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COMMUNICATION

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

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Cationic electron donor-acceptor dyads are incorporated into a supercage of zeolite Y by cation exchange depending on the size of the dyad cations. 3-Mesityl-1-methylquinolinium ion was small enough to be incorporated into the zeolite supercage, exhibiting long-lived charge separation upon photoexcitation.

Artificial photosynthesis attracts many researchers to realise a sustainable society relying on solar energy.^{1–5} To achieve artificial photosynthesis, light-harvesting, charge-separation and catalytic units should be developed and combined together.^{6,7} For the light harvesting and charge separation, a variety of electron donor-acceptor linked molecules, which mimic charge-separation processes in the photosynthetic reaction centre, have been developed.^{8–10} A class of donor-acceptor linked molecules form a long-lived electron-transfer (ET) state by photoirradiation in organic media.^{11,12} Recently, the lifetime of the ET state longer than that of the natural photosynthesis centre has been realised by supporting donor-acceptor linked dyads on mesoporous silica-alumina, in which intermolecular event resulting in back electron transfer can be effectively retarded.^{13,14} The long-lived ET state of a donor-acceptor linked dyad can be observed even in water,^{15–22} which is beneficial to realise greener artificial photosynthesis.

3-Mesityl-1-methylquinolinium perchlorate ($\text{Qu}^+\text{-Mes}$ ClO_4^-) was synthesised by Suzuki-Miyaura coupling between (2,4,6-trimethylphenyl)boronic acid and bromoquinoline, followed by methylation with methyl iodide, which are characterised as given in ESI. An acetonitrile (MeCN) solution of $\text{Qu}^+\text{-Mes}$ ClO_4^- was mixed with 200 mg of NaY after 8 h calcination in the air at 473 K and stirred for 12 h at room temperature. The amount of Na^+ -cation exchange with $\text{Qu}^+\text{-Mes}$ increased with increasing concentration of $\text{Qu}^+\text{-Mes}$ to reach a constant value as shown in Fig. 1 (red points). The maximum amount of $\text{Qu}^+\text{-Mes}$ incorporated into zeolite Y

corresponds to 2.2 molecules per 10 supercages. When $\text{Qu}^+\text{-Mes}$ was replaced by 9-mesityl-10-methylacridinium ion ($\text{Acr}^+\text{-Mes}$), no $\text{Acr}^+\text{-Mes}$ molecules were incorporated into zeolite Y (black points in Fig. 1) because of the large molecular size of $\text{Acr}^+\text{-Mes}$ (9.0 Å) as compared with that of the zeolite supercage (7.0 Å), which is slightly larger than that of $\text{Qu}^+\text{-Mes}$ (6.8 Å). $\text{Qu}^+\text{-Mes}$ incorporated into zeolite Y exhibits the same absorption maximum ($\lambda_{\text{max}} = 325$ nm) as that in solution

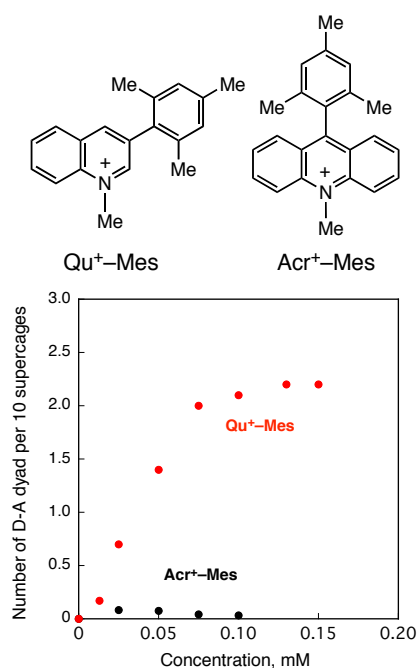


Fig. 1 (a) Chemical structures of 3-mesityl-1-methylquinolinium ion ($\text{Qu}^+\text{-Mes}$) and 9-mesityl-10-methylacridinium ion ($\text{Acr}^+\text{-Mes}$) used in this study perchlorate salts. (b) Plots of number of cation molecules incorporated into zeolite Y (0.5 mg) suspended in MeCN (1.0 mL) vs. concentrations of cations.

Scheme 1.

