

Supporting Information

Novel Energy Relay Dyes for High Efficiency Dye-Sensitized Solar Cells

Md. Mahbubur Rahman^a, Min Jae Ko^b, and Jae-Joon Lee^{a*}

^aNanotechnology Research Center and Department of Applied Life Science, College of Biomedical and Health Science, Konkuk University, Chungju 380-701, Republic of Korea

^bPhoto-Electronic Hybrids Research Center, Korea Institute of Science and Technology (KIST), Seoul 136-791, Republic of Korea

*Address correspondence to jjlee@kku.ac.kr (J.-J. Lee).

Materials

HPLC and TLC grade of 4',6-diamidino-2-phenylindole (DAPI), 2'-(4-ethoxyphenyl)-5-(4-methyl-1-piperazinyl)-2,5'-bi-1H-benzimidazole tri-hydrochloride (H33342), 3,6-bis-diethylamino-9-(2',4'-disulfophenyl)-xanthylium-sodium (sulforhodamine B sodium, SRB), and 2',4',5',7'-Tetrabromofluorescein (Eosin-Y) were purchased from Sigma-Aldrich. The electrolytes were prepared by dissolving 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII, Solaronix SA), 0.1 M lithium iodide (LiI), 0.05 M iodine (I₂), and 0.5 M 4-*tert*-butylpyridine (tBP) in 3-methoxypropionitrile (MPN) along with different concentrations of the energy relay dyes (ERDs).

Instrumentation

UV-Vis absorption and emission spectra were measured by a spectrophotometer (Perkin Elmer, Lambda 35, USA) and spectrofluorometer (Horiba, Fluorolog-3, USA), respectively. Electrochemical experiments were performed using a potentiostat (CHI430A, CH Instruments Inc., USA). A conventional three-electrode system was used; where a platinum electrode (3 mm diameter), a platinum wire, and a Ag/Ag⁺ were used as working, counter, and reference electrode, respectively. A solar simulator equipped with a 200 W Xenon lamp (McScience, Polaronix[®] K201) was used to generate simulated light AM 1.5. A photovoltaic power meter (McScience, Polaronix[®] K101 LAB20) was used to measure the current density-voltage (*J-V*) curves. The incident light intensity was adjusted to 100 mWcm⁻² (1 sun) by a standard mono-Si solar cell (PV Measurement Inc, PVM 396) certified by the U.S. National Renewable Energy Laboratory. Incident-photon-to-current conversion efficiency (IPCE) spectra were measured by an IPCE measurement system (McScience, Polaronix[®] K3100) with 300 W xenon light source. The

intensity of the incident monochromatic light was also calibrated with the same standard mono-Si solar cell. Electrochemical impedance spectra (EIS) were obtained under open-circuit and dark conditions at frequencies of 10^5 - 0.1 Hz with a 5 mV ac amplitude (Zahner-Elektrik GmbH & Co. KG, IM6ex). The measured spectra were fitted to an equivalent circuit appropriate for DSSCs using Z-view software (Scribner Associates Inc., version 3.1).

Device fabrication

Fluorine-doped Tin Oxide (FTO) glass plates (Pilkington TEC Glass-TEC 8, Solar, 2.3 mm thickness) were cleaned in a detergent solution using an ultrasonic bath for 30 min and then rinsed with water and ethanol. The FTO glass plates were immersed in TiCl_4 (40 mM) at 70 °C for 30 min and washed with water and ethanol. A transparent nanocrystalline TiO_2 layer on the FTO glass plates was prepared by screen printing TiO_2 paste (TTPH-20N, ENBKOREA Co., Ltd., Korea, particle size 20 nm) and then drying at 120 °C. The TiO_2 electrodes were gradually heated under an air flow at 350 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min. A paste for the scattering layer containing 500 nm anatase particles (STP-500N, ENBKOREA Co., Ltd., Korea) was deposited by screen printing and then dried for 1 h at 120 °C. Then, the TiO_2 electrodes were gradually heated under an air flow at 350 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min. The resulting layer was composed of a 6 μm thick transparent layer and a 4 μm thick scattering layer. The TiO_2 electrodes were treated again with TiCl_4 at 70 °C for 30 min and sintered at 500 °C for 30 min.

