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Coupled Sensitizer–Catalyst Dyads: Electron-Transfer Reactions in a Perylene–Polyoxometalate Conjugate

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Abstract: A new strategy is introduced that permits covalent attachment of an organic chromophore to a polyoxometalate (POM) cluster. Two examples are reported that differ according to the nature of the anchoring group and the flexibility of the linker. Both POMs are functionalized with perylene monoimide units, which function as photon collectors and form a relatively long-lived charge-transfer state under illumination. They are reduced to a stable π-radical anion by electrolysis or to a protonated dianion under photolysis in the presence of aqueous triethanolamine. The presence of the POM opens up an intramolecular electron-transfer route by which the charge-transfer state reduces the POM. The rate of this process depends on the molecular conformation and appears to involve through-space interactions. Prior reduction of the POM leads to efficient fluorescence quenching, again due to intramolecular electron transfer. In most cases, it is difficult to resolve the electron-transfer products because of relatively fast reverse charge shift that occurs within a closed conformer. Although the POM can store multiple electrons, it has not proved possible to use these systems as molecular-scale capacitors because of efficient electron transfer from the one-electron-reduced POM to the excited singlet state of the perylene monoimide.

Keywords: dyes/pigments · electron transfer · fluorescence · photochemistry · polyoxometalates

Introduction

The ever-increasing demands for renewable energy supplies have led to increased effort being devoted to the design of artificial photosynthetic systems able to generate a chemical fuel under visible-light illumination. Although much fundamental research has been conducted over the past four decades or so, many severe barriers remain, and we are still unable to engineer a viable photosystem for this purpose. One of the critical steps relates to the need to charge selec-

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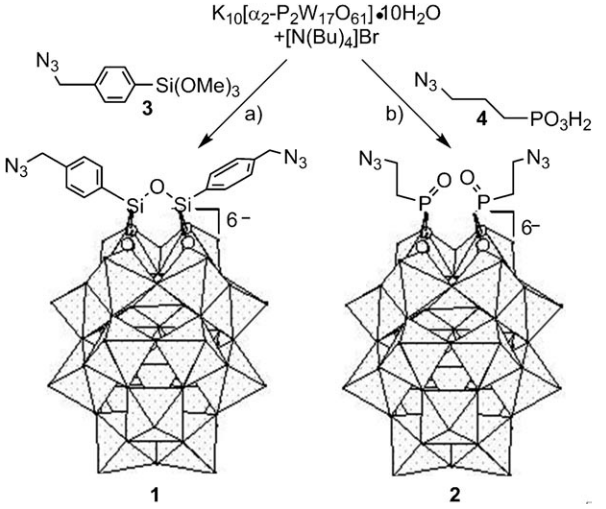
tive catalysts with redox equivalents generated during the photochemical event. Bearing in mind that fuel production is a multi-electron process,[1] while light-induced redox reactions invariably proceed by one-electron steps,[2] this is a major problem. The most successful artificial systems use colloidal redox catalysts to drive the multi-electron chemistry,[3–5] with the catalyst fulfilling the vital role of storing the charges, at least in a temporary sense. Such systems have proved to be invaluable in optimizing catalyst performance in sacrificial systems (i.e., in which the fuel is produced from a disposable organic substrate), but have evident limitations under real-world conditions. Consequently, one of the main requirements for sustained production of a useful chemical fuel relates to the identification of alternative catalysts and new routes by which to charge them with the appropriate number of redox equivalents.[6]

Herein we introduce a soluble polyoxometalate (POM) cluster as a redox catalyst,[7] functionalized with a perylene-based photon collector. The intention was to explore the electron-transfer chemistry of the resultant conjugate following illumination into the perylene-based unit. In principle, several dyes can be attached to the surface of a given POM, and thereby offer the possibility to accumulate successive charges on the catalyst, but first it is necessary to fully characterize the initial steps. The perylene monoimide dye used here is a close relative of compounds known to form a charge-transfer state under illumination in a polar solvent.[8,9] This unit is attached to the POM through a short covalent tether intended to minimize the distance over which secondary electron-transfer reactions must occur. Direct attachment of the dye to the surface is a nontrivial task[10] and we have used two different types of tether. These differ in terms of their internal flexibility and, most notably, in their ability to keep the reactants apart. The POM was selected for its facile multi-electron reduction,[11] and we employed an organic solvent to prevent rapid discharge of electrons accumulated on the catalyst.

Results and Discussion

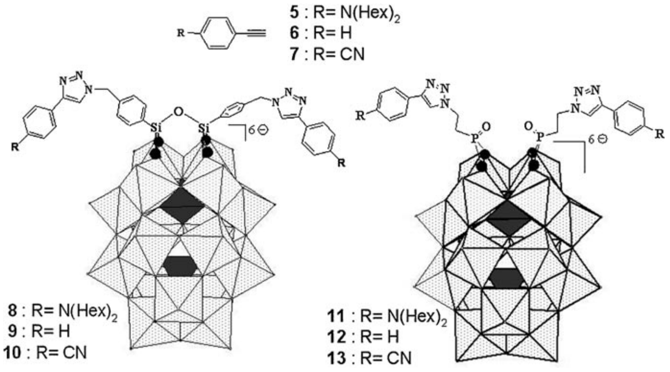
Synthesis: Usually, the association of a molecular unit to a POM is attained by way of electrostatic interactions.[12,13] However, we prefer to use a covalent linkage to increase the stability of the conjugate, especially in polar solvents. Furthermore, the former supramolecular approach is restricted to utilization of positively charged adsorbates. To the best of our knowledge, only two reports describe covalent attachment of a sensitizer to a POM. The first example concerns functionalization of a lacunary decatungstosilicate with an organosilyl fulleropyrrolidine by Bonchio and coworkers.[14a] In the second example, Peng and co-workers[14b] connected hexamolybdate clusters to a conjugated polymer. We initially developed a mild and efficient synthetic approach to covalently attach two functional groups to a Dawson polyoxometalate. To this end, Huisgen 1,3-dipolar cycloaddition was particularly appealing, since Sharpless et al. and Meldal et al. independently discovered that copper(I) catalyzes this reaction very efficiently with exclusive formation of the 1,3-triazole.[15] Recently, during the course of this work, Malacria et al. reported the monofunctionalization of Keggin-type polyoxometalates with floppy organotin groups and their post-functionalization by the Huisgen reaction.[16,17] Synthetic strategies allowing the bis-functionalization of POMs are limited,[18] although they could be useful if one envisions attaching several organic units to a single POM or preparing copolymers based on a POM monomer.[19] To this end, the new polyoxometalates **1** and **2** were first prepared in good yield by treating $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 20H_2O$ with an excess of 4-azidomethylphenyltrimethoxysilane (**3**) and 2-azido ethylphosphonic acid (**4**), respectively (Scheme 1). The tetrabutylammonium salts of POMs **1** and **2** were isolated as air-stable white powders in good yield (about 75–80 %), and they are soluble in CH_3CN and DMF. In POMs **1** and **2**, the characteristic IR signature of the two azido groups could be observed at 2097 cm^{-1}.

