Electronic Supplementary Information

Photoinduced Electron Transfer Between a Donor and an Acceptor Separated by a Capsular Wall

Mintu Porel,[a] Steffen Jockusch,[b] Anand Parthasarathy,[a] V. Jayathirtha Rao,[a] Nicholas J. Turro[b] and V. Ramamurthy[a]*

[a]Department of Chemistry, University of Miami, Coral Gables, Florida 33124, USA.

[b]Department of Chemistry, Columbia University, New York, New York 10027, USA.

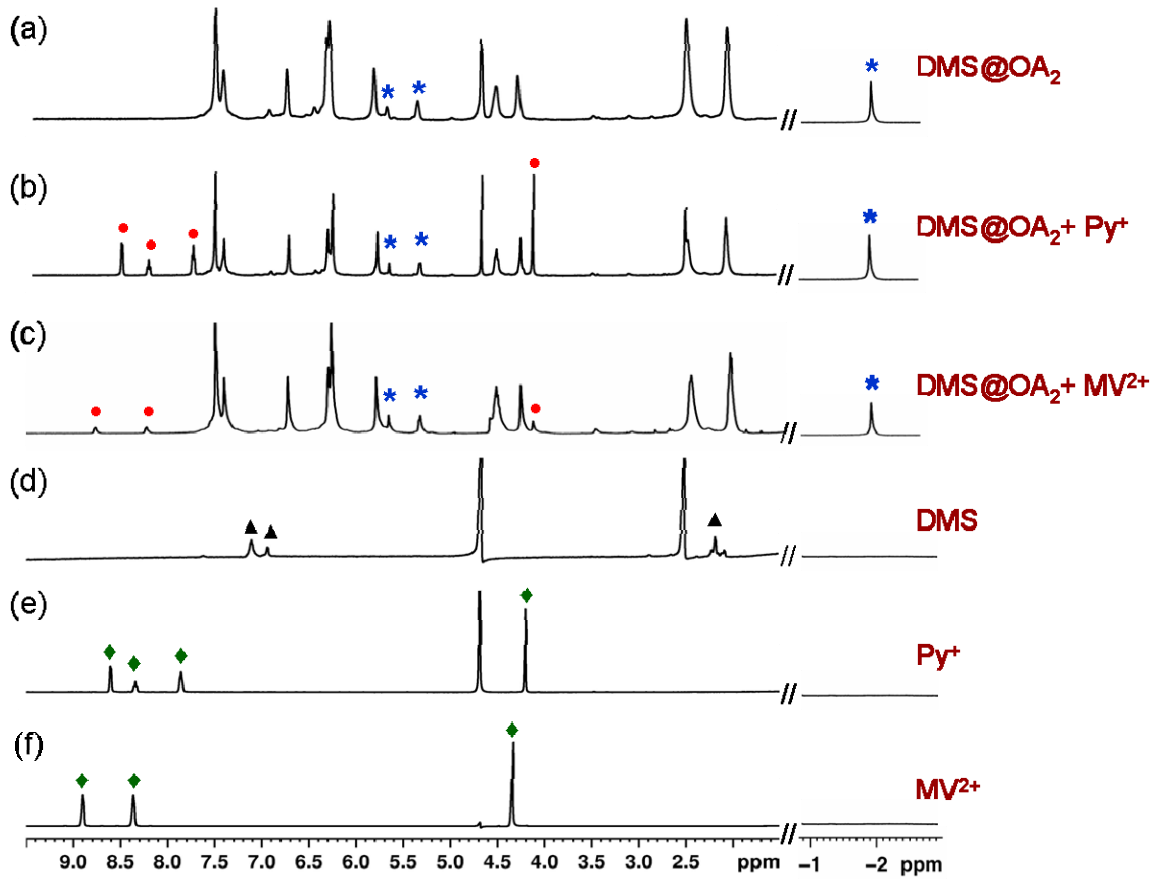


Figure S1. ^{1}H NMR (500 MHz, D_2O) spectra of (a) DMS@OA_2, (b) DMS@OA_2 + Py^+, (c) DMS@OA_2 + MV^{2+}, (d) DMS, (e) Py^+, (f) MV^{2+}; [DMS] = 0.5 mM, [OA] = 1 mM, [Py^+] = 1 mM and [MV^{2+}] = 1 mM in 10 mM sodium tetraborate buffer; "*", "●", "▲" and "♦" represent bound DMS protons, bound Py^+ and MV^{2+} protons, free DMS protons and free Py^+ and MV^{2+} protons signal, respectively.