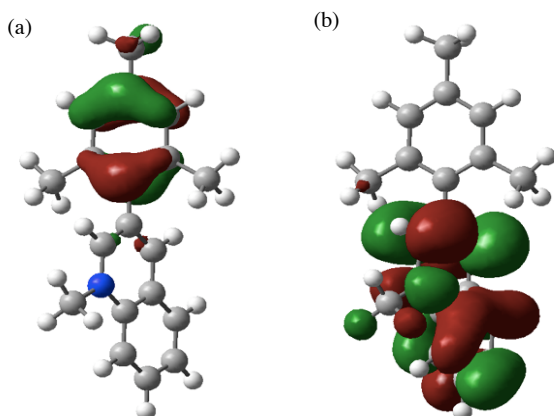
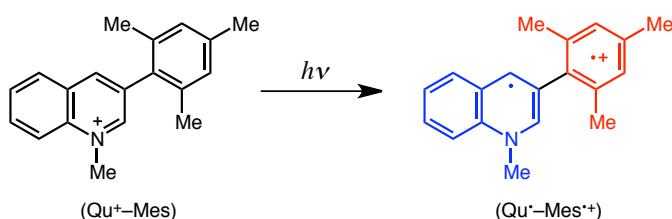


Fig. 2 (a) HOMO and (b) LUMO orbitals with optimised structure of Qu^+-Mes calculated by the B3LYP/6-31G(d) level of theory.

(Fig. S1 in the electronic supplementary information (ESI[†])).

The HOMO and LUMO orbitals of Qu^+-Mes are localised on the Mes and Qu^+ moieties, respectively (Fig. 2), supporting the formation of the ET state ($\text{Qu}^{\bullet}-\text{Mes}^{\bullet+}$) upon photoexcitation (Scheme 1). The one-electron oxidation (E_{ox}) and reduction (E_{red}) potentials of Qu^+-Mes were determined by cyclic voltammetry and second harmonic AC voltammetry (SHACV),²² respectively, where the experimental conditions are shown in the electronic supplementary information (ESI). The reversible wave for the reduction of the quinolinium moiety was observed in the CV measurements. The E_{red} value was determined to be -0.77 V vs. SCE in MeCN. The E_{ox} value for the oxidation of the mesitylene moiety was 2.02 V vs. SCE, which was determined by SHACV. The energy of charge-separated state is calculated from the redox potentials to be 2.79 eV, which is smaller than the value of the singlet excitation energy of quinolinium ion (3.53 eV). Thus, photoinduced electron transfer from the mesitylene moiety to the singlet excited state of quinolinium is energetically favourable because of the positive driving force of electron transfer ($-\Delta G_{\text{ET}} = 0.74$ eV).

Femtosecond laser excitation at 380 nm of a deaerated MeCN solution of Qu^+-Mes (5.0×10^{-4} M) results in formation of the ET state ($\text{Qu}^{\bullet}-\text{Mes}^{\bullet+}$), which has transient absorption bands at 470 nm and 530 nm due to mesitylene radical cation and quinolinyl radical, respectively, as shown in Fig. 3a. The

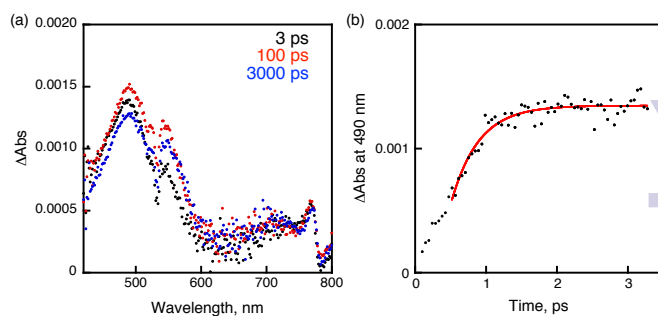


Fig. 3 (a) Transient absorption spectra of a deaerated MeCN solution of Qu^+-Mes observed upon femtosecond pulse laser excitation (fwhm = 130 fs). (b) Rise time profile of absorbance at 500 nm due to $\text{Qu}^+-\text{Mes}^{\bullet+}$.

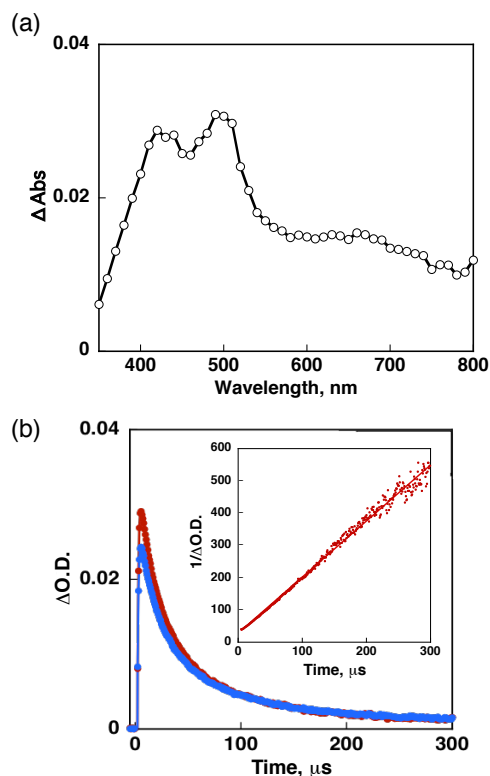
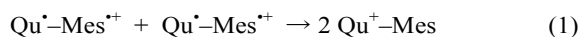