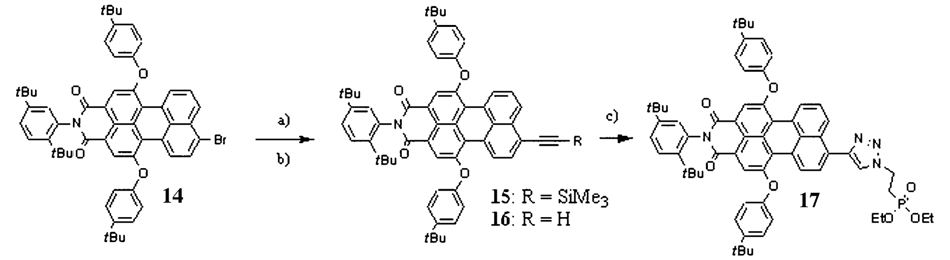


Scheme 1. Outline of the route used for preparation of the key POM synthons **1** and **2**. a) CH_3CN/H_2O, HCl, RT, 75 %; b) CH_3CN, HCl, reflux, 80 %.

The Huisgen reaction was then tested with POMs **1** and **2** with three aromatic alkynes bearing substituents with electronic properties varying from electron-donating dihexylamino (**5**) through neutral, unsubstituted (**6**) to electron-withdrawing cyano (**7**) groups. The classical conditions ($CuSO_4\cdot 6H_2O$ with ascorbic acid in DMF at 50 °C for 64 h) afforded the expected bis-coupled products **8**–**13** in high yield. In the resulting POMs **8**–**13**, the intense IR band of the azido group has disappeared completely.

To extend this approach to grafting light-harvesting antenna to the above POMs **1** and **2**, we prepared novel perylene monoimide (PMI) **16** bearing a terminal alkyne group and the corresponding benchmark reference **17** (Scheme 2). Compound **16** results from the Sonogashira reaction between the trimethylsilylacetylene and the known 2,5-di-*tert*-butylphenoxyperylene-1,6-bis(4-*tert*-butyl-phenoxy)-9-

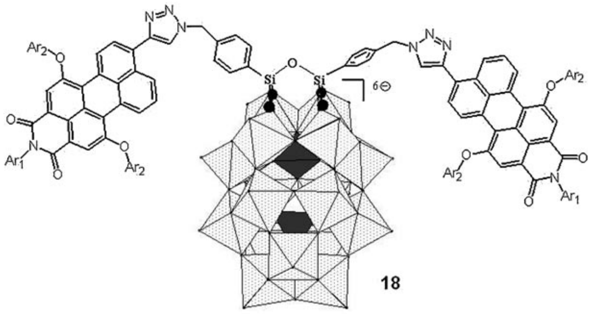




Scheme 2. Synthetic route to **16** and **17**. Reagents and conditions: a) Trimethylsilylacetylene, [PdCl$_2$(PPh$_3$)$_2$], CuI, toluene, Et$_3$N, 50 °C, overnight, 87 %; b) Potassium carbonate, CH$_2$Cl$_2$, methanol, RT, 1 h, 100 %; c) DMF, CuSO$_4$•5 H$_2$O, ascorbic acid, 2-azidoethyl diethyl phosphonate, 50 °C, 16 h, 100 %.

bromo-3,4-dicarboximide (**14**)[20,21] followed by cleavage of the trimethylsilyl group by potassium carbonate. Again, the copper-catalyzed Huisgen reaction between PMI **16** and 2-azidoethyl diethyl phosphonate gives **17** in quantitative yield.

We then adapted the click-chemistry procedure to prepare triads **18** and **19** with perylene monoimide sensitizer **16**. Reaction of PMI **16** with POMs **1** and **2** under the above conditions gave respectively POMs **18** and **19** in good yield. The two new POMs **1** and **2** are valuable precursors in which the organic arm is connected either by semirigid (**1**) or floppy (**2**) spacers, and thus allow construction of triads with different conformational freedoms and electronic couplings. Besides, these azido-substituted polyoxometalates **1** and **2** make it possible to functionalize a Dawson-type polyoxometalate with a wide diversity of substituents, since terminal alkynes could be attached by copper-catalyzed Huisgen reaction.[17]



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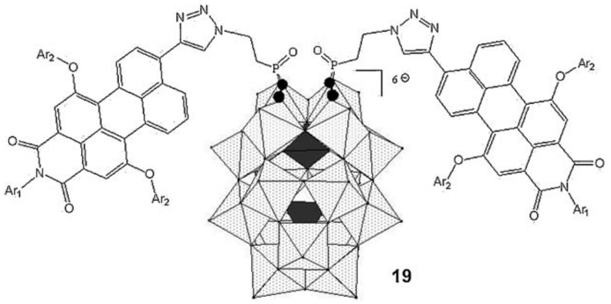

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Model compound PER: The absorption spectrum of POM-free reference compound PER (**17** in the synthetic schemes) is given in Figure 1 and shows an intense set of transitions with a maximum at 525 nm in DMF. The entire absorption envelope can be resolved into a series of four bands of equal half-width and with a vibrational spacing of 1300 cm^{-1}. The corresponding fluorescence spectrum shows reasonably good mirror symmetry with the absorption transition and has a maximum at 585 nm in DMF. The emission maximum shifts towards lower energy with increasing dielectric constant of the solvent (Figure 1), but the absorption spectrum is less affected. This behavior confirms that a marked increase in the molecular dipole moment occurs on promotion to the first excited singlet state. Indeed, fitting the experimental data to the Lippert–Mataga expression[22] allows us to conclude that the dipole moment of the first excited singlet state exceeds that of the ground state by about 16 D. This value is reached on the basis that the molecule resides in a cavity of radius 5 Å. Furthermore, DFT calculations at the B3LYP/6-311+G* level give a ground-state