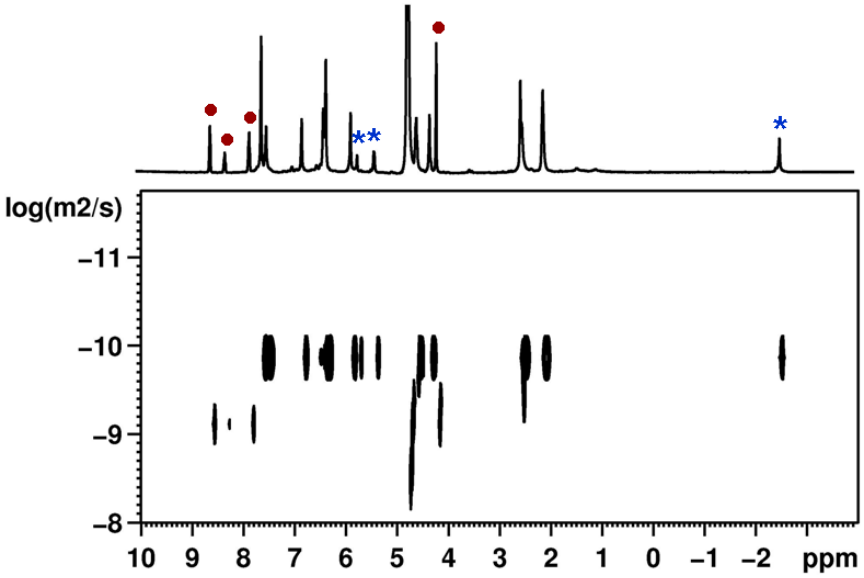


Figure S2. 2D DOSY (500 MHz, D_2O) spectra of DMS@OA_2 + Py^+; [DMS] = 0.5 mM, [OA] = 1 mM, [Py^+] = 1 mM; "*" and "•" represent bound DMS proton and Py^+ proton signals, diffusion constant of DMS@OA_2 and Py^+ are 1.2×10^{-10} m^2/s and 4.8×10^{-10} m^2/s, respectively.

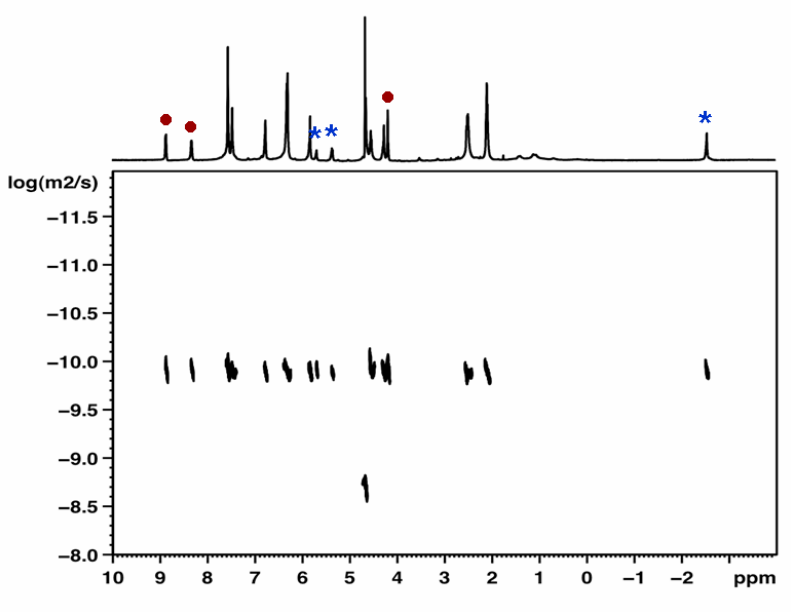


Figure S3. 2D DOSY (500 MHz, D_2O) spectra of DMS@OA_2 + MV^{2+}; [DMS] = 0.5 mM, [OA] = 1 mM, [MV^{2+}] = 0.5 mM; "*" and "•" represent bound DMS proton and MV^{2+} proton signals, diffusion constant of DMS@OA_2 and MV^{2+} are 1.25×10^{-10} m^2/s and 1.17×10^{-10} m^2/s, respectively.

