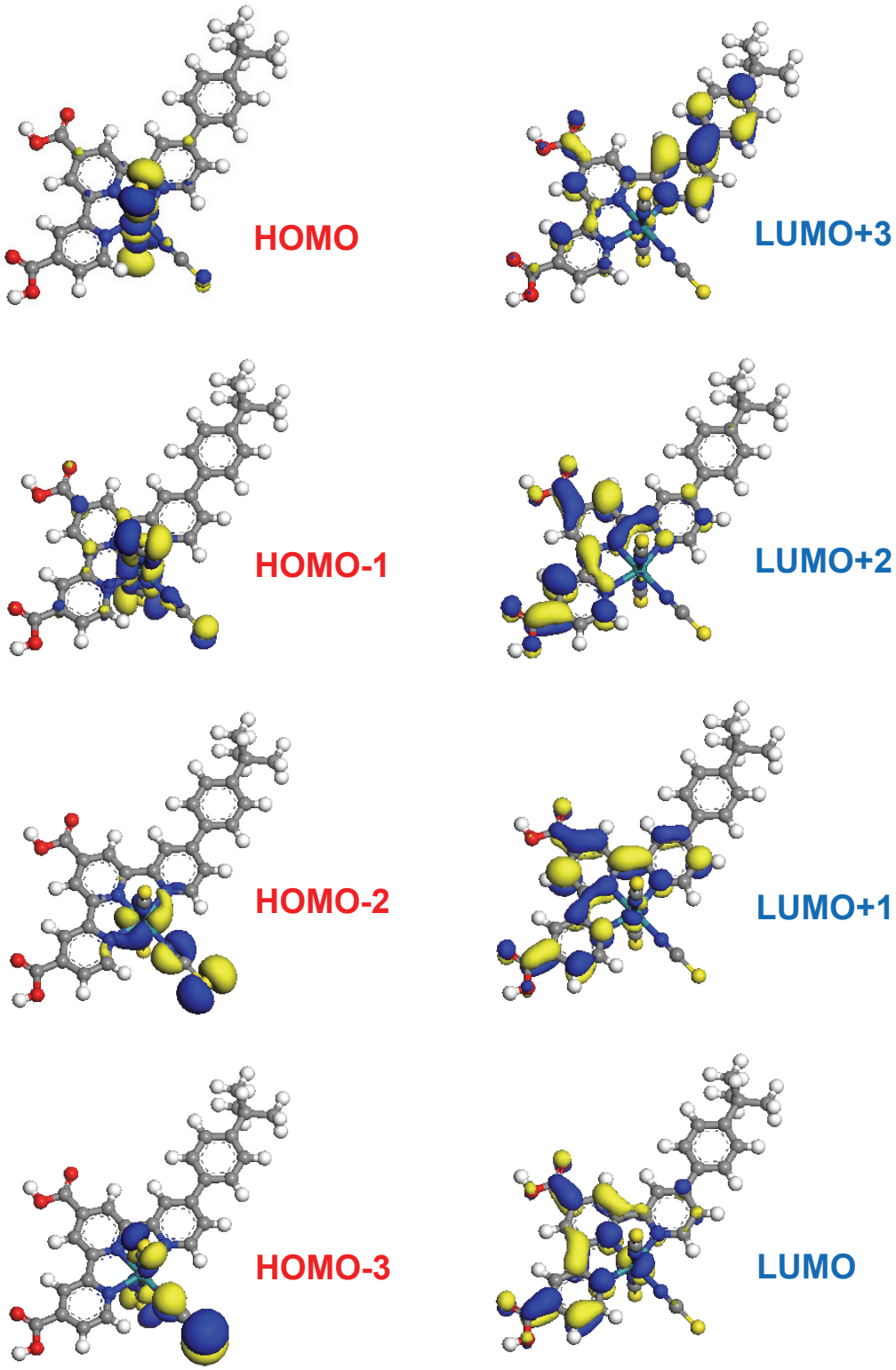

Figure S3. Frontier molecular orbitals (occupied and unoccupied MOs) of a fully optimized structure of **TUS-39** in acetonitrile.