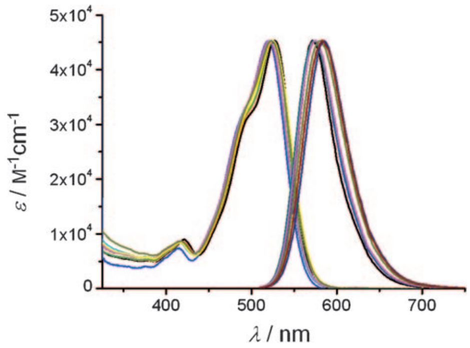


Figure 1. Absorption and fluorescence spectra of PER recorded in a range of organic solvents of differing polarity. The excitation wavelength for the emission spectra was 490 nm.

dipole moment of 4.8 D; hence, the dipole moment of the S_1 state must be about 21 D. This behavior is in general agreement with earlier work with closely related compounds.[8,9]

The S_1 state is highly fluorescent in solution.[23] The emission quantum yield Φ_F recorded in dilute DMF is 0.58, while the excited state lifetime τ_S is 5.4 ns. Decay curves were well represented by single-exponential kinetics. Again, the derived photophysical values are consistent with earlier reports.[8,9] The spectral data can be used to determine the energy level of the S_1 state as 2.22 eV. Even in a nonpolar solvent, the emission spectrum is relatively broad and featureless and there is no clear indication for initial formation of a π,π* excited state. At 77 K, the fluorescence spectrum recorded in a butyronitrile glass is blue-shifted by about 20 nm and shows some fine structure (see Supporting Information). The individual bands resolved by a Gaussian analysis remain fairly broad, while the Stokes shift is reduced to 900 cm^{-1}. Thus, the S_1 state has less charge-transfer character under these conditions, but a significant change in geometry on excitation still occurs.[24] In a butyronitrile glass containing 15% iodoethane and maintained at 77 K, we were unable to detect phosphorescence at $\lambda < 800$ nm. Likewise, nanosecond laser flash photolysis of PER in deoxygenated DMF did not detect a transient species that might be the triplet excited state.[25] Under these conditions ($\lambda = 532$ nm, full width at half-maximum (FWHM) = 4 ns), a small amount of sample decomposition led to formation of the π-radical anion as a permanent species.[26] Aeration of the solution reduced the lifetime of this species to about 2 μs. The yield of the π-radical anion was very low and probably reflects reaction of the polar S_1 state with reducing impurities present in the solvent.

The cyclic voltammogram recorded for PER in DMF shows that the compound readily undergoes both reductive and oxidative electrochemical steps.[27] Indeed, the voltammogram shows four one-electron waves, some of which are quasi-reversible. On reductive scans, two one-electron waves are seen and allow determination of the corresponding half-wave potentials as −0.92 and −1.36 V versus a normal hydrogen electrode (NHE). The corresponding one-electron waves seen on oxidative scans are poorly reversible and correspond to peak potentials of 1.25 and 1.58 V versus NHE, respectively. Poor reversibility is a common feature of the oxidation of aryl hydrocarbons[28] and is often associated with formation of a dimer radical cation.[29] Spectro-electrochemical studies in dry DMF were performed to follow the course of the reductive scans, and it was found that electrolysis at −0.85 V versus NHE results in clean conversion of PER to the corresponding π-radical anion[26] (Figure 2). A clear isosbestic point at 560 nm is preserved throughout electrolysis. The π-radical anion has a narrow and intense absorption band centered at 620 nm, with additional bands prominent at 808 and 864 nm. There is no indication for disproportionation of the π-radical anion under these conditions, and this finding is consistent with the large spacing ($\Delta E = 0.44$ eV) between successive reduction waves in the cyclic voltammograms.

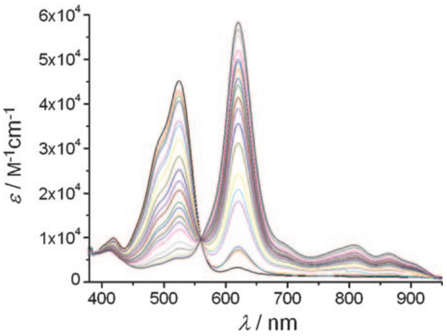


Figure 2. Spectro-electrochemical investigation of the reduction of PER in DMF containing background electrolyte and after thorough deoxygenation. Electrolysis was carried out at −0.85 V versus NHE for incremental time periods.

To investigate the photochemical reduction of PER, a set of experiments was performed following addition of triethanolamine (TEOA). It is well known that oxidation of TEOA, for which the one-electron oxidation potential is reported to be 0.82 V versus NHE,[30] is followed by loss of a proton and concomitant formation of a reducing radical.[31] Thus, one molecule of TEOA provides two reducing equivalents. A linear Stern–Volmer plot was obtained for the quenching of the PER S_1 state by TEOA in wet DMF, from which the bimolecular rate constant was found to be $(1.2 \pm 0.2) \times 10^9\,M^{-1}s^{-1}$. The thermodynamic driving force for this reaction is estimated to be about 0.48 eV from the respective reduction potentials. Steady-state illumination of PER in deoxygenated DMF containing TEOA and 5 vol% water leads to rapid buildup of the PER π-radical anion (Figure 3), which accumulates in solution but disappears on aeration. Longer irradiation leads to formation of a second species, which absorbs primarily at 490, 608, and 647 nm. This species, which can be assigned to a protonated form of the PER π dianion,[32] presumably arises because of the presence of small amounts of water in the system. Indeed, laser flash photolysis of PER in deoxygenated, wet DMF containing TEOA (0.01 M) confirmed formation of the π-

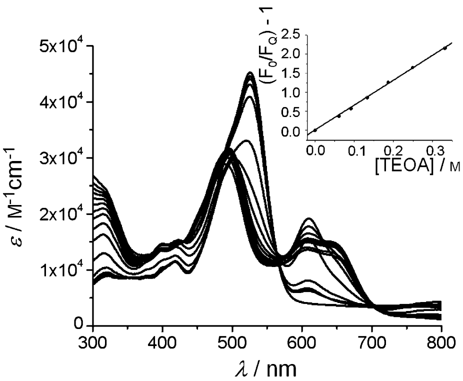


Figure 3. Absorption spectral changes recorded during steady-state irradiation of PER in deoxygenated DMF containing water (5% v/v) and TEAO (0.1 M). The inset shows a Stern–Volmer plot for quenching of the PER S_1 state by TEOA under the same conditions.

radical anion. Under these conditions, this species decays with second-order kinetics with a half-life of about 450 µs. Using the molar absorption coefficient derived by spectro-electrochemistry ($\varepsilon_{620} = 56300\,\text{M}^{-1}\text{cm}^{-1}$), the corresponding bimolecular rate constant becomes $1.9 \times 10^{9}\,\text{M}^{-1}\text{s}^{-1}$. This decay process is presumed to involve concomitant protonation and disproportionation.[33] Again, oxygen catalyzes the return to the ground-state dye; in air-equilibrated DMF the lifetime falls to about 2 µs.

