Photoinduced Electron Transfer Across a Molecular Wall: Coumarin Dyes as Donors and Methyl viologen and TiO_2 as Acceptors

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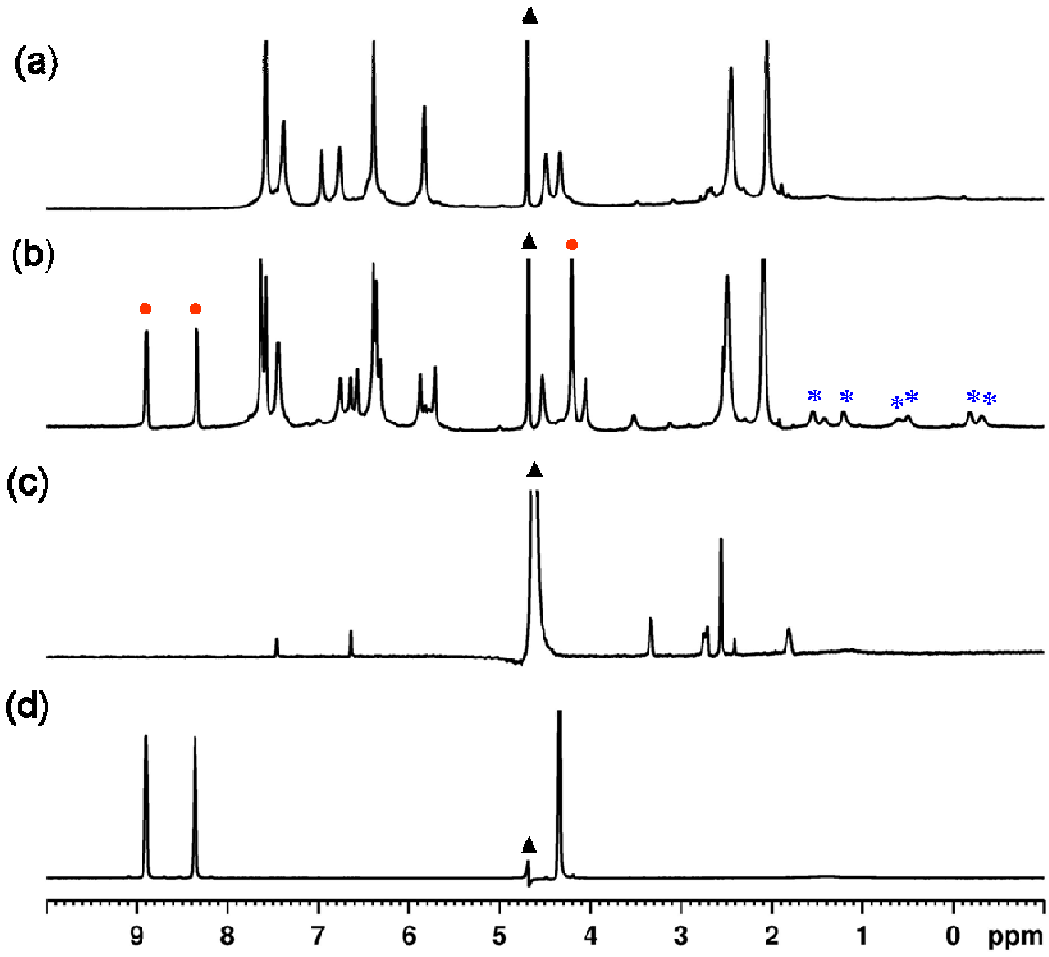

Figure S1. ^{1}H NMR (500 MHz, D_2O) spectra of (a) OA, (b) C-153@OA_2 + MV^{2+}, (c) C-153 and (d) MV^{2+}; [C-153]= 0.5 mM, [OA]=1 mM, [MV^{2+}]= 1 mM and in 10 mM sodium tetraborate buffer; "*", "•"and "▲"represent bound C-153 protons, MV^{2+} protons and residual proton signal in D_2O respectively.