The TiO_2 electrodes were dipped separately into 0.4 mM ethanolic solution of N719 (Solaronix SA) for 20 h. The N3, Ru505, and Z907 sensitized TiO_2 photoelectrodes were

prepared as same. The ERDs were adsorbed on TiO₂ and the N719-loaded TiO₂ from their 1 mM ethanolic solutions for 20 h and 6 h, respectively.

The counter electrodes were prepared by spin coating of 5 mM ethanolic solution of chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O) on FTO and sintered in an electric muffle furnace at 400 °C for 20 min. The dye loaded photoelectrodes (active area *ca.* 0.2 cm²) and Pt counter electrodes were sandwiched by heating at 80 °C with a hot-melt film (60 μm thickness, Surlyn) as a spacer between the electrodes. The liquid-type electrolyte with/without ERDs was injected directly into the cell through the drilled holes at the counter electrode and the holes were temporarily sealed with transparent scotch tape.

Quantum yield (Q_d) calculation

Fluorescence quantum yield (Q_d) is the ratio of photons absorbed to photons emitted through fluorescence, which was calculated for the ERDs by the procedure reported elsewhere.^{S1} Briefly, Eosin-Y and SRB were selected as two standard compounds. Figure S1 shows the plot of the absorbance vs. the integrated fluorescence intensity of DAPI, H33342, SRB, and Eosin-Y. Using the two standard samples and their reported Q_d values (Eosin-Y, Q_d = 0.67, SRB, Q_d = 0.91),^{S2, S3} the Q_d values of Eosin-Y and SRB were determined to be 0.63 and 0.917, respectively according to the equation S1.

$$Q_x = Q_{ST} \left(\frac{\text{Grad}_x}{\text{Grad}_{ST}} \right) \left(\frac{\eta_x}{\eta_{ST}} \right)^2 \quad (\text{S1})$$

where, the subscripts ST and X denote standard and test respectively, *Grad* the gradient, and η the refractive index of the solvent.

Therefore, calculating the *Grad* of the plot of absorbance vs. integrated fluorescence intensity of DAPI and H33342 and cross-calibrated by two standards, the Q_d values was determined to be 0.69 and 0.63, respectively, which is high enough to obtain a reasonable Förster radius (R_0) between the ERDs and N719.

