Electronic Supplementary Information (ESI)

Organic dye-sensitized TiO_2 for the redox conversion of water pollutants under visible light

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1. Organic dye (OD) synthesis

Synthesis of 4-[5'-(5,5-Dimethyl-1,3-dioxan-2-yl)[2,2'-bithiophen]-5-yl]benzenamine (2).
To a stirred solution of 4-bromoaniline (0.42 g, 2.46 mmol) and $Pd(PPh_3)_4$ (85 mg, 0.07 mmol) in tetrahydrofuran (10 mL) were added a THF solution (10 mL) of 4,4,5,5-tetramethyl-2-(5-(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)-thiophen-2-yl)-1,3,2-dioxaborolane **1**[1] (1.00 g, 2.46 mmol) and potassium carbonate (1.36 g, 9.84 mmol) and then H_2O (10 mL). The mixture was refluxed for 12 h, cooled to rt, extracted with CH_2Cl_2, and dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, flash chromatography of the residue over silica gel using ethylacetate/hexane (v/v = 1:2) as eluent gave the product **2** as a yellow powder. Yield: 0.65 g (71%). ^1H NMR ($CDCl_3$): δ 7.39 (d, 2H, ArH), 7.08 (d, 1H, ArH), 7.04 (d, 1H, ArH), 7.02 (s, 2H, ArH), 6.69 (d, 2H, ArH), 5.62 (s, 1H, -CH-), 3.77 (d, 2H, $-CH_2-$), 3.75 (s, 2H, $-NH_2$), 3.64 (d, 2H, $-CH_2-$), 1.29 (s, 3H, $-CH_3$), 0.80 (s, 3H, $-CH_3$). HRMS(FAB) calcd for $C_{20}H_{21}NO_2S_2$: 371.1014. Found: 371.1021 $[M]^+$. Anal. Calcd for $C_{20}H_{21}NO_2S_2$: C, 64.66; H, 5.70; N, 3.77. Found: C, 64.61; H, 5.68; N, 3.76.

Synthesis of 1-Bromo-4-[[2-(2-methoxyethoxy)ethoxy]methyl]benzene (3).
A solution of diethylene glycol monoethyl ether (1.13 ml, 9.57 mmol) in dry THF (20 mL) was added to a rapidly stirred suspension of sodium hydride (0.689 g, 28.72 mmol) in dry THF (10 mL). After stirring at room temperature for 30 min, 4-bromobenzyl bromide (2.39 g, 9.57 mmol) was added to the solution. The resulting mixture was stirred at room temperature for 6 h and then quenched with a saturated ammonium chloride solution. After removal of the solvent with a rotary evaporator under reduced pressure, the residue was diluted with water and extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. Flash chromatography of the residue over silica gel using ethylacetate/hexane (v/v =1:3) as eluent gave the product **3** as a colorless oil. Yield: 2.91 g (91%). ^1H NMR ($CDCl_3$): δ 7.46 (d, 2H, ArH), 7.22 (d, 2H, ArH), 4.51 (s, 2H, $-CH_2-$), 3.69–3.63 (m, 6H), 3.57–3.54 (m, 2H), 3.38 (s, 3H, $-OCH_3$). HRMS(FAB) calcd for $C_{12}H_{17}BrO_3$: 288.0361. Found: 288.0370 $[M]^+$. Anal. Calcd for $C_{12}H_{17}BrO_3$: C, 49.84; H, 5.93. Found: C, 49.81; H, 5.91.

Synthesis of 4-((2-(2-methoxyethoxy)ethoxy)methyl)-N-(4-((2-(2-methoxyethoxy)ethoxy) methyl)phenyl)-N-(4-(5-(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)thiophen-2-yl) phenyl)benzenamine (4).
A toluene solution (20 mL) containing a mixture of **2** (0.50 g, 1.35 mmol), **3** (0.90 g, 3.1 mmol), $Pd_2(dba)_3$ (0.085 g, 3 mol%), Xantphos (0.054 g, 3 mol%), and NaOtBu (1.04 g, 10.77 mmol) was stirred under N_2 at 110 °C for 12 h, hydrolyzed with water, extracted with CH_2Cl_2, and dried over $MgSO_4$. After removal of the solvent under reduced pressure, silica gel column chromatography of the residue using ethylacetate/hexane (1:4) as eluent gave the product **4** was obtained as a yellow oil. Yield: 0.64 g (61%). ^1H NMR ($CDCl_3$): δ 7.43 (d, 2H, ArH), 7.24 (d, 4H, ArH), 7.11-7.03 (m, 10H, ArH), 5.62 (s, 1H, -CH-), 4.51 (s, 4H, $-CH_2-$), 3.77 (d, 2H), 3.72-

