

# Long-lived charge separation in a donor–acceptor dyad adsorbed in mesoporous MCM-41

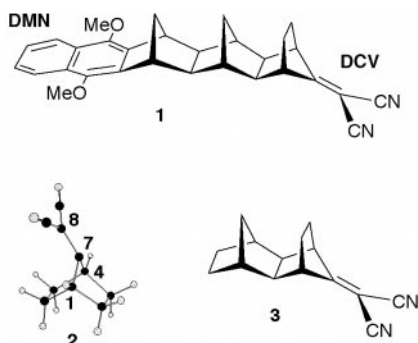
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**Irradiation of a rigid donor–[6-bond-bridge]–acceptor dyad [donor = dimethoxynaphthalene (DMN); acceptor = dicyanovinyl (DCV)] occluded within the pores of mesoporous MCM-41 containing aluminium leads to the formation of the DCV radical anion of the dyad with a lifetime of days.**

Photoinduced charge separation in covalently linked dyads such as **1** occurs extremely rapidly, a result of strong electronic coupling mediated by a through-bond (TB) mechanism.<sup>1</sup> However the lifetimes of the resulting charge-separated (CS) states are short (nanosecond scale<sup>2</sup>), which is also a consequence of strong TB electronic coupling. We now report that photolysis of **1**,<sup>1b</sup> which has been occluded within the pores of mesoporous MCM-41, leads to a charge separation in which the host material participates, the final state of which has a lifetime measured in days.

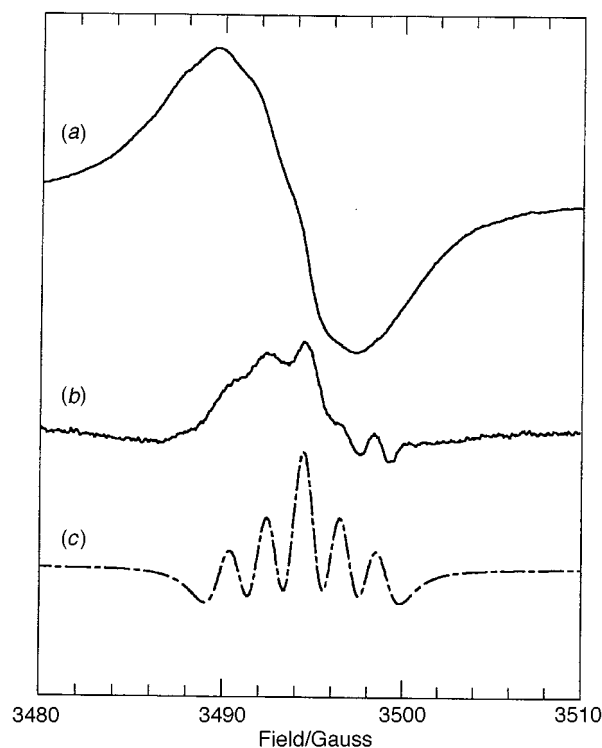


The ability of microporous zeolite hosts to stabilize organic radical cations and anions is well documented.<sup>3</sup> Mallouk *et al.* showed that the rates of charge recombination in a series of Ru<sup>II</sup>–viologen dyads adsorbed at the external surface of several microporous zeolites were slowed by a factor of 10<sup>5</sup> relative to the same molecules in solution.<sup>4</sup> This dramatic stabilization of the charge-separated state in a molecule only partly occluded within a porous solid prompted us to begin a study of dyads totally occluded within the pores of the larger pore size (mesoporous) zeolite analog, MCM-41. The test dyad selected was **1**, which comprises a dimethoxynaphthalene (DMN) donor coupled to a dicyanovinyl (DCV) acceptor covalently linked to a rigid  $\sigma$ -bonded hydrocarbon bridge.

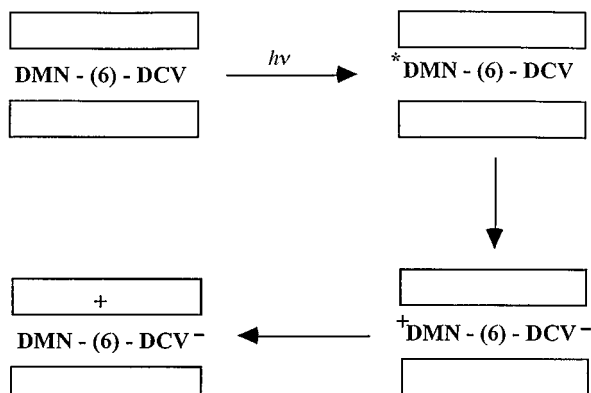
MCM-41 is a mesoporous silica containing a regular array of uniform linear one-dimensional pores with an approximately hexagonal cross section and a diameter determined by the particular surfactant molecule used in the synthesis.<sup>5,6</sup> Although the original preparations of MCM-41 were pure silica materials, it is also possible to incorporate aluminium into the synthesis to form mesoporous aluminosilicate zeolite analogs (hereafter designated AIMCM-41) with pores large enough to easily accommodate molecules such as **1**.<sup>7</sup> The pore volume of AIMCM-41 (0.22 cm<sup>3</sup> g<sup>-1</sup>) is sufficient to occlude up to 50 wt% of **1**. FTIR and <sup>13</sup>C NMR measurements on samples of AIMCM-41 (Si:Al = 15) loaded up to this level by impregnating the dehydrated AIMCM-41 with a CH<sub>2</sub>Cl<sub>2</sub> solution of **1** under nitrogen showed that the molecule was adsorbed intact into the pores of the AIMCM-41. † Irradiation of loaded samples