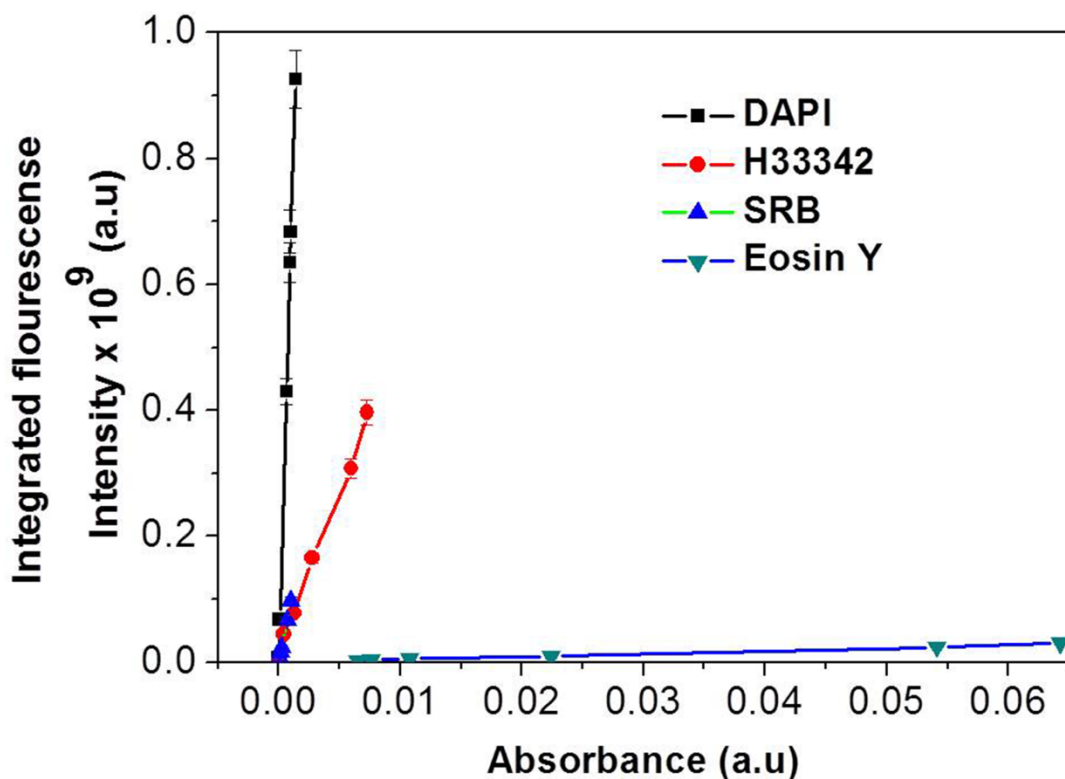


Figure S1: Plots of $\lambda_{\max, \text{abs.}}$ vs. integrated fluorescence intensity of different concentration of the ERDs.

Förster radius (R_0) calculation

Förster radius (R_0) illustrates the donor-acceptor separation at which the energy transfer efficiency is 50%, which was calculated according to the equation S2^{S4} between the ERDs and N719.

$$R_0^6 = 8.79 \times 10^{-25} \left\{ Q_d k^2 n^{-4} J \right\} \text{ cm}^6 \quad (\text{S2})$$

Where, $J = \int F_D \varepsilon_A(\lambda) \lambda^4 d\lambda$ in $\text{M}^{-1} \text{ cm}^3$

Using the calculated spectral overlap (J), Q_d , and the reported orientation factor for the dipole moment (k^2) = $2/3$,^{S4} and refractive index (n) = 1.5 for DSSCs,^{S4} the calculated R_0 for the N719/DAPI, N719/H33342 pairs were 2.14 and 1.93 nm, respectively, which is favorable for high energy transfer efficiency between the ERDs and N719.

Optimization of the ERDs concentration

The $J-V$ characteristics of DSSCs with different concentrations of DAPI and H33342 as additive in the electrolytes are shown in Figure S2. The maximum power conversion efficiency (PCE) was attained using 5 mM DAPI and H33342, and considered as optimal concentration.

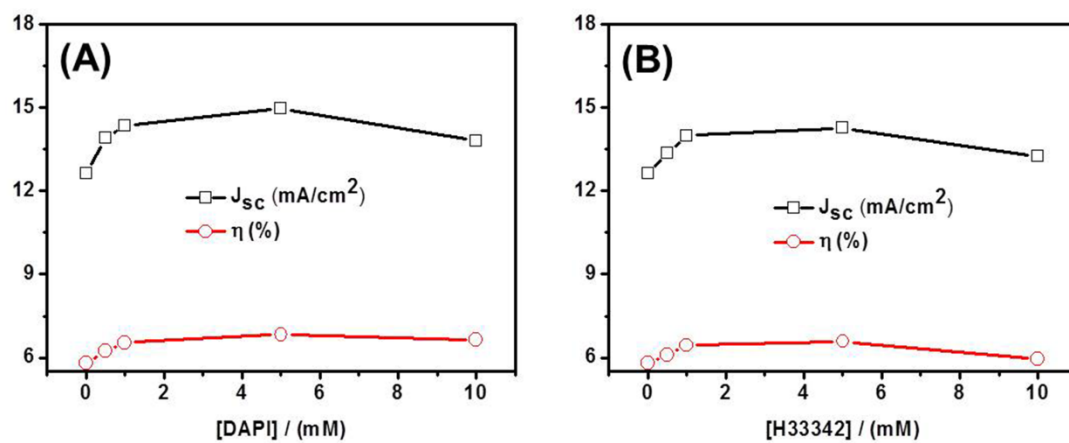


Figure S2: Photocurrent density-voltage (J - V) characteristics of DSSCs with different concentrations of DAPI and H33342 in electrolytes. The thicknesses of the nanocrystalline TiO_2 photoelectrodes were *ca.* 5 μm .