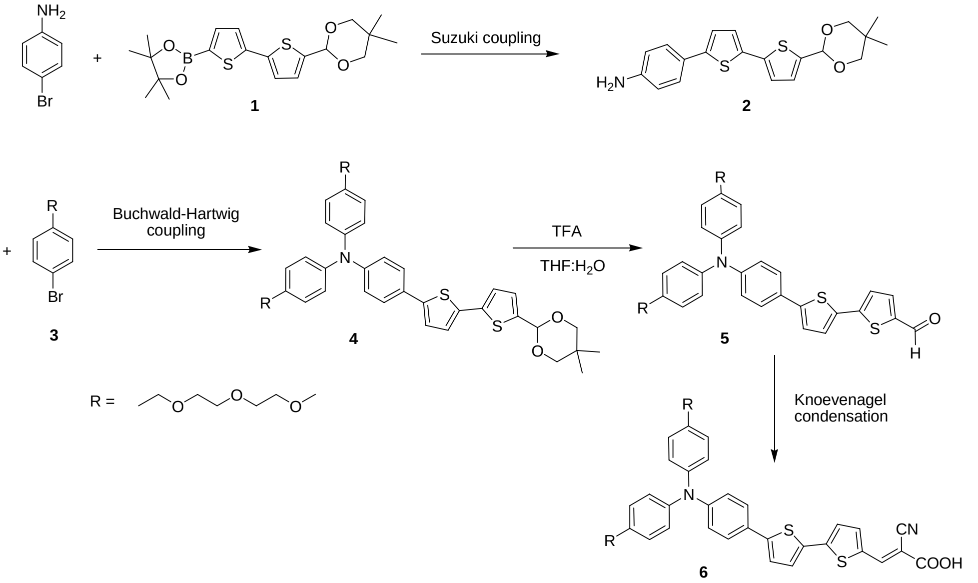
3.63 (m, 14H), 3.57-3.55 (m, 4H), 3.39 (s, 6H, $-OCH_3$), 1.29 (s, 3H, $-CH_3$), 0.80 (s, 3H, $-CH_3$). HRMS(FAB) calcd for $C_{44}H_{53}NO_8S_2$: 787.3213. Found: 787.3222 $[M]^+$. Anal. Calcd for $C_{44}H_{53}NO_8S_2$: C, 67.06; H, 6.78; N, 1.78. Found: C, 67.02; H, 6.74; N, 1.75.

Synthesis of 5'-{4-[Bis-(4-((2-(2-methoxyethoxy)ethoxy)methyl)-phenyl)-amino]-phenyl} -[2,2']bithiophenyl-5-carbaldehyde (5).

To acetal **4** (0.64 g, 0.81 mmol) placed in a flask were added THF (100 ml), water (25ml) and then TFA (22 ml). The resulting mixture was stirred for 2 h at room temperature, quenched with saturated aqueous sodium bicarbonate, and extracted with dichloromethane. The combined dichloromethane phases were then washed with aqueous sodium bicarbonate and dried $MgSO_4$. After removal of the solvent under reduced pressure, silica gel column chromatography of the residue using ethylacetate/hexane (3:1) as eluent gave the product **5** was obtained as an orange oil. Yield: 0.38 g (67%). ^1H NMR ($CDCl_3$): δ 9.83 (s, 1H, -COH), 7.65 (d, 1H, ArH), 7.44 (d, 2H, ArH), 7.30 (d, 1H, ArH), 7.26-7.21 (m, 5H, ArH), 7.16 (d, 1H, ArH), 7.09-7.03 (m, 6H, ArH), 4.51 (s, 4H, $-CH_2-$), 3.69-3.63 (m, 12H), 3.58-3.54 (m, 4H), 3.38 (s, 6H, $-OCH_3$). HRMS(FAB) calcd for $C_{39}H_{43}NO_7S_2$: 701.2481. Found: 701.2490 $[M]^+$. Anal. Calcd for $C_{39}H_{43}NO_7S_2$: C, 66.74; H, 6.17; N, 2.00. Found: C, 66.71; H, 6.13; N, 1.99.

Synthesis of 3-(5'-{4-[Bis-(4-((2-(2-methoxyethoxy)ethoxy)methyl)-phenyl)-amino]-phenyl}-[2,2']bithiophenyl-5-yl)-2-cyanoacrylic acid (6, OD).