Studies on PSI–POM: In PSI–PER, two PER units are attached to a single POM residue by way of a silyl anchoring group (compound **18** in the synthetic schemes). In DMF, the absorption and fluorescence spectra remain unaffected by the presence of the cluster; this indicates the absence of any significant electronic interactions between these units. There is a modest decrease in Φ_F (i.e., 40 %), while the emission decay curves are nonexponential. Reasonable, but far from perfect, analyses can be obtained by a biexponential fit with lifetimes of 5.3 (67) and 1.0 ns (33 %). Cyclic voltammetry shows that the oxidative electrochemistry of the PER units remains unchanged from that recorded for PER, but several new quasireversible, one-electron reduction waves are apparent (Figure 4). These peaks, which have half-wave potentials of −0.59 and −0.84 V versus NHE, are due to reduction of the POM cluster.[34] The second reduction step overlaps with the first reduction wave associated with the PER unit. These data can be used to estimate the thermodynamic driving force for electron transfer from the PER S_1 state to the nearby POM as 0.34 eV. We attribute the observed fluorescence quenching process to intramolecular electron transfer from the initially formed charge-transfer state to the POM.

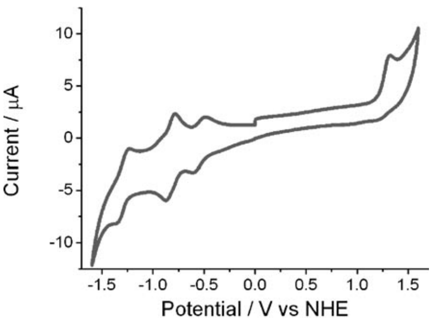


Figure 4. Cyclic voltammogram recorded for PSI–POM **18** in dry DMF containing background electrolyte and after thorough deoxygenation.

Spectro-electrochemical studies in deoxygenated DMF showed that reductive electrolysis leads to buildup of the reduced POM cluster (Figure 5). This product displays weak absorption over the 600–1100 nm range and has a clear blue color.[35] The one-electron-reduced POM is stable over many hours in the absence of oxygen.[36] Further electrolysis at −0.89 V versus NHE results in the appearance of the PER π-radical anion. Clearly, this species can coexist with the reduced form of the POM cluster. According to the cyclic voltammograms, reduction of the PER unit occurs after addition of two electrons to the POM.

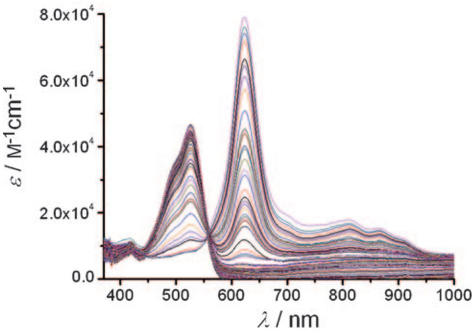


Figure 5. Spectro-electrochemical investigation of the stepwise reduction of PSI–POM **18** in deoxygenated DMF. The applied potential was initially −0.5 V versus NHE and finally −0.89 V versus NHE.

The linkage used to attach the PER unit to the surface of the POM is semirigid and favors the existence of different conformations.[37] In a crude sense, we can assign the longer lifetime found in the time-resolved emission records to a conformation in which the PER and POM units are held far apart. Consequently, the shorter lifetime can be assigned to species having the two units in relatively close contact. This type of analysis does not rule out the presence of conformers in which the redox-active units are in direct contact and, in fact, integrating the decay curves for PER and PSI–POM suggests that about 17 % of the ground-state mixture exists in such a closed conformation that does not fluoresce. Thus, the combined fluorescence data require the coexistence of a minimum of three families of conformers that differ according to their ability to undergo intramolecular electron-transfer reactions. This situation was confirmed by a series of laser flash photolysis studies with excitation into the PER unit ($\lambda = 532$ nm, FHWM = 20 ps). Thus, the transient absorption spectrum recorded 30 ps after excitation of PSI–POM is identical to that recorded for PER in dry DMF (Figure 6). This spectrum shows bleaching of the ground-state absorption bands and strong absorption centered at around 620 nm that is reminiscent of the PER π-radical anion. There is no clear spectroscopic signature for the oxidized component of the charge-transfer state at wavelengths between 420 and 700 nm (see Supporting Information). The transient signal returns to the ground state by way of nonexponential kinetics. However, decay profiles recorded at 620 and 525 nm are remarkably similar, and there is no sign of either the one-electron-reduced POM or the oxidized donor. The latter species would be most apparent as delayed return of the ground-state absorption, since it has no clear spectral signature. The transient absorption signal observed at longer wavelengths, at which the reduced POM is the sole absorber, were too small to provide useful kinetic information.

We can conclude, therefore, that charge recombination ($\Delta G^0 = -1.84$ eV) is faster than intramolecular electron

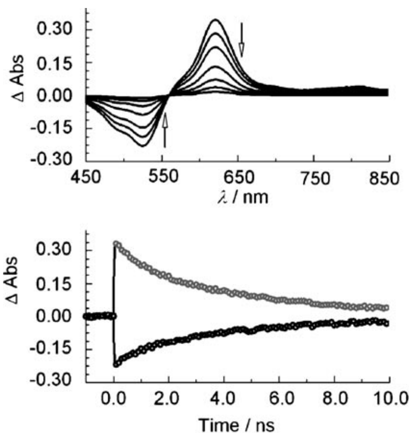
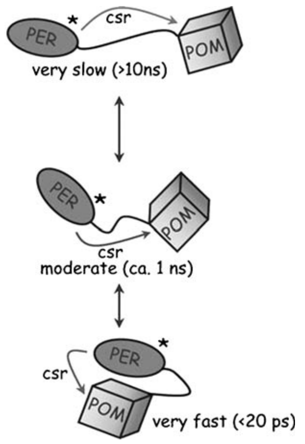


Figure 6. Top: Transient differential absorption spectra recorded at different time delays following pulsed laser excitation of PSI–POM in deoxygenated DMF. Bottom: Decay traces recorded at 620 (gray) and 520 nm (black).

transfer in this system. A possible explanation for this behavior is that electron transfer to the POM takes place through folded conformers in which the reactants are in close contact (Scheme 3). The rate constant for electron transfer is difficult to resolve from the diffusional processes. However, charge recombination is facilitated since the required geometry has already been attained. The modest fraction of ground-state dyad that exists in a folded conformation (i.e., ca. 17 % as deduced from the fluorescence studies) does not provide evidence for a relatively long lived species in which the charge is transferred to the POM.

