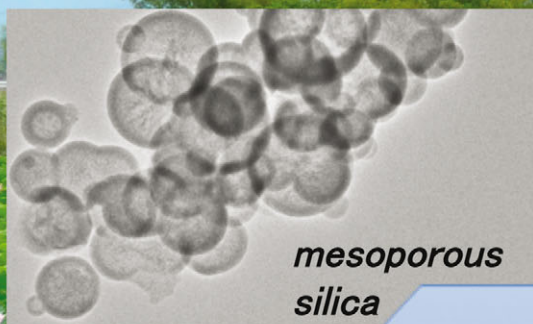


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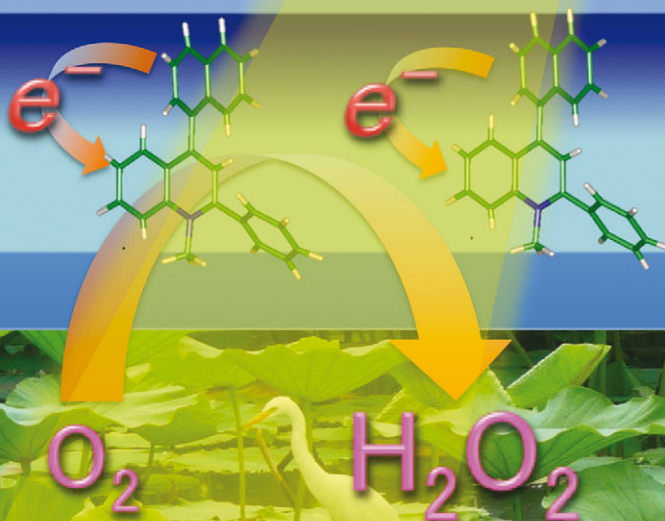
Chemical Communications

www.rsc.org/chemcomm

Volume 49 | Number 45 | 7 June 2013 | Pages 5093–5238



inside mesopore



ISSN 1359-7345

RSC Publishing

**COMMUNICATION**

Shunichi Fukuzumi *et al.*

The long-lived electron transfer state of the 2-phenyl-4-(1-naphthyl)quinolinium ion incorporated into nanosized mesoporous silica–alumina acting as a robust photocatalyst in water



1359-7345(2013)49:45;1-#

## The long-lived electron transfer state of the 2-phenyl-4-(1-naphthyl)quinolinium ion incorporated into nanosized mesoporous silica–alumina acting as a robust photocatalyst in water†

Cite this: *Chem. Commun.*, 2013, **49**, 5132

Received 1st March 2013,  
Accepted 14th March 2013

DOI: 10.1039/c3cc41575a

www.rsc.org/chemcomm

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**A simple electron donor–acceptor linked dyad, the 2-phenyl-4-(1-naphthyl)quinolinium ion (QuPh<sup>+</sup>–NA), was incorporated into nanosized mesoporous silica–alumina to form a composite, which is highly dispersed in water and acts as an efficient and robust photocatalyst for the reduction of O<sub>2</sub> by oxalate to produce hydrogen peroxide with a quantum yield of 10%.**

Artificial photosynthesis attracts many researchers to realize a sustainable society depending mainly on solar energy.<sup>1</sup> A variety of electron donor–acceptor linked molecules, which mimic charge-separation processes in the photosynthetic reaction centre, have been utilized in photocatalytic systems to produce high-energy chemicals.<sup>2,3</sup> The donor–acceptor linked molecules form an electron-transfer (ET) state upon photoirradiation in reaction media, usually in organic solvents.<sup>4–6</sup> Even if an electron donor–acceptor linked molecule exhibits a long-lived ET state in the isolated state, *e.g.*, in frozen media, the lifetime of its ET state in a solution is much shorter than that in the isolated state, because of facile intermolecular back electron transfer.<sup>6</sup>

To avoid such an intermolecular event in solution, electron donor–acceptor linked molecules have been isolated on a metal oxide support. For example, 9-mesityl-10-methylacridinium ion (Acr<sup>+</sup>–Mes), which forms an ET state upon photoirradiation, has been supported on mesoporous silica–alumina by ion exchange, exhibiting the ET state lifetime longer than a second when suspended in acetonitrile (MeCN) at room temperature.<sup>7</sup> Among the reaction media used for chemical reactions, water is the most commonly used solvent owing to its abundance, ubiquitous nature and environmentally benign properties.