An acetonitrile solution (10 mL) containing **5** (0.38 g, 0.54 mmol), cyanoacetic acid (46 mg, 0.54 mmol), and piperidine (0.07 ml, 0.71 mmol) was refluxed for 6 h, cooled to rt, and then quenched with 1M HCl. After removal of acetonitrile in vacuo, the crude product was extracted with CH_2Cl_2 and dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, flash chromatography of the residue over silica gel using ethylacetate/MeOH (v/v = 9:1) as eluent gave the product **6** was obtained as a red powder. Yield: 0.35 g (84%). ^1H NMR (DMSO-d6): δ 8.04 (s, 1H, =CH-), 7.64-7.58(m, 3H, ArH), 7.46-7.42 (m, 3H, ArH), 7.28 (d, 4H, ArH), 7.04 (d, 4H, ArH), 6.97 (d, 2H, ArH), 4.44 (s, 4H, $-CH_2-$), 3.56-3.51 (m, 12H), 3.45-3.43 (m, 4H), 3.23 (s, 6H, $-OCH_3$). 13C NMR (DMSO-d6): 164.4, 147.8, 146.5, 144.5, 142.1, 141.2, 137.0, 136.1, 134.4, 134.3, 129.7, 127.5, 127.3, 127.1, 124.8, 123.2, 119.8, 109.3, 72.3, 71.9, 70.4, 70.2, 69.8, 58.7. HRMS(FAB) calcd for $C_{42}H_{44}N_2O_8S_2$: 768.2539. Found: 768.2542 $[M]^+$. Anal. Calcd for $C_{42}H_{44}N_2O_8S_2$: C, 65.60; H, 5.77; N, 3.64. Found: C, 65.55; H, 5.75; N, 3.62.



2. Catalyst Preparation

TiO_2 Powder (Degussa P25), a mixture of anatase and rutile (8:2) with a BET surface area of 50 m^2/g and primary particle size of 20-30 nm, was used as a base catalyst material. Chemical substrates used in this study include 4-chlorophenol (4-CP, Sigma), $Na_2Cr_2O_7$ (Cr^{VI}, Aldrich), $NaAsO_2$ (As^{III}, Aldrich), $Na_2S_2O_8$ (Aldrich). All reagents were used as received. A platinum plate (1×1 cm^2, 0.125 mm thick, 99.9%, Aldrich), lithium perchlorate(99.9%, Aldrich), and $FeCl_3\cdot6H_2O$ (>99%, Kanto) were used in photoelectrochemical experiments.

RuL_3 adsorbed well on TiO_2 in aqueous suspensions. RuL_3/TiO_2 sample was prepared by dispersing 0.1 g of TiO_2 powder in 10 mL aqueous RuL_3 solution (100 μM) at pH 3. Whereas, OD /TiO_2 sample was prepared by dispersing 0.1 g of TiO_2 powder in 10 mL OD solution (100 μM in TBA+ACN(1:1) organic solvent). The molar concentration of OD added in OD/TiO_2 was identical to that of RuL_3 in RuL_3 /TiO_2 as 10 μmol g^{-1}. The solution was stirred for 3 h, then the dye/TiO_2 was collected by filtering. After drying in an oven (85 ^{o}C), orange colored powder of dye/TiO_2 were obtained.

The organic dye-supported on SiO_2 (OD/SiO_2) was prepared as a control sample in comparison with OD/TiO_2. All procedure is identical to that of OD/TiO_2, but the solvent was evaporated instead of the filtration. The electrodes of OD/TiO_2/FTO (fluorine-doped SnO_2, Pilkington, 1.65 cm^2), RuL_3/TiO_2/FTO were prepared for the stability test of dye/TiO_2. Prior to the dye adsorption, TiO_2-coated electrode (loaded TiO_2 amount ≈ 0.0045 g) was prepared. TiO_2 paste was prepared by adding poly(ethylene glycol) (PEG, Aldrich, molecular weight 20 kDa) in distilled water (50 wt% solution) and spreading it on a FTO plate using doctor-blade method with tracks of two layers of Scotch Magic Tape. After the TiO_2-coated electrode was calcined at 450 ^{o}C for 30 min, it was cooled to room temperature and immediately immersed into the solution of dye (100 μM) over 12 h to make dye/TiO_2/FTO. The RuL_3 solution were prepared in water at pH 3, whereas OD was dissolved in ACN+TBA(1:1).

3. Photocatalytic Activity Test

Sample powder was dispersed in distilled water (1 g/L). An aliquot of the substrate stock solution was subsequently added to the suspension to give a desired substrate concentration, then the initial pH of the suspension was adjusted with $HClO_4$ or NaOH standard solution. When the anoxic condition was needed, the reactor was purged continuously with nitrogen gas during irradiation. The irradiation employed a 300-W Xe arc lamp (Oriel) as a light source. Light passed through a 10-cm IR water filter and a UV cutoff filter ($\lambda > 420$ nm for visible light illumination), then the filtered light was focused onto a 30-mL Pyrex reactor with a quartz window. The incident light intensity ($\lambda < 500$ nm) was determined by ferrioxalate actinometry to be 6.7×10^{-4} einstein L^{-1} min^{-1}.

