positions, riding on their carbon atoms. Crystal data for **3**: $C_{17}H_{17}Mn_{1.5}NO_{6.5}S_{1.5}$, $M_r = 469.82$, monoclinic, space group $C2/c$, $a = 39.700(3)$, $b = 8.3664(6)$, $c = 24.390(2)$ Å, $\beta = 90.128(2)°$, $V = 8101.0(11)$ Å^3, $Z = 16$, $\rho_{calcd} = 1.541$ g cm^{-3}, $\mu = 1.139$ mm^{-1}, $F(000) = 3832$, θ range 1.03–26.40°, 520 variables refined with 8304 independent reflections to final R indices $[I > 2\sigma(I)]$ of $R_1 = 0.0676$ and $wR_2 = 0.1892$, and GOF = 1.025. Crystals of **4** suitable for X-ray studies were grown from a solution in DMA. Crystal data for **4**: $C_{26}H_{26}Mn_3N_2O_{12}$, $M_r = 723.31$, monoclinic, space group $P2_1/c$, $a = 12.939(2)$, $b = 10.0886(15)$, $c = 12.9121(19)$ Å, $\beta = 90.128(2)°$, $V = 1510.0(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.591$ g cm^{-3}, $\mu = 1.299$ mm^{-1}, $F(000) = 734$, θ range 2.68–26.36°, 206 variables refined with 12734 independent reflections to final R indices $[I > 2\sigma(I)]$ of $R_1 = 0.0570$ and $wR_2 = 0.1397$, and GOF = 0.979. CCDC-182869 and -186586 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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Reversible Photoinsertion of Ferrocene into a Hydrophobic Semiconductor Surface: A Chemionic Switch[**]

Masahiro Muraoka, Stephen L. Gillett, and Thomas W. Bell[*]

Molecular devices are currently of intense interest,[1] but functional supramolecular devices are shorter term candidates for various applications including signal processing[2] and separation.[3] Control of the self-assembly[4] of photonic, electronic, and ionic supramolecular, or "chemionic",[2a,5] devices remains an important challenge. We have devised a surprisingly simple, self-reversing, photoredox system that functions as a chemionic switch (Figure 1). This bi-stable supramolecular device can be switched "on" by light and "off" by chemical oxidation. Light is an attractive agent for mediating self-assembly, and this has led us to base our chemionic switch on a photoredox reaction driven by an illuminated semiconductor.[6] Electron–hole pairs formed near the surface of the semiconductor by the absorption of

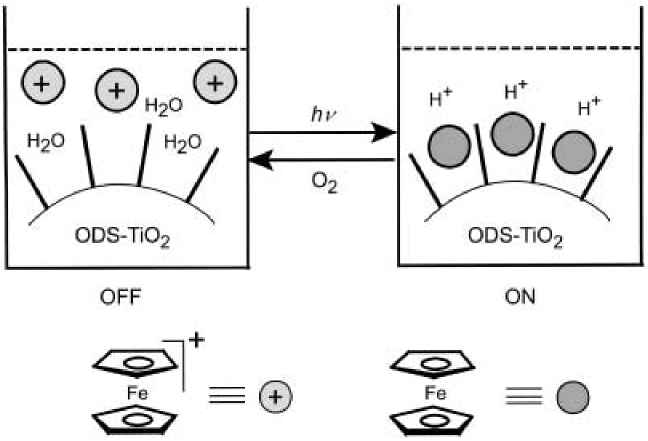

Figure 1. Illustration of the self-reversing chemionic switch. "ODS-TiO_2" describes TiO_2 particles surface-functionalized with octadecyltrichlorosilane (ODS). Holes generated by near-UV illumination oxidize the solvent to generate hydrogen ions, while photogenerated electrons reduce solution ferrocenium (Fc^+) to ferrocene (Fc), which dissolves into the hydrophobic monolayer on the surface of the TiO_2. After storing the sample in the dark for several hours the ferrocene spontaneously reoxidizes by reaction with atmospheric O_2.

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photons that have energy greater than its band-gap are highly active "reagents" for driving redox reactions.