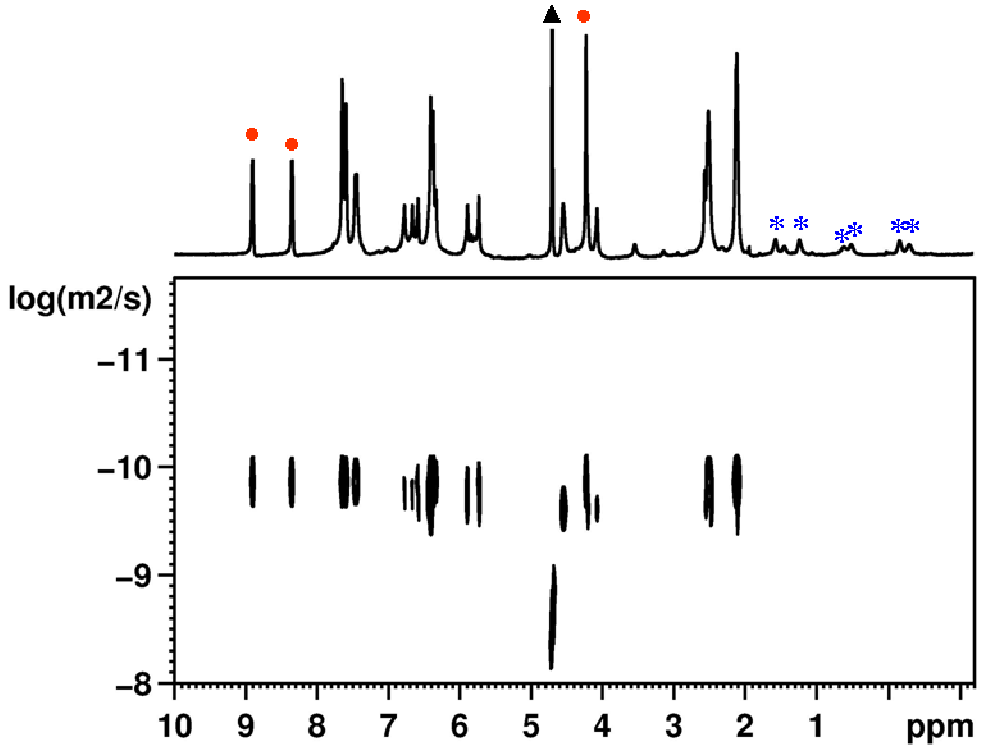

Figure S2. 2D DOSY (500 MHz, D_2O) spectra of C-153@OA_2 + MV^{2+}; [C-153]= 0.5 mM, [OA]=1 mM, [MV^{2+}]= 1 mM; "*" and "•" represent bound C-153 and MV^{2+} proton signals, diffusion constant of C-153@OA_2 and MV^{2+} are 1.19×10^{-6} cm^2/s and 1.2×10^{-6} cm^2/s respectively.

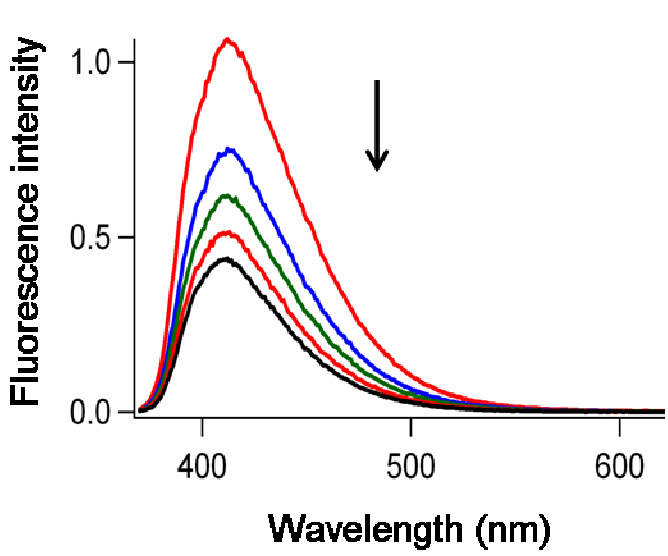

Figure S3. Fluorescence titration spectra of C-1@OA_2 with $MV^{2+;}$ λ_{ex} = 350 nm; [C-1] = 2×10^{-5} M, [OA] = 1×10^{-4} M, [MV^{2+}] = 1.5×10^{-5} M to 4×10^{-5} M in 10 mM sodium tetraborate buffer.

