

Supplementary Information

**Photoinduced electron injection from organic dye having pyridyl
anchor to Lewis acid site of TiO₂ surface**

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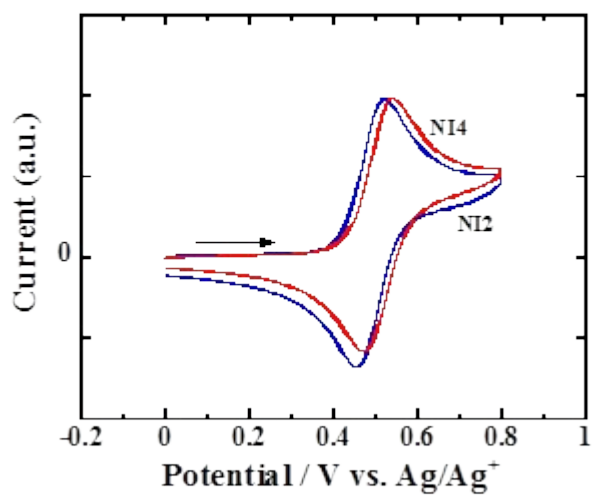


Fig. S1 CV curves of **NI2** and **NI4** at 100 mV s^{-1} in MeCN/TBAP(0.1 M).

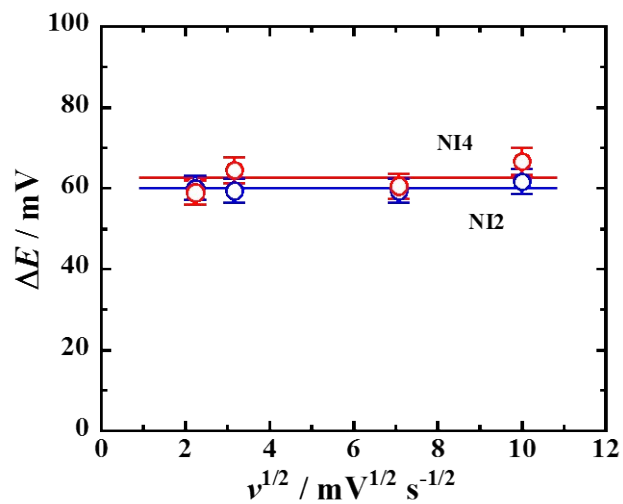


Fig. S2 Peak separations (ΔE) of CV curves for **NI2** and **NI4** with a square root of a potential scan rate ($v^{1/2}$).

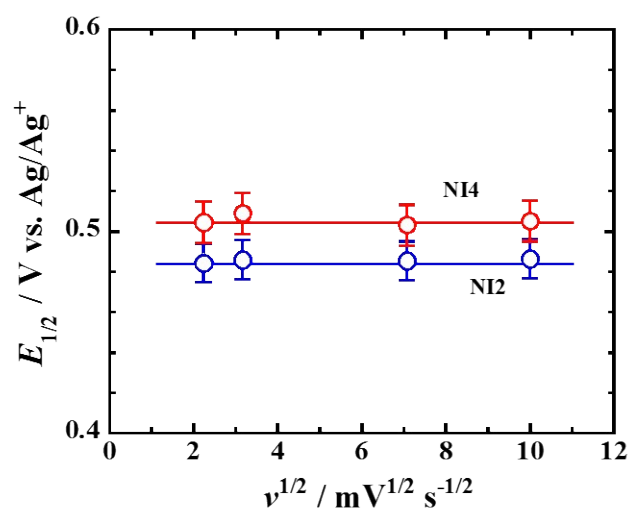


Fig. S3 Half-wave potentials ($E_{1/2}$) of CV curves for NI2 and NI4 with $v^{1/2}$.

