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[26] Compound **4a** ($C_{52}H_{62}O_2Si_2Y_2{\cdot}2\,C_6D_6$) crystallizes from benzene in the monoclinic space group $P2_1/c$ with $a = 11.7875(2)$, $b =$ 14.0396(3), $c = 16.8378(4)$ Å, $\beta = 104.2053(12)°$, $V =$ 2701.31(10) Å^3, and $\rho_{calcd} = 1.364\ \mathrm{g\,cm^{-3}}$ for $Z = 2$. Data were collected at 193 K on a Nonius Kappa-CCD system. The structure was solved by Patterson methods, and least-square refinement of the model based on 3682 reflections ($I > 2.0\sigma(I)$) converged to a final $R1 = 4.0\,\%$ ($wR2 = 8.1\,\%$). Except H(1), all hydrogen atoms were placed in calculated positions. H(1) was located in difference Fourier maps and refined with isotropic thermal parameters. CCDC-188842 (**4a**) 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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Photocatalytic Oxidation

An Efficient and Selective Photocatalytic System for the Oxidation of Sulfides to Sulfoxides**

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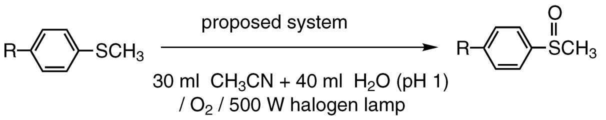
The selective oxidation of organic sulfides to sulfoxides without any overoxidation to sulfones is a challenging research interest in synthetic organic chemistry, partly because of the importance of sulfoxides as intermediates in biologically active compounds.[1] Of the many classical oxidants, H_2O_2-based systems are considered to be relatively clean and free of pollution.[2] Nevertheless, under catalytic conditions, the choice of H_2O_2 conditions and the stoichiometry with respect to the catalyst are critical to the selectivity of the reaction. Herein, we report a novel heterogeneous photochemical system for the selective transformation of organic sulfides to sulfoxides in the presence of oxygen using a nafion membrane doped with a lead ruthenate pyrochlore (Pyc) catalyst and a $[Ru(bpy)_3]^{2+}$ photosensitizer (designated as $|NPyc^{x-}$–$Ru(bpy)|$). Figure 1a illustrates the typical procedure for the incorporation of Pyc into a nafion membrane.[3] The membrane (5 × 5 cm) was first soaked with a mixture of Pb^{2+} and Ru^{3+} ions (1.5:1), which led to electrostatic exchange of ions into the hydrophilic sites of nafion. The precipitation of Pyc (designated as $|NPyc^{x-}|$) was done by treating the ion-exchanged membrane in 1.1 M KOH at 53 °C for 24 h with continuous purging of O_2.[3a] The formation of Pyc was confirmed by X-ray diffraction analysis.[3a] The $|NPyc^{x-}|$ membrane was found to be highly stable in organic media.[4] Finally, a suitable amount of $[Ru(bpy)_3]^{2+}$ was doped into the $|NPyc^{x-}|$ membrane simply by an ion-exchange process from a solution containing 1 mM $[Ru(bpy)_3]^{2+}$. This membrane (designated as $|NPyc^{x-}$–$Ru(bpy)|$) was then used in organic syntheses. Very few photochemical reactions have so far been reported for the sulfide oxidation reaction (SOR), and all the cases resulted in a mixture of products from C–S bond breakage and overoxidation through radical combination reactions.[5] In the present study a clean reaction [Eq. (1)] occurs, and the controlled catalytic oxygen reduction reaction (ORR) to H_2O_2 at the Pyc active sites is essential to the SOR (see below).



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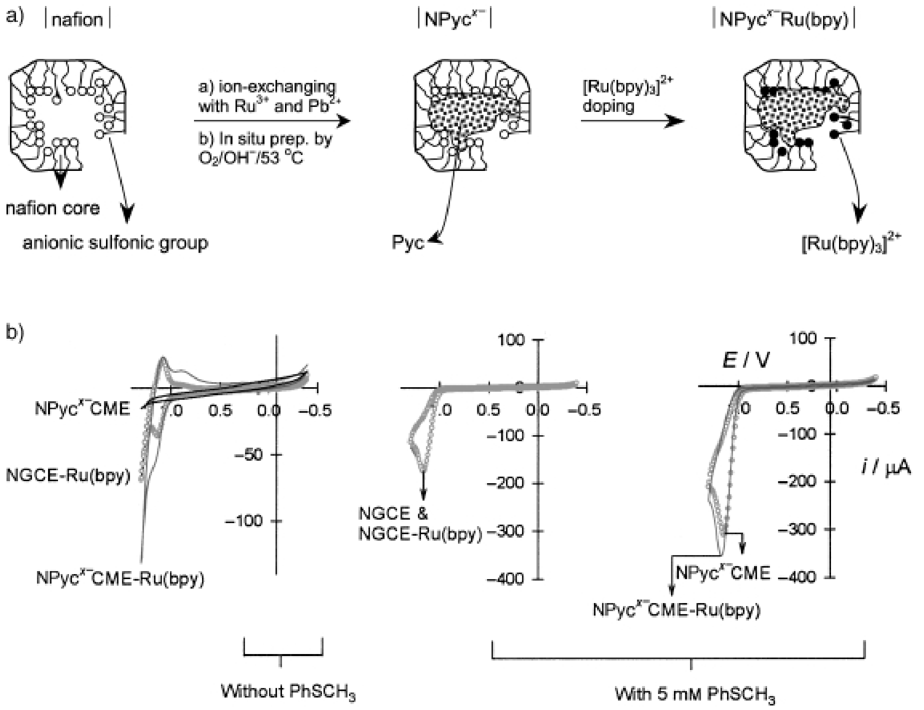