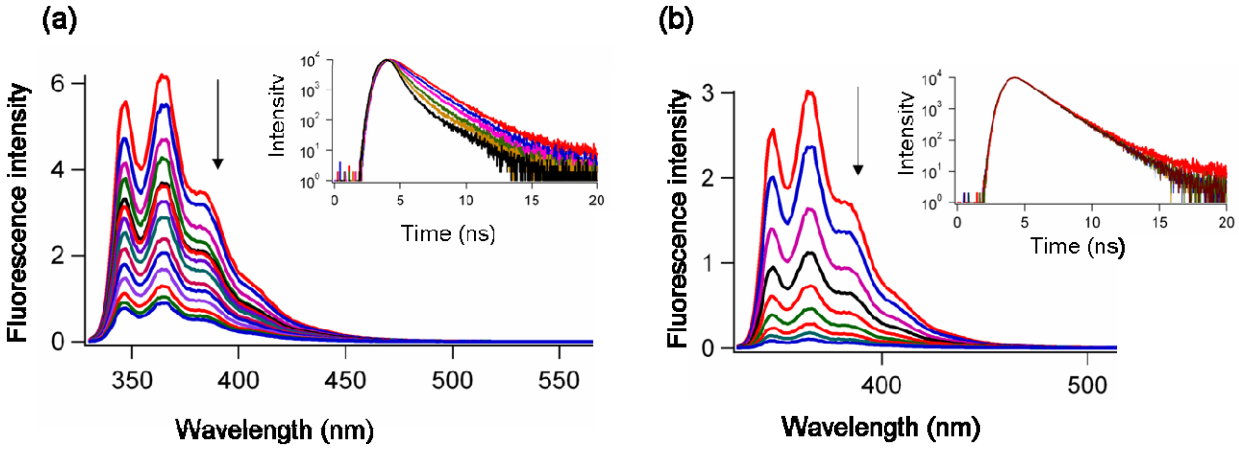


Figure S4. (a) Fluorescence quenching titration of DMS@OA_2 with Py^+, Inset: time resolved quenching titration of DMS@OA_2 with Py^+ and (b) Fluorescence quenching titration of DMS@OA_2 with MV^{2+}, Inset: time resolved quenching titration of DMS@OA_2 with MV^{2+}; λ_{ex}= 320 nm, λ_{em}= 365 nm; [DMS] = 1.25×10^{-5} M, [OA] = 2.5×10^{-5} M and [Py^+] = 0 to 31.75×10^{-5} M and [MV^{2+}] = 0 to 2.5×10^{-5} M in 10 mM sodium tetraborate buffer.

