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Highly efficient sensitization of titalium oxide

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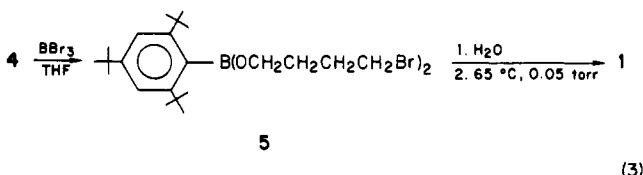
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product is obtained upon similar hydrolysis and dehydration of bis(4-bromobutoxy)(2,4,6-tri-*tert*-butylphenyl)borane (**5**), obtained by the reaction of **4** with boron tribromide in tetrahydrofuran (eq 3).[8]


5   (3)

Compound **1** reacts with water and oxygen; when heated to 85 °C it decomposes with loss of two molecules of 2-methylpropene to form a second diboradioxetane, **6**, also a pale yellow oil (eq 4).[9] Both **1** and **6** show rather positive ^{11}B chemical shift values,

6   (4)
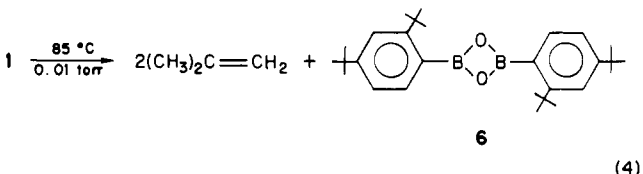
+32.37 and 33.01 ppm, respectively. The deshielding of the boron nucleus in these species is consistent with a strained ring structure.[10] The Raman spectrum of **1** exhibits a strong line at 905 cm^{-1} with satellites at 927 and 944 cm^{-1}, assigned to the symmetric ring stretching of the B_2O_2 framework. These frequencies are about 100 cm^{-1} higher than for related six-membered rings, $R_3B_3O_3$.[11]

Photolysis of **1** in the presence of trapping agents led to products which may arise from the intermediate oxoborane **2**.[12] Thus irradiation at 254 nm of a solution of **1** in *tert*-butyl methyl ketone produced the dioxaboretane **7**,[13] and similar photolysis in the presence of 2,2,4,4-tetramethyl-2,4-disila-1-oxacyclopentane gave the product **8**[14] (eq 5), both in nearly quantitative yields.

8

7   (5)
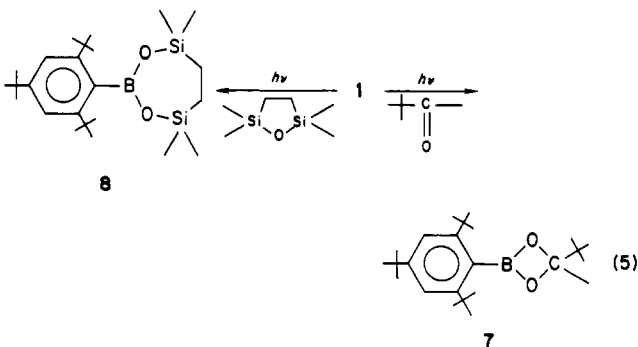
(7) ^1H NMR δ 1.43 (s, 9), 1.59 (s, 18), 7.56 (s, 2); ^{11}B NMR 32.37 ppm; UV, hexane λ$_{max}$ 268, 232, 220 cm^{-1}; Raman 905, 927, 944 (16:4:1). Molecular weight 544.4623 (calcd), 544.4755 (found); MS, *m/e* 544 (M$^+$, 0.9%), 489 (1.9), 418 (7.8), 272 (0.6), 256 (50.3), 57 (100.0), 54 (43.8). In repeated mass spectral and GC–MS experiments under various conditions, no peaks with higher mass were ever detected.

(8) Kuchen, W.; Brinckmann, R. D. *A. Anorg. Allg. Chem.* 1963, *325*, 225.

(9) ^1H NMR δ 1.32 (s, 9), 1.52 (s, 9), 7.25 (m, 1), 7.53 (m, 1), 7.72 (m, 1); ^{11}B NMR 33.01 ppm; molecular weight 432.3371 (calcd), 432.3370 (found); MS, *m/e* 432 (M$^+$, 5.7%), 417 (1.5), 303 (6.1), 288 (5.7), 216 (7.7), 171 (5.0), 57 (100.0).

