Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information

A Simple Triaryl Amine-based Dual Functioned Co-adsorbent for Highly Efficient Dye-sensitized Solar Cells

Hae Min Song, Kang Deuk Seo, Min Soo Kang, In Tack Choi, Sang Kyun Kim, Yu Kyung Eom, Jung Ho Ryu, Myung Jong Ju and Hwan Kyu Kim*

[*]Center for Advanced Photovoltaic Materials (ITRC), Department of Advanced Materials Chemistry, Korea University, 208 Seochang, Jochiwon, Chungnam, 339-700, Korea. E-mail: hkk777@korea.ac.kr

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Possible energy transfer pathway investigation for understanding the cell performance enhancement by HC-acid

Experimental

Absorption spectra were recorded with a Shimadzu UV-2401PC spectrophotometer and photoluminescence spectra with a Fluorolog FL-3-22 fluorometer from Horiba-Jobin-Yvon Ltd. Equipped with a 450W Xe-lamp. Visible emission spectra were detected with a Hamamatsu R928 photomultiplier at room temperature.

Results and discussion

To clarify the further effect of HC-Acid co-adsorbent on the photovoltaic performance of NKX2677-sensitized solar cells, the photophysical properties of HC-Acid and NKX2677 were studied in solution state. For effective energy transfer processes, high Förster resonant energy transfer (FRET) rates (k_{FRET}) are essentially required to quickly transfer the energy from the donor of the excited energy relay dye (ERD) (e.g. HC-Acid) to the certain acceptor of sensitizing dye (e.g. NKX2677(SD)) before the non-radiative decay processes of the excited ERD. The FRET rate is dependent upon the Förster radius (R_o) between the ERD and the SD or the separation distance between the ERD and the SD interface. The Förster radius, in which Förster energy transfer efficiency of 50 % occurs between two individual chromophores, can be calculated using equation (1):[1]

$$R_o^{\,6} = \frac{9000 \cdot (\ln 10)\kappa^2 Q_D}{128 \cdot \pi^5 n^4 N_A} \int F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda \qquad (1)$$

where n is the index of refraction of the host medium (1.4~1.5 for the DSC electrolyte), k^2 the orientational factor (2/3 for random orientation), N_A Avogadro's number, Q_D the photoluminescence (PL) efficiency, F_D the emission profile of the donor and ε_A (λ) is the molar extinction coefficient. The rate of the FRET between isolated chromophores, known as point-to-point transfer, is given by $k_{FRET} = k_o(R_o)^6/r^6$, where r is the separation distance. A high energy-transfer efficiency between energy donor and acceptor has been observed if the following conditions are fulfilled: 1) a sufficient overlap of the emission spectrum of the donor with the absorption spectrum of the acceptor, 2) an energy donor with a high fluorescence quantum efficiency, 3) a small interchromophore distance, and 4) a molecular orientation allowing suitable dipole-dipole interactions (e.g. freely rotating chromophore groups).[2]

Figure S1 shows the emission and absorption overlapping spectra among HC-Acid, NKX2677 and I_2. The NKX2677 dye absorption and the PL emission of the HC-Acid overlaps significantly, but the I_2 absorption and the PL emission of the HC-Acid overlaps relatively weak. Given the absorption of the NKX2677 or I_2 and emission profile of HC-Acid, the Förster radius between HC-Acid and NKX2677, HC-Acid and I_2 are estimated to be 11.9 nm and 4.92 nm, respectively.

For an example, it is essential for high FRET that PTCDI as an ERD has high PL quantum efficiency (> 90%), fast fluorescence lifetime, excellent photo- and air-stability, and high absorption coefficient of 50,000 M^{-1}

cm^{-1} at 580 nm,[3] TT1 as a SD has a high molar extinction coefficient of 191,500 M^{-1} cm^{-1} centered at 680 nm.[4]

In this study, the molar extinction coefficients of HC-Acid used as co-adsorbent (ERD) and NKX2677 used as sensitizing dye (SD) are estimated to be 37,400 M^{-1} cm^{-1} and 50,400 M^{-1} cm^{-1}, centered at 354 nm and 491 nm, respectively, and the PL quantum efficiency of HC-Acid is not relatively high to be about 45%.

Figure S2 shows the UV-vis absorption/emission spectra and the molar excitation coefficients of NKX2677 in acetonitrile. Two peaks, appeared around 391 nm and 491 nm, presumely correspond to the Raman spectra of OH vibration stretching modes. When the excitation wavelength (λex) was increased, the PL emission intensity of NKX2677 around 600 nm increased gradually.

Figure S3 shows the excitation spectra of HC-Acid, NKX2677, and a mixture of HC-Acid and NKX2677 in acetonitrile. The excitation spectra profiles of HC-Acid (λ_{em} = 414 nm) and NKX2677 (λ_{em} = 670 nm) are almost similar to UV-vis absorbance spectra of HC-Acid and NKX2677 as shown in **Figure S1**.