Fig. 4 (a) Transient absorption spectra of a deaerated MeCN solution of Qu^+-Mes observed upon nanosecond pulse laser excitation at 1.6 μs . (b) Decay time profile of the absorbance at 500 nm due to $\text{Qu}^+-\text{Mes}^{\bullet+}$. Inset shows the second-order plot.

rate constant of formation of the ET state was determined from the rise of the absorbance at 490 nm (Fig. 3b) to be $2.6 \times 10^{12} \text{ s}^{-1}$ [$= (0.39 \text{ ps})^{-1}$]. The extremely fast electron transfer from mesitylene moiety to the singlet excited state of quinolinium ion moiety occurs to form the ET state (Scheme 1). The resulting absorption due to the ET state exhibited no decay by 3 ns (Fig. 3a), which is the delay time limit for our setup femtosecond transient absorption spectroscopy.

Nanosecond laser pulse excitation of an MeCN solution of Qu^+-Mes resulted in formation of the ET state ($\text{Qu}^{\bullet}-\text{Mes}^{\bullet+}$) which exhibited transient absorption bands at 420 and 490 nm

due to the Qu^\bullet and Mes^{++} moieties, respectively (Fig. 4a).^{11,12} The transient absorption shift relative to those in the femtosecond transient absorption bands is attributed to the formation of the dimer radical cation between the electron-transfer state and the ground state of Qu^+-Mes in MeCN.¹² The decay of absorbance at 500 nm obeyed second-order kinetics (Inset of Fig. 4b). This indicates that back electron transfer from the Qu^\bullet moiety to the Mes^{++} moiety occurs via the bimolecular reaction of two $\text{Qu}^\bullet-\text{Mes}^{++}$ molecules (eq. 1) with the rate constant of $\sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, which is faster than the intramolecular back electron transfer in $\text{Qu}^\bullet-\text{Mes}^{++}$.



The ET state was detected by EPR measurements during photoexcitation of Qu^+-Mes at low temperature as shown in Fig. 5a, where the EPR signals due to Qu^\bullet and Mes^{++} are overlapped.²³ The decay of EPR signal due to $\text{Qu}^\bullet-\text{Mes}^{++}$ obeyed first-order kinetics (Inset of Fig. 5b), indicating that the bimolecular back electron transfer between two $\text{Qu}^\bullet-\text{Mes}^{++}$ molecules is prevented by incorporation of Qu^+-Mes into zeolite Y. The lifetime of the ET state was determined to be as long as 500 s at 223 K (Fig. 5b). The decay rate constant is highly temperature dependent and the Eyring plot (Fig. 6) afforded the activation enthalpy of 14 kcal mol⁻¹. Such a large temperature dependence of the k_{BET} value indicates that the

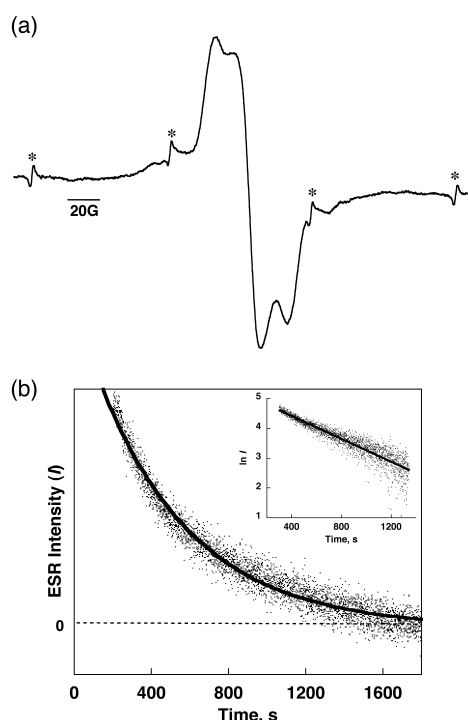


Fig. 5 (a) EPR spectrum observed during photoirradiation of a deaerated MeCN solution of Qu^+-Mes incorporated into zeolite Y at 77 K. Asterisks denote Mn^{2+} markers to determine g value; (b) Decay time profile of EPR intensity of $\text{Qu}^\bullet-\text{Mes}^{++}$ at zeolite Y generated by photoirradiation at 223 K. Inset: first-order plot.