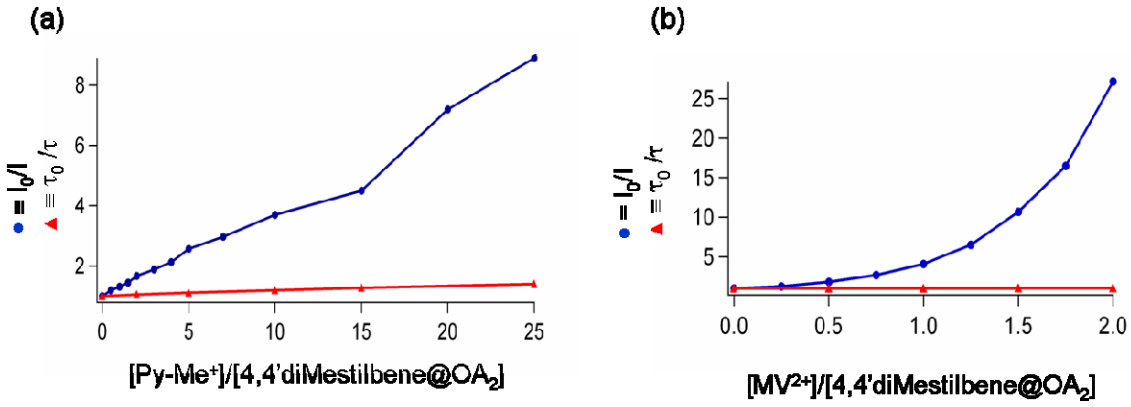


Figure S5. Stern-Volmer plot of quenching study of DMS@OA_2 with (a) Py^+, dynamic rate constant = 7.8×10^{11} $M^{-1}s^{-1}$ and (b) MV^{2+}; [DMS] = 1.25×10^{-5} M, [OA] = 2.5×10^{-5} M, [Py^+] = 0 to 31.25×10^{-5} M and [MV^{2+}] = 0 to 2.5×10^{-5} M in 10 mM sodium tetraborate buffer; "●"and "▲"represent steady state and time resolved study, respectively.

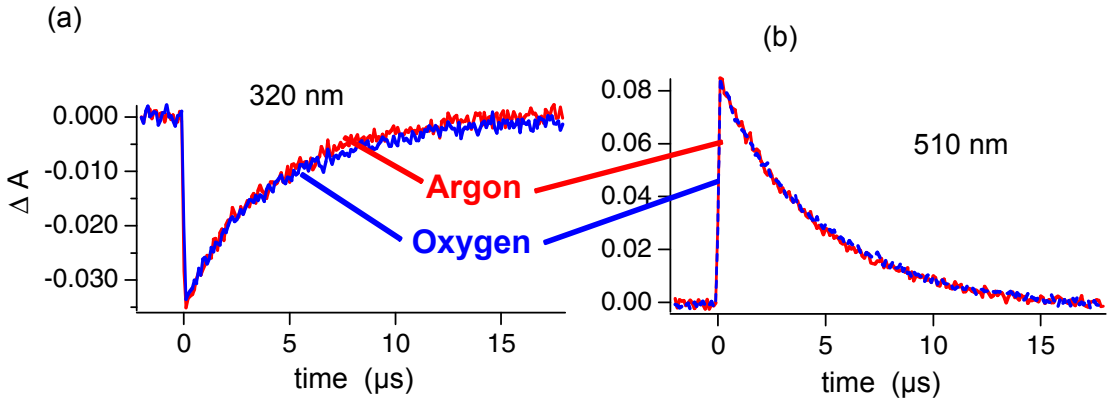


Figure S6. Kinetic traces of transient absorption at 320nm (a) and 510 nm (b) of argon (red) and oxygen (blue) saturated soutions of DMS (1.25×10^{-5} M), OA (2.5×10^{-5} M) and Py^{+} (31.25×10^{-5} M) in 10 mM sodium tetraborate buffer; Laser pulse: 308 nm, pulse width: 15 ns. No change in kinetics after oxygen saturation is observed. This shows that the transient at 510 nm is not quenched by oxygen, which is consistent with assignment to $DMS^{+}\bullet@OA_2$.

