Supplementary Information: **From Black Pigment to Green Energy: Shedding Light on Melanin Electrochemistry in Dye-Sensitized Solar Cells**

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Melanin-DSSC fabrication

The fluorine-doped tin oxide (FTO) conducting glass (Nippon Sheet Glass Co., Ltd.) was sonicated for 15 minutes each in the sequence of deionized water, acetone, and ethanol. Following sonication, the FTO glass was exposed to ultraviolet/O_3 for 20 minutes, and subsequently immersed in a 40 mM $TiCl_4$ aqueous solution at 70 °C for 30 min in an oven to form a blocking TiO_2 compact layer. The 0.16 cm^2 (0.4 × 0.4 cm^2) TiO_2 photoactive layer was prepared by depositing the opaque TiO_2 pastes (18 NR-AO, Greatcell Solar Limited) containing dispersed scattering particles via the screen-printing method (MESH S/T250, Emulsion 12 μM). The screen-printed TiO_2 photoanode was subjected to sequential sintering processes at the following temperatures and durations: 150 °C for 10 min, 325 °C for 5 min, 375 °C for 5 min, 450 °C for 15 min, and 500 °C for 30 min. After the sintering process, the TiO_2 photoanode was immersed in the 40 mM $TiCl_4$ aqueous solution at 70 °C for 15 min in the oven and then washed with DI water and ethanol, followed by a second sintering process at 500 °C for 30 minutes. The mesoporous TiO_2 photoanodes were dipped in a melanin solution, which was prepared by dissolving 10 mg of synthetic eumelanin (Sigma-Aldrich) in a 20 mL binary solvent of DMSO and methanol (volume ratio, 1:19), for 16 hours at room temperature. For the fabrication of counter electrodes, holes for electrolyte injection were drilled into the FTO glasses using a hand drill, and the subsequent washing process was identical to that of the photoanode. For I^-/I_3^- electrolyte application, the cleaned glasses were coated with 10 mM $H_2PtCl_6 \cdot 6H_2O$ (~40% Pt, Sigma-Aldrich) ethanol solution, and then subjected to sintering at 400 °C for 20 minutes. In the case of $Co^{(3+/2+)}(bpy)_3$ or $Cu^{(2+/1+)}(tmby)_2$ electrolyte utilization, poly(3,4-ethylenedioxythiophene) (PEDOT) was deposited on the cleaned glass by supplying 0.5 mA for 30 seconds in an acetonitrile solution containing 0.01 M of 3,4-ethylenedioxythiophene (EDOT, 97%, Aldrich) and 0.1 M of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 98+%, Fisher Scientific Korea Ltd.). The 25 μm thick Surlyn films (Meltonix 1170-25, Solaronix) were used to integrate the prepared photo and counter electrodes into the sandwich-

type cells, which were pressed at 110 °C to seal. The iodine electrolyte was injected into the vacant space of the sandwich cells by vacuum back-filling through the hole in the counter electrode, and then the hole was enclosed with the Surlyn films and a cover glass.

Electrolyte preparation

The iodine electrolyte (I^-/I_3^-) was prepared in a mixed sovlent of acetonitrile and valeronitrile (volume ratio, 85:15) with 0.055 M I_2 (≥99.8% Aldrich), 0.5 M 4-tert-butylpridine (96%, Aldrich), 0.6 M 1,2-dimethyl-3propylimidazolium iodide (DMPII, Solaronix), 0.05 M guanidine thiocyanate (≥97%, Aldrich), and 0.025 M LiI (99.9% trace metals basis, Aldrich). The cobalt electrolyte ($Co^{(3+/2+)}(bpy)_3$) was synthesized following the procedure outlined in the 'Synthesis of cobalt complexes' section of the Supporting Information, utilizing 0.25 M $Co^{2+}(bpy)_3(PF_6)_2$, 0.02 M $Co(bpy)_3(PF_6)_3$, 0.1 M LiTFSI (98+%, Alfa Aesar), and 0.5 M 4-tert-butylpyridine in acetonitrile (Sigma-Aldrich). The copper electrolyte ($Cu^{(2+/1+)}(tmby)_2$) was prepared in an acetonitrile solution, comprising 0.2 M $Cu^{1+}(tmby)_2$TFSI (bis-(4,4',6,6'-tetramethyl-2,2'-bipyridine)copper(I) bis(trifluoromethanesulfonyl)imide, Dyenamo, DN-Cu09), 0.09 M $Cu^{1+}(tmby)_2(TFSI)_2$ (bis-(4,4',6,6'-tetramethyl-2,2'-bipyridine)copper(II) bis[bis(trifluoromethanesulfonyl)imide, Dyenamo, DN-Cu10), 0.6 M 4-tert-butylpyridine (96%, Aldrich), and 0.1 M LiTFSI (98+%, Alfa Aesar).