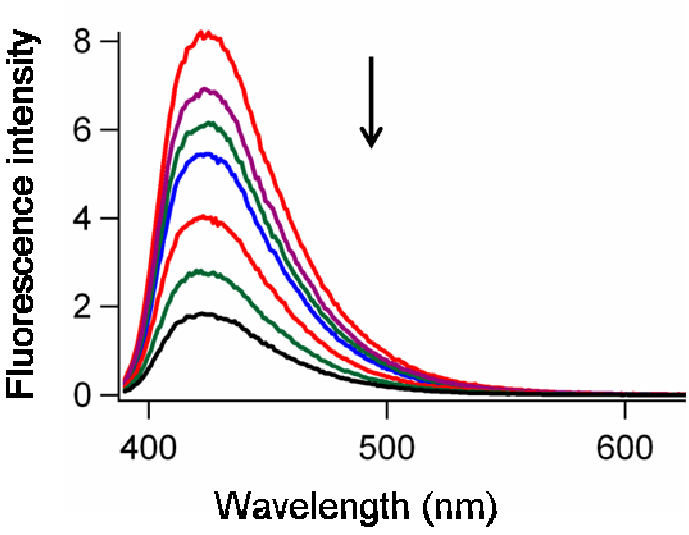

Figure S4. Fluorescence titration spectra of C-480@OA_2 with $MV^{2+;}$ λ_{ex} = 380 nm; [C-480] = 2×10^{-5} M, [OA] = 1×10^{-4} M, [MV^{2+}] = 1.5×10^{-5} M to 5×10^{-5} M in 10 mM sodium tetraborate buffer.

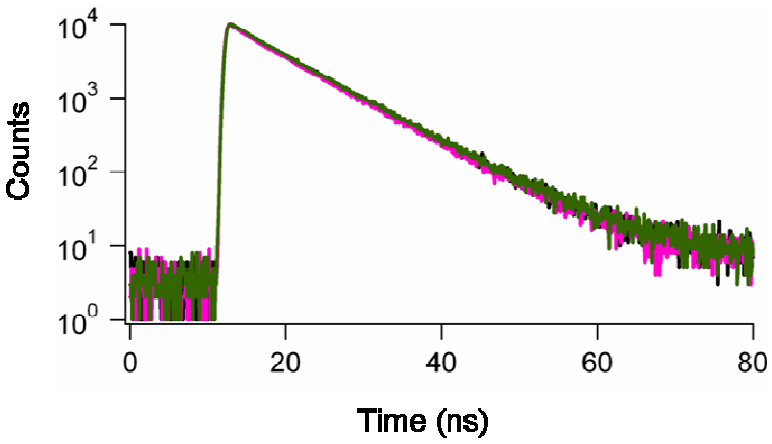

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Figure S5. Time resolved titration spectra of C-153@OA_2 with MV^{2+}; λ_{ex} = 420 nm, λ_{em} = 480 nm, [C-153] = 1.5×10^{-5} M, [OA] = 1×10^{-4} M and [MV^{2+}] = 1.5×10^{-5} M to 7.5×10^{-5} M in 10 mM sodium tetraborate buffer; Lifetime τ = 7.3 ns.