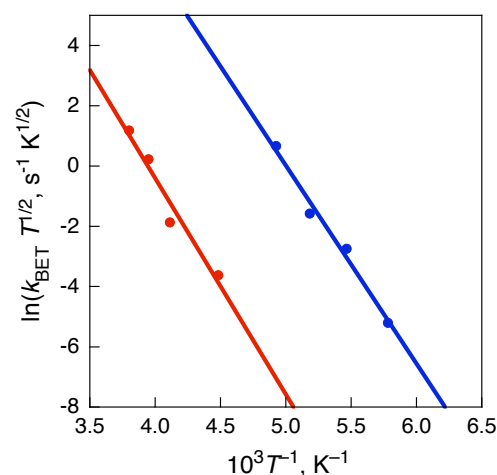


Fig. 6 Marcus plots obtained from the temperature dependence of decay rate constant of back electron transfer in $\text{Qu}^\bullet-\text{Mes}^{++}$ incorporated into the zeolite Y supercage (red) and in MeCN (blue).

BET process is deeply in the Marcus inverted region because of the small reorganisation energy necessary for electron transfer in $\text{Qu}^\bullet-\text{Mes}^{++}$ and the BET rate constant decreases as the driving force increases.²⁴ From the slopes and intercepts of Fig. 6 the values of the reorganisation energies of electron transfer (λ) and electronic coupling matrix elements (V) were determined as $\lambda = 1.16 \text{ eV}$ and $V = 220 \text{ cm}^{-1}$ in MeCN and $\lambda = 1.12 \text{ eV}$ and $V = 21 \text{ cm}^{-1}$ in the zeolite Y supercage, respectively, calculated by eq. 2,

$$k_{\text{BET}} = \left(\frac{4\pi^3}{h^2 \lambda k_B T} \right) V^2 \exp \left[- \frac{(\Delta G_{\text{BET}} + \lambda)^2}{4 \lambda k_B T} \right] \quad (2)$$

where k_B is the Boltzmann constant, h is the Planck constant and T is the absolute temperature.²⁵ The V value in the zeolite Y supercage is smaller than that in an MeCN solution, probably because of the interaction with the cation exchange site, which may prohibit the interaction between the donor and acceptor moieties.

In conclusion, size selective incorporation of 3-methyl-1-methylquinolinium cation into zeolite Y and photoexcitation resulted in formation of the long-lived electron transfer state. The lifetime of the ET state is 400 s at 223 K, being highly temperature dependent with a large activation enthalpy of 14 kcal mol⁻¹. Incorporation of electron donor-acceptor linked cation molecules into zeolite Y provides a convenient way to elongate the lifetime of the ET state by preventing the bimolecular reaction.

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Notes and references

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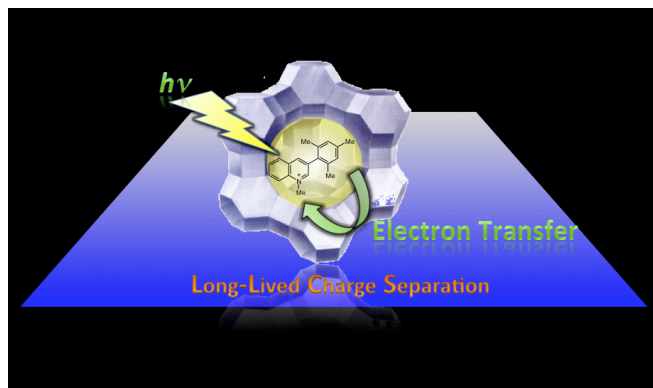
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† Electronic Supplementary Information (ESI) available: [Experimental details and synthesis of $\text{Qu}^+-\text{Mes ClO}_4^-$]. See DOI: 10.1039/c0xx00000x/