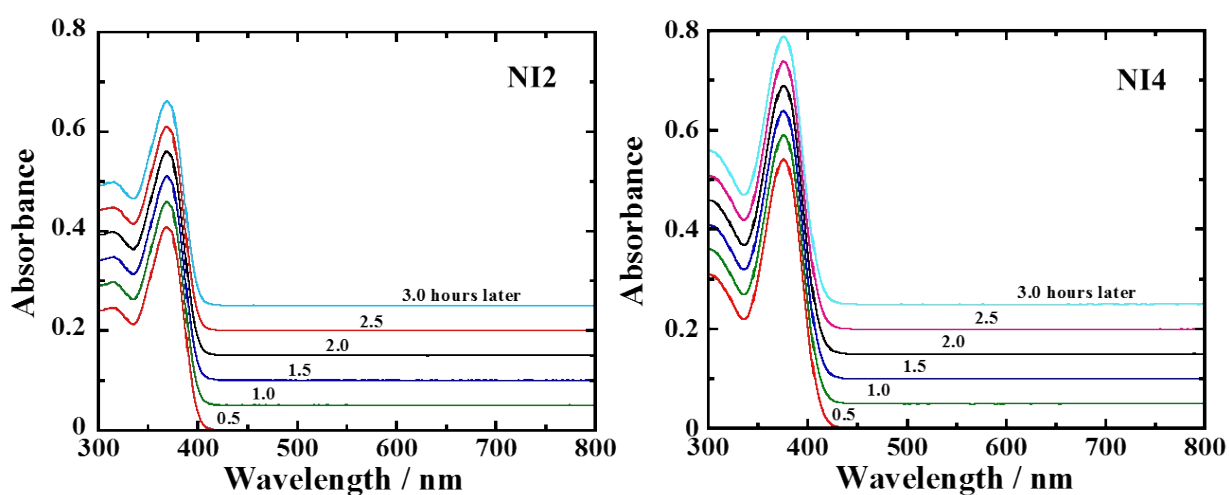


Fig. S4 Time-courses of absorption spectra of NI2 and NI4 in mixed solutions (THF:DMSO:H₂O (1M NaOH) = 5:4:1, v:v:v).

Transient absorption spectroscopy

The transient absorption measurements were performed by the conventional pump and probe technique to account for the recombination kinetics between the NI2 or NI4 cations and electrons injected into the TiO₂ film.^{S1,S2} The dyes adsorbed on TiO₂ film were excited at 400 nm by a dye laser pumped by a N₂ laser (0.6 ns pulse duration, 6 Hz repetition). The resulting photoinduced

change in optical density (OD) was monitored by employing a probe light of 850 nm corresponding nearly to absorption peaks of dye cations, a photosensor (Hamamatsu Photonics C8366 PIN photodiode), and a digital storage oscilloscope (IWATSU DS-4372). Fig. S5 shows absorption spectra of cation radicals of **NI2** and **NI4** obtained by oxidizing neutral dyes with tris(4-bromophenyl)aminium hexachloroantimonate (TAH) in CH₂Cl₂. Absorption peaks of **NI2** and **NI4** cations are located at 897 and 860 nm, respectively.