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(13) ^1H NMR δ 0.95 (s, 3), 1.40 (s, 9), 1.55 (s, 18), 1.79 (s, 9), 7.59 (s, 2); ^{11}B NMR 33.52 ppm; molecular weight 315.2495 (M − 57 calcd), 315.2337 (M − 57 found); MS 372 (M$^+$ − 15, 1.3%), 315 (M$^+$ − 57, 7.7), 300 (3.0), 256 (1.5), 245 (23.7), 71 (11.7), 57 (100.0), 56 (18.3), 43 (47.2).

(14) ^1H NMR δ 0.15 (s, 12), 0.73 (s, 4), 1.38 (s, 9), 1.52 (s, 18), 7.52 (s, 2); ^{11}B NMR 30.48 ppm; molecular weight 432.3051 (calcd), 432.3011 (found); MS, *m/e* 432 (M$^+$, 2.9%), 417 (1.2), 360 (1.0), 245 (4.5), 231 (19.7), 187 (9.8), 115 (10.4), 72 (14.6), 57 (100.0).

Irradiation of **1** at −196 °C in 3-methylpentane glass led to formation of a weak UV absorption band at 314 nm which may be due to free **2**. Further investigations of this new species are being carried out.

Highly Efficient Sensitization of Titanium Dioxide

Jean Desilvestro, Michael Grätzel,* Ladislav Kavan,[1] and Jacques Moser

Institut de Chimie Physique
Ecole Polytechnique Fédérale
CH-1015 Lausanne, Switzerland

Jan Augustynski

Institut de Chimie Minérale, Analytique et
Appliquée, Université de Genève
CH-1211 Genève, Switzerland

Received December 6, 1984

The photosensitization of wide-bandgap oxide semiconductors is the subject of an intensive investigation, mainly due to its importance for solar energy conversion.[2] Of particular interest is the combination of chromophores such as Ru(bpy)$_3^{2+}$ with TiO$_2$ or SrTiO$_3$ since this offers the possibility to shift the water cleavage activity of these oxides into the visible.[3] However, the efficiencies achieved so far with such devices have been disappointingly low, mainly due to poor light energy harvesting and small quantum yields for charge injection. We have achieved strikingly high efficiencies in the sensitization of colloidal anatase particles and polycrystalline electrodes using tris(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II) dichloride[4], (**1**) as a sensitizer.

(1) Visiting scientist from the Heyrovsky Institute of Physical Chemistry and Electrochemistry, 10200 Prague, 10, CSSR.

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(4) **1** was synthesized according to C. Foreman: Foreman, C. Ph.D. Thesis, University of North Carolina, Chapel Hill, NC. We thank Prof. D. G. Whitten for providing us with a copy of this thesis.
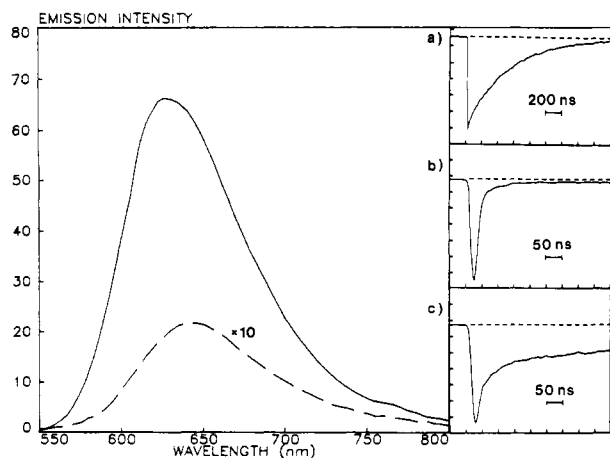
Figure 1. Effect of colloidal TiO_2 on the luminescence of **1** in aqueous solution of pH 2, concentration of sensitizer 5×10^{-6} M. Solid line, no TiO_2 present; dashed line, $[TiO_2]$ = 0.5 g/L, gain 10 times increased; insert, laser photolysis of **1** in aqueous solution of pH 2, (a) emission at 630 nm in the absence of TiO_2, (b) emission at 630 nm in the presence of 1 g/L TiO_2, (c) bleaching of ground-state absorption of **1** at 450 nm.