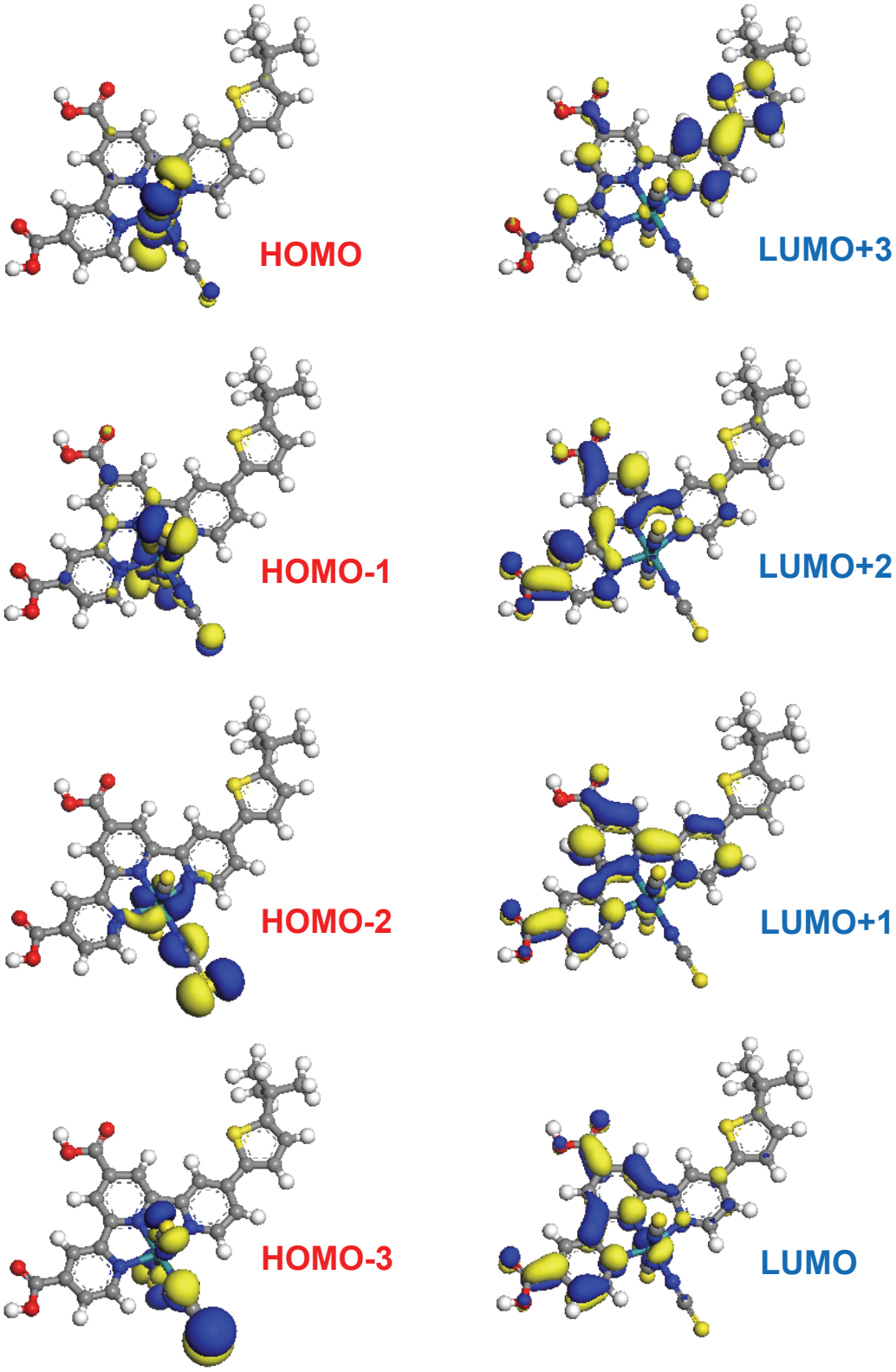

Figure S4. Frontier molecular orbitals (occupied and unoccupied MOs) of a fully optimized structure of **TUS-41** in acetonitrile.

Preparation of the TiO_2 photoelectrodes and the DSCs

TiO_2 pastes were prepared using titanium(IV) tetraisopropoxide.[1] Nanocrystalline TiO_2 photoelectrodes were prepared by screen printing the TiO_2 paste on fluorine-doped SnO_2 conducting glasses (FTO, Nippon Sheet Glass Co., 10 Ω/square). TiO_2 thin films were composed of seven layers (from the bottom to the third layer: 20 nm TiO_2 particles, the fourth and the fifth layers: a 8:2 mixture of 20 nm and 100 nm particles, the sixth layer: a 6:4 mixture of 20 nm and 100 nm particles, and the top layer: 400 nm TiO_2 particles; film thickness: approximately 40 μm).[2] TiO_2 photoelectrodes were calcinated at 520 °C after each layer was coated. The active areas of these TiO_2 photoelectrodes were determined by a KEYENCE VHX-200 digital microscope (0.25~0.26 cm^2). **TUS-38**, **TUS-39**, **TUS-41** and Black dye were dissolved in a 1-propanol solution at the concentration of 0.2 mM, which contains 20 mM DCA as a coadsorbent.[3] TiO_2 photoelectrodes were immersed in this dye-adsorption solvent for 24 h at 20 ºC, 4 ºC, and -18 ºC to adsorb the dye onto the TiO_2 surface. Photoelectrochemical measurements were performed in a two-electrode sandwich cell configuration made up of the dye-adsorbed TiO_2 photoelectrode, a platinum-sputtered counter electrode, a spacer film (50 μm), and an electrolyte solution (an acetonitrile solution containing 0.05 M I_2, 0.1 M LiI, 0.6 M DMPImI and 0.3 M TBP; an acetonitrile solution containing 0.05 M I_2, 0.02 M LiI, 0.6 M EMImI and 0.3 M TBP). All adsorbed dyes were desorbed from the TiO_2 photoelectrodes by immersing into a NaOH solution (0.05 M). The amount of dye adsorption was estimated from the absorption spectrum of the resulting solution.