Figure 1. a) Conceptional representation for the preparation of |NPyc^{x-}Ru(bpy)|. b) Cyclic voltammetric response of various chemically modified electrodes at pH 1 in a supporting electrolyte consisting of a mixture of CH_3CN and H_2O (3:4) without and with 5 mM $PhSCH_3$ at $\upsilon = 50\ mV\,s^{-1}$.

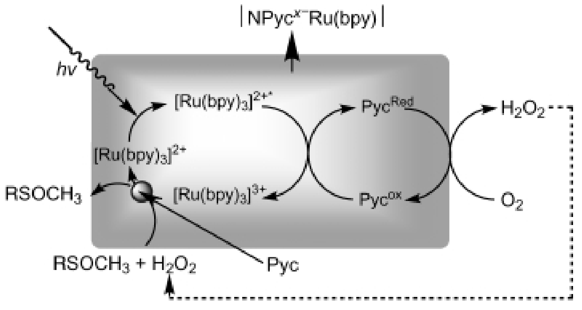
To electrochemically characterize the multicomposite |NPyc^{x-}-Ru(bpy)| membrane and to study the photoconversion of $[Ru(bpy)_3]^{2+} \rightarrow [Ru(bpy)_3]^{3+}$ (via $[Ru(bpy)_3]^{2+}$*) in the presence of Pyc, a simulated chemically modified electrode (designated as NPyc^{x-}-CME-Ru(bpy)) was prepared. The only difference in preparing the NPyc^{x-}-CME was that a nafion-coated glassy carbon electrode (NGCE) was first prepared by dip coating with 5 µL of a 5 wt% solution of nafion. As shown in Figure 1b, a well-defined redox peak at approximately 1.1 V versus Ag/AgCl corresponding to the $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$ couple was observed at the NPyc^{x-}-CME.[6] The anodic peak current (i_{pa}) was much higher than that observed at the $[Ru(bpy)_3]^{2+}$-doped NGCE (NGCE-Ru(bpy)). The increase in the current response clearly has something to do with the existence of active Pyc catalyst inside nafion. The catalyst can somehow assist the reaction of $[Ru(bpy)_3]^{2+} \rightarrow [Ru(bpy)_3]^{3+}$ via $[Ru(bpy)_3]^{2+}$*. The importance of the active Pyc site in nafion was further demonstrated by the following two experiments. First, an irreversible oxidation peak at the redox potential of the $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$ couple with a much higher i_{pa} value with NPyc^{x-}-CME than with NGCE was observed on addition of 5 mM $PhSCH_3$. Secondly, virtually no change in the i_{pa} value was observed on using NGCE and NGCE-Ru(bpy); while a net increase of approximately 60 µA in the i_{pa} value was observed at the NPyc^{x-}-CME-Ru(bpy) than that at the NPyc^{x-}-CME. In other words, there is no intrinsic effect on the SOR by using $[Ru(bpy)_3]^{2+}$ without the assistance of the active Pyc site in nafion. These preliminary electrochemical results can indeed help to explain the reaction mechanism of the photochemical oxidation of $RSCH_3$ (R = Ph, $PhCOCH_3$, and $PhOCH_3$) at the |NPyc^{x-}-Ru(bpy)| membrane (see below).