*in vacuo* at wavelengths where the DMN chromophore absorbs (below 310 nm) gave the EPR signal shown in Fig. 1(a). This signal grew in intensity with irradiation time for several hours, and was stable in the dark *in vacuo* for at least one day. The first derivative spectrum shows evidence of poorly resolved hyperfine splitting ‡ which was enhanced by recording the second harmonic spectrum [Fig. 1(b)]; this shows clearly five hyperfine components. The second harmonic spectrum could be approximately simulated by assuming an isotropic hyperfine coupling with two equivalent <sup>14</sup>N nuclei and a coupling constant of 1.8 Gauss [Fig. 1(c)]. The actual hyperfine coupling in the observed spectra is clearly not completely isotropic; nevertheless the spectrum appears to be that expected for the DCV radical anion moiety in **1**. This identification was supported by B3LYP<sup>8</sup> DFT calculations of the isotropic hyperfine coupling constant for the model dicyanovinylbornane radical anion **2**. § The calculated coupling constants are 1.76 and 1.34 Gauss using the 3-21G and 631G basis sets, respectively.

No EPR signal was observed when the corresponding experiment was carried out in MCM-41 containing no aluminium, *i.e.* the photoinduced formation of the radical anion of **1** appears to require the presence of aluminium on the MCM-41 framework. Conventional aluminosilicate zeolites are known to contain electron donor sites capable of transferring an electron to strong acceptors such as tetracyanoethylene.<sup>9</sup> Adsorption of TCNE from CH<sub>2</sub>Cl<sub>2</sub> solution into dehydrated MCM-41 gave the



**Fig. 1** (a) EPR spectrum of **1** in AIMCM-41 following irradiation *in vacuo* at room temperature; (b) second harmonic EPR spectrum; (c) computer simulation of (b) assuming isotropic hyperfine coupling to two equivalent <sup>14</sup>N nuclei of 1.8 Gauss.



**Fig. 2** Schematic of the proposed mechanism for the formation of the long-lived radical anion of **1**.

EPR spectrum of the radical anion only when the MCM-41 contained aluminium, and not with the all-silica form, confirming the role of aluminium in the framework in generating electron donor sites.

It is unlikely that the radical anion of **1** is formed in AIMCM-41 by direct electron transfer from the host, since the reduction potential of the DCV group is 1.5 V more negative than that of TCNE,<sup>10</sup> and the EPR signal was not observed without irradiation. This was confirmed by adsorbing the molecule **3** which contains no electron donor group into AIMCM-41; this gave no EPR signal in the dark or upon irradiation.

Our proposed explanation for the observed photoformation of the stable radical anion of **1** when it is adsorbed in AIMCM-41 (but not MCM-41 containing no aluminium) is shown schematically in Fig. 2: photoinduced intramolecular charge separation is followed immediately by hole transfer from the DMN cation radical to the MCM-41, leaving a stable DCV radical anion.

The ability of the host to stabilize the radical anion in this way clearly depends critically on the relative rates of charge recombination within the charge-separated state of the dyad and hole transfer to the host. We plan flash photolysis experiments to quantify these rates and to determine quantum yields, as has been done in solution<sup>1</sup> and for zeolite adsorbed species.<sup>4</sup> Better characterization of the electron donor (hole acceptor) sites in the AIMCM-41 host is also necessary. The many variations possible in this system (varying the Al content of the host, the pore size, the length of the hydrocarbon spacer and the redox properties of the dyad) provide intriguing opportunities to understand more fully and control electron transfer processes in heterogeneous systems.

An exciting aspect of our preliminary findings is that they offer the possibility of transducing photonic energy into truly

long-lived energetic species possessing useful chemical potential. Furthermore, the generation of long-lived charge separation in mesoporous materials need not be restricted to rigid multichromophoric systems, but should occur with non-rigid systems as well. This is a very important conjecture, from the viewpoint of synthetic facility, and its validity will be tested.

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## Notes and references

† The adsorbed molecule gave FTIR and <sup>13</sup>C NMR spectra closely similar to those of the parent compound. Primary evidence for adsorption within the pores of MCM-41 came from observation of FTIR spectra: the  $\nu(\text{OH})$  band due to silanol groups within the pores of MCM-41 was broadened and shifted to lower frequency, indicating a weak hydrogen bonding interaction with **1**.

‡ No improvement in resolution was achieved by recording the spectrum at 77 K.

§ Geometry optimization of **2** was carried out under  $C_s$  symmetry constraint using the UB3LYP theoretical model and the 3-21G and 6-31G(d) basis sets. The UB3LYP/6-31G(d) and UB3LYP/3-21G optimized structures are nearly identical.

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