The photocurrent-voltage (*I-V*) characteristics of the DSCs were measured on a Keithley 2400 source meter under irradiation of AM 1.5, 100 mW/cm^2 (1 sun) supplied by a solar simulator (Yamashita Denso, YSS-150A). The incident light intensity was calibrated with a grating spectroradiometer LS-100 (EKO Instruments) and a reference Si solar cell equipped with a heat absorbing filter (BS520-BK, Bunko Keiki). The incident monochromatic photon-to-current conversion efficiency (IPCE) was measured on a PEC-S10 (Peccell Technologies). Electrochemical impedance spectroscopic (EIS) studies were conducted using an electrochemical interface SI 1287 (Solartron) and a frequency response analyzer 1255B (Solartron).

Table S1. Solar cell performances of the DSCs with **TUS-38**, **TUS-39**, **TUS-41**, and Black dye[a]

sensitizer	*J*sc [mA/cm^2]	*V*oc [V]	*FF*	η [%]	Amount of dye adsorption [$\times 10^{-7}$ mol/cm^2]
TUS-38	23.56	0.664	0.692	10.83	1.8
	24.34	0.666	0.673	10.91	1.8
	23.69	0.666	0.680	10.73	1.9
	23.54	0.657	0.702	10.86	1.8
TUS-38[b]	23.88	0.674	0.688	11.07	1.7
	24.01	0.672	0.688	11.10	1.7
	23.30	0.679	0.691	10.93	1.4
TUS-39	22.62	0.631	0.661	9.43	1.7
	21.54	0.636	0.695	9.52	1.6
	22.13	0.638	0.678	9.57	1.6
	22.48	0.626	0.667	9.39	1.6
TUS-39[b]	22.82	0.641	0.665	9.73	1.5
	22.28	0.649	0.658	9.53	1.4
TUS-41	22.20	0.626	0.679	9.44	1.5
	21.73	0.628	0.697	9.51	1.5
	21.07	0.645	0.688	9.35	1.5
	21.99	0.645	0.687	9.74	1.5
TUS-41[b]	22.47	0.636	0.680	9.72	1.3
	21.74	0.651	0.686	9.71	1.3
	22.64	0.649	0.676	9.93	1.3
Black dye	22.11	0.691	0.715	10.92	2.1
	21.52	0.694	0.724	10.81	2.1
	22.34	0.690	0.713	10.99	2.1
	23.10	0.680	0.695	10.92	2.1
Black dye[b]	21.83	0.689	0.726	10.92	1.8
	22.46	0.685	0.713	10.97	1.9
	22.45	0.679	0.701	10.69	1.7
	22.22	0.683	0.704	10.69	1.8

[a] The electrolyte was an acetonitrile solution containing 0.05 M I_2, 0.1 M LiI, 0.6 M DMPImI and 0.3 M TBP. TiO_2 film thickness and active area were ca. 40 μm and 0.26 cm^2, respectively. Irradiation was carried out by using a solar simulator (AM 1.5, 100 mW/cm^2). [b] Solar cell performances of the DSCs, where dye adsorption to the TiO_2 photoelectrode was carried out at 4 ºC.