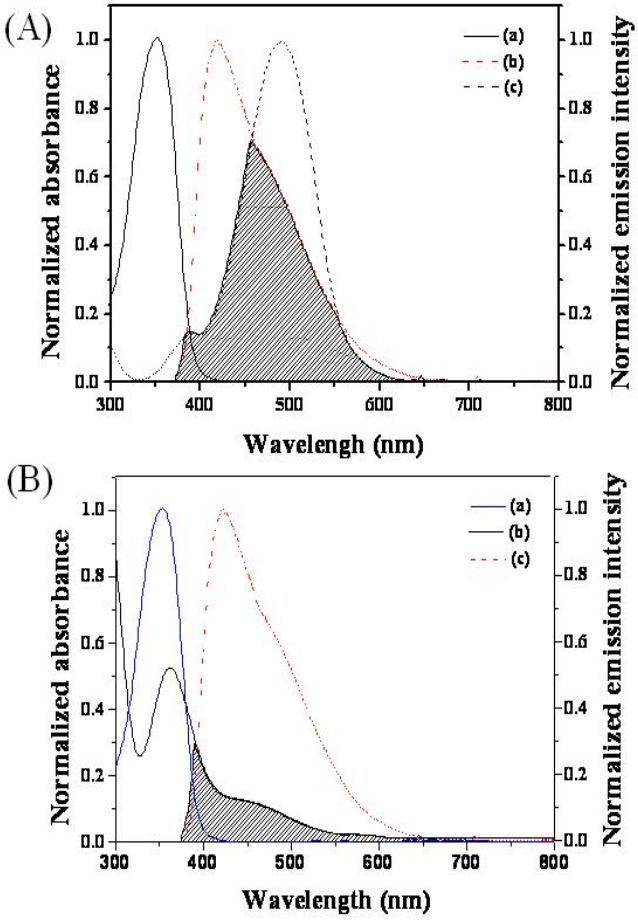

Figure S1. **(A)** UV-vis absorption of HC-Acid (9.9×10^{-6} M) (a), HC-Acid emission (b), and NKX2677 (6.6×10^{-6} M) absorption (c) in acetonitrile; **(B)** UV-vis absorption of HC-Acid (a), UV-vis absorption of I_2 (1.25×10^{-5} M) (b), and HC-Acid emission (c) in acetonitrile.

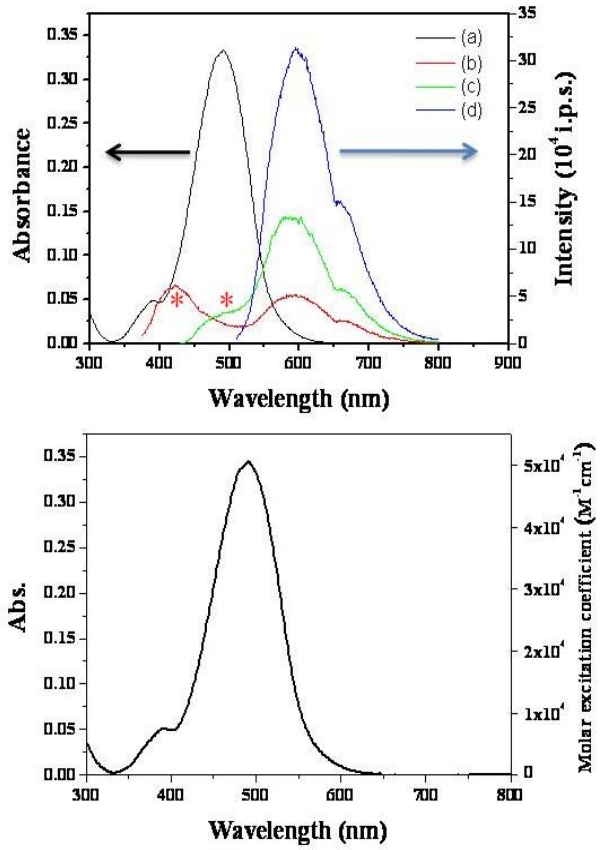

Figure S2. (Top): UV-vis absorption and emission spectra of NKX2677 in acetonitile solution. (a) UV-vis absorption spectrum of NKX2677, (b), (c) and (d) emission spectra of NKX2677 at λ_{ex} of 354 nm, 418 nm and 500 nm, respectively. **(Bottom)**: UV-vis absorption and molar excitation coefficients of NKX2677 in acetonitrile. * corresponds to the spectra originating from the Raman spectra of OH vibration stretching modes.

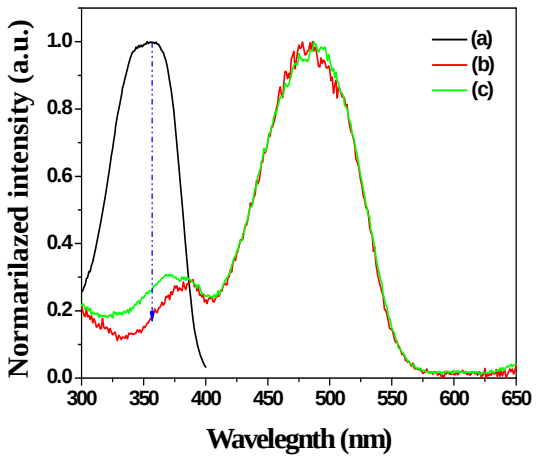

Figure S3. Excitation spectra of (a) HC-Acid (λ_{em} = 414 nm), (b) NKX2677 (λ_{em} = 670 nm) and (c) the mixture of HC-Acid and NKX2677 (λ_{em} = 670 nm) in acetonitrile. Concentration of HC-Acid and NKX2677 is 9.9 x 10^{-6} M and 6.6 x 10^{-6} M, respectively.

References

1. T. Förster, *Discuss. Faraday Soc*., 1959, **27**, 7
2. C. Siegers, J. Hohl-Ebinger, B. Zimmermann, U. Würfel, R. Mülhaupt, A. Hinsch, and R. Haag, *ChemPhysChem*., 2007, **8**, 1548.
3. F. Wurthner, *Chem. Commun*., 2004, 1564.
4. J. J. Cid, J.-H. Yum, S.-R. Jang, M. K. Nazeeruddin, E. M. Ferrero, E. Palomares, J. Ko, M. Grätzel, and T. Torres, *Angew. Chem.*, 2007, **119**, 8510.