Synthesis of cobalt complexes

For the cobalt electrolyte ($Co^{(3+/2+)}(bpy)_3$) synthesis, $CoCl_2·6H_2O$ (98%, Alfa Aesar), 2,2'-bipyridine (99%, Alfa Aesar), NH_4PF_6 (99.5%, Alfa Aesar), and $NOPF_6$ (96%, Alfa Aesar) were used in the molar ratio of 1:3:4:1.2, respectively. $CoCl_2·6H_2O$ and 2,2-bipyridine were added to degassed methanol under N_2 and the mixture was stirred for 2 hours. NH_4PF_6 was added to the mixture and the resulting solution was filtered to obtain a solid product. The filtered

product was washed successively with diethyl ether, methanol, and ethanol, and subsequently dried under vacuum, and the resulting complex was utilized without undergoing any additional purification.

For synthesizing $Co^{3+}(bpy)_3(PF_6)_3$, $NOPF_6$ was added dropwise to an acetonitrile solution with $Co^{2+}(bpy)_3(PF6)_2$ and the solution was stirred for 30 minutes under N_2 conditions. The resulting mixture was evaporated via a rotary evaporator and then the small volume of acetonitrile for redissolving and diethyl ether for precipitating were added. The precipitated compound was filtered, washed with methanol, and finally dried under vacuum. The resulting complex was utilized without any additional purification.

Photoelectrochemical Measurements

The class AAA solar simulator system equipped with a 150 W xenon arc lamp (PEC-L01, Peccell) was calibrated to a 100 mW/cm^2 (standard AM 1.5G condition) using a PEC-SI01 (Peccell) Si reference cell certified by Bunkoukeiki, before starting solar measurements. The photoelectrochemical properties including J-V or dark characteristics were conducted using a potentiostat/galvanostat (Vertex, Ivium Technologies). The PEIPCE120 system (HS Technologies) was employed to investigate the IPCE of the fabricated melanin-DSSCs. An IPCE system, comprising of an AM 1.5G solar simulator equipped with a 150 W xenon arc lamp (Abet Technologies), splitting system, and potentiostat/galvanostat (Vertex, Ivium Technologies) was employed without additional background light. During IPCE measurements, the AM 1.5G condition was calibrated using a standard PEC-SI02 (Peccell) Si reference cell certified by Bunkoukeiki. EIS was measured with a direct current (DC) forward bias using a potentiostat/galvanostat (Vertex, Ivium Technologies) without additional background light. The perturbation amplitude was set at 10 mV within a frequency range from 10^6 to 10^{-1} Hz, and

ZView software (Scribner Associates, Inc.) was used for fitting the obtained Nyquist plots with appropriate equivalent circuits.

Stability Test

For the 1 sun light stability test, the certificated class ABA LED solar simulator (LSH-7320, Newport) was employed. For the UV aging test, a 365-nm UV lamp (FL20SBLB, Sankyo Denki) was used. The photovoltaic parameters of the aged devices were characterized using the class AAA solar simulator system equipped with a 150 W xenon arc lamp (PEC-L01, Peccell) and a potentiostat/galvanostat (Vertex, Ivium Technologies), in the same way as above.

Table S1. Summarized DSSC performance data of relevant literature devices.

Sensitizer[a]	V_{oc} (V)	J_{sc} (μA/cm^2)	FF^b (%)	PCE (%)	Reference
Mussel-inspired polydopamine	0.385	5500	56.5	1.20	[1]
Electropolymerized melanin-like poly indolequinone	0.33	228	25	0.34	[2]
Retinoic acid-based pigment	0.339	398	57	0.109	[3]
Melanin-based pigment	0.387	186	49.0	0.0503	[3]
Hemin-based pigment	0.449	71.2	70	0.032	[3]
Bacterial pigment from *Streptomyces fildesensis*	0.493	91	57.9	0.026	[4]
Yellow and pink oyster mushroom dyes	0.499	397	53.8	0.107	[5]
Black dye producing fungi (*Aspergillus sp.*)	0.463	70.6	44.27	0.0144	[6]

Red dye producing fungi (*Penicillium sp.*)	0.559	37.1	55.23	0.0114	6
Bare TiO$_2$ alone (18NR-AO) without melanin	0.52	144	74.8	0.056	our work
Synthetic melanin	0.47	777	64.5	0.24	our work
Synthetic melanin (after UV-treatment)	**0.42**	**1475**	**68.2**	**0.42**	**our work**

(a) Measured under AM 1.5G 100mW/cm^2 sunlight. (b) Fill factor (*FF*).