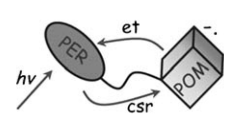


Scheme 3. Light-induced electron transfer from the excited singlet state of the PER-based chromophore to the POM in the different families of conformations present in slow equilibrium (csr = charge-shift reaction).

The residual fluorescence from the PER S_1 state in PSI–POM was quenched by TEOA in wet DMF, and a linear Stern–Volmer plot was obtained. Under the assumption that the longer-lived species will be more susceptible to bimolecular quenching, the derived rate constant is estimated as $1.2\times10^{9}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$. Again, this quenching process is attributed to reduction of the S_1 state to form the corresponding PER-based π-radical anion. Thus, steady-state illumination of PSI–POM in deoxygenated wet DMF containing excess TEOA leads to accumulation of the reduced POM (see Supporting Information). On prolonged irradiation, there was no clear indication for further reduction to give the PER π-radical anion and, in particular, no bleaching of the PER absorption bands occurred. This is because the S_1 state localized on the PER unit undergoes an electron-transfer reaction with the reduced POM in preference to electron abstraction from TEOA. This step was confirmed by fluorescence spectro-electrochemistry, which showed that prior reduction of the POM lowered Φ_F for the PER unit from 0.35 to 0.09. The fluorescence lifetime is decreased to about 1 ns. It is also notable that absorption spectra recorded for the reduced POM in dry and wet DMF are different. Presumably, this is because of protonation of the reduced POM in the presence of water.

Nanosecond laser flash photolysis studies in the presence of excess TEOA (0.1 M) in deoxygenated wet DMF failed to detect transient formation of the π-radical anion. Presumably, this is because the rate constant for intramolecular electron transfer to the appended POM is too high; we can estimate the lower limit for this value as being $>2\times10^{8}\,\mathrm{s}^{-1}$. Even with improved temporal resolution it was not possible to obtain a good estimate for this rate constant, because the rate of formation of the PER π-radical anion remains modest ($k\approx7\times10^{8}\,\mathrm{s}^{-1}$) even when the concentration of TEOA is increased to 0.6 M. Under these conditions, the lifetime of the PER π-radical anion is less than 5 ns.

Laser flash photolysis studies were also performed with a sample in which the POM had been reduced. Here, the S_1 state of the PER chromophore is seen immediately after excitation ($\lambda = 400$ nm; FWHM = 20 ps). This species decays with first-order kinetics, with a lifetime of 0.8 ± 0.2 ns, to restore the pre-pulse baseline. We attribute this quenching process to intramolecular electron transfer from the reduced POM to the PER S_1 state to form the PER π-radical anion (Scheme 4). This reaction is extremely favorable, with a thermodynamic driving force of about 1.9 eV, and is likely to fall within the Marcus inverted region.[38] Light-induced electron transfer is followed by a thermal electron-transfer step to recover the reduced POM; the driving force for this second step is 0.34 eV. Under these conditions, it was not possible to observe intermediate formation of the π-radical anion, since the rate for the return charge-shift reaction exceeds that for the forward reaction. Furthermore, we are unable to distinguish between through-bond and through-space processes on the basis of these results alone and, as a consequence, attention was turned to the more flexible PP–POM system.



Scheme 4. Light-induced electron transfer (et) from the reduced POM to the excited singlet state of the PER-based chromophore (csr = charge-shift reaction).

Studies on PP–POM: The PP–POM system has two PER units covalently attached to a POM residue by way of flexible linkages with phosphoryl anchoring groups (compound **19** in the synthetic schemes). Again, the presence of the POM had no evident effect on either absorption or fluorescence spectra recorded in DMF. In this case, however, fluorescence from the PER S_1 state was heavily quenched, and Φ_F fell to 0.02. Time-resolved fluorescence decay curves could be analyzed satisfactorily in terms of two exponential components, with lifetimes of 5.5 (8) and 0.38 ns (92 %). As above, fluorescence quenching is attributed to intramolecular electron transfer from the PER S_1 state to the POM, for which the thermodynamic driving force is 0.87 eV. The decay records do not eliminate the presence of very fast components, and integration of the entire signal suggests that such species make an important contribution. Indeed, we estimate that some 75 % of the dyad must exist in a non-fluorescent form. These different lifetimes are assigned to conformations that differ according to their propensity to undergo light-induced electron transfer. They may differ in terms of mutual separation distance[39] and/or orientation.[40] The fact that PP–POM is more heavily quenched than PSI–POM, in which the linker is more rigid, can be used to argue that light-induced electron transfer requires orbital contact between the redox-active units.

Laser flash photolysis of PP–POM in dry DMF (λ = 400 nm; FWHM = 20 ps) confirmed formation of the PER S_1 state within the excitation pulse. The derived decay profiles were complex, but most of the initial signal (60–70 % in a typical experiment) decayed rapidly with a lifetime of about 60 ps. We attribute this process to intramolecular electron transfer from S_1 to the POM in a family of folded conformers (Scheme 3). This situation appears to be fully consistent with the fluorescence results mentioned above. The decay process is most notable at 620 nm, where the PER π-radical anion is the dominant absorber. On longer timescales, the PER S_1 state decays by nonexponential kinetics to restore the pre-pulse baseline. Overall, this behavior is consistent with the forward reaction being slower than the reverse process. This can be well explained in terms of the forward reaction being limited by the need for mass transfer, while the reverse step occurs within the resultant conformer.

Spectro-electrochemical reduction of PP–POM in dry DMF shows stepwise buildup of the reduced POM, followed by the appearance of the PER π-radical anion, as described above for PSI–POM (see Supporting Information). Prior reduction of the POM does not prevent electron addition to the PER unit. Photoreduction of PP–POM in wet DMF containing excess TEOA (0.5 M) leads to the slow accumulation of the reduced POM (see Supporting Information). Again, the absorption spectra are somewhat different to those obtained by electrochemical reduction in dry DMF and most likely correspond to a protonated species. Under photochemical conditions, the PER π-radical anion does not accumulate even on prolonged irradiation. This behavior is easily explained in terms of intramolecular electron transfer from the reduced POM to the PER S_1 state, followed by a charge-shift reaction to restore the reduced POM (Scheme 4). In this case, the rather low fluorescence quantum yield found for PP–POM prevented monitoring this process by steady-state fluorescence spectroscopy. Because of the extensive quenching of the S_1 state by the POM, it was difficult to conduct meaningful laser flash photolysis studies in the presence of TEOA.