- 1 (a) N. S. Lewis and D. G. Nocera, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 15729; (b) H. B. Gray, *Nat. Chem.*, 2009, **1**, 7; (c) J. H. Alstrum-Acevedo, M. K. Brennaman and T. J. Meyer, *Inorg. Chem.*, 2005, **44**, 6802.
- 2 (a) T. A. Faunce, W. Lubitz, A. W. Rutherford, D. MacFarlane, G. F. Moore, P. Yang, D. G. Nocera, T. A. Moore, D. H. Gregory, S. Fukuzumi, K. B. Yoon, F. A. Armstrong, M. R. Wasielewski and S. Styring, *Energy Environ. Sci.*, 2013, **6**, 695; (b) L. Duan, F. Bozoglian, S. Mandal, B. Stewart, T. Privalov, A. Llobet and L. Sun, *Nat. Chem.*, 2012, **4**, 418.
- 3 K. Kalyanasundaram, J. Kiwi and M. Grätzel, *Helv. Chim. Acta*, 1978, **61**, 2720.
- 4 A. Kudo and Y. Miseki, *Chem. Soc. Rev.*, 2009, **38**, 253.
- 5 K. Maeda and K. Domen, *J. Phys. Chem. Lett.*, 2010, **1**, 2655.
- 6 P. V. Kamat, *J. Phys. Chem. Lett.*, 2012, **3**, 663.
- 7 (a) T. Toyao, M. Saito, Y. Horiuchi, K. Mochizuki, M. Iwata, H. Higashimura and M. Matsuoka, *Catal. Sci. Technol.*, 2013, **3**, 2092; (b) T. Kamegawa, S. Matsuura, H. Seto and H. Yamashita, *Angew. Chem., Int. Ed.*, 2013, **52**, 916.
- 8 A. J. Cowan and J. R. Durant, *Chem. Soc. Rev.*, 2013, **42**, 2281.
- 9 M. R. Wasielewski, *Acc. Chem. Res.*, 2009, **42**, 1910.
- 10 S. Fukuzumi, K. Ohkubo and T. Suenobu, *Acc. Chem. Res.*, 2014, **47**, 1455.
- 11 S. Fukuzumi, H. Kotani, K. Ohkubo, S. Ogo, N. V. Tkachenko and H. Lemmetyinen, *J. Am. Chem. Soc.*, 2004, **126**, 1600.
- 12 H. Kotani, K. Ohkubo and S. Fukuzumi, *Faraday Discuss.*, 2012, **155**, 89.
- 13 (a) S. Fukuzumi, K. Doi, A. Itoh, T. Suenobu, K. Ohkubo, Y. Yamada and K. D. Karlin, *Proc. Natl. Acad. Sci. U. S. A.*, 2012, **109**, 15572; (b) S. Fukuzumi, A. Itoh, T. Suenobu and K. Ohkubo, *J. Phys. Chem. A*, 2014, **118**, 24188.
- 14 Y. Yamada, A. Nomura, K. Ohkubo, T. Suenobu and S. Fukuzumi, *Chem. Commun.*, 2013, **49**, 5132.
- 15 H. Kotani, T. Ono, K. Ohkubo and S. Fukuzumi, *Phys. Chem. Chem. Phys.*, 2007, **9**, 1487.
- 16 H. Kotani, K. Ohkubo, Y. Takai and S. Fukuzumi, *J. Phys. Chem. B*, 2006, **110**, 24047.
- 17 S. Fukuzumi, Y. Yamada, T. Suenobu, K. Ohkubo and H. Kotani, *Energy Environ. Sci.*, 2011, **4**, 2754.
- 18 H. Kotani, R. Hanazaki, K. Ohkubo, Y. Yamada and S. Fukuzumi, *Chem.–Eur. J.*, 2011, **17**, 2777.
- 19 Y. Yamada, T. Miyahigashi, H. Kotani, K. Ohkubo and S. Fukuzumi, *J. Am. Chem. Soc.*, 2011, **133**, 16136.
- 20 Y. Yamada, T. Miyahigashi, H. Kotani, K. Ohkubo and S. Fukuzumi, *Energy Environ. Sci.*, 2012, **5**, 6111.
- 21 Y. Yamada, T. Miyahigashi, K. Ohkubo and S. Fukuzumi, *Phys. Chem. Chem. Phys.*, 2012, **14**, 10564.
- 22 T. G. McCord and D. E. Smith, *Anal. Chem.*, 1969, **41**, 1423.
- 23 The spin state of the electron-transfer state may be triplet produced via the intersystem crossing, resulting in the long lifetime because of the spin forbidden back electron transfer as reported in ref. 13a.
- 24 The predicted lifetimes of electron-transfer state at room temperature (298 K) are estimated to be 0.3 ms in MeCN and 300 ms in zeolite Y, respectively, calculated from the Marcus plot obtained from the temperature dependence as shown in Fig. 6.
- 25 (a) R. A. Marcus, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1111; (b) R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta Rev. Bioenerg.*, 1985, **811**, 265.

TOC Graphic



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