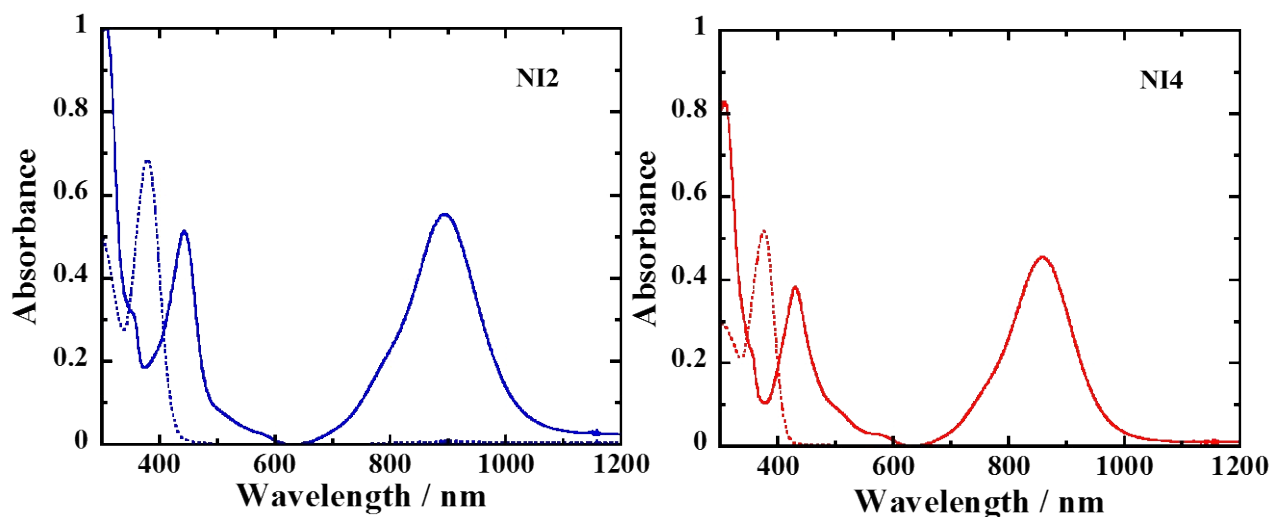


Fig. S5 Absorption spectra of neutral dyes **NI2** (0.02 mM) and **NI4** (0.015 mM) (broken lines), and their corresponding cations (solid lines) in CH_2Cl_2 .

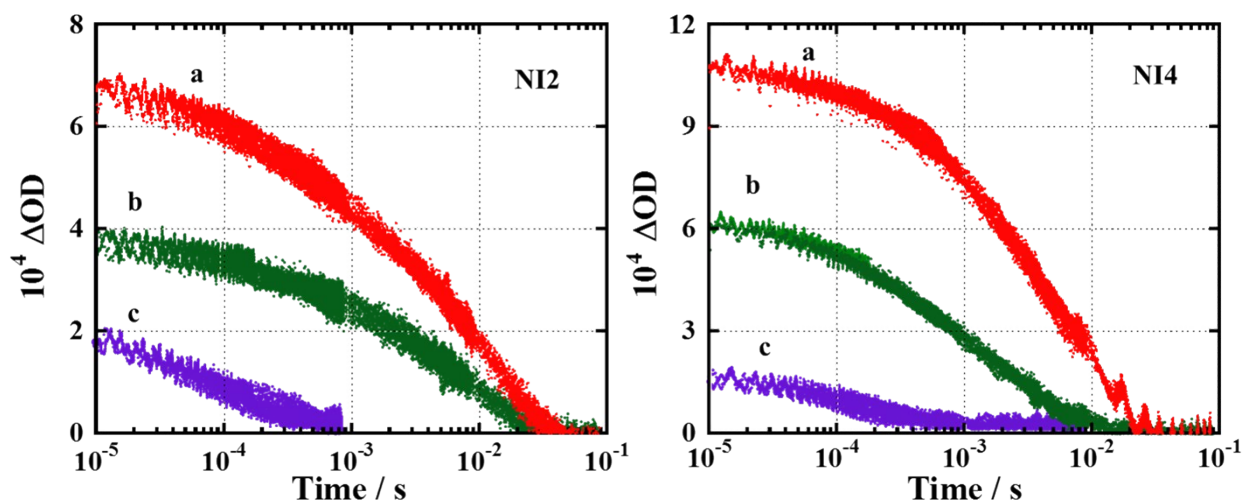


Fig. S6 Transient absorption data of **NI2**- and **NI4**-coated TiO_2 in contact with a) a neat MeCN, and b) 1/80 and c) 1/40 diluted solutions of MeCN containing 0.1 M LiI, 0.05 M I_2 , and 0.6 M DMPPrII. Experiments were carried out under open-circuit conditions.

Decay of the cation absorption band at 850 nm for the **NI2**- and **NI4**-DSSCs in neat MeCN is very slow, as shown in Fig. S6. By increasing the concentrations of the redox electrolyte, the absorption decay is greatly enhanced, demonstrating that the recombination kinetics between the dye cations and electrons injected into the TiO_2 film that are responsible for reduction of

photocurrents are negligibly slow for both dyes compared with the electron injection kinetics from I⁻ to dye cations.

REFERENCES

- (S1) Haque, S.A.; Tachibana, Y.; Willis, R.L.; Moser, J.E.; Grätzel, M.; Klug, D.R.; Durrant, J.R. Parameters Influencing Charge Recombination Kinetics in Dye-Sensitized Nanocrystalline Titanium Dioxide Films. *J. Phys. Chem. B* **2000**, *104*, 538-547.
- (S2) Green, A.N.M.; Palomares, E.; Haque, S.A.; Kroon, J.M.; Durrant, J.R. Charge Transport versus Recombination in Dye-Sensitized Solar Cells Employing Nanocrystalline TiO₂ and SnO₂ Films. *J. Phys. Chem. B* **2005**, *109*, 12525-12533.