Titanium dioxide (TiO_2) is a well-known semiconductor for photoinduced redox reactions,[7] and is indefinitely stable when in contact with aqueous solutions. Its threshold band-gap energy lies in the near-UV (ca. 390 nm). Ferrocene (Fc) was employed as the redox-active species because of the well-known stability of the ferrocene/ferrocenium (Fc/Fc^+) redox couple.[8] The ferrocene moiety has also been incorporated into a vast number of derivatives, which suggests that more elaborate redox-active molecular systems based on ferrocene might be achieved. Ferrocenium (Fc^+) salts are soluble in polar solvents, but reduction produces a nonpolar species (Fc). We formed a covalently bonded hydrophobic monolayer on the TiO_2 particles by treating them with octadecyltrichlorosilane (ODS) to produce "ODS-TiO_2."[9]

Solutions of ferrocenium tetrafluoroborate in various solvents containing suspensions of ODS-TiO_2 particles were subjected to near-UV radiation (details in Supporting Information). In most cases, UV irradiation resulted in a striking visual change: the blue Fc^+ solution became colorless, while the suspended, white TiO_2 particles turned yellowish beige. UV/Vis absorption spectroscopic analysis showed that decolorization of the blue Fc^+ solution corresponded to a decrease in the intensity of the Fc^+ absorption at 618 nm (Figure 2). After illumination, the mixtures were then stirred in the dark at room temperature for varying lengths of time. Over the course of 10–20 minutes, a 1 M HCl solution containing the yellow-beige particles became pale blue, while the ODS-TiO_2 particles became white.

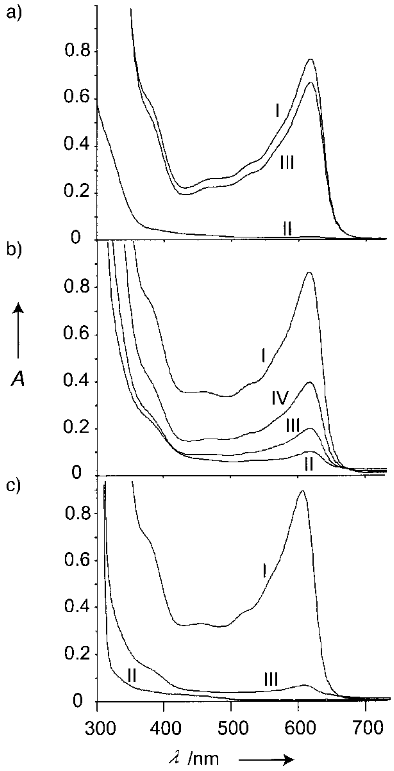

Figure 2. UV/Vis absorption spectra of supernatant solutions from suspensions of ODS-TiO_2 showing the redox-switching of ferrocene/ferrocenium (Fc/Fc^+); initial $[Fc^+BF_4^-] = 2$ mM. a) 1 M HCl solution in ethanol. I: Initial Fc^+ solution; II: after UV-irradiation for 25 min; III: after stirring in the dark for 14 h. b) 0.1 M HCl solution in ethanol. I: Initial Fc^+ solution; II: after UV-irradiation for 60 min; III: after stirring in the dark for 40 h; IV: after stirring in the dark for 70 h. c) 0.01 M HBF_4 solution in ethanol. I: Initial Fc^+ solution; II: after UV-irradiation for 40 min; III: after stirring in the dark overnight (ca. 14 h).

These observations are interpreted as follows: the holes generated by UV absorption react with water to yield hydrogen ions (e.g., Eq. (1)). Holes produced in TiO_2 are known to react quickly with the surrounding solvent.[10] While in contrast, electrons are relatively slow to react and thus are available for reduction of solution species such as dyes[11] and metal ions.[12] In this case, the electrons reduce the Fc^+ ions in solution to Fc [Eq. (2)], which is consistent with its standard reduction potential (versus a normal hydrogen electrode (NHE)) of 0.4 V.[13] The nonpolar Fc was then extracted into the hydrophobic layer on the TiO_2, which accounts for the color change of the TiO_2 particles. In the dark, the Fc in the Fc/ODS/TiO_2 system was evidently reoxidized slowly to form Fc^+ ions, which in turn redissolved into the supernatant, as is shown by UV/Vis spectroscopy (Figure 2a). The oxidation is presumably because of the presence of atmospheric O_2 and the strongly acidic conditions. The overall process is shown in Figure 1.

$$h^+ + H_2O \rightarrow H^+ + \tfrac{1}{2}H_2O_2 \qquad (1)$$

$$Fc^+ + e^- \rightarrow Fc \qquad (2)$$

This mechanism is supported by three lines of evidence. First, Fc was extracted by dichloromethane from the yellowish beige ODS-TiO_2 particles and identified by ^1H NMR spectroscopy. ODS-TiO_2 particles that are yellowish beige because of ferrocene dissolved in the ODS layer will be termed "Fc-ODS-TiO_2". The ODS-TiO_2 particles became white after this extraction was carried out.

Second, when the suspension was saturated with O_2 prior to UV illumination, not all of the Fc^+ ions were reduced (Figure 3a). In contrast, saturation with air or N_2 led to complete or near-complete photoreduction (Figure 3b, c). Reoxidation in the dark (described below) also proceeded more quickly with O_2 than with air (Figure 3b) but was almost completely inhibited under N_2.