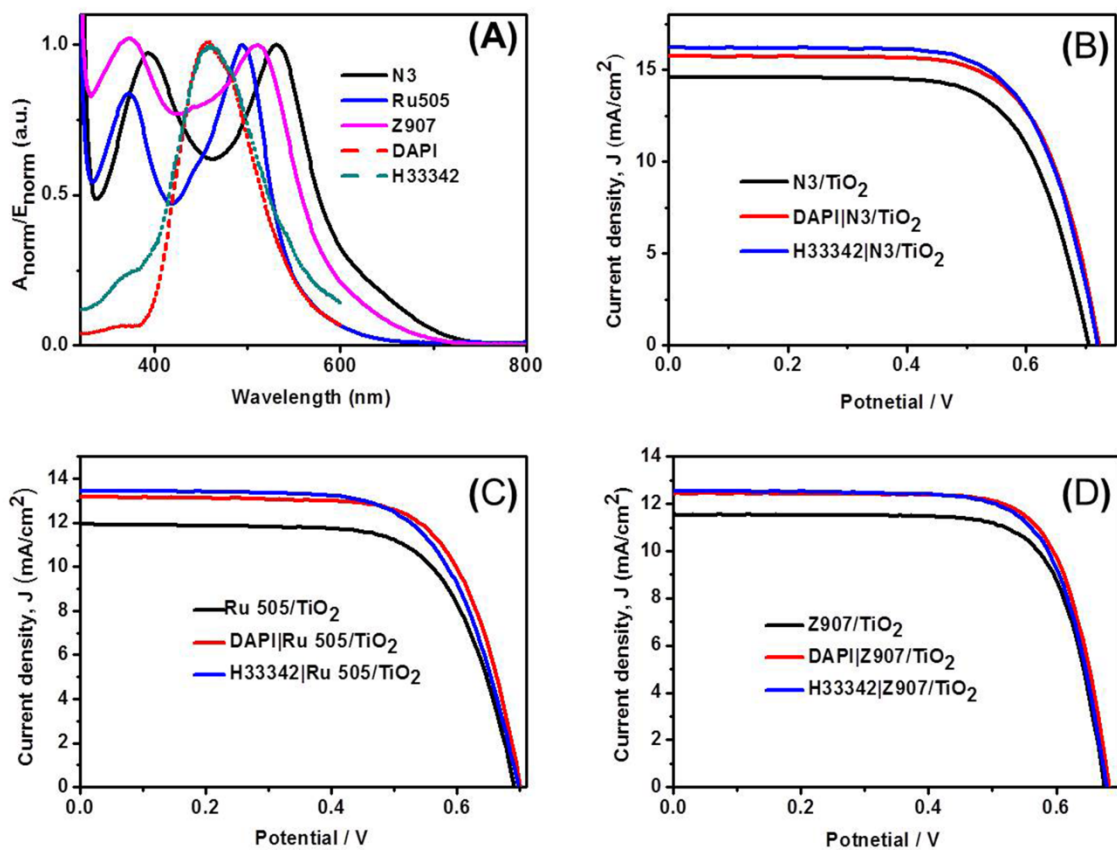


Figure S3: Normalized absorption spectra of N3, Ru505, and Z907 dyes together with the emission spectra of DAPI and H33342 (A), and the Current density-voltage (J - V) plots of N3, Ru505, and Z907 sensitized DSSCs with/without ERDs added into I^-/I_3^- based electrolyte (B-D).

References

- S1.** A. T. R. Williams, S. A. Winfield and J. N. Miller, *Analyst*, 1983, **108**, 1067–1071.
- S2.** H. Du, R. A. Fuh, J. Li, A. Corkan and J. S. Lindsey, *Photochem. Photobiol.*, 1998, **68**, 141–142.
- S3.** M. Dashtiev, V. Azov, V. Frankevich, L. Scharfenberg, and R. Zenobi, *J. Am. Soc. Mass Spectrom.*, 2005, **16**, 1481–1487.
- S4.** J.-H. Yum, B. E. Hardin, S.-J. Moon, E. Baranoff, F. Nüesch, M. D. McGehee, M. Grätzel and M. K. Nazeeruddin, *Angew. Chem. Int. Ed.*, 2009, **48**, 9277–9280.