Laser excitation of PP–POM after prior reduction of the POM in dry DMF generates the PER S_1 state (Figure 7). This species decays over about 100 ps with nonexponential kinetics. As the signal decays, a slight blueshift (5–10 nm) and narrowing of the absorption band occur, possibly due to the expected light-induced charge-shift reaction (Scheme 4). However, there are no evident spectroscopic signatures by which to monitor this process. Kinetic measurements indicate that part of the signal grows in after the excitation pulse, and this must be indicative of the charge-shift reaction. On the basis of a global analysis of the spectroscopic data, it can be argued that the PER S_1 state has an average lifetime of about 70 ps, while mono-reduced POM is restored with a lifetime of about 160 ps in DMF at room temperature (Figure 8).

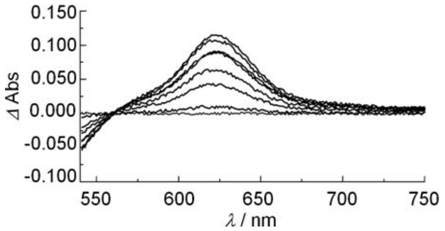


Figure 7. Transient differential absorption spectra recorded at different time delays following pulsed laser excitation of PP–POM in deoxygenated DMF after prior reduction of the POM. Delay times are 0, 20, 40, 80, 120, 180, 250, and 500 ps.

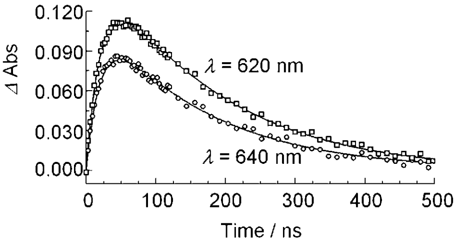


Figure 8. Typical decay traces recorded for the system described in the legend to Figure 7. The PER π-radical anion absorbs more strongly than the PER S_1 state at 620 nm, while they show comparable absorption coefficients at 640 nm. The solid line running through each data set corresponds to the results of a global fit to the spectroscopic data in which the lifetime of the S_1 state is 70 ps and that of the charge-shifted state is 160 ps.

Conclusion

We have described a methodology for the covalent attachment of organic chromophores to the surface of a redox-active POM. The linking tether is either flexible, and thereby facilitates close contact between chromophore and POM, or semirigid. The resultant dyads undergo successive electrochemical reduction steps in which the POM stores two electrons before the PER unit is reduced. Both the reduced POM and the PER π-radical anion are susceptible to protonation when water is added to a solution of the samples in DMF. The PER π-radical anion can also be formed by photochemical reduction using TEOA as a sacrificial electron donor. A major point of interest in this work is intramolecular electron transfer between the terminals, and several such steps have been identified. Firstly, the excited singlet state resident on the PER chromophore transfers an electron to the POM. Electron transfer from the S_1 state, which has considerable charge-transfer character,[8,9] appears to take place within a folded conformation that brings the reactants into close proximity. Thus, the dynamics of the overall process involve a combination of mass transfer and electron transfer. In this respect, the flexible tether provides for faster rates of electron transfer and more extensive fluorescence quenching. The charge-shifted products are not seen, because the rate of the reverse process exceeds that of the forward step. Likewise, except in one case, we were unable to record the kinetics for intramolecular electron transfer from the PER π-radical anion to the appended POM. The problem here is related to the relatively long timescale associated with generation of the PER π-radical anion. For PP–POM **19**, this reaction has a half-life of about 160 ps.

Finally, the S_1 state of the PER chromophore enters into electron-transfer reactions with the one-electron-reduced form of the POM.[41] In DMF at ambient temperature, this is a fairly fast reaction that takes place preferentially within folded conformations. It is followed by a thermal charge-shift reaction to restore the original system. In principle, the PER S_1 state could transfer an electron to the mono-reduced POM to form the doubly reduced species. Such reactions would be facilitated by a high photon flux, as is easily achieved with short laser pulses, and are an essential feature of a molecular-scale capacitor. This study shows that the addition of a second electron to the POM is not observed under our conditions with **18** and **19**, although the thermodynamics are favorable. This is ascribed to the fact that second electron transfer does not compete with the intramolecular charge shift from the excited-state sensitizer to the mono-reduced POM. This aspect could be very useful to take into consideration in the future for the design of new photochemical devices to achieve photo-accumulative electron transfer, which is an important function for mimicking artificial photosynthesis.

Experimental Section

Experimental details for the preparation of the various compounds and their characterization are collected in the Supporting Information. Absorption spectra were recorded with a Hitachi U3310 or Perkin–Elmer Lambda 35 UV/Visible spectrophotometer, while fluorescence studies were made with a Hitachi F-4500 fluorescence spectrophotometer in DMF. Measurements were made on optically dilute solutions after deoxygenation by purging with N_2. Fluorescence quantum yields were measured by comparison to standard fluorophores.[42] Corrected excitation spectra were also recorded under optically dilute conditions. Fluorescence lifetimes were measured by time-correlated, single-photon counting following excitation with an ultrashort laser diode emitting at 525 nm by using a PTI Easy-Life spectrometer. After deconvolution of the instrumental response function, the temporal resolution of this setup was about 50 ps. Steady-state irradiations were performed in DMF by using a Fiber Lite PT 900 regulated illuminator with a 150 W quartz-halogen bulb with <400 nm filtering and by using a sealed, N_2 purged cuvette.

Cyclic voltammetry experiments were performed using an HCH Instruments Electrochemical Analyzer and a three-electrode setup consisting of a platinum working electrode, a platinum wire counterelectrode, and a silver wire reference electrode. All studies were performed in deoxygenated dichloromethane containing tetra-*n*-butylammonium tetrafluoroborate (TBATFB, 0.1 M) as background electrolyte and ferrocene as internal standard. The solute concentrations were typically 0.5 mM. Reduction potentials were reproducible to within ±15 mV. Spectro-electrochemical fluorescence experiments were performed by using a Specac Omnicell, which was aligned 45° to the excitation source and illuminated at 495 nm. Scattered and incident light was removed by a 515 nm filter placed before the detector. For bulk electrolysis on a HCH instruments electrochemical analyzer, the working electrode potential was set at −0.61 V. Emission spectra were monitored over time.

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[1] J. R. Darwent, P. Douglas, A. Harriman, G. Porter, M.-C. Richoux, *Coord. Chem. Rev.* **1982**, *44*, 83–126.

