Electronic Supplementary Information (ESI)

Size-selective incorporation of donor-acceptor linked dyad cations into zeolite Y and long-lived charge separation

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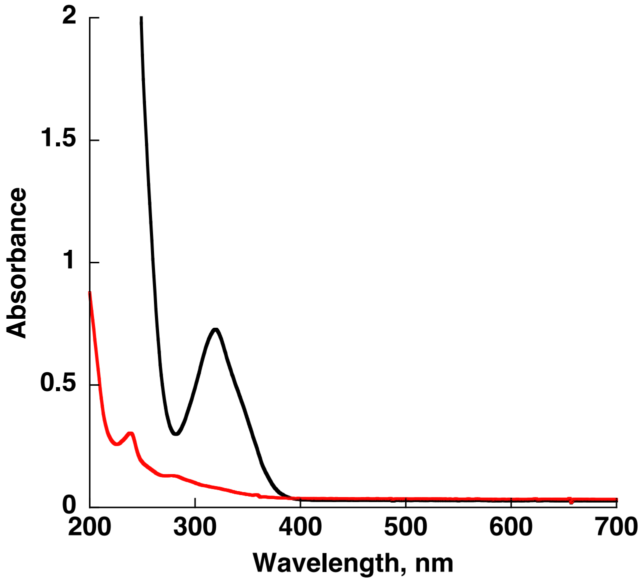

Fig. S1 UV-vis absorption spectra of an acetonitrile solution of Qu^{+}–Mes (black) and a supernatant acetonitrile solution after addition of zeolite Y.

Experimental

Materials

9-Mesityl-10-methylacridinium perchlorate, Acr^+–$Mes(ClO_4^-)$ was commercially obtained from Tokyo Chemical Industry Co., Ltd. Spectroscopic grade acetonitrile (MeCN) used as a solvent was purchased from Nacalai Tesque. Zeolite Y (NaY; Molecular Sieve SK-40) was obtained from GL Sciences. NaY was activated by heating in a furnace (in air) at 473 K for 8 h before use.

Synthesis of 3-mesityl-1-methylquinolinium perchlorate.

A mixture of (2,4,6-trimethylphenyl)boronic acid (1.6 g, 10 mmol) and 3-bromoquinoline (1.2 g, 6.0 mmol) dissolved in dimethoxyethane (8.0 mL) was added into aqueous solution (2.0 mL) of K_2CO_3 (2.0 M) and tetrakis(triphenylphosphine) palladium(0) [$Pd(PPh_3)_4$, 60mg, 0.052 mmol], and was refluxed at 90 °C for 12 h. After cooling, chloroform (100 mL) and distilled water (100 mL) were added to the reaction mixture. The organic layer was separated, washed with water (100 mL) two times and brine (50 mL), and then evaporated. The crude product was purified by column choromatography eluted with dichloromethane to give 3-mesityl-1-methylquinoline as pale-yellow solid (500 mg, 34%). A mixture of 3-mesityl-1-methylquinoline (500 mg, 2.0 mmol) and methyl iodide (8.0 mmol) dissolved in acetone (80 mL) was stirred at room temperature for 10 h. After removal of the solvent, the residue was stirred in MeOH (30 mL) and then $NaClO_4$ (0.12 g, 1.0 mmol) was added to the solution. The solution was evaporated and subsequent recrystallisation from MeOH gave 3-mesityl-1-methylquinolinium perchlorate as a yellow solid (105 mg, 14%): ^{1}H NMR (300 MHz, CD_3CN) δ 8.93(s, 1H), 8.90(s, 1H), 8.39 (d, J = 7.8 Hz, 1H), 8.33 (d, J = 7.8 Hz, 1H), 8.26 (t, J = 7.8 Hz, 1H), 8.04 (t, J = 7.8Hz, 1H), 7.08 (s, 2H), 2.04 (s, 6H), 4.57 (s, 3H), 2.35 (s, 3H), MALDI-TOF-MS *m/z* 262 (M^+ Calcd for $C_{19}H_{20}N$ 261.8). Anal. Calcd for $C_{19}H_{20}ClNO_4$: C, 63.07; H, 5.57; N, 3.87. Found: C, 62.91; H, 5.49; N, 3.89.