Thus, efficient photocatalytic processes using a long-lived ET state in water are highly desired. However, organic donor–acceptor linked molecules are yet to be employed as photocatalysts in water because of their insolubility in water.

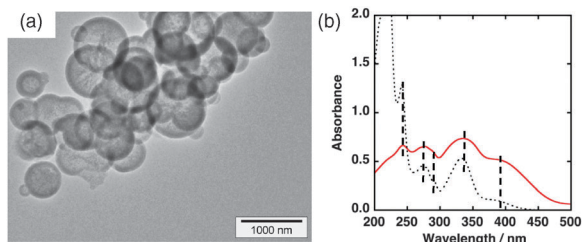
We report herein the incorporation of the 2-phenyl-4-(1-naphthyl)quinolinium ion (QuPh<sup>+</sup>–NA), which also forms the ET state acting as a strong oxidant and reductant ( $E_{\text{red}} = 1.87$  V and  $E_{\text{ox}} = -0.90$  V vs. SCE in MeCN) upon photoirradiation,<sup>5</sup> into nanosized mesoporous silica–alumina with a spherical shape (sAlMCM-41) by cation exchange and utilization of the composite (QuPh<sup>+</sup>–NA@sAlMCM-41) as a photocatalyst in aqueous media. The composite affords the extremely long-lived ET state (QuPh<sup>•</sup>–NA<sup>•+</sup>@sAlMCM-41) upon photoirradiation even in the presence of water. Thus, the photocatalytic activity of the composite was investigated for O<sub>2</sub> reduction by the oxalate anion to produce H<sub>2</sub>O<sub>2</sub> in water. Oxalate is converted into two equivalents of CO<sub>2</sub> after the reaction, therefore, pure H<sub>2</sub>O<sub>2</sub> in water can be easily obtained by just removing the catalytic nanocomposite by filtration or sedimentation.

Na<sup>+</sup>-exchanged sAlMCM-41 has been prepared according to a reported method with modifications.<sup>8</sup> TEM images of the synthesized Na<sup>+</sup>-exchanged sAlMCM-41 are displayed in Fig. 1a and Fig. S1 in ESI.† N<sub>2</sub> adsorption and desorption isotherms for Na<sup>+</sup>-exchanged sAlMCM-41 afforded a Brunauer–Emmett–Teller (BET) surface area of 520 m<sup>2</sup> g<sup>−1</sup> with a pore diameter of 1.8 nm determined by the Barrett–Joyner–Halenda (BJH) method (Fig. S2 in ESI†). The Na<sup>+</sup>-exchanged sAlMCM-41 was ion-exchanged with QuPh<sup>+</sup>–NA to prepare the QuPh<sup>+</sup>–NA@sAlMCM-41 composite. Because the molecular size of QuPh<sup>+</sup>–NA is small compared with the pore size of sAlMCM-41, cation exchange with QuPh<sup>+</sup>–NA occurs spontaneously upon mixing Na<sup>+</sup>-exchanged sAlMCM-41 with QuPh<sup>+</sup>–NA(ClO<sub>4</sub><sup>−</sup>) in MeCN as observed by UV-vis absorption of the supernatant (Fig. S3, ESI†). The amount of adsorbed QuPh<sup>+</sup>–NA was determined by the decrease in absorption of the solution at 333 nm owing to QuPh<sup>+</sup>–NA. The number of Al atoms on the surface of sAlMCM-41 estimated from the used amount of Al source was  $1.05 \times 10^{-3}$  mol g<sup>−1</sup>, thus, 7.9% of all the Na<sup>+</sup>-sites was

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† Electronic supplementary information (ESI) available: Experimental details, Fig. S1–S4 (TEM images of Na<sup>+</sup>-exchanged sAlMCM-41, the N<sub>2</sub> isotherm curve and the BJH plot, UV-vis absorption change and time courses of EPR signals). See DOI: 10.1039/c3cc41575a