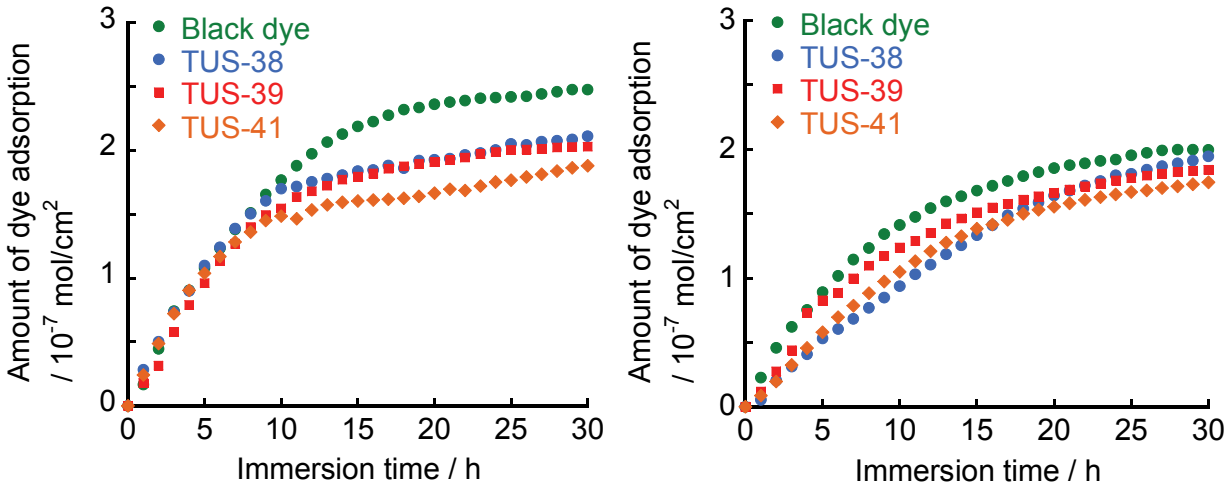

Figure S5. Adsorption profiles of **TUS-38**, **TUS-39**, **TUS-41** and **Black dye** to the TiO_2 photoelectrode at 20 ºC (left), and at 4 ºC (right). The concentration of each dye-adsorption solvent (1-propanol) is 0.2 mM, which contains 20 mM DCA as a coadsorbent. The film thickness and active area of the TiO_2 photoelectrode are approximately 40 μm and 0.26 cm^2, respectively.

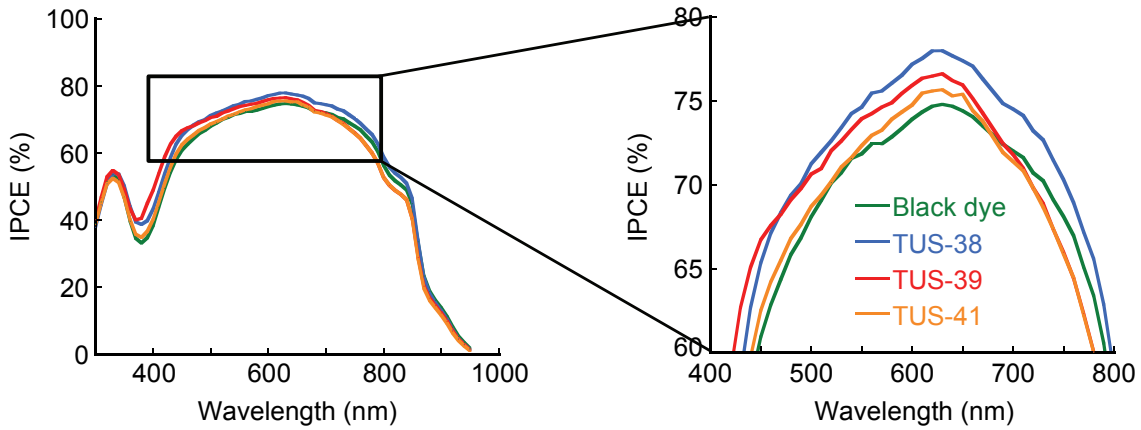

Figure S6. IPCE spectra of the DSCs with **TUS-38**, **TUS-39**, **TUS-41** and **Black dye**.