1 in acidic aqueous solution is strongly adsorbed to the surface of TiO_2. When TiO_2 powder is introduced into $2 \leqslant$ pH $\leqslant 5$ solutions of **1**, a bright red color develops onto the particles whose reflectance spectrum in the visible is practically identical with the absorption spectrum of **1**. The supernatant spectrum shows simply the disappearance of free **1**. Figure 1 demonstrates that the emission of **1** with a maximum at 640 nm is very efficiently quenched by colloidal TiO_2 paraticles (particle radius 60 Å, produced via hydrolysis of $TiCl_4$[5]). Inserted are oscillograms from time-resolved studies which employed a 530-nm Nd:YAG laser to excite **1**. In water (pH 2), τ_f = 600 ns while in the presence of TiO_2 the emission follows essentially the time profile of the laser pulse. Single-photon counting analysis gives τ_f = 19 ns.[6] The ground-state bleaching at 450 nm shows a short-lived component matching the luminescence decay, followed by a slower recovery in the microsecond domain. The appearance of this long-lived bleaching component is due to oxidative quenching of the excited chromophore:[7]

$$*Ru(bpy(COO^-)_2)_3^{4-} \xrightarrow{k_{inj}} Ru(bpy(COO^-)_2)_3^{3-} + e_{CB}^-(TiO_2)$$
$$(1)$$
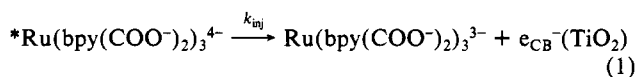
Using previously published actinometry,[8] we obtain a quantum yield of 60 ± 10% for charge injection. Since $k_{inj} = \phi_{inj}/\tau_f$, the rate constant for electron injection is 3.2×10^7 s^{-1}. The slower bleaching recovery in Figure 1 is due to recapture of conduction band electrons by $Ru(bpy(COO^-)_2)_3^{3-}$ and occurs at a rate constant[9] of $k_b \simeq 4 \times 10^5$ s^{-1}, which is typical for such intraparticle back-electron-transfer processes:[10]

$$Ru(bpy(COO^-)_2)_3^{3-} + e_{CB}^-(TiO_2) \xrightarrow{k_b} Ru(bpy(COO^-)_2)_3^{4-}$$
$$(2)$$
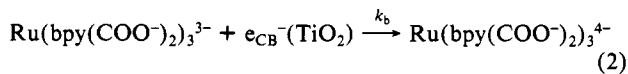
In contrast to **1**, the emission of $Ru(bpy)_3^{2+}$ at pH 2 is not quenched by colloidal TiO_2 up to a concentration of 10 g/L.[11]

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(6) A small fraction of the luminescence signal was found to decay with a longer lifetime of $\tau_f \simeq 50$ ns.

(7) In eq 1 we have formulated **1** as a tetraanion. Acid base titration shows that the pK value for the first protonation is 6.5. At pH <2.5 three more protons are added leading to the precipitation of the Zwitterion of **1**. Therefore, **1** exists as a trianion at $2.5 \leqslant$ pH $\leqslant 6$. Below the isoelectric point the surface pH of TiO_2 is 1–2 units higher than in the bulk. This will shift the domain where **1** is a trianion to lower values.

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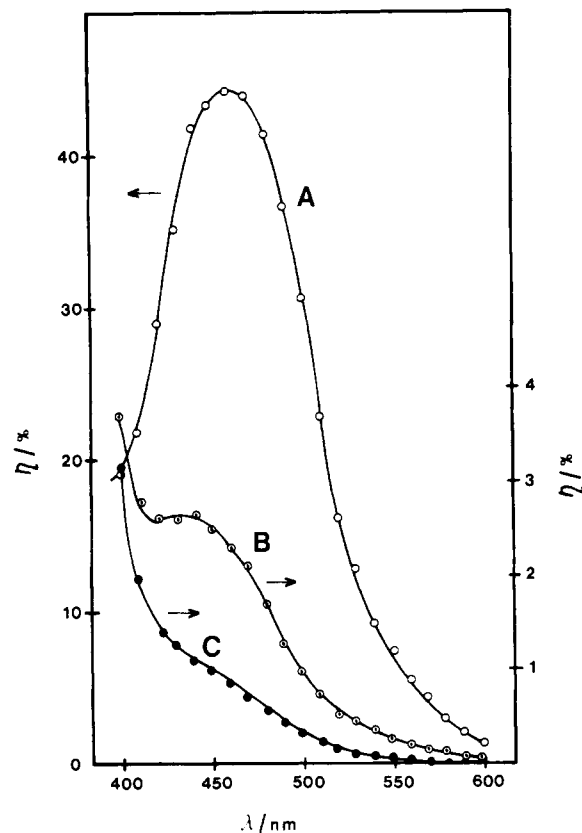(10) Moser, J.; Grätzel, M. *J. Am. Chem. Soc.* **1984**, *106*, 6557.