Cation-exchange procedure to prepare Qu^+–Mes incorporated into zeolite Y

Qu^+–Mes@zeolite Y was prepared by exchanging sodium ion (Na^+) with Qu^+–Mes cation incorporated into zeolite Y (NaY). A small amount of NaY (0.20 g) powder was suspended by stirring in MeCN solution (200 mL) containing 1.0×10^{-4} M Qu^+–$Mes(ClO_4^-)$ (7.2 mg, 2.0×10^{-2} mmol) for 12 h at room temperature. The suspension was then centrifuged and the precipitate was repeatedly washed 3 times with MeCN. Then, the solid precipitate was dried at room temperature in vacuo. The incorporation of Acr^+–Mes (λ = 423 nm, $\varepsilon = 5.6 \times 10^3$ M^{-1} cm^{-1} in MeCN) into NaY was tried in the same manner under otherwise the same experimental conditions. The content of Qu^+–Mes ion incorporated into NaY by cation exchange was determined from the absorption spectral change of the supernatant measured before and after centrifugation.

EPR measurements

EPR spectra of the ET states of Qu^+–Mes in MeCN and Qu^+–Mes@zeolite Y were recorded on a JEOL X-band spectrometer (JES-RE1XE) with a quartz EPR tube (4.5 mm i.d.) *in vacuo* under photoirradiation with a high-pressure mercury lamp (USH-1005D) through a UV-light (λ < 310 nm) cut filter (Toshiba L31). The vacuum level attained during data acquisition was better than 5×10^{-5} torr.

Theoretical calculations

Density functional theory (DFT) calculations of Qu^+–Mes were performed with Gaussian 09 (Revision A.02, Gaussian, Inc.).[S1] The calculations were performed on a 32-processor QuantumCube^{TM} at the B3LYP/6-31G(d) level of theory.[S2] Graphical outputs of the computational results were generated with the *GaussView* software program (ver. 3.09) developed by Semichem, Inc.[S3]

Electrochemical measurements. Cyclic voltammetry (CV) and second harmonic AC voltammery (SHACV) measurements of Qu^+–Mes were performed with an ALS630B electrochemical analyser in deaerated acetonitrile containing 0.1 M $Bu_4N^+PF_6^-$ ($TBAPF_6$) as a supporting electrolyte at 298 K. The platinum working electrode (BAS, surface i.d. 1.6 mm) was polished with BAS polishing alumina suspension and rinsed with acetone before use. The counter electrode was a platinum wire (0.5 mm dia.). The measured potentials were recorded with respect to an $Ag/AgNO_3$ (0.01 M) reference electrode. The values of redox potentials (vs $Ag/AgNO_3$) are converted into those vs SCE by addition of 0.29 V.[S4]

Transient absorption measurements. Femtosecond transient absorption spectroscopy experiments were conducted using an ultrafast source: Integra-C (Quantronix Corp.), an optical parametric amplifier: TOPAS (Light Conversion Ltd.) and a commercially available optical detection system: Helios provided by Ultrafast Systems LLC. The source for the pump and probe pulses were derived from the fundamental output of Integra-C (780 nm, 2 mJ/pulse and fwhm = 130 fs) at a repetition rate of 1 kHz. 75% of the fundamental output of the laser was introduced into TOPAS which has optical frequency mixers resulting in tunable range from 285 nm to 1660 nm, while the rest of the output was used for white light generation. Prior to generating the probe continuum, a variable neutral density filter was inserted in the path in order to generate stable continuum, then the laser pulse was fed to a delay line that provides an experimental time window of 3.2 ns with a maximum step resolution of 7 fs. In our experiments, a wavelength at 380 nm of TOPAS output, which is fourth harmonic of signal or idler pulses, was chosen as the pump beam. As this TOPAS output consists of not only desirable wavelength but also unnecessary wavelengths, the latter was deviated using a wedge prism with wedge angle of 18°. The desirable beam was irradiated at the sample cell with a spot size of 1 mm diameter where it was merged with the white probe pulse in a close angle (< 10°). The probe beam after passing through the 2 mm sample cell was focused on a fibre optic cable that was connected to a CCD spectrograph for recording the time-resolved spectra (410-800 nm). Typically, 2500 excitation pulses were averaged for 5 seconds to obtain the transient spectrum at a set delay time. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. All measurements were conducted at room temperature, 295 K.

Nanosecond time-resolved transient absorption measurements were carried out using the laser system provided by UNISOKU Co., Ltd. The measurements were performed according to the following procedure. A deaerated MeCN solution containing a Qu^{+}–Mes in a quartz cell (1 cm × 1 cm) was excited by a Nd:YAG laser (Continuum SLII-10, 4-6 ns fwhm, λ_{ex} = 355 nm, 5 mJ/pulse). The photodynamics were monitored by continuous exposure to a xenon lamp (150 W) as a probe light and a photomultiplier tube (Hamamatsu 2949) as a detector. The solution was deoxygenated by nitrogen purging for 15 min prior to measurements.

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