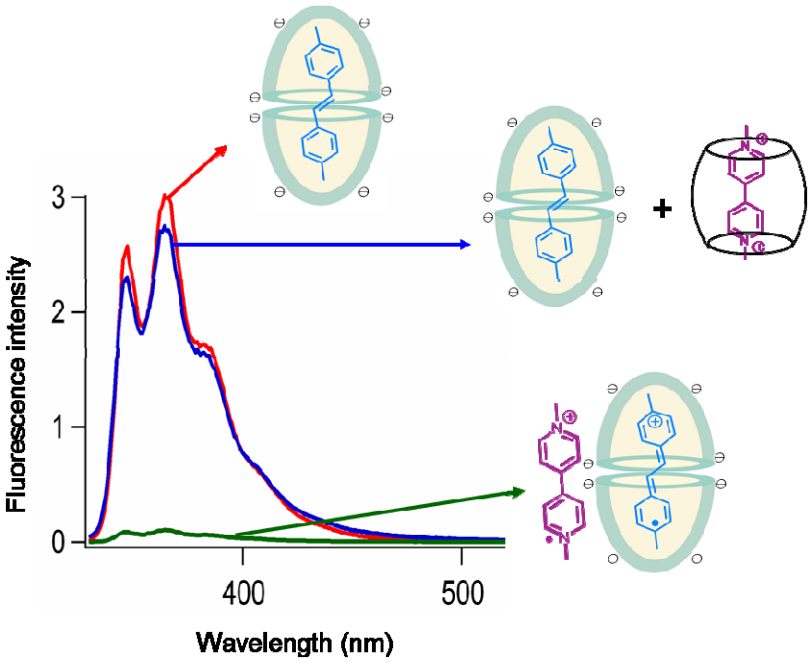


Figure S7. Fluorescence spectra of $DMS@OA_2$, $DMS@OA_2 + MV^{2+}$ and $DMS@OA_2 + MV^{2+}@CB7$; [DMS] = 1.25×10^{-5} M, and [OA] = [MV^{2+}] = [CB7] = 2.5×10^{-5} M in 10 mM sodium tetraborate buffer; λ_{ex}: 320 nm.

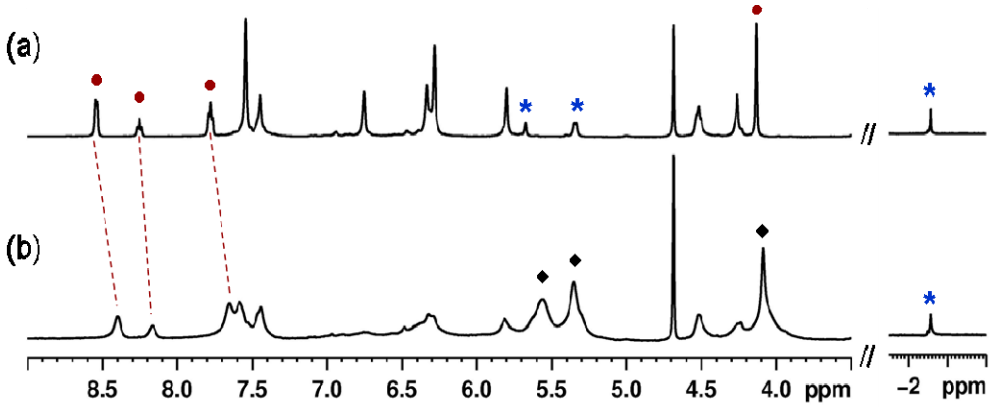


Figure S8. ^{1}H NMR (500 MHz, D_2O) spectra of (a) DMS@OA_2 + Py^+ and (b) DMS@OA_2 + Py^+@CB7; [DMS] = 0.5 mM, [OA] = [Py^+] = [CB7] = 1 mM; "*", "●" and "♦" represent bound DMS proton, Py^+ and CB7 proton signals, respectively.