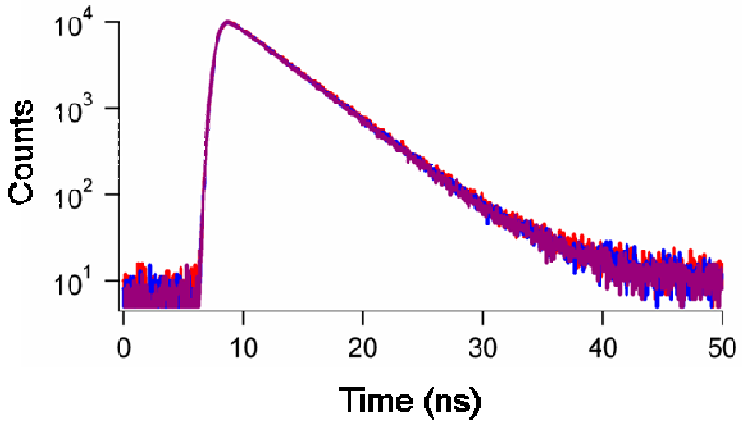

Figure S6. Time resolved titration spectra of C-1@OA_2 with MV^{2+}; λ_{ex} = 350 nm, λ_{em} = 412 nm, [C-1] = 2×10^{-5} M, [OA] = 1×10^{-4} M and [MV^{2+}] = 1.5×10^{-5} M to 4×10^{-5} M in 10 mM sodium tetraborate buffer; Lifetime τ = 4.3 ns.

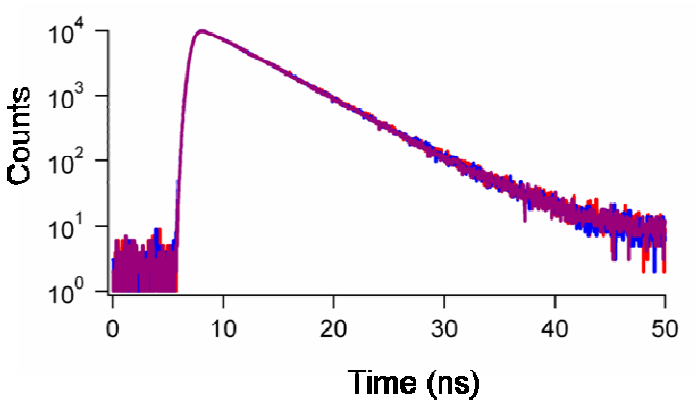

Figure S7. Time resolved titration spectra of C-480@OA_2 with MV^{2+}; λ_{ex} = 380 nm, λ_{em} = 435 nm, [C-480] = 2×10^{-5} M, [OA] = 1×10^{-4} M and [MV^{2+}] = 1.5×10^{-5} M to 5×10^{-5} M in 10 mM sodium tetraborate buffer; Lifetime τ = 4.7 ns.

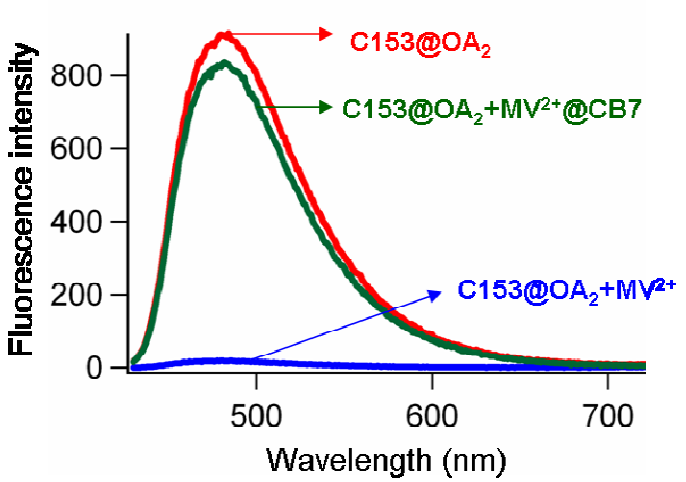

Figure S8. Fluorescence spectra of C-153@OA_2 in presence of MV^{2+} and MV^{2+}@CB7, λ_{ex} = 420 nm; [C-153] = 1.5×10^{-5} M, [OA] = 1×10^{-4} M and [MV^{2+}] = 7.5×10^{-5} M and [CB7] = 7.5×10^{-5} M in 10 mM sodium tetraborate buffer.

