Supplementary Material (ESI) for Journal of Materials Chemistry

Electronic Supplementary Information

Organization of supramolecular assembly of 9-mesityl-10-carboxymethylacridinium ion and fullerene clusters on TiO_2 nanoparticles for light energy conversion

Taku Hasobe,[a,b] Shigeki Hattori,[a,b] Prashant V. Kamat,*,[c] Yuji Wada,[a] and Shunichi Fukuzumi*,[a,b]

Department of Material and Life Science, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

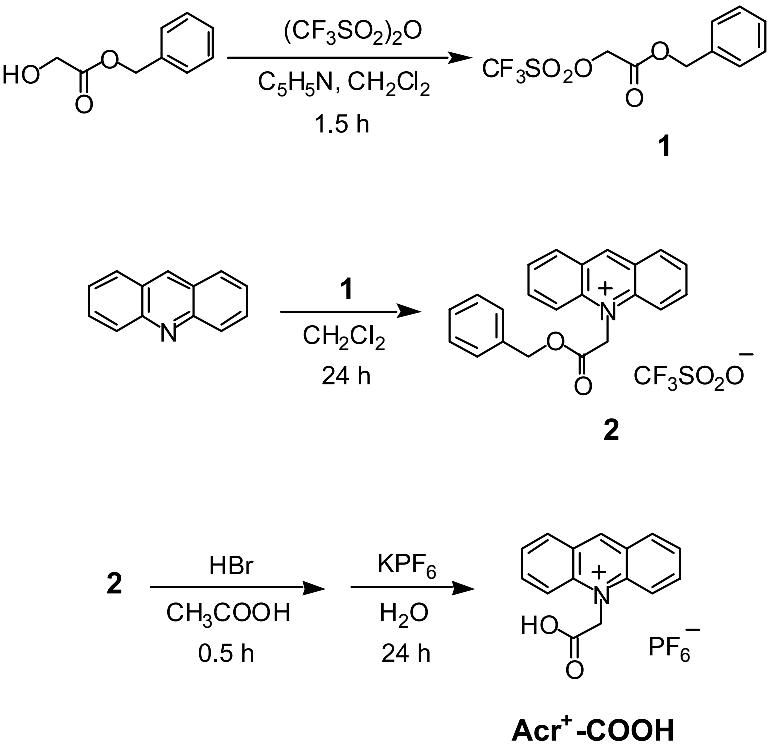
CREST, Japan Science and Technology Agency, Suita, Osaka 565-0871, Japan

Radiation Laboratory and Department of Chemical & Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana 46556, USA

---

[a] Osaka University, [b] CREST, [c] University of Notre Dame

Synthesis



Scheme S1. Synthesis of Acr^+-COOH

Triflate of benzylglycolate 1:[1] **1** was prepared using a slight modification of the reported literature methods. To a solution of benzyl glycolate (1.66 g, 10.0 mmol) and pyridine (0.89 mL, 11.0 mmol) in CH_2C1_2 (40 mL) at -20 °C was added triflic anhydride (1.84 mL, 11.0 mmol) over a period of 5-10 min. After complete addition, the reaction mixture was stirred for 30 min and warmed to rt, and stirred for additional 30 min. The reaction mixture was evaporated and rapidly passed through a short column of silica gel eluting with CH_2C1_2. The fractions containing triflate were combined, the solvent was evaporated, and the residue was subjected to a second rapid chromatography (1/1, CH_2Cl_2/hexane) to provide 2.24 g of the triflate as a pale yellow oil which solidified at 0 °C. This material was suitable for use directly without any further purification: ^{1}H NMR δ4.93 (s, 2H), 5.28 (s, 2H), 7.38 (s, 5H).

10-Benzyloxycarbonylmethylacridinium triflate 2:[2] To a solution of acridine (0.060 g, 0.336 mmol) and in CH_2C1_2 (0.764 mL) at -15 °C was added triflate of benzylglycolate (0.11 g, 0.370 mmol) over a period of 5-10 min. After complete addition, the reaction mixture was stirred for 30 min and warmed to rt, and stirred for additional 24 h. Dried diethylether was added to the reaction mixture and precipitated crystals were filtered, yielding an acridinium ester protected by a benzyl group. (0.13 g, 0.272 mmol, 83%): ^{1}H NMR (CD_3CN): δ5.28 (s, 2H, CH_2), 6.15 (s, 2H, CH_2), 7.38 (s, 5H, Ar-H), 8.01 (t with J = 8 Hz, 2H, Ar-H) , 8.35-8.44 (m, 4H, Ar-H) , 8.58 (d with J = 8 Hz, 2H, Ar-H), 9.99 (s, 1H, Ar-H). MALDI-TOF-MS *m/z* 328.0 (Calcd for $C_{22}H_{18}NO_2^+$ *m/z* 328.1).