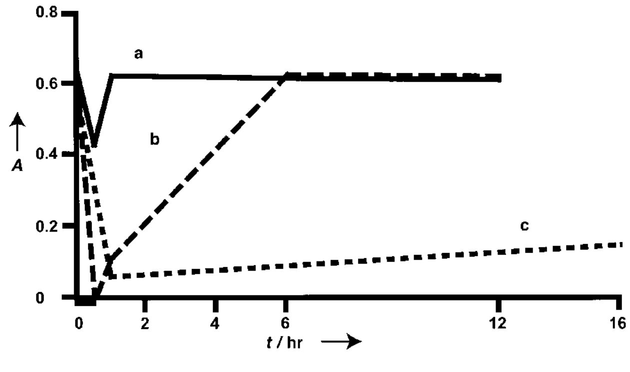

Figure 3. Change in the intensity of the ferrocenium absorption band (618 nm) upon UV illumination for 30 min (marked by bar along abscissa) followed by the bubbling of gases through the TiO_2 suspension in darkness (see text). a) ——: O_2; b) – – –: air; c) - - - -: N_2.

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Third, a roughly quantitative decrease in the pH value of the solution was detected upon irradiation in a separate experiment. An aqueous solution of $FcBF_4$ (10^{-3} M) in which unfunctionalized P25 TiO_2 had been suspended was adjusted to pH 6.4 with NaOH and subjected to UV irradiation for 30 min. The pale-blue solution again turned colorless while the TiO_2 particles became yellowish beige. The pH value of the supernatant, after separation from the TiO_2 by centrifugation, was 3.7. Full reduction of Fc^+ should yield a final pH value of approximately 3, but competing reactions such as those shown in Equations (3) and (4) probably account for this discrepancy.[14] Although oxidation of chloride ions may also occur[15] in 1M HCl, similar results were found when experiments were conducted in 1M HBF_4, so reduction does not depend on the nature of the anion.

$$H^+ + e^- \rightarrow H^{\cdot} \qquad (3)$$

$$H^+ + O_2^- \rightarrow H^{\cdot} + O_2 \qquad (4)$$

As the experiment above shows, the same set of photoreactions also proceeded quickly in mixtures of plain (that is, non-ODS-functionalized) TiO_2 in near-neutral aqueous solution. However, no reduction of Fc^+ species was observed in reaction mixtures of plain TiO_2 in 1M HCl. Presumably under such conditions, reoxidation of Fc to Fc^+ by atmospheric O_2 occurs so swiftly that no Fc accumulation takes place. Strongly acidic conditions are known to facilitate the oxidation of Fc by O_2 [Eq. (5)].[16] Fc accumulation (indicated by the color change of the TiO_2 particles) is observed with ODS-TiO_2 because dissolution of Fc into the hydrophobic ODS layer hinders this reoxidation. Moreover, chloride adsorption at the plain TiO_2 surface may inhibit electron transfer,[17] while the ODS layer will drastically alter the adsorption properties of the TiO_2 surface.

$$2\,Fc + {}^1\!/_2 O_2 + 2\,H^+ \rightarrow 2\,Fc^+ + H_2O \qquad (5)$$

When acetonitrile was used as solvent, the photoreduction of Fc^+ by ODS-TiO_2 was very slow (16 h) as compared with combinations that included water as a cosolvent, in which reactions took less than 1 h. These results further suggest that water facilitates the reduction of Fc^+ on irradiated ODS-TiO_2 suspensions by acting as a hole scavenger [Eq. (1)]. Furthermore, the Fc in Fc-ODS-TiO_2 was not completely reoxidized to Fc^+ in 0.1M HCl (Figure 2b) and 0.01M HBF_4 (Figure 2c) solutions in ethanol even after more than two days in the dark. Presumably the pH value of these solutions is too high for reoxidation to occur. Remarkably, and contrary to our initial expectations, photogenerated holes also do not oxidize Fc to Fc^+ on continued irradiation of Fc-ODS-TiO_2. This is probably a result of the large difference in oxidation potential between Fc and the holes.

We have demonstrated a remarkably simple chemionic switch involving the reduction of ferrocenium (off) to ferrocene (on) and reoxidation to ferrocenium. Reduction is driven by near-UV light and the spontaneous reversion by atmospheric oxygen (Figure 1). This spontaneously reversing system is an attractive model for a light-driven "self-eluting" adsorbing surface for the particularly promising application of solute extraction. Photoreduction of a redox-active solution species causes its precipitation, with elution occurring on reoxidation by atmospheric O_2. A spontaneously reversing system for the extraction of Cu^{2+} ions has been demonstrated, but in contrast to our system, the photoreduction does not work in air.[18] Although recovery of metals by semiconductor-mediated photoreduction has been the subject of much study,[19] the difficulty of eluting the precipitated metal has so far prevented practical applications.