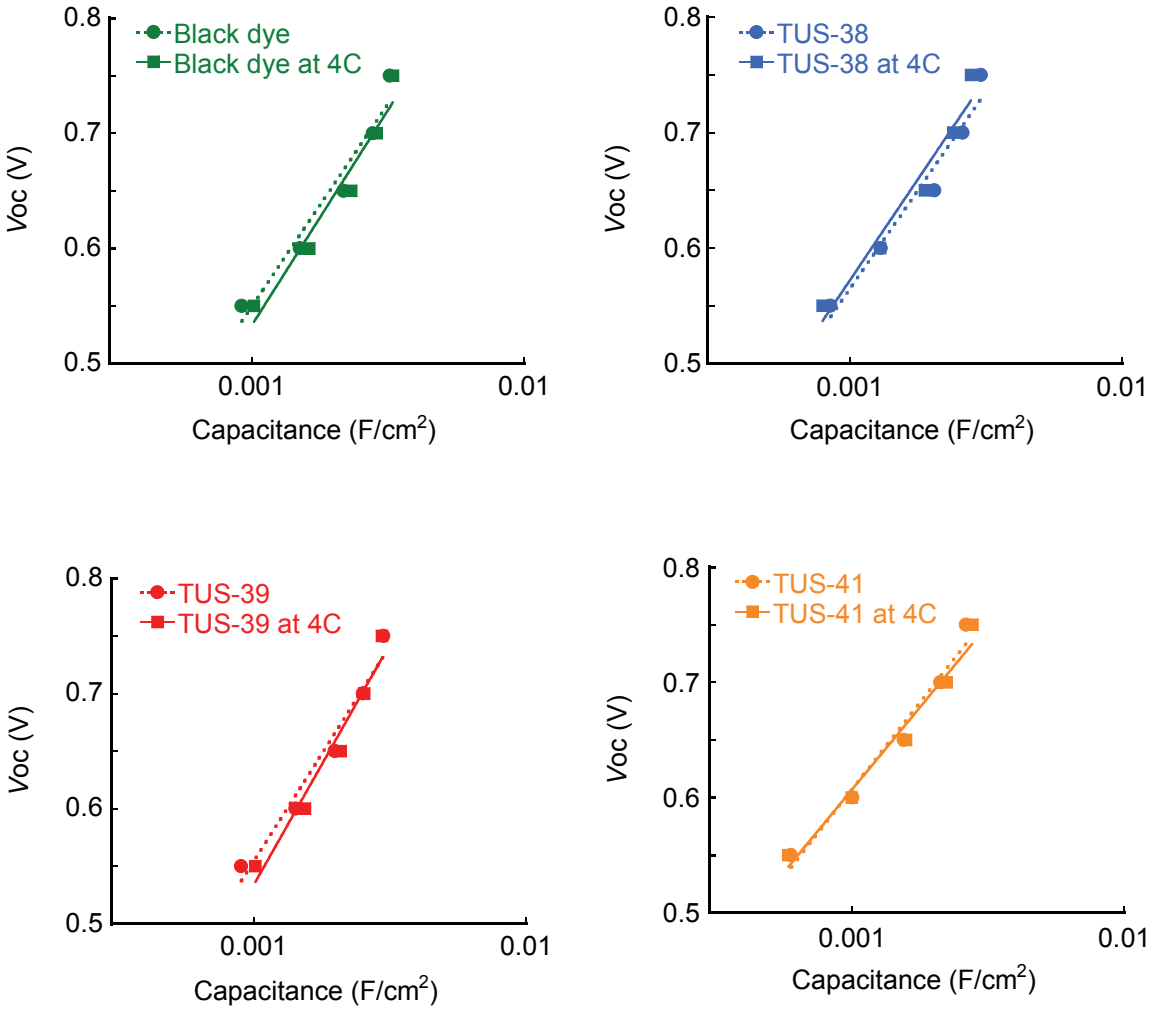

Figure S7. *V*oc as a function of capacitance of the DSCs with **TUS-38**, **TUS-39**, **TUS-41** and **Black dye**.