Table S2. Photovoltaic parameters for melanin-DSSCs with different redox mediators.

Electrolyte[a]	V_{oc} (V)	J_{sc} (μA/cm^2)	FF^b (%)	PCE (%)
I$^-$/I^{3-}	0.47	777	64.5	0.24
Co$^{(3+/2+)}$(bpy)$_3$	0.20	61	38.2	0.0047
Cu$^{(2+/1+)}$(tmby)$_2$	0.13	99	27.3	0.0035

(a) Photovoltaic performances were measured under AM 1.5G 100mW/cm^2 sunlight. (b) Fill factor (*FF*).
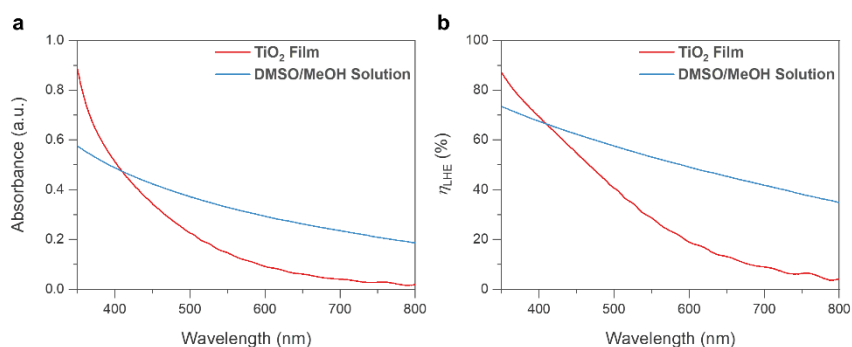
SI Fig. S1. Absorption properties of melanin in a mesoporous film and in solution. (**a**) UV-vis absorption spectra and (b) the light harvesting efficiency (LHE) of the melanin were measured on a 1.8 μm TiO$_2$ active layer (blue line) and in solution (red line). Melanin was dissolved in a DMSO/MeOH (1:19) solution and a 18NR-T TiO$_2$ paste containing particles with similar size (~20 nm) without scattering particles compared to 18NR-AO was used. The FTO-TiO$_2$ glass was immersed in the same solution condition for 16 hours at room temperature for adsorption. The equation, $\eta_{\text{LHE}}(\lambda) = 1 - 10^{-A(\lambda)}$ was used to calculate the LHE from the absorbance (a).
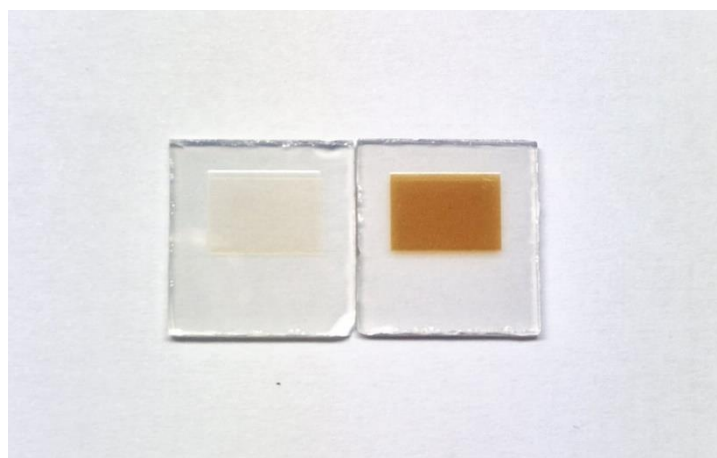