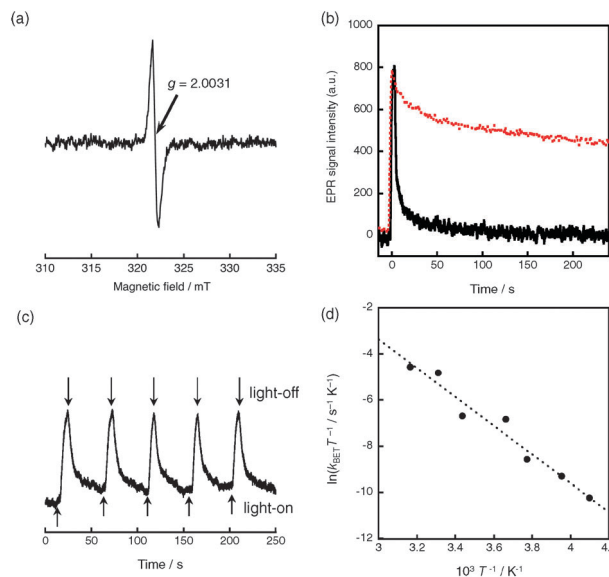


**Fig. 1** (a) Transmission electron microscope (TEM) image of Na<sup>+</sup>-exchanged sAlMCM-41. (b) Diffuse reflectance UV-vis spectrum of the QuPh<sup>+</sup>-NA@sAlMCM-41 composite (red solid line) compared with the UV-vis absorption spectrum of the QuPh<sup>+</sup>-NA ion in MeCN (black dotted line). Positions of peaks and shoulders are indicated by broken lines.

occupied by QuPh<sup>+</sup>-NA. The diffuse reflectance UV-vis spectrum of the QuPh<sup>+</sup>-NA@sAlMCM-41 composite shown in Fig. 1b (red solid line) shows that the positions of peaks and shoulders of the spectrum are quite similar to those of the QuPh<sup>+</sup>-NA ion in MeCN (black dotted line in Fig. 1b).

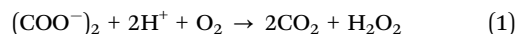
Photoirradiation of the QuPh<sup>+</sup>-NA@sAlMCM-41 composite using a 1000 W high-pressure mercury lamp through a UV-light cutting filter ( $\lambda > 340$  nm) results in the formation of the ET state (QuPh<sup>•</sup>-NA<sup>•+</sup>@sAlMCM-41) via photoinduced electron transfer from the naphthalene (NA) moiety to the singlet excited state of the quinolinium ion (QuPh<sup>+</sup>) moiety as evidenced by EPR measurements. An EPR signal at  $g = 2.0031$  appearing upon photoirradiation (Fig. 2a) assures formation of a radical species. The decrease in the EPR signal intensities observed by cutting off the light obeyed first-order kinetics for a prolonged time after 20 s as shown in Fig. 2b (red dotted line), revealing the intramolecular back electron transfer of the ET state of QuPh<sup>+</sup>-NA. Based on the rate constant of the decay curve, the lifetime of the ET state is longer than 190 s at 316 K. The ET state lifetime in the presence of water significantly decreased as compared with that observed in the absence of water (Fig. 2b, black solid line). Water vapour was adsorbed on the composite at 313 K under reduced pressure for several hours, because the presence of bulk water strongly interferes the observation of EPR signals. The EPR signal intensity oscillated by the intermittent photoirradiation for 2 seconds followed by 48 s in the dark as indicated in Fig. 2c. The similar signal intensity obtained at each cycle resulted from the photo-robustness of the composite. An Eyring plot in Fig. 2d for the rate constant of intramolecular back electron transfer in the ET state of the composite indicates that the activation enthalpy ( $\Delta H^\ddagger$ ) of the composite was determined to be  $12(\pm 2)$  kcal mol<sup>-1</sup>. A large  $\Delta H^\ddagger$  value [ $20(\pm 1)$  kcal mol<sup>-1</sup>] has also been reported for Acr<sup>+</sup>-Mes supported on AlMCM-41 in MeCN,<sup>7</sup> resulting from a large driving force for the back electron transfer in the Marcus inverted region,<sup>9</sup> because of decreased solvation in the pores of sAlMCM-41.