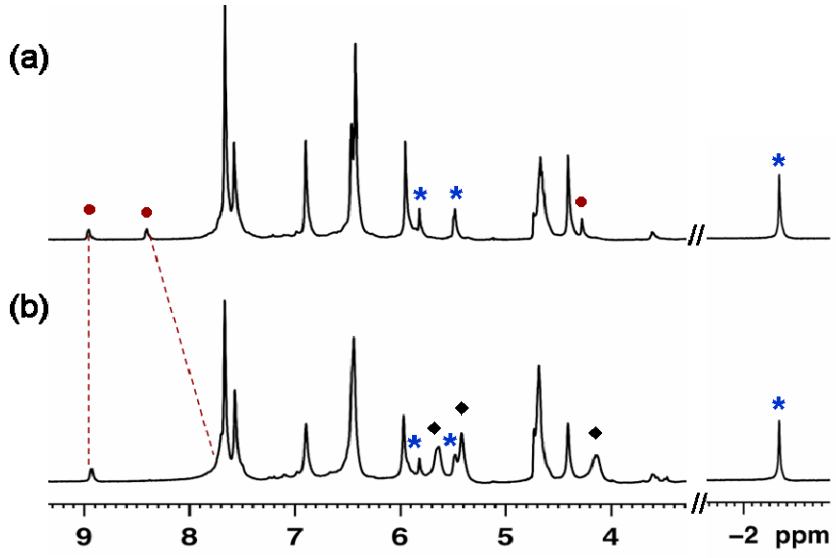


Figure S9. ^{1}H NMR (500 MHz, D_2O) spectra of (a) DMS@OA_2 + MV^{2+} and (b) DMS@OA_2 + MV^{2+}@CB7; [DMS] = 0.5 mM, [OA] = [MV^{2+}] = [CB7]= 1 mM; "*", "●" and "♦" represent bound DMS proton, MV^{2+} and CB7 proton signals, respectively.

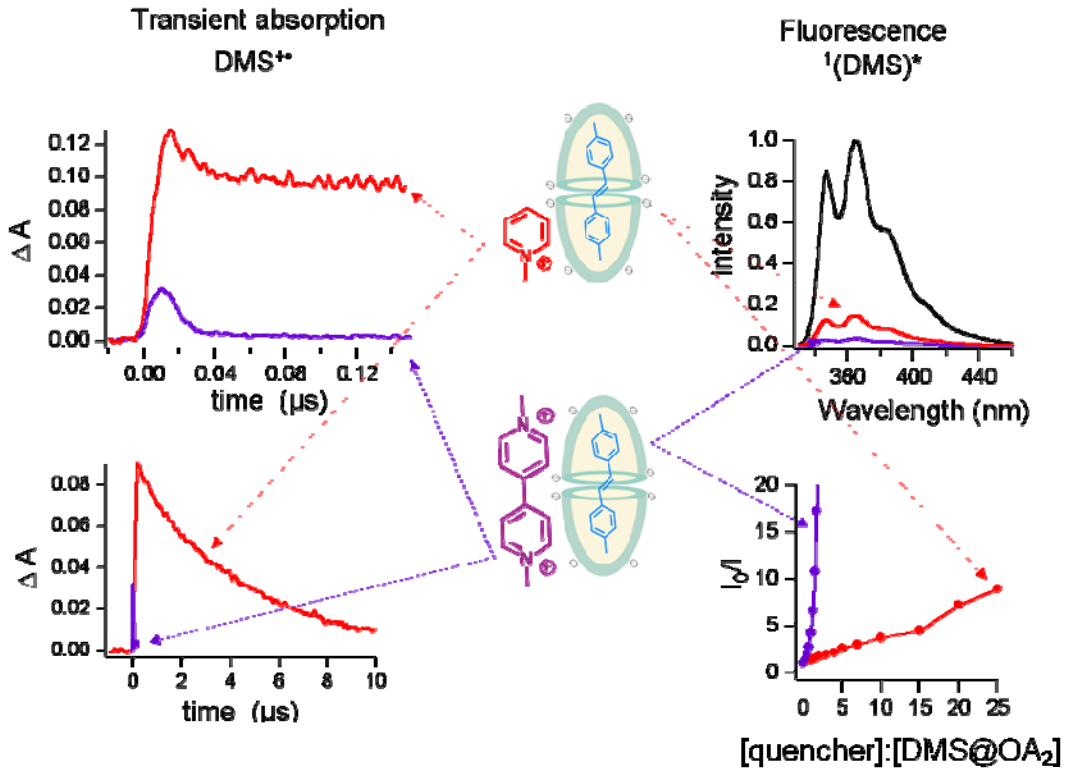


Figure S10. Comparison of electron transfer processes from DMS@OA_2 to Py^+ and MV^{2+} by transient absorption at 510 nm of $DMS^+\bullet$ (left) and fluorescence from $^1(DMS)^*$ (right). For experimental details see Figs. 1 and 2. Although quenching of $^1(DMS)^*$ is more efficient with MV^{2+} compared to Py^+ (see fluorescence), the observed transient absorption of $DMS^+\bullet$ is significantly smaller for MV^{2+}. This is probably caused by fast back electron transfer from $MV^+\bullet$ to $DMS^+\bullet$ on a time scale to fast to be observed with our experimental setup. The kinetic transient absorption trace of $DMS^+\bullet$ in the presence of Py^+ shows a minor fast decay component on early time scales (top left, red line) which is probably caused by fast back electron transfer of a minor fraction of the radical pair before escape and diffusion of Py• into the solution occurred