Sample aliquots were withdrawn from the reactor intermittently during the illumination and filtered through a 0.45-μm PTFE syringe filter (Millipore). Duplicate or triplicate photocatalytic activity measurements were carried out under the identical experimental condition to confirm reproducibility. The degradation of 4-CP and the production of chloride were monitored using a high performance liquid chromatograph (Agilent 1100 series) and an ion chromatograph (Dionex DX-120), respectively. The conversion of Cr^{VI} to Cr^{III} was tested. The concentration of Cr^{VI} was analyzed using a colorimetric method that uses 1,5-diphenylcarbazide (DPC) reagent.[2] The color change was monitored at 540 nm ($\varepsilon = 4 \times 10^4$ Lmol^{-1}cm^{-1}) using a UV-Vis spectrophotometer (Agilent 8453). Quantitative analysis of As(V) was performed using an ion chromatograph (IC, Dionex DX-120), which was equipped with a Dionex IonPac As 14 (4 mm × 250 mm) columm and a conductivity detector. The eluent solution was 3.5 mM Na_2CO_3/ 1 mM $NaHCO_3$**.**

The oxygen evolution was analyzed with an oxygen electrode (Thermo Orion 850 DO meter). The oxygen electrode was zero-calibrated with 20% Na_2SO_3 solution prior to the measurement. Nitrogen gas was purged through the suspension for 1 h and then the reactor with the oxygen electrode was sealed from the ambient air. Dissolved oxygen was measured in the presence of an alternative electron acceptor (10 mM $S_2O_8^{2-}$) and the reactor temperature was controlled using a cooling fan. Other experiment conditions were the same as those of the photocatalytic experiment.

4. Photocatalyst Characterization

DRUVS was measured using an UV-vis spectrophotometer (Shimadzu UV-2401PC) equipped with an integrating sphere attachment (Shimadzu ISR 2200). Measurements of the photocurrent collected on an inert electrode (Pt) immersed in aqueous suspension of dye/TiO_2 samples were carried out as described previously.[3] Fe^{3+}/Fe^{2+} redox couple was used as an electron shuttle that carries the electron from the photocatalyst particles to the Pt electrode. And acetate and lithium perchlorate were used as an electron donor and electrolyte, respectively. A Pt plate (1×1 cm^2), an Ag/AgCl electrode, and a graphite rod were used as a working, a reference and a counter electrode, respectively. Nitrogen gas was continuously purged though the suspension. Photocurrents were collected in the suspension by applying a potential (+0.7 V vs Ag/AgCl) to the Pt working electrode using a potentiostat (Gamry, Reference 600) connected to a computer.

Cyclic voltammetry (CV) experiments for OD was performed using a BAS 100 electrochemical analyzer. Glassy carbon, platinum wire, and Ag/$AgNO_3$ (0.10 M) were used as the working, counter, and reference electrodes, respectively. The CV experiment was performed using these three electrodes immersed in a solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in anhydrous THF at room temperature under argon with a scan rate of 0.1 V/s.

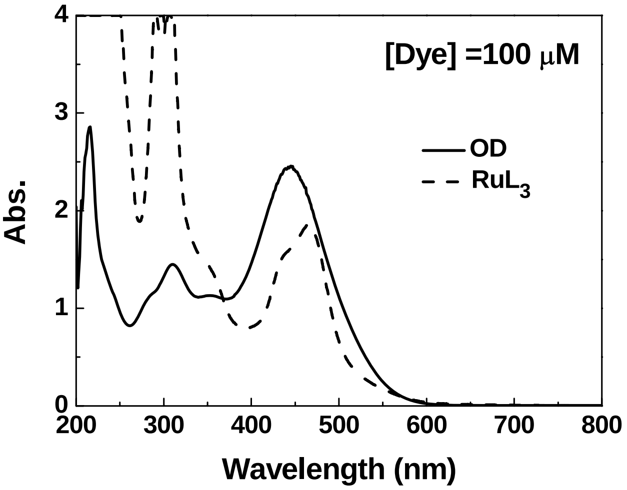


Fig. S1. UV-visible absorption spectra of **OD** (in acetonitrile and *tert*-butyl alcohol 1:1 mixture) and **RuL_3** (in water). [Dye] = 100 μM.

References

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