[2] a) A. Krasna, *Photochem. Photobiol.* **1979**, *29*, 267–271; A. Harriman, *J. Photochem.* **1984**, *25*, 33–36.

[3] J.-M. Lehn, J.-P. Sauvage, *Nouv. J. Chim.* **1977**, *1*, 441–446.

[4] A. Moradour, E. Amouyal, P. Keller, H. Kagan, *Nouv. J. Chim.* **1978**, *2*, 547–551.

[5] A. Harriman, G. Porter, M.-C. Richoux, *J. Chem. Soc. Faraday Trans. 2* **1981**, *77*, 1939–1948.

[6] a) B. Hinnemann, P. G. Moses, J. Bonde, K. P. Jorgensen, J. H. Nielsen, S. Horch, I. Chorkendorff, J. K. N. Orskov, *J. Am. Chem. Soc.* **2005**, *127*, 5308–5309; b) P. Liu, J. A. Rodriguez, *J. Am. Chem. Soc.* **2005**, *127*, 14871–14878; c) I. Bhugun, D. Lexa, J.-M. Savéant, *J. Am. Chem. Soc.* **1996**, *118*, 3982–3983; d) P. V. Bernhardt, L. A. Jones, *Inorg. Chem.* **1999**, *38*, 5086–5090.

[7] a) E. Gkika, P. Kormally, S. Antonaraki, D. Dimoticali, E. Papaconstantinou, A. Hiskia, *Int. J. Photoenergy* **2004**, *6*, 227–231; b) A. Hiskia, A. Mylonas, E. Papaconstantinou, *Chem. Soc. Rev.* **2001**, *30*, 62–69; c) K. Karnicka, M. Chojak, K. Miecznikowski, M. Skunik, B. Baranowska, A. Kolary, A. Piranska, B. Palys, L. Adamczyk, P. J. Kulesza *Bioelectrochemistry* **2005**, *66*, 79–87; d) E. Gkika, P. Kormali, S. Antonaraki, D. Dimoticali, E. Papaconstantinou, A. Hiskia, *Int. J. Photoenergy* **2004**, *6*, 227–231; e) T. Kida, *Langmuir* **2008**, *24*, 7648–7650.

[8] a) S. E. Miller, Y. Zhao, R. Schaller, V. Mulloni, E. M. Just, R. C. Johnson, M. R. Wasielewski, *Chem. Phys.* **2002**, *275*, 167–183; b) D.

Gosztola, M. P. Niemczyk, W. Svec, A. S. Lukas, M. R. Wasielewski, *J. Phys. Chem. A* **2000**, *104*, 6545–6551.

[9] a) L. E. Sinks, B. Rybtchinski, M. Limura, B. A. Jones, A. J. Goshe, X. B. Zuo, D. M. Tiede, X. Y. Li, M. R. Wasielewski, *Chem. Mater.* **2005**, *17*, 6295–6303; b) S. Q. Xiao, M. E. El-Khouly, Y. L. Li, Z. H. Gan, L. Jiang, Y. Araki, O. Ito, D. Zhu, *J. Phys. Chem. B* **2005**, *109*, 3658–3667; c) A. Marcos Ramos, E. H. A. Beckers, T. Orfermans, S. C. J. Meskers, R. A. J. Janssen, *J. Phys. Chem. A* **2004**, *108*, 8201–8211; d) C. Flors, I. Oesterling, T. Schnitzler, E. Fron, G. Schweitzer, M. Sliwa, A. Herrmann, M. van der Auweraer, F. C. De Schryver, K. Mullen, J. Hofkens, *J. Phys. Chem. C* **2007**, *111*, 4861–4870.

[10] a) M. J. Calhorda, *J. Organomet. Chem.* **1994**, *475*, 149–155; b) S. Triki, L. Ouaheb, J. Padiou, D. Grandjean, *J. Chem. Soc. Chem. Commun.* **1989**, 1068–1070; c) M. H. Alizadeh, M. Mirzaei, H. Razavi, *Mater. Res. Bull.* **2008**, *43*, 546–555; d) T. Kida, K. Lemura, H. Kai, M. Nagano, *J. Am. Ceram. Soc.* **2007**, *90*, 618–621; e) M. K. Seery, N. Fay, T. McCormac, E. Dempsey, R. J. Forster, T. E. Keyes, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3426–3433.

[11] a) D. Ingersoll, P. J. Kulesza, L. R. Faulkner, *J. Electrochem. Soc.* **1994**, *141*, 140–147; b) L. H. Bi, T. McCormac, S. Beloshapkin, E. Dempsey, *Electroanalysis* **2008**, *19*, 37–46; c) K. Karnicka, M. Chojak, K. Miecznikowski, M. Shunik, B. Baranowska, A. Kolary, A. Piranska, B. Palys, L. Adamczyk, P. J. Kulesza, *Bioelectrochemistry* **2005**, *66*, 79–87.

[12] a) T. E. Keyes, E. Gicquel, L. Guerin, R. J. Forster, V. Hultgren, A. M. Bond, A. G. Wedd, *Inorg. Chem.* **2003**, *42*, 7897–7905; b) C. Allain, S. Favette, L.-M. Chamoreau, J. Vaissermann, L. Ruhlmann, B. Hasenknopf, *Eur. J. Inorg. Chem.* **2008**, 3433–3441.

[13] a) T. Tachikawa, S. Tojo, M. Fujitsuka, T. Majima, *Chem. Eur. J.* **2006**, *12*, 3124; b) J. Xie, B. F. Abrahams, A. G. Wedd, *Chem. Commun.* **2008**, 576–577; c) A. Yokoyama, T. Kojima, K. Ohkubo, S. Fukuzumi, *Chem. Commun.* **2007**, 3997–3998; d) A. Tsuda, E. Hirahara, Y.-S. Kim, H. Tanaka, T. Kawai, T. Aida, *Angew. Chem.* **2004**, *116*, 6487–6491; *Angew. Chem. Int. Ed.* **2004**, *43*, 6327–6331.

[14] a) M. Bonchio, M. Carraro, G. Scorrano, A. Bagno, *Adv. Synth. Catal.* **2004**, *346*, 648–654; b) B. Xu, M. Lu, J. Kang, D. Wang, J. Brown, Z. Peng, *Chem. Mater.* **2005**, *17*, 2841 and 2851.

[15] a) V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Angew. Chem.* **2002**, *114*, 2708–2711; *Angew. Chem. Int. Ed.* **2002**, *41*, 2596–2599; b) C. W. Tornøe, C. Christensen, M. Meldal, *J. Org. Chem.* **2002**, *67*, 3057–3064.

