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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,15-20 which is beneficial to realise greener artificial photosynthesis.

3-Mesityl-1-methylquinolinium perchlorate (Qu–MesClO₄) 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 ESL. An acetonitrile (MeCN) solution of Qu–MesClO₄ 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 Qu–Mes increased with increasing concentration of Qu–Mes to reach a constant value as shown in Fig. 1 (red points). The maximum amount of Qu–Mes incorporated into zeolite Y corresponds to 2.2 molecules per 10 supercages. When Qu–Mes was replaced by 9-mesityl-10-methylacridinium ion (Acr–Mes), no Acr–Mes molecules were incorporated into zeolite Y (black points in Fig. 1) because of the large molecular size of Acr–Mes (9.0 Å) as compared with that of the zeolite supercage (7.0 Å), which is slightly larger than that of Qu–Mes (6.8 Å). Qu–Mes incorporated into zeolite Y exhibits the same absorption maximum (λmax = 325 nm) as that in solution.

![Chemical structures of 3-mesityl-1-methylquinolinium ion (Qu–Mes) and 9-mesityl-10-methylacridinium ion (Acr–Mes) used in this study.](image-url)

**Fig. 1** (a) Chemical structures of 3-mesityl-1-methylquinolinium ion (Qu–Mes) and 9-mesityl-10-methylacridinium ion (Acr–Mes) used in this study. (b) Plots of number of cation molecules incorporated into zeolite Y (0.5 mg) suspended in MeCN (1.0 mL) vs. concentrations of cations.
and quinolinyl radical, respectively, as shown in Fig. 3a. The bands at 470 nm and 530 nm due to mesitylene radical cation (Mes•+).

The positive driving force of electron transfer (ΔG_{ET}) potentials of Qu•−–Mes and Qu•−–MeCNO, respectively, where the experimental conditions were determined by cyclic voltammetry and second harmonic AC voltammetry (SHACV), 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 (−ΔG_{ET} = 0.74 eV).

Femtosecond laser excitation at 380 nm of a deaerated MeCN solution of Qu•−–Mes (5.0 x 10^{-4} M) results in formation of the ET state (Qu•−–MeCNO), 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 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 x 10^{12} s^{-1} [= (0.39 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 (Qu•−–MeCNO) which exhibited transient absorption bands at 420 and 490 nm.
due to the Qu’ and Mes’ moieties, respectively (Fig. 4a).\textsuperscript{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.\textsuperscript{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’ moiety to the Mes’ moiety occurs via the bimolecular reaction of two Qu’–Mes’’ molecules (eq. 1) with the rate constant of $\sim 10^{10}$ M$^{-1}$ s$^{-1}$, which is faster than the intramolecular back electron transfer in Qu’–Mes’’.

$$\text{Qu’–Mes’’} + \text{Qu’–Mes’’} \rightarrow 2 \text{Qu’–Mes}$$ (1)

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’ and Mes’ are overlapped.\textsuperscript{23} The decay of EPR signal due to Qu’–Mes’’ obeyed first-order kinetics (Inset of Fig. 5b), indicating that the bimolecular back electron transfer between two Qu’–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 $k_{\text{BET}}$ value indicates that the BET process is deeply in the Marcus inverted region because the small reorganisation energy necessary for electron transfer in Qu’–Mes’’ and the BET rate constant decreases as the driving force increases.\textsuperscript{24} From the slopes and intercepts of Fig. 6 the values of the reorganisation energies of electron transfer ($\lambda$) and electronic coupling matrix elements ($V$) were determined as $\lambda = 1.16$ eV and $V = 220$ cm$^{-1}$ in MeCN and $\lambda = 1.12$ eV and $V = 21$ cm$^{-1}$ in the zeolite Y supercage respectively, calculated by eq. 2,

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

where $k_B$ is the Boltzmann constant, $h$ is the Planck constant and $T$ is the absolute temperature.\textsuperscript{25} The $V$ value in the zeolite 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-methyquinolinium 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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temperature dependence as shown in Fig. 6. respectively, calculated from the Marcus plot obtained from the 
(298 K) are estimated to be 0.3 ms in MeCN and 300 ms in zeolite Y, 
produced via the intersystem crossing, resulting in the long 
spin state of the electron 

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.
3-Mesityl-1-methylquinolinium ion is incorporated into a supercage of zeolite Y, exhibiting long-lived charge separation upon photoexcitation.