The QuPh<sup>+</sup>-NA@sAlMCM-41 composite was examined as a photocatalyst for the production of H<sub>2</sub>O<sub>2</sub> in an aqueous solution. H<sub>2</sub>O<sub>2</sub> can be simply prepared by reduction of atmospheric O<sub>2</sub> by oxalate, which is capable of acting as a strong reductant ( $E^\circ = -0.48$  V vs. NHE).<sup>10</sup> Oxalate can be easily found in the soil and leaves of various vegetables at a high



**Fig. 2** (a) EPR spectrum of the QuPh<sup>+</sup>-NA@sAlMCM-41 composite in the presence of adsorbed water under photoirradiation using a high-pressure mercury lamp and a UV cut-off filter ( $\lambda > 340$  nm). (b) Time profile of the EPR signal intensity for QuPh<sup>+</sup>-NA<sup>•+</sup>@sAlMCM-41 in the absence (red dotted) or presence (black solid) of water at 316 K. (c) Time profile of the EPR signal intensity for QuPh<sup>+</sup>-NA<sup>•+</sup>@sAlMCM-41 in the presence of water upon intermittent photoirradiation for 2 seconds followed by 48 seconds in the dark at 316 K. (d) Plot of  $\ln(k_{\text{BET}} T^{-1})$  vs.  $T^{-1}$  for intramolecular back electron transfer of QuPh<sup>+</sup>-NA@sAlMCM-41 in the presence of water. The water-adsorbed sample was prepared by exposure of QuPh<sup>+</sup>-NA@sAlMCM-41 to water vapour at 313 K overnight under reduced pressure. The time profile at each temperature is indicated in Fig. S4 in ESI.†

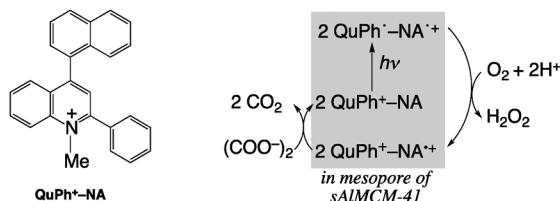
content of  $\sim 1$  wt%.<sup>11</sup> Nature utilizes oxalate as an electron donor for producing H<sub>2</sub>O<sub>2</sub> in the enzymatic active centre of oxalate oxidase, which catalyses the oxidation of oxalate, reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> and formation of two moles of CO<sub>2</sub> [eqn (1)].<sup>12</sup> In this process, CO<sub>2</sub> is solely produced as a



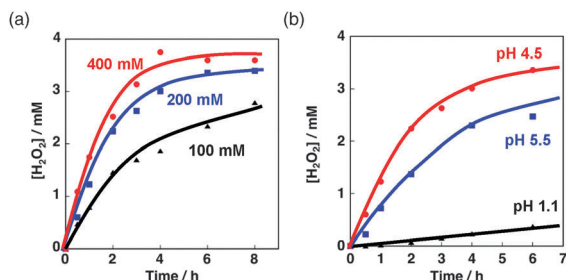
by-product. However, no functional model of oxalate oxidase has been reported, because the C-C bond of oxalate is kinetically stable. The property of oxalate, which can be converted into CO<sub>2</sub> after oxidation, benefits efficient photocatalytic reactions because of prevention of back electron transfer. In our photocatalytic system, oxalate can be used as a natural electron donor to reduce O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> using the QuPh<sup>+</sup>-NA@sAlMCM-41 composite as a photocatalyst in water. Scheme 1 depicts the overall catalytic cycle for H<sub>2</sub>O<sub>2</sub> production by O<sub>2</sub> reduction using QuPh<sup>+</sup>-NA and oxalate as a photocatalyst and an electron donor, respectively.

The photocatalytic H<sub>2</sub>O<sub>2</sub> production has been performed by photoirradiation ( $\lambda > 340$  nm) of an oxygen-saturated aqueous suspension (1.3 mM, 2.0 mL) containing QuPh<sup>+</sup>-NA@sAlMCM-41 (QuPh<sup>+</sup>-NA, 0.22 mM) and oxalate (100–400 mM). Fig. 3a shows the time courses of H<sub>2</sub>O<sub>2</sub> production in the photocatalytic reaction. The initial H<sub>2</sub>O<sub>2</sub> formation rate (1 h) increased from 1.6  $\mu\text{mol h}^{-1}$  to 2.5 and 3.5  $\mu\text{mol h}^{-1}$  upon increasing the concentration of oxalate from 100 mM to 200 and 400 mM in the reaction solution. The pH of the reaction solution was





**Scheme 1** Chemical structure of QuPh<sup>+</sup>-NA and overall catalytic cycle for H<sub>2</sub>O<sub>2</sub> production.