10-Carboxylmethylxacridinium hexafluorophosphate Acr$^+$-COOH:[3] The acridinium ester protected by a benzyl group **2** (0.13 g, 0.279 mmol) was suspended in a 30% solution of hydrogen bromide/acetic acid (3.00 mL), and heated for 30 minutes at 50 °C, and the solvent was removed in vacuo. The resulting solid was dissolved in distilled water and was added to a solution of potassium hexafluorophosphate (2.96 g, 16.1 mmol) in 34.0 mL of distilled water. The resulting solution was stirred for 24h at room temperature, and precipitated crystals were filtered, yielding an acridinium carboxyl derivative (**Acr$^+$-COOH**) (0.059 g, 0.153 mmol, 55%): UV-VIS (CH_3CN) λ_{max} (ε) 344 (14560), 359 (26830), 419 (6340 mol^{-1} dm^3 cm^{-1}) nm. ^{1}H NMR (CD_3CN): δ5.95 (s, 2H, CH_2), 7.95 (t with J = 7 Hz, 2H, Ar-H), 8.33 (t with J = 7 Hz, 2H, Ar-H), 8.43 (d with J = 7 Hz, 2H, Ar-H) , 8.51 (d with J = 7 Hz, 2H, Ar-H). 9.88 (s, 1H, Ar-H). MALDI-TOF-MS *m/z* 238.0 (Calcd for $C_{15}H_{12}NO_2^+$ *m/z* 238.1).

Preparation of TiO_2 nanocrystallites films modified with Mes-Acr$^+$-COOH (denoted as OTE/TiO_2/Mes-Acr$^+$-COOH). Nanoporous TiO_2 electrodes were prepared by dropping the colloidal suspensions of TiO_2 nanoparticles (P25, d = 21 nm, Nippon Aerogel) on optically transparent electrode (OTE) (Nippon Sheet Glass, SnO_2:F, 8 Ω/square) with a glass rod and adhesive tapes as a spacer. The resulting electrodes (OTE/TiO_2) were annealed at 450 °C in air for 30 min. The thickness of the electrodes ranged between 13 and 14 μm as measured by a profiler. Coloration of the TiO_2 surface with the **Mes–Acr$^+$–COOH** was carried out by immersing the film (still warm, i.e., 80 ~ 100 °C) for 12 h in acetonitrile containing 3.0×10^{-4} mol dm^{-3} of **Mes–Acr$^+$–COOH**. After completion of the **Mes–Acr$^+$–COOH** adsorption, the electrode was withdrawn from the solution, washed with acetonitrile, and dried. The TiO_2 nanocrystallites films modified with **Acr^+–COOH** (denote as OTE/TiO_2/**Acr^+–COOH**) were similarly prepared.

References

(1) Triflate of benzylglycolate was synthesized according to the procedure in: V. R. Escher, and P. Bünning, *Angew. Chem.,* 1986, **98**, 264

(2) For the synthesis of acridinium ester, see: N. Sato, *Tetrahedron Lett.*, 1996, **37**, 8519.

(3) Debenzylation was performed according to the procedure in ref. 2.