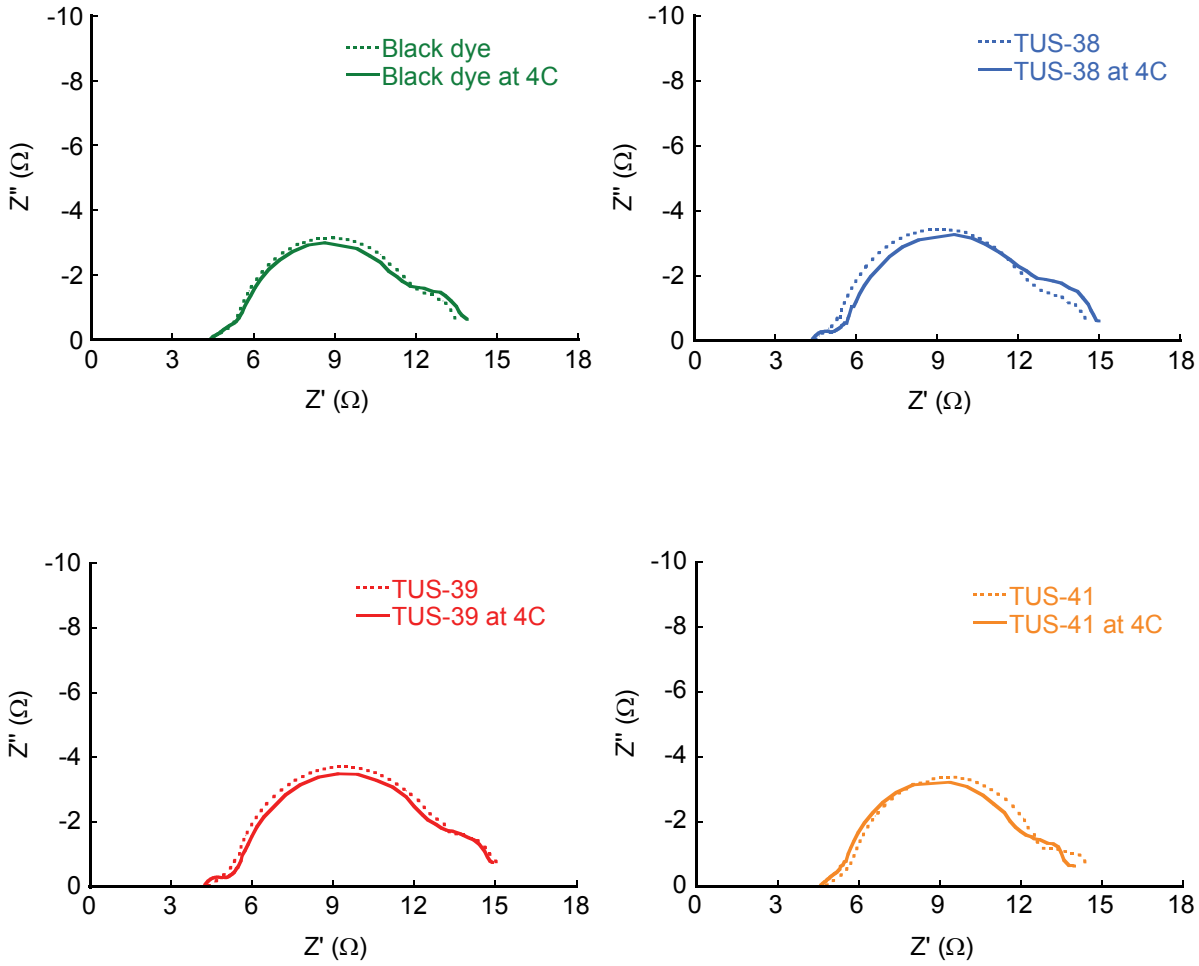

Figure S8. Nyquist plots of the DSCs with **TUS-38**, **TUS-39**, **TUS-41** and **Black dye** under AM 1.5 (100 mW/cm^2) irradiation and the open-circuit conditions.