Fig. S2. Displayed are photoanodes of bare TiO$_2$ (left) and melanin-sensitized TiO$_2$ (right) following the immersion process.
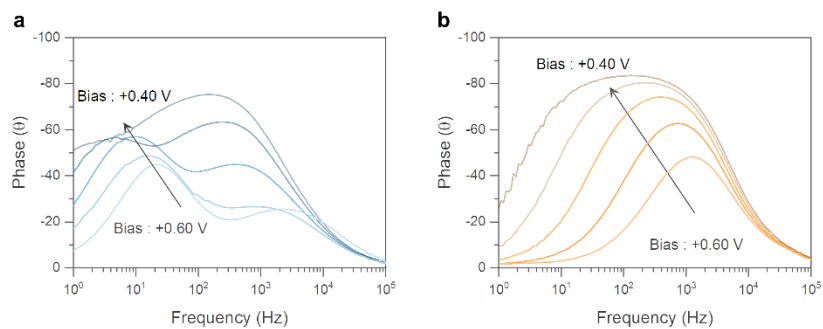
Fig. S3. Bode plots of (a) bare TiO$_2$ and (b) melanin DSSCs. Under the dark condition, the spectra were obtained from various V_{bias} from + 0.40 V to + 0.60 V in (a) bare-TiO$_2$ DSSCs and in (b) melanin-DSSCs.
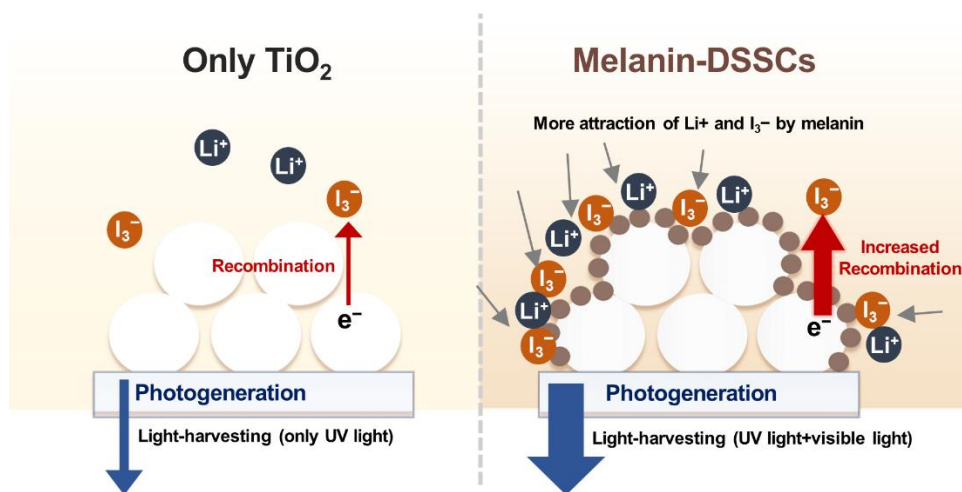

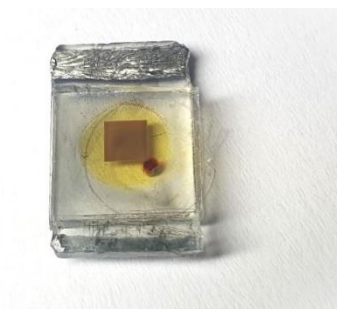**Fig. S4.** Graphical scheme of recombination kinetics in bare-TiO$_2$ and melanin-DSSCs.

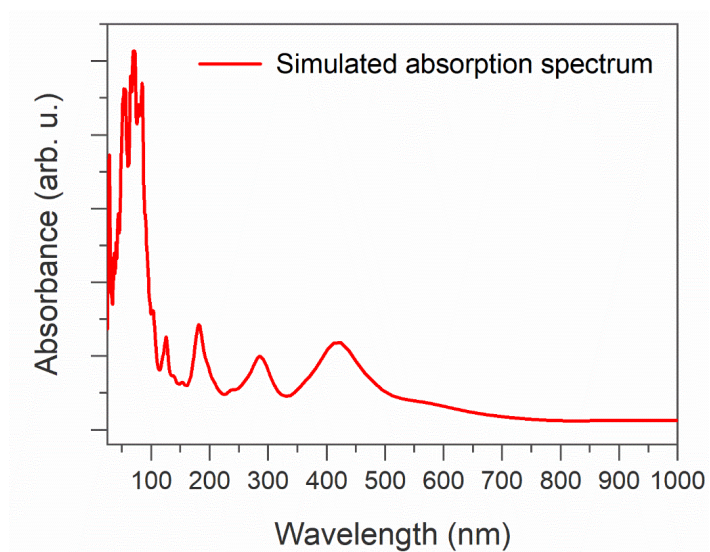**Fig. S5.** A photograph of fabricated melanin-DSSC device.

Fig. S6. Unedited and expanded simulated absorption spectrum of a gas-phase melanin tetramer in the "6 H structure"[7] calculated using MOLGW[8] on the BHLYP/cc-pVDZ(-RI)[9-11] level of theory.

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