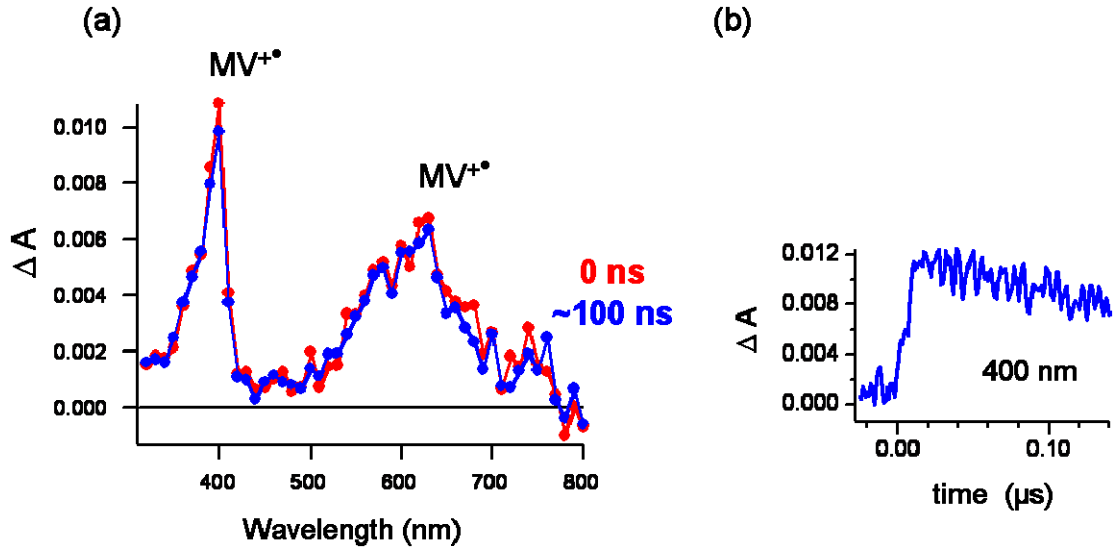


Figure S11. Transient absorption spectra (a) and decay trace (b) of the radical cation of MV^{2+} generated by laser excitation (308 nm, pulse width 15 ns) of argon saturated solutions of OA (2.5×10^{-5} M) in the presence of MV^{2+} (2.5×10^{-5} M); sodium tetraborate buffer solution (10 mM).

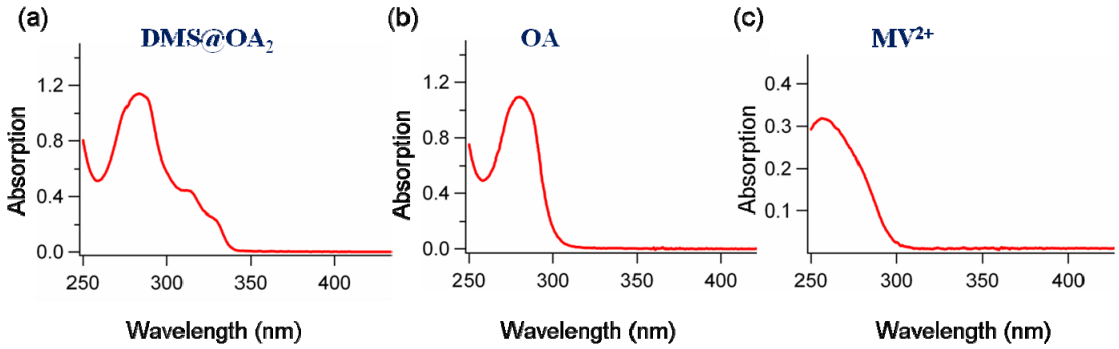
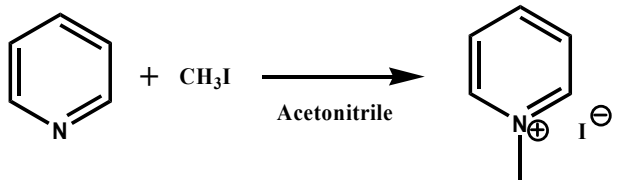