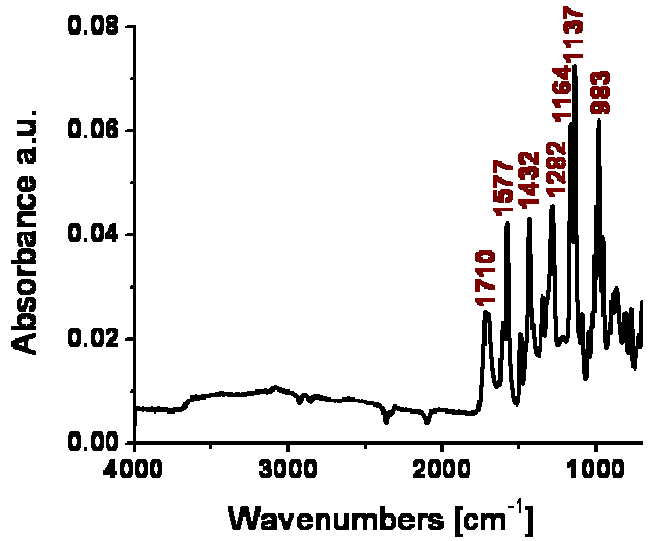

Figure S9. FTIR-ATR spectra of OA (solid)

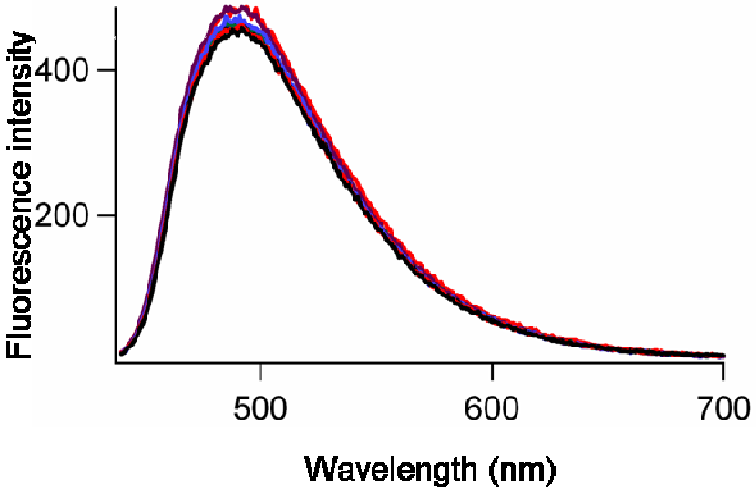

Figure S10. Fluorescence titration spectra of C-153@OA_2 with ZrO_2 colloidal solution; λ_{ex} = 440 nm; [C-153] = 1.5 × 10^{-5} M, [OA] = 1 × 10^{-4} M in water.

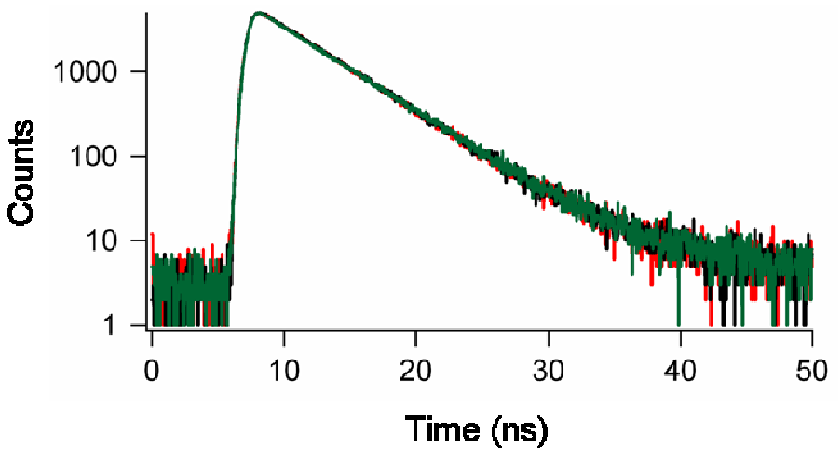

Figure S11. Time resolved titration spectra of C-153@OA_2 with TiO_2 solution; λ_{ex} = 440 nm, λ_{em} = 480 nm, [C-153] = 1.5 × 10^{-5} M and [OA] = 1 × 10^{-4} M in water; Lifetime τ = 7.3 ns.