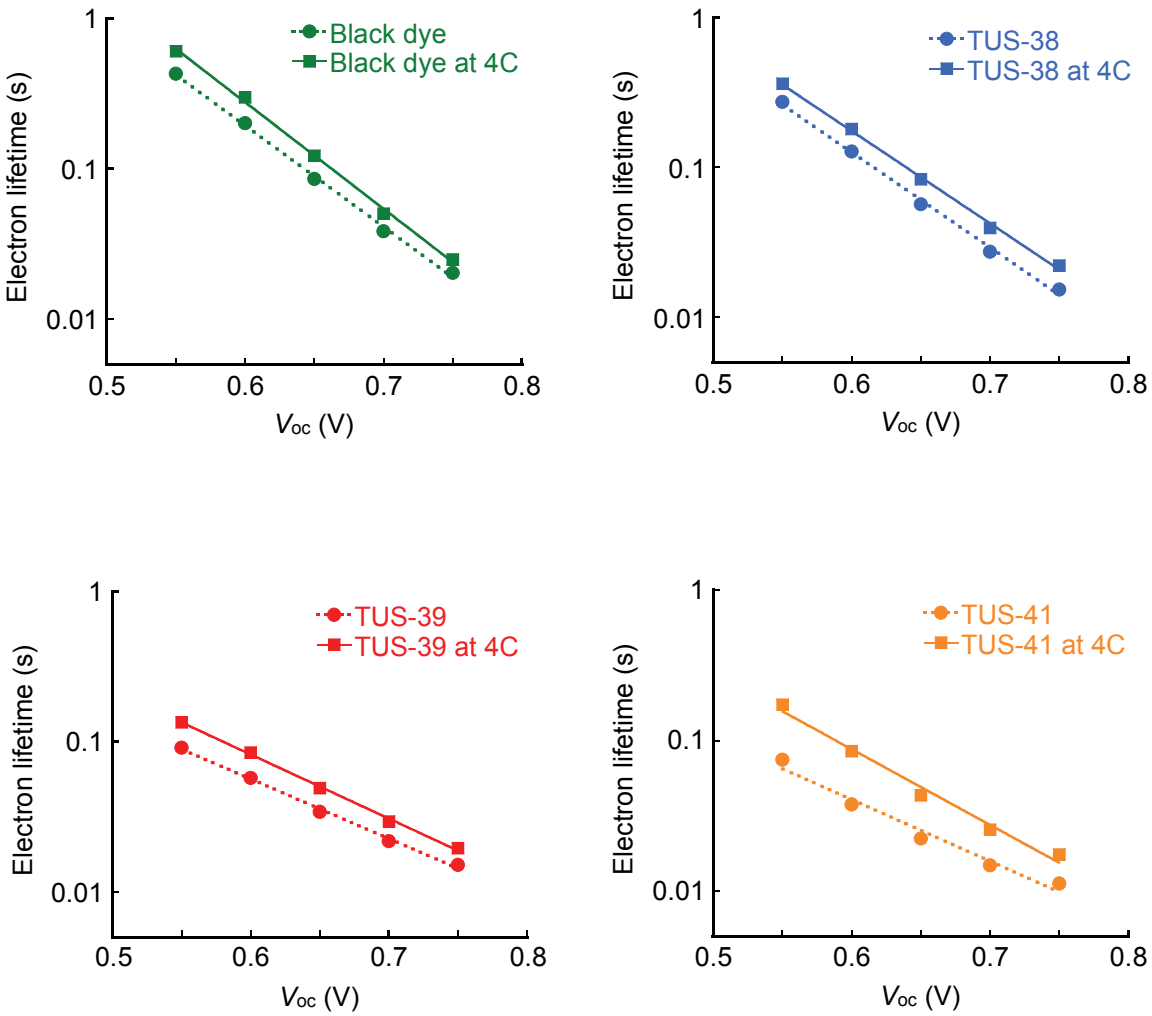

Figure S9. Electron lifetime in the TiO_2 photoelectrode as a function of *V*oc of the DSCs with **TUS-38**, **TUS-39**, **TUS-41**, and Black dye.

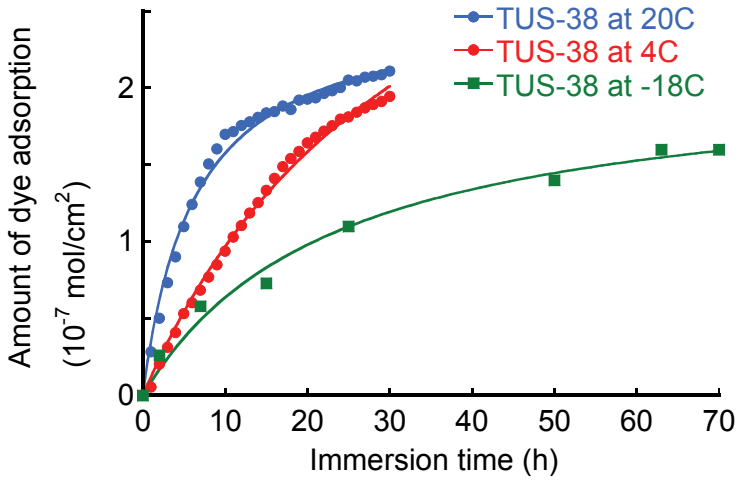

Figure S10. Adsorption profiles of **TUS-38** to the TiO_2 photoelectrodes at 20 ºC, 4 ºC, and -18 ºC using 1-propanol as a dye-adsorption solvent. The concentration of dye-adsorption solvent (1-propanol) is 0.2 mM, which contains 20 mM DCA as a coadsorbent. The film thickness and active area of the TiO_2 photoelectrode are approximately 40 μm and 0.26 cm^2, respectively.

Table S2. Solar cell performances of the DSCs with **TUS-38**[a]

Dye	J_{sc} (mA/cm^2)	V_{oc} (V)	*FF*	η (%)	Amount of dye adsorption (x 10^{-7} mol/cm^2)
TUS-38(20 °C)	24.05	0.632	0.686	**10.43**	1.9 (24 h immersion)
	24.29	0.630	0.676	**10.34**	1.9 (24 h immersion)
TUS-38(4 °C)	22.94	0.667	0.702	**10.74**	1.6 (24 h immersion)
	23.68	0.654	0.691	**10.70**	1.7 (24 h immersion)
	23.58	0.651	0.691	**10.61**	1.6 (24 h immersion)
TUS-38(-18 °C)	23.02	0.660	0.692	**10.51**	1.3 (50 h immersion)
	22.54	0.665	0.707	**10.60**	1.4 (50 h immersion)
TUS-38(-18 °C)	23.28	0.669	0.692	**10.78**	1.6 (70 h immersion)
	22.71	0.672	0.695	**10.61**	1.7 (70 h immersion)

[a]The electrolyte was an acetonitrile solution containing 0.05 M I_2, 0.1 M LiI, 0.6 M DMPImI, and 0.3 M TBP (TiO_2 film thickness: 40 μm, active area: 0.26 cm^2). Irradiation was carried out by a solar simulator (AM 1.5, 100 mW/cm^2).