Figure S12. Absorption spectra of (a) DMS@OA_2 (molar extinction coefficient at 308 nm is 7500 $M^{-1}cm^{-1}$); (b) OA (molar extinction coefficient at 308 nm is 530 $M^{-1}cm^{-1}$) and (c) MV^{2+} (molar extinction coefficient at 308 nm is 200 $M^{-1}cm^{-1}$); [OA] = 6×10^{-5} M, [DMS] = 3×10^{-5} M and [MV^{2+}] = 6×10^{-5} M in 10 mM sodium tetraborate buffer.

Experimental Section

Materials and Methods: The hosts octa acid[1], cucurbit[7]uril[2] were synthesized following published procedures. The guest DMS was synthesized following the published procedure[3] and MV^{2+} was used as received from Sigma-Aldrich/Acros.

Synthesis of Py^+I^-:



Equal molar equivalents of pyridine and methyl iodide were dissolved in acetonitrile and refluxed at 80 °C for 16 h. The reaction mixture was cooled to room temperature and then ethyl acetate was added slowly until precipitation was observed. The precipitate was washed with ethyl acetate and dried under vacuum. The purity was checked by ^{1}H NMR.

General protocol for NMR study:

^{1}H NMR studies were carried out on a Bruker 500 MHz NMR spectrometer at 25 °C. 600 µL of a D_2O solution of host OA (1mM OA in 10 mM $Na_2B_4O_7$) was taken in a NMR tube and to this 0.5 equivalent increments of DMS (5 µL of a 60 mM solution in DMSO-d_6) was added. The ^{1}H NMR experiments were carried out after shaking the NMR tube for 5 min after addition. Completion of complexation was monitored by the disappearance of the free host OA signals upon addition of guest. The required amount of quencher solution (Py^+ and MV^{2+}; stock solutions of 30 mM were prepared in D_2O) was added and 1H NMR was recorded after shaking the NMR tube for 5 min. For experiments in the presence of CB7, the calculated amount of CB7 (solid) was added to DMS@OA_2 + quencher solutions and shaken properly before ^{1}H NMR spectra were recorded.

General protocol for fluorescence study:

Fluorescence emission spectra were recorded on a FS920CDT Edinburgh steady-state fluorimeter and the lifetime measurements on FL900CDT fluorescence lifetime spectrometer. Capsular assemblies (0.5 mM) were made by adding 5 μL of 60 mM solution of DMS (in DMSO solution) to 0.6 mL of 1 mM OA in 10 mM borate buffer in H_2O. It was diluted appropriately with 10 mM buffer solution to have the required concentration of host/guest complex. Calculated amounts of quencher solution (stock solutions in H_2O) were added and mixed thoroughly and then the fluorescence spectra were recorded. The required amount of CB7 (stock solution was prepared in H_2O) was added to the solution (host/guest + quencher) and fluorescence spectra were recorded.

General protocol for transient absorption study:

Laser flash photolysis experiments employed the pulses from a Lambda Physik Lextra 50 excimer laser (308 nm, pulse width 15 ns) and a home built system, which has been described elsewhere.[4]

Reference:

[1] C. L. D. Gibb; B. C. Gibb *J. Am. Chem. Soc.* 2004, **126**, 11408–11409.

[2] A. Day; A. P. Arnold; R. J. Blanch; B.. Snushall *J. Org. Chem.* 2001, **66**, 8094.

[3]A. Parthasarathy; V. Ramamurthy *Photochem. Photobiol. Sci.* 2011, **10**, 1455-1462.

[4]Y. Yagci, S. Jockusch, N. J. Turro *Macromolecules* 2007, **40**, 4481-4485.