Figure 2. Photocurrent action spectrum in the visible of the polycrystalline TiO_2 (anatase) electrode sensitized by **1** (A), $Ru(bpy)_3^{2+}$ (B), and without sensitizer (C). Current efficiencies were calculated by dividing the photocurrent density by the incident monochromatic light flux. Solutions contain 10^{-2} M NaCl and 10^{-3} M hydroquinone. Higher hydroquinone concentrations did not improve efficiencies. Conditions: (A) pH 2.6, adjusted with HCl, 0.0 V (SCE); (B) 1.5×10^{-4} M $Ru(bpy)_3^{2+}$, pH 7, –0.1 V (SCE); (C) no sensitizer, pH 7, –0.1 V (SCE).

At pH 10, where $Ru(bpy)_3^{2+}$ is adsorbed onto TiO_2,[12] k_{inj} = 1.5 $\times 10^5$ s^{-1} and $k_b \simeq 4 \times 10^5$ s^{-1}.

In Figure 2 we compare the performance of the two sensitizers in photoelectrochemical experiments that employed a rough polycrystalline anatase electrode[13] (area 0.28 cm^2, thickness 10 μm, roughness factor ca. 100) irradiated with an Oriel 250-W tungsten halogen lamp through a Kratos monochromator. Hydroquinone, 10^{-3} M, was employed as a cosensitizer. The electrode was loaded with **1** by dipping it for 30 min in a 5×10^{-4} M solution of **1** (pH 3.5) and subsequent rinsing with water. The maxima of the photocurrent action spectrum for **1** and $Ru(bpy)_3^{2+}$ are at around 460 and 440 nm, respectively. In agreement with the laser photolysis data, sensitization by $Ru(bpy)_3^{2+}$ was observed only at pH $\geqslant 4$, attaining its optimum efficiency at pH 7.

The current density obtained for **1** at an incident monochromatic light flux of 0.22 mW/cm^2 at 460 nm is 36 μA/cm^2. This corresponds to an incident photon to current conversion efficiency (η) of 44%. A light flux of 0.2 mW/cm^2 at 440 nm gave for $Ru(bpy)_3^{2+}$ a sensitization current of 1.1 μA/cm^2. Thus, for $Ru(bpy)_3^{2+}$, η = 1.5%. Polychromatic irradiation (420-nm cutoff combined with a Balzers K-45 band-pass filter, 10^{-2} M hydroquinone, other conditions as in Figure 2) gave for an incident light flux of 15 mW/cm^2 a current density of 0.57 mA/cm^2. After 6.6 C/cm^2 had passed through the electrode, the current was 0.46

(11) Given an error limit of 5% in the experimental determination of τ_f and ϕ_f the value of k_{inj} is smaller than 10^5 s^{-1} at pH 2 and a TiO_2 particle concentration of 7×10^{-6} M. For diffusion-controlled injection one would expect k_{inj} to be 4×10^5 s^{-1} under these conditions.

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mA/cm². At this time the turnover number of **1** was at least 10^4, assuming complete coverage of the electrode by a monolayer of **1**, a roughness factor of 100, and a radius for **1** of ca. 8 Å.

The achievement of 44% incident photon to current conversion efficiency is unprecedented. Apart from the rough structure of the electrode surface acting as a light trap, this is due to the unique sensitizing properties of **1**. In the pH domain of interest, **1** is an anion and therefore electrostatically attracted to the semiconductor. In addition, carboxylate groups adsorb specifically at the surface of TiO_2[14] resulting in the intimate contact required for efficient sensitization.[15] For $Ru(bpy)_3^{2+}$, the ratio of charge injection to recombination rates is unfavorable. Interstingly, ruthenium bis(2,2′-bipyridyl)(2,2′-bipyridyl-4,4′-dicarboxylate) (**2**), chemically attached to a TiO_2 electrode, gives only ϕ_{inj} = 0.0025.[3e,f,g] The current action spectrum of **2** is structureless, indicating that chemical attachment of **2** to the surface of TiO_2 creates semiconductor (t_{2g})/dye (π^*) surface states acting as recombination centers.[3f] This increases k_b sharply, reducing drastically the efficiency of sensitization. The action spectrum obtained for **1** matches its absorption spectrum indicating that this type of interaction is absent in the case of **1**.

