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A Highly Photoactive Bilayer Lipid Membrane Doped with a Rare-Earth Complex

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Bilayer lipid membranes (BLMs) doped with synthetic sensitizers are of current interest because of their potential applications in the simulation of photosynthesis, mitochondrial respiration, and visual transduction process and to the design of molecular systems for solar energy conversion.[1−4] Very recently, Hwang and Mauzerall[5] made a striking improvement on the photoresponse of a BLM system doped with C_{70}. They obtained a photocurrent density 40 times higher than that of the carotene−porphyrin−quinone system,[4] previously the most efficient artificial system. Here we report a novel rare-earth coordination compound, (*E*)-1-hexadecyl-4-(2-(4-(dimethylamino)phenyl)ethenyl)-pyridinium tetrakis(1-phenyl-3-methyl-4-benzoylpyrazolone-5)ytterbium ($PYbL_4$), (see Figure 1) as a new sensitizer, which can be doped into a bilayer lipid membrane to produce photocurrent 10 times higher than that of C_{70}−BLMs at comparable light intensities. In addition, this BLM system shows excellent properties in photoelectric reversibility and constancy. A complex coupling mechanism is proposed, and the enhancement of the photocurrent is attributed to the charge mediating by nonphotosensitive counteranion (YbL_4^-). A prospect for getting more efficient sensitizers is anticipated based on the discovery.

The synthesis and characterization of the rare-earth complex ($PYbL_4$) used was described by one of the authors.[6] Egg phosphatidylcholine (EPC, Sigma) and other reagents are of analytical grade.

The BLM forming solution was prepared from 1% EPC and 2% cholesterol in a mixture of *n*-decane and isobutyl alcohol (3:1). $PYbL_4$−BLM-forming solution was prepared by adding aliquots of solid $PYbL_4$ into the BLM-forming solution described above; the final concentration of $PYbL_4$ was 1.5 mM. All the bathing solutions were made up from the aqueous solution containing 0.5 M KBr (tridistilled water was used). The asymmetric condition was gotten by adding an aliquot of $FeCl_3$ into one side of the bathing solution.

The two chambers of the cell were connected with two saturated calomel electrodes (SCE) via salt bridges to the circuit. A picoammeter (Model Wuda-1, Wuhan University, China), a high-impedance millivoltmeter (Model Orion 811) and PAR-370 electrochemical system (EG&G) were used to study the electrical properties of the BLM systems. Photopotentials were measured under open-circuit conditions ($Z \geq 10^{13}\ \Omega$) or by the "null current method".[7] The BLMs were formed by introducing a small amount of membrane forming solutions with the aid of a syringe onto the aperture (φ = 1 mm) of the Teflon film separating two chambers (1 × 3 cm) filled with bathing solutions. The thinning and blackening of the membrane was monitored by a low-power microscope (×40). The incident beam was introduced by a coherent optical fiber bundle from a xenon lamp (200 W) and measured with a photopower meter (Model LM- 91, National Institute of Metrology, Beijing, China). The absorption spectra were recorded on a Shimadzu 2100 UV−vis spectrometer.

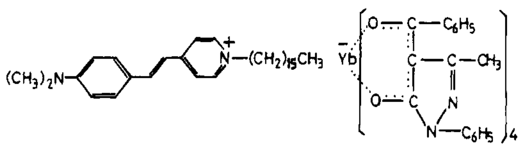

Figure 1. Structure formula of $PYbL_4$.

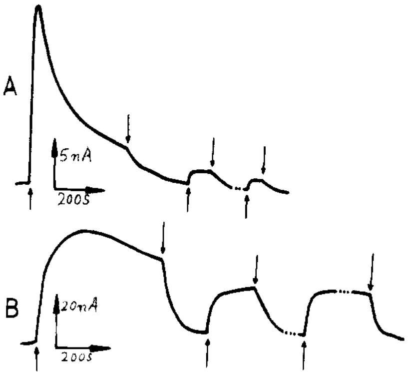

Figure 2. Development of the photocurrents under continuous illumination with 300 mW cm^{-2} light at wavelength ≈ 400−600 nm (through a 1-cm $CuSO_4$ aqueous solution) for BLMs containing 1.5 mM $PYbL_4$ (curve B) and 1.5 mM PI (curve A). (↑ light on, ↓ light off). Both BLMs were formed in 0.5 M KBr solutions. The out chamber contained 5 mM $FeCl_3$.

The membrane-forming solutions and bathing solutions must be freshly prepared each day. If the solutions were kept overnight, the photoresponses would be reduced. The following conditions could be used to make sure that the electric responses in the experiments are mainly due to the electronic process induced by light. The direction of the incident light does not influence the sign and the magnitude of the photoresponses. The concentration gradient of non-redox electrolyte such as KBr, KCl, HCl, etc., do not give any photoresponses. In the absence of $PYbL_4$ or $FeCl_3$, no steady-state photocurrent will be recorded.