In addition, although metallocene–metallocenium couples have been widely used in determining photopotentials,[20] our system also seems to be the first quantitative out-of-solution photoreduction of a metallocenium species. Finally, this chemionic switch further indicates how light can be utilized to drive molecular organization, in this case through photoreduction, which induces the insertion of the hydrophobic Fc into the ODS layer on the TiO_2 surface.

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Gram-Scale Synthesis of Suspension-Polymerized Styrene–Divinylbenzene-Based Resins Using an Oscillatory Baffled Reactor

David C. Sherrington,* Andreas Lanver, Hans-Günther Schmalz, Bruce Wilson, Xiong-Wei Ni, and Siguo Yuan

The use of spherical particulate cross-linked vinyl polymer beads or resins produced by free-radical suspension polymerization is now widespread in both synthetic and screening methodologies.[1–3] Increasingly, however, they are also being exploited as the basis of heterogeneous reagents, catalysts, and scavengers to facilitate the synthesis of target molecules in solution.[4,5] The work-horse species are styrene–divinylbenzene-based resins, which are synthesized on a large industrial scale (ca. 1000 kg) by using a batch polymerization procedure carried out in steel, stirred-tank reactors (STR).[6] Laboratory-scale syntheses are performed similarly by using a glass reactor typically of 0.5–2.0 L in volume.[7] A major technical challenge is to avoid particle aggregation, and this is usually achieved by dissolving a suitable suspension stabilizer in the aqueous phase, coupled with efficient stirring. In practice, stabilization conditions are usually optimized by experimentation, and no universal procedure is available that is suitable for all polymerization mixtures. Since aggregation is associated primarily with surface phenomena, that is, particle–particle, particle–reactor, and particle–stirrer interactions, and since the surface/volume ratio increases as the scale of the process is reduced, aggregation becomes more problematic. Suspension polymerization to produce high-quality beads in good yield on a gram scale is therefore difficult to achieve. This situation is unfortunate because an attractive strategy for synthesizing complex functional resins is to use an appropriate functional (for example, styryl) monomer in a suspension polymerization to produce resin beads with a predetermined loading, cross-link ratio, and morphology. Since laboratory resin synthesis is problematic below the 10–20 g scale, and some optimization program is almost always necessary for each functional comonomer, there is a considerable deterrent to investing in complex monomer synthesis in view of the likely wastage that will ensue in implementing successful suspension polymerization.

We have now developed a robust suspension polymerization procedure by using a small oscillatory baffled reactor (OBR) capable of providing good yields of high-quality resin beads, of both gel-type and various macroporous morphologies, and operating on a gram scale. We have also shown that a functional styryl co-monomer can be employed in the system with no deterioration in the yield nor physical quality of the resin beads obtained.

The design and underlying principles of the OBR have been reported by Mackley and co-workers,[8–10] and the appropriate choice of the dimensions of the reactor and the oscillating baffles, together with the frequency and amplitude of oscillation, leads in effect to each baffled cell acting as if it were a continuously stirred tank.[9,10] Ni et al. have reported the results of remarkable flow-visualization experiments[11] and computational fluid-dynamic simulations[12] which confirm this picture. The successful application of OBRs in suspension polymerization by the same group[13–16] prompted us to investigate the possibility of scaling down the reactor size to carry out gram-scale suspension polymerizations.

Accordingly, the glass OBR shown in Figures 1 and 2 was constructed. The reactor consists of a vertical glass tube 25 mm in diameter and 137 mm tall (ca. 70 mL volume) with a water jacket 53.5 mm in diameter and 158 mm tall. The top of the reactor is a conventional glass flange arrangement that allows the use of an N_2 supply and a condenser. The oscillatory motion in the reaction mixture is achieved by moving a set of stainless steel baffles up and down. The set consists of two or three orifice baffles (with orifice diameters of 11 mm) and an upper coupling plate into which is located the driving con-rod. The latter is 6.3 mm in diameter and 190 mm in length and is connected non-centrally to a rotating wheel which thus provides the oscillatory vertical motion. The con-rod moves within a long teflon bearing in the glass flange lid so as to maintain a vertical alignment of the baffles within the reactor. The baffles are made of 3-mm thick stainless-steel plate, and are connected to each other and the coupling plate by two 1.5-mm stainless-steel rods. The distance between the lower baffle and the reactor bottom is 6 mm (at full extension) and the oscillation amplitude is set at 21 mm. The free baffle area ratio (defined as the ratio of baffle orifice area to the tube

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