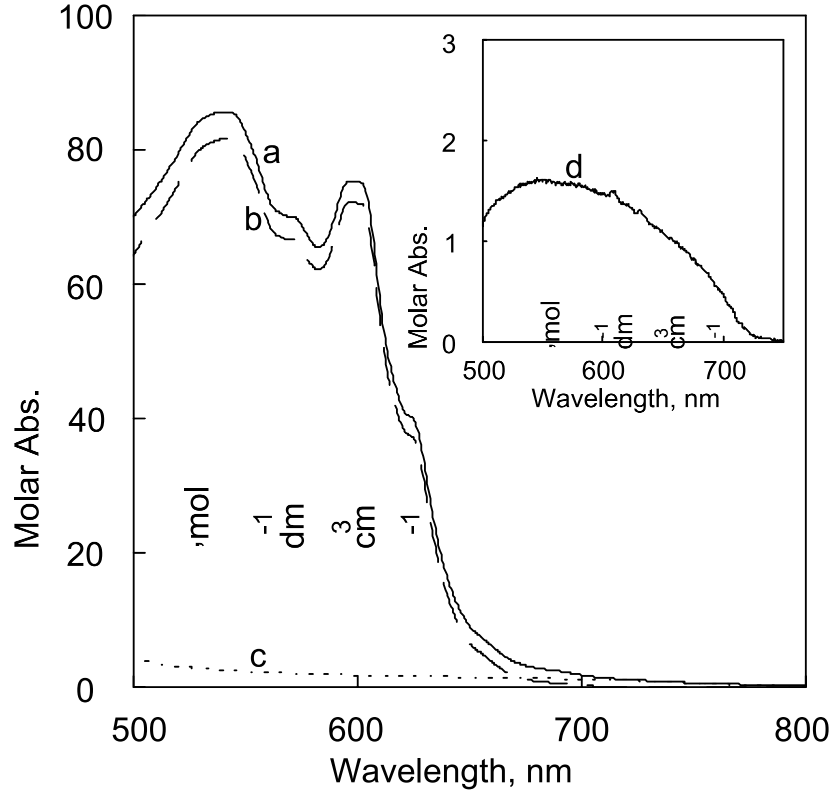


Fig. S1. Absorption spectra of (a) the mixture of **Mes-Acr$^+$** (1.0 × 10^{-2} M) with C_{60} (1.0 × 10^{-2} mol dm^{-3}), (b) C_{60} (1.0 × 10^{-2} mol dm^{-3}), and (c) **Mes-Acr$^+$** (1.0 × 10^{-2} mol dm^{-3}) in *o*-dichlorobenzene. Absorption spectrum of (d) the CT absorption of **Mes-Acr$^+$** with C_{60} obtained by subtracting the absorptions of C_{60} (1.0 × 10^{-2} mol dm^{-3}) (b) and **Mes-Acr$^+$** (1.0 × 10^{-2} mol dm^{-3}) (c) from the absorption of mixture of **Mes-Acr$^+$** (1.0 × 10^{-2} mol dm^{-3}) with C_{60} (1.0 × 10^{-2} mol dm^{-3}) (a) in *o*-dichlorobenzene.

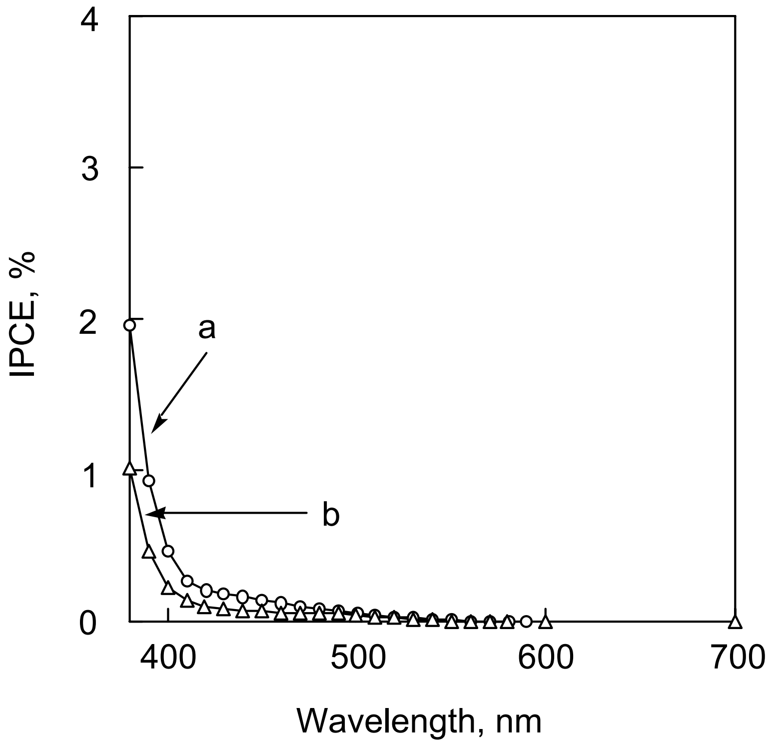


Fig. S2. Photocurrent action spectra (IPCE *vs.* wavelength) of (a) OTE/TiO_2/**Mes-Acr$^+$-COOH** electrode and (b) OTE/TiO_2/**Acr$^+$-COOH** electrode.