[16] K. Micoine, B. Hasenknopf, S. Thorimbert, E. Lacote, M. Malacria, *Org. Lett.* **2007**, *9*, 3981–3984.

[17] V. D. Bock, H. Hiemstra, J. H. van Maarseveen, *Eur. J. Org. Chem.* **2006**, 51–68.

[18] a) J. Kang, B. Xu, Z. Peng, X. Zhu, Y. Wei, D. R. Powell, *Angew. Chem.* **2005**, *117*, 7062–7065; *Angew. Chem. Int. Ed.* **2005**, *44*, 6902–6905; b) Z. Peng, *Angew. Chem.* **2004**, *116*, 948–953; *Angew. Chem. Int. Ed.* **2004**, *43*, 930–935.

[19] a) S. Binauld, F. Boisson, T. Hamaide, J.-P. Pascault, E. Drockenmuller and E. Fleury, *J. Polym. Sci. Polym. Chem. Ed.* **2008**, *46*, 5506–5517; b) D. J. V. C. van Steenis, O. R. P. David, G. P. F. van Strijdonck, J. H. van Maarseveen, J. N. H. Reek, *Chem. Commun.* **2005**, 4333–4335.

[20] R. T. Hayes, M. R. Wasielewski, D. Gosztola, *J. Am. Chem. Soc.* **2000**, *122*, 5563–5567.

[21] A. Morandeira, J. Fortage, T. Edvinsson, L. Le Pleux, E. Blart, G. Boschloo, A. Hagfeldt, L. Hammarström, F. Odobel, *J. Phys. Chem. C* **2008**, *112*, 1721–1728.

[22] a) E. Lippert, *Z. Naturforsch.* **1955**, *10*, 541–546; b) N. Mataga, Y. Kaitu, M. Koizumi, *Bull. Chem. Soc. Jpn.* **1955**, *28*, 690–695.

[23] M. Sliwa, C. Flors, I. Oesterling, J. Hotta, K. Mullen, F. C. de Schryver, J. Hotkens, *J. Phys. Condens. Matter* **2007**, *19*, 445004.

[24] M. Goes, M. De Groot, M. Koeberg, J. W. Verhoeven, N. R. Lokan, M. J. Shephard, M. N. Paddon-Row, *J. Phys. Chem. A* **2002**, *106*, 2129–2134.

[25] a) W. E. Ford, P. V. Kamat, *J. Phys. Chem.* **1987**, *91*, 6373–6380; b) A. Prodi, C. Chiorboli, F. Scandola, E. Leugo, E. Alessio, R. Dobrawa, F. Wurther, *J. Am. Chem. Soc.* **2005**, *127*, 1454–1462.

[26] M. Andrzejak, M. Sterzel, M. T. Pawlikowski, *Spectrochim. Acta A* **2005**, *61*, 2029–2032.

[27] J. Cremer, P. Bauerle, *J. Mater. Chem.* **2006**, *16*, 874–884.

[28] S. K. Lee, Y. Zu, A. Herrmann, Y. Geerts, K. Mullen, A. J. Bard, *J. Am. Chem. Soc.* **1999**, *121*, 3513–3520.

[29] J. L. Sessler, Y. Kubo, A. Harriman, *J. Phys. Org. Chem.* **1992**, *114*, 5714–5722.

[30] V. Anbazhagan, A. Kathiravan, M. Asha Jhonsi, R. Renganathan, *Z. Phys. Chem. (Muenchen Ger.)* **2007**, *221*, 929–939.

[31] M. Kirch, J.-M. Lehn, J.-P. Sauvage, *Helv. Chim. Acta* **1979**, *62*, 1345–1384.

[32] K. Kano, K. Mori, T. Konse, B. Uno, T. Kubota, *Anal. Sci.* **1989**, *5*, 651–656.

[33] L. Michaelis, *Chem. Rev.* **1935**, *35*, 243–270.

[34] a) M. Fromon, C. Triener, R. Bury, M. Fournier, *J. Chem. Soc. Faraday Trans. 1* **1985**, *81*, 2513–2523; b) R. Wlodarczyk, M. Chojak, K. Miecznikowski, A. Kolary, P. J. Kulesza, R. Marassi, *J. Power Sources* **2006**, *159*, 802–809; c) P. J. Kulesza, M. Skunik, B. Baranowska, K. Miecznikowski, M. Chojak, K. Karnicka, E. Frackowiak, F. Beguin, A. Kuhn, M.-H. Delville, B. Starobrzynska, A. Ernst, *Electrochim. Acta* **2006**, *51*, 2373–2379.

[35] a) G. J. Zhang, H. H. Ke, T. He, D. B. Xiao, Z. H. Chen, W. S. Yang, J. N. Yao, *J. Mater. Res.* **2004**, *19*, 496–500; b) Y. Shan, G. Yang, Y. Sun, S. Pang, J. Gong, Z. Su, L. Qu, *Electrochim. Acta* **2007**, *53*, 569–574.

[36] T. Rüther, V. M. Hultgren, B. P. Timko, A. M. Bond, W. B. Jackson, A. G. Weddi, *J. Am. Chem. Soc.* **2003**, *125*, 10133–10143.

[37] a) Z. Bajzer, F. G. Prendergast, *Biophys. J.* **1993**, *65*, 2313–2323; b) A. T. Russo, L. Brand, *J. Fluoresc.* **2004**, *14*, 333–342; c) C. K. Johnson, B. D. Slaughter, J. R. Unruh, E. S. Price, *Rev. Fluoresc.* **2006**, 239–259; d) G. Blondeel, D. De Keeukeleire, A. Harriman, L. R. Milgrom, *Chem. Phys. Lett.* **1985**, *118*, 77–82.

[38] R. A. Marcus, *J. Chem. Phys.* **1956**, *24*, 966–971.

[39] J. Zhou, L. V. Lukin, C. L. Braun, *J. Phys. Chem. A* **2008**, *112*, 7507–7513.

[40] L. A. Curtiss, C. A. Naleway, J. R. Miller, *Chem. Phys.* **1993**, *176*, 387–405.

[41] J. C. Scaiano, C. Aliaga, M. N. Chretien, M. Frenette, K. S. Focaneanu, L. Mikelsons, *Pure Appl. Chem.* **2005**, *77*, 1009–1018.

[42] D. Magde, J. Brannol, T. Cremers, J. Olmsted, *J. Phys. Chem.* **1979**, *83*, 696–699.

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