**Fig. 3** (a) Time courses of H<sub>2</sub>O<sub>2</sub> production by photoirradiation ( $\lambda > 340$  nm) of an aqueous suspension containing (COO<sup>-</sup>)<sub>2</sub> (400 mM, red; 200 mM, blue; 100 mM, black, [(COOK)<sub>2</sub>]/[(COOH)<sub>2</sub>] = 3) and the QuPh<sup>+</sup>-NA@sAlMCM-41 composite ([QuPh<sup>+</sup>-NA]: 0.2 mM). (b) Time courses of H<sub>2</sub>O<sub>2</sub> production under different pH conditions. The pH value of each aqueous medium was controlled to 1.1 (black), 4.5 (red) or 5.5 (blue) by changing the ratio of (COOH)<sub>2</sub> to (COOK)<sub>2</sub>. The total concentration of the oxalate anion was fixed at 200 mM.

controlled by changing the ratio of the amount of oxalic acid to that of disodium oxalate keeping the concentration of oxalate constant (200 mM) as shown in Fig. 3b. The initial H<sub>2</sub>O<sub>2</sub> formation rate (1 h) reached the maximum around pH 4.5. A further increase or decrease in pH decelerated the H<sub>2</sub>O<sub>2</sub> formation. At lower pH, the oxalate dianion is protonated to produce the monoanion and oxalic acid, which cannot act as an electron donor in the photocatalytic system. At higher pH, reduction of O<sub>2</sub> is thermodynamically unfavourable, because the one-electron reduced species of O<sub>2</sub> (O<sub>2</sub><sup>•-</sup>) cannot be protonated to produce HO<sub>2</sub><sup>•</sup> that disproportionates to yield H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub>. Thus, the H<sub>2</sub>O<sub>2</sub> formation rate reached maximum around pH 4.5, which is close to the pK<sub>a2</sub> of oxalic acid (4.27) and the pK<sub>a</sub> of HO<sub>2</sub><sup>•</sup> (4.9).<sup>13</sup>

The efficiency of the photocatalytic reaction can be evaluated by the quantum yield ( $\Phi$ ) of the products, where the  $\Phi$  value is defined as the mole number of H<sub>2</sub>O<sub>2</sub> produced divided by that of photons absorbed by the photocatalyst. In previous reports, the  $\Phi$  value of H<sub>2</sub>O<sub>2</sub> production has been determined to be 4.2% by photoirradiation (340 nm) of an oxygen-saturated buffer (pH 7.5–8.0) containing ZnO colloid and oxalate.<sup>14</sup> The  $\Phi$  value of the H<sub>2</sub>O<sub>2</sub> production in an aqueous solution containing the QuPh<sup>+</sup>-NA@sAlMCM-41 composite ([QuPh<sup>+</sup>-NA]: 0.2 mM) and oxalate (200 mM) was determined to be 10% using a ferrioxalate actinometer under photoirradiation with monochromatised light of 334 nm. Such a high quantum yield originated from the high oxidizing and reducing abilities of

photogenerated QuPh<sup>+</sup>-NA<sup>•+</sup>, which are sufficient for both the oxidation of oxalate and the reduction of O<sub>2</sub>.<sup>5</sup>

In summary, a long-lived ET state was attained in pure water for the first time by supporting QuPh<sup>+</sup>-NA on nanosized mesoporous silica-alumina. The formation of the long-lived ET state of the QuPh<sup>+</sup>-NA@sAlMCM-41 composite was confirmed by EPR measurements. The composite has been shown to act as an efficient photocatalyst for H<sub>2</sub>O<sub>2</sub> production by reducing O<sub>2</sub> with oxalate in water. The high quantum yield of 10% for H<sub>2</sub>O<sub>2</sub> production in water without any organic solvent was comparable to that achieved in the homogeneous reaction system using an organic solvent.<sup>15</sup>

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