Controlled experiments were carried out under various experimental conditions (Table 1) to rationalize the reaction mechanism. It is clear that the success of the system lies in the proper combination of catalyst, photosensitizer, solvent composition, pH value, O_2, and light illumination. A possible reaction mechanism based on these results is shown in Scheme 1, where Pyc plays a dual catalytic role both in the ORR (dark reaction) and the SOR (light reaction). It is noteworthy that, since the Pyc is opaque, only $[Ru(bpy)_3]^{2+}$ can be involved in light

Table 1: The influence of the reaction conditions on the selective photochemical oxidation of $RPhSCH_3$ to $RPhSOCH_3$.[a]

Entry	Membrane catalyst		Solution					
	Pyc	$[Ru(bpy)_3]^{2+}$	CH_3CN:H_2O	pH[b]	O_2	$h\nu$[c]	t [h]	yield [%]
1	+	–	3:4	1	+	+	8	–
2	–	+	3:4	1	+	+	8	–
3	+	+	3:4	1	+	–	8	–
4	+	+	1:4	ca. 7	+	+	8	–
5	+	+	3:4	1	–	+	8	23
6	+	+	14:1	1	+	+	8	37
7	–	–	3:4	1	1 mL of 30% H_2O_2 added	–	3	47
8	+	+	3:4	ca. 7	+	+	8	49
9	+	+	3:4	1	+	+	3	>97

[a] +: presence, –: absence, [$RPhSCH_3$: R = H, $COCH_3$, OCH_3] = 17 mM, Entries 1–8 tested with $PhSCH_3$. [b] Adjusted with dilute HCl. [c] A 500-W halogen lamp was used as the light source. As for entry 9, the yields for the substituted organic sulfides are: R = $COCH_3$: 96% and R = OCH_3: 90%.



Scheme 1. Reaction mechanism for the photochemical sulfide oxidation reaction.

absorption in the membrane. The active Pyc site was reported to be an efficient catalyst for the ORR,[3b,7] and hence, the purging O_2 is essential for the formation of H_2O_2 during the reaction. The control experiment in pure H_2O_2 gave only about 47 % conversion with poor selectivity (Table 1). However, the assistance of Pyc and $[Ru(bpy)_3]^{2+}$ in the SOR was supported by the indirect electrochemical studies mentioned earlier. The efficiency of the SOR was then evaluated by putting a 4.5×2 cm $|NPyc^{x-}Ru(bpy)|$ in a mixture of CH_3CN (30 mL), H_2O (40 mL), and 17 mM $RSCH_3$ (R = Ph, $PhCOCH_3$, and $PhOCH_3$) at pH 1, with constant purging of O_2 under illumination (500 W halogen lamp) for 3 h. The products were analyzed simply by evaporation of the solution of the separated reaction product in $CHCl_3$ with a rotary-vacuum system. All reactions gave a single product of sulfoxide (that is, no sulfone was observed on the TLC plate and was further confirmed by NMR and mass spectroscopic studies) in > 90 % yield. The high selectivity of the current approach was clearly demonstrated. Finally, three repeated experiments were performed with $PhSCH_3$ to test the recyclability of the $|NPyc^{x-}Ru(bpy)|$ system, and almost the same yield was observed.

In conclusion, we have demonstrated a clean and highly selective photochemical oxidation of sulfide to sulfoxide on a novel heterogeneous multicomponent nafion membrane containing a Pyc catalyst and a $[Ru(bpy)_3]^{2+}$ photosensitizer. The high sulfoxide selectivity, lack of pollution, ease of product separation, and recyclable nature of the muticomponent membrane has a clear advantage over classical approaches. Further investigations are currently underway to expand the scope of this reaction to sulfide compounds containing more complicated organic structures and to a macroscale synthesis.

Experimental Section

Photochemical experiments were carried out at pH 1 (adjusted with HCl) in a mixture of CH_3CN and H_2O (3:4, ca. 70 mL) in a closed round-bottomed flask sealed with a gasket-septum under constant purging of O_2 gas. Cyclic voltammetric (CV) experiments were performed using a CHI workstation with a three-electrode system of working (0.071 cm^2), reference (Ag/AgCl), and counter (Pt disc, 0.071 cm^2) electrodes between −0.4 to 1.4 V. A negative current in the cyclovoltammograms denotes an anodic response, while a positive current denotes a cathodic current. The oxidized product was separated into $CHCl_3$ and then analyzed by NMR spectroscopic (in $CDCl_3$) and mass spectrometric techniques after rotary-vacuum evaporation. The yield of the products was determined on the basis of the ratio between the molar weight of the reactant and the product.

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Stereoselective Alkylation

Highly Stereoselective N-Terminal Functionalization of Small Peptides by Chiral Phase-Transfer Catalysis**

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Peptide modification is an essential yet flexible synthetic concept for screening targets efficiently and optimizing lead structures in the application of naturally occurring peptides as pharmaceuticals.[1,2] The introduction of side chains directly to a peptide backbone is a powerful method for preparing nonnatural peptides. The achiral glycine subunit has generally been used for this purpose[3] and glycine enolates,[4–8] radicals,[9–11] and glycine cation equivalents[12,13] have been ex-

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