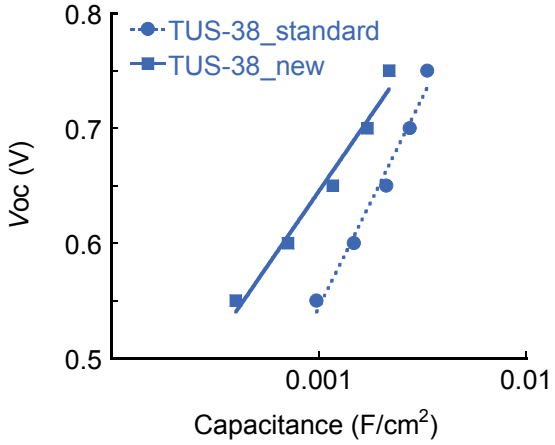

Figure S11. *V*oc as a function of capacitance of the DSCs with **TUS-38** using two kinds of electrolyte solutions. Dye adsorption to the TiO_2 photoelectrodes was carried out at 4 ºC.

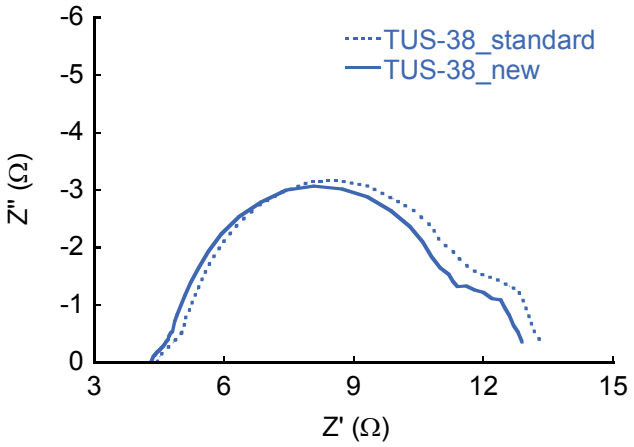

Figure S12. Nyquist plots of the DSCs with **TUS-38** using two kinds of electrolyte solutions under AM 1.5 (100 mW/cm^2) irradiation and the open-circuit conditions. Dye adsorption to the TiO_2 photoelectrode was carried out at 4 ºC.

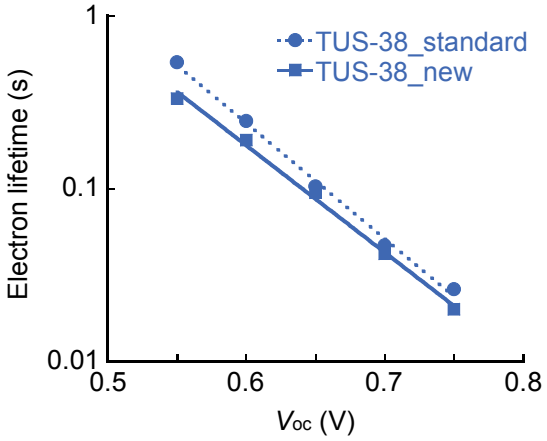

Figure S13. Electron lifetimes in the TiO_2 photoelectrode as a function of *V*oc of the DSCs with **TUS-38** using two kinds of electrolyte solutions. Dye adsorption to the TiO_2 photoelectrode was carried out at 4 ºC.

References

[1] M. K. Nazeeruddin, P. Péchy, T. Renouard, S. M. Zakeeruddin, R. Humphyry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi, *J. Am. Chem. Soc.,* **2001**, *123*, 1613-1624.

[2] (a) H. Ozawa, K. Fukushima, A. Urayama, H. Arakawa, *Inorg. Chem.*, **2015**, *54*, 8887-8889. (b) H. Ozawa, Y. Yamamoto, H. Kawaguchi, R. Shimizu, H. Arakawa, *ACS Appl. Mater. Interfaces*, **2015**, *7*, 3152-3161. (c) H. Ozawa, T. Sugiura, R. Shimizu, H. Arakawa, *Eur. J. Inorg. Chem.*, **2014**, 4734-4739. (d) H. Ozawa, T. Sugiura, R. Shimizu, H. Arakawa, *Inorg. Chem.*, **2014**, *53*, 9375-9384. (e) H. Ozawa, K. Fukushima, T. Sugiura, A. Urayama, H. Arakawa, *Dalton Trans.*, **2014**, *43*, 13208-13218. (f) H. Ozawa, Y. Okuyama, H. Arakawa, *ChemPhysChem*, **2014**, *15*, 1201-1206.

[3] H. Ozawa, M. Awa, T. Ono, H. Arakawa, *Chem. Asian J.*, **2012**, *7*, 156-162.