Experimental Section

Material: The hosts octa acid[1], cucurbit[7]uril[2] were synthesized following published procedures. Laser grade coumarin 153 (C-153), coumarin 1 (C-1) and coumarin 480 (C-480) were used as received from Sigma-Aldrich/Acros.

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 coumarin (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 (MV^{2+}; stock solutions of 30 mM were prepared in D_2O) was added and ^{1}H 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 coumarin@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. A 30 mM stock solution of the guest was prepared in $CHCl_3$. The host (OA) aqueous solution was prepared in 10 mM sodium tetraborate buffer (1 mM). The complex solutions were prepared by adding required amount of guest solution in a vial, evaporating the solvent, and adding to the vial 2.5 mL of the host solution. The resulting aqueous solution was sonicated for 30 min. Calculated amounts of quencher solution (aqueous MV^{2+} solution, TiO_2 and ZrO_2 colloidal solution) were added and mixed thoroughly and then the fluorescence spectra were recorded. The required amount of CB7 was added to the solution (host/guest + MV^{2+}), sonicated and fluorescence spectra were recorded.

pH adjustment

Capsular assembly (C-153@OA_2) was made in sodium tetraborate buffer (pH~9) and its emission was recorded. At each step of the acid-titration, aqueous HCl was added drop wise and pH of the solution was checked. After adjusting a certain pH, emission of the solution was recorded. It was observed that upto pH~7, λ_{max} of complex emission remain almost same. From pH=7, λ_{max} was gradually red shifted with increasing pH of the solution indicating that C-153 was decomplexing from OA capsule. Depending upon this result pH of C-153@OA_2 was fixed at 7 for binding study with TiO_2.

Mesoporous metal oxide film preparation and binding

Binding was done on semiconducting TiO_2 (E_b = 3.2 eV) films, as well as insulating ZrO_2 (E_b = 5 eV) films to study excited states. Synthesis of TiO_2 / ZrO_2 nanoparticles were carried out by acidic hydrolysis of titanium(IV) iso-propoxide and zirconium(IV) propoxide under nitrogen atmosphere and autoclaved at 200 ^oC for 8 hours as previously described [3,4]. Poly(ethylene glycol) (PEG 2,000) was added (6g/L) to the colloidal pastes of TiO_2/ $ZrO_2$to optimize the solution viscosity of the pastes. The pastes were applied to a micro cover glass (VWR) or a conductive glass (FTO, TEC 7 by Pilkington, with 8 – 10

Ω/sq resistance of the sheet). TheTiO_2 / ZrO_2 pastes were spread on a conductive glass by using a glass test tube and holding the edge of a conductive glass by the tape. The films were air dried and then sintered in the oven at 450 ^oC for 30 minutes under oxygen flow. Then, the films were cooled down before using, or stored in a desiccator in dark.

The binding of C153@OA_2 complexes onto TiO_2 and ZrO_2 films was performed by immersing the MO_n films in 1 mM aqueous solutions of the complex overnight in the dark. The functionalized films were rinsed with water, dried, and then used for the spectroscopic measurements.

General protocol for FTIR-ATR study of the films

All FTIR-ATR spectra for OA (soild) and C-153@OA_2 (at pH=7) on TiO_2/ZrO_2 films were recorded on a Thermo Scientific, Nicolet 6700Ft-IR. The films were dried by heating in the oven to 110 ^oC for 30 minutes before all measurements.

General protocol for emission study of the films

Fluorescence emission spectra of the C-153@OA_2 (at pH=7) binding on TiO_2/ ZrO_2 films were collected on a Cary Eclipse, Varian fluorescence spectrometer. The fluorescence spectra were recorded at λ_{ex} = 420 nm. Before the spectroscopic measurements all films were heated in the oven to 110 ^oC for 30 minutes to remove moisture.

Reference

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

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

[3] Taratula, O.; Wang, D.; Chu D.; Galoppini, E.; Zhang Z.; Chen, H.; Saraf, G; Lu, Y; *J. Phys. Chem. B,* **2006**, *110,* 6506-6515.

[4] Rochford, J.; Chu, D.; Hagfeldt, A.; Galoppini, E.; *J. Am. Chem. Soc.*, **2007**, 129, 4655.