Acknowledgment. This work was supported by the Swiss National Science Foundation and the Gas Research Institute, Chicago, IL (subcontract with the Solar Energy Research Institute, Golden, CO). We are grateful to Dr. Robin Humphry-Baker and Paul Liska for experimental help.

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Photoinduced Aggregation Changes in Photochromic Polypeptides

O. Pieroni,*[†,‡] A. Fissi,[†] J. L. Houben,[†] and F. Ciardelli[‡,§]

*CNR–Institute of Biophysics, 56100 Pisa, Italy
Institute of Industrial Organic Chemistry
University of Pisa, 56100 Pisa, Italy
CNR-Center for the Study of Stereoordered and
Optically Active Macromolecules, 56100 Pisa, Italy*

Received November 26, 1984

Several photoresponsive effects have been recently observed in azobenzene-containing photochromic systems.[1–16] Here we report

† Institute of Biophysics.
‡ Institute of Industrial Organic Chemistry.
§ Center for the Study of Stereoordered and Optically Active Macromolecules.

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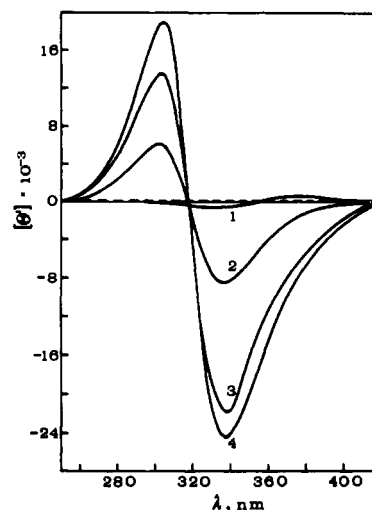(14) Pieroni, O.; Houben, J. L.; Fissi, A.; Costantino, P.; Ciardelli, F. J. Am. Chem. Soc. 1980, 102, 5913–5915.

Figure 1. Poly(L-glutamic acid) containing 21 mol % azobenzene units. Time dependence of side-chain CD bands in TMP/H_2O = 50/50. (1) Freshly prepared solution, (2) 1-day old solution; (3) 2-day old solution, (4) 3-day old solution. (—) Dark-adapted, (---) irradiated at any time. Data are expressed in terms of azobenzene molar ellipticity.
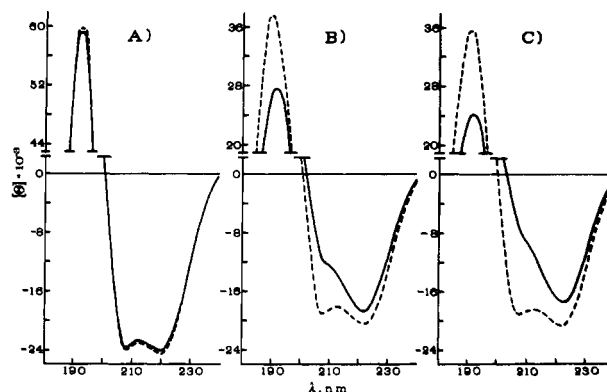

Figure 2. Poly(L-glutamic acid) containing 21 mol % azobenzene units. CD spectra in TMP/H_2O = 50/50, recorded at various aging times. (A) Freshly prepared, (B) 1-day old, (C) 2-day old solution. (—) Dark-adapted, (---) irradiated samples. Molar ellipticity is based on the mean residue weight.

some CD data providing evidence that azobenzene-containing poly(L-glutamic acid) can undergo reversible "aggregation changes" upon exposure to light or dark conditions.

A photochromic polymer containing 21 mol % azo units was obtained by modification of poly(L-glutamic acid) ($\bar{M}_v$ = 200 000), as previously described.[16,17] Its photochromic behavior is correlated with the reversible trans ⇌ cis photoisomerization of azobenzene moieties. High trans-to-cis photoconversions can be obtained by irradiating at λ = 370 nm. The opposite cis-to-trans isomerization is obtained by irradiating at λ = 450 nm or by dark adaptation.[16,17]

The CD spectra in trimethyl phosphate (TMP) exhibit the two negative bands at 222 and 208 nm typical of α-helical polypeptides. The dark-adapted samples (all trans azo groups) show also an intense positive CD couplet centered at 350 nm, in correspondence to the π–π^* transition of the azo chromophore.[16,17]

Remarkable variations of the CD spectra occur when increasing amounts of water are added to the TMP solutions stored in the dark. Side-chain CD bands progressively decrease by increasing water concentration and disappear when its concentration is higher

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