Unlike the conventional pigments, $PYbL_4$ doped in BLM can enhance the stability of the BLM and make it easy to get to the black state. This may be due to the good solubility of $PYbL_4$ in the BLM-forming solutions and the satisfactory orientations in the membranes.

As shown in Figure 2A, the highest photocurrent across the $PYbL_4$−BLM may reach to about 50 nA under continuous illumination and then slowly decay to a steady state of about 20 nA. At the steady state, the photopotential is about 40 mV (measured by the "null

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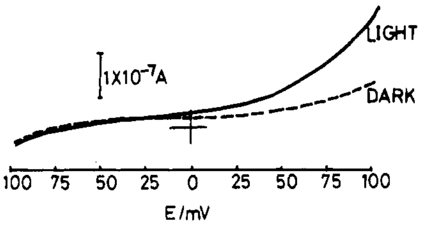

Figure 3. Current/voltage curves of $PYbL_4$–BLMs. The other conditions are the same as in Figure 2.

current method"). The membrane resistance measured by DC method is about $(3 \pm 0.5) \times 10^9\ \Omega$. The curve shows a good reversibility and constancy to the light excitations. The attenuation of the steady-state photocurrent is about 10% for the whole life of the BLM (~1 h). The main limiting factors of the photoresponses are found to be the concentration of $PYbL_4$ in the forming solution and $FeCl_3$ in the bathing solutions, the light intensity, and the applied voltage. In the lower concentration range (<1 mM), the photocurrent increases linearly with increasing concentration of $FeCl_3$ and tend to a saturation state in the higher concentration ranges. The variation of the photocurrent with the intensity of the incident light is similar to that of the conventional systems.[1] After a linear part in lower intensity range (>400 mW cm^{-2}), the photocurrent gradually reaches the saturation state. The applied voltages increase the photocurrent steeply when its direction was the same as the photocurrent (i.e., same polarity as the BLM) and decrease the photocurrent slowly when its direction is opposite to that of the BLMs (Figure 3).

The significant difference between the curve A, for PI, and curve B, for $PYbL_4$, as shown in Figure 2 indicates that the photocurrent of the chromophore is strongly anion dependent. More than 1 order of magnitude of the enhancement of photocurrent has been obtained by replacing the water-soluble anion (I^-) with hydrophobic rare-earth complex anion (YbL_4^-). Since the spectra of the two compounds (Figure 4) are similar, the big enhancement of the photocurrent cannot be attributed to the resonance between the hemicyanine cation and the counteranion YbL_4^-. Hence, the counteranion YbL_4^- acts only as a promoter for the charge transfer through the membrane.

Since no added donor molecules existing in the bathing solution, it is entirely conceivable that water could serve as an effective donor, being oxidized in the process. This is similar to the case of Chl–BLM.[8] Taking account of the large size of the complex anion (~120 Å^2 in cross section[6]) and the mismatch structures between the lipid chains and the complex anions, we can reasonably infer that the free diffusion of YbL_4^- may be very slow; instead, it exists in the membrane and serves as the charge-trapping sites, which may dramatically decrease the effective site-to-site tunneling distances for the transfer of charges. Therefore, we may come to the conclusion that the great enhancement of the photoresponses in $PYbL_4$–BLMs is due to the promotion of charge transfer across the membrane by the complex anion (YbL_4^-).

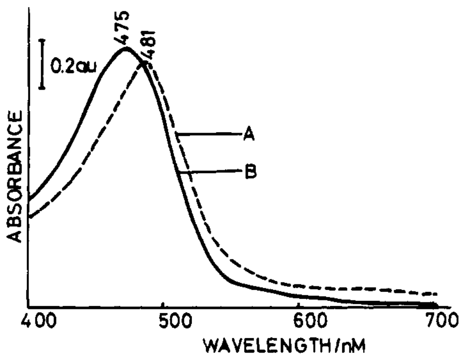

Figure 4. Absorption spectra of $PYbL_4$ (curve A) and PI (curve B) in the BLM forming solutions. Both in the concentrations of 0.1 mM.

For comparison, other representative examples of rare-earth complex anions incorporated with hemicyanine cations have also been investigated. The steady-state photocurrents from the doped BLMs are listed here:

compound	$PLaL_4$	$PNdL_4$	$PEuL_4$	$PDyL_4$	$PYbL_4$
photocurrents (nA)	4.0	5.1	15.4	16.0	20.0

The results show that the complex anions listed can all promote the charge transfer through the BLM to a certain extent. The activity increased with the increasing atomic numbers of the central elements or decreasing atomic radii.

Although there are still some details about the mechanism and membrane structure of $PYbL_4$–BLM remaining to be explored, the notable advantages such as being less expensive (compared with C_{70}) and having a high photoresponse and high stability should make the compound a hopeful candidate for solar energy conversion. Obviously, by replacing the hemicyanine cation and/or counteranion, one can get more $PYbL_4$-like coordination compounds to develop the high photoresponse.

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