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Bis(phthalocyaninato)lanthanoid(III)-catalyzed Photoreduction of Methylviologen

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The title complex catalyzes a photoreduction of methylviologen in methanol upon irradiation at λ >440 nm. The catalytic reaction is affected by ionic radius of the lanthanoid(III) ion of the complex.

Photoinduced hydrogen evolution from water has received considerable attention for the storage of solar energy and its conversion into chemical energy. The metal complexes such as $[Ru(bpy)_3]^{+2}$ 1) and tetraphenyl porphyrin derivatives2,3) have been used as a sensitizer for the photochemical decomposition of water to hydrogen. It is one of the most important points that visible light can be used for the conversion of solar energy. In this regard, phthalocyanine derivatives which show strong absorption bands in wavelength region from 600 to 700 nm should be attractive candidates for the photosensitizer. We report here that bis(phthalocyaninato)lanthanoid(III), HPcLnPc (Fig. 1), acts as the sensitizer for the photoreduction of methylviologen, MV^{+2}, in a methanol solution with an irradiation of visible light.

The complexes were prepared according to the literature.5) A methanol solution containing the HPcNdPc complex (1.00×10^{-6} mol dm^{-3}), MV^{+2}(1.00×10^{-1} mol dm^{-3}), and triethanolamine (1.00×10^{-1} mol dm^{-3}) in a glass cell with a 1 cm-light path length was purged by N_2 and was irradiated with a 300-W tungsten lamp through a color glass filter (λ >440 nm) under N_2 at 25 °C. As the reaction proceeded, new bands appeared at 570^{sh}, 603, 670^{sh}, and 730 nm being ascribed to the radical cation of MV^{+}. After 60 min, the amount of the radical cation generated was estimated to be ca. 250 times that of the complex. Without the complex, the radical cation was not generated under irradiation. When air was introduced into the irradiated TEOA-complex-MV^{+2} system in order to oxidize MV^{+}, the visible spectrum of the system became identical with that before irradiation. That is, in the course of the photoreduction, the complex can effectively catalyze the reaction.

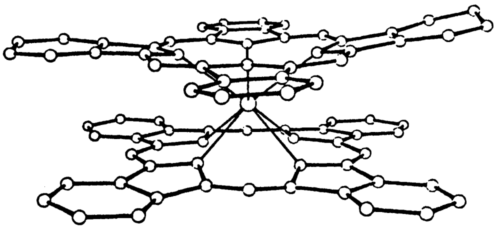

Fig. 1. Molecular structure of bis(phthalocyaninato)neodymium(III).4)

It is reported that triplet excited MV^{2+} itself undergoes photoreduction by TEOA under irradiation at λ <440 nm to yield the $\dot{MV}^{+}$ radical cation.6) This is the reason why the light of λ <440 nm was excluded in this experiment.

A relative quantum yield (RQY) increases with the decrease of ionic radius of the lanthanoid(III) ion (Fig. 2).7) This might be interpreted by an energy level of the HOMO of rings, as was shown in the case of a photooxidation of the complexes in the presence of dichloromethane.8) However, the yield may be affected not only by the energy level of the HOMO, but also by a factor such as the probability of separation of ion pairs. Further studies are required to elucidate the reaction mechanism.9)

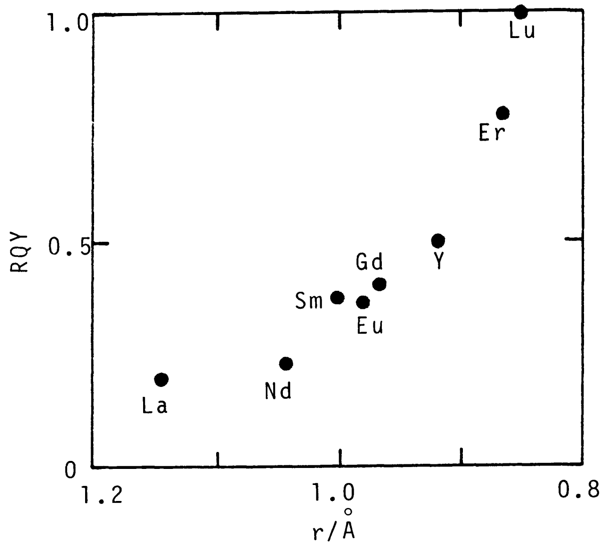

Fig. 2. Plots of the RQY against ionic radii of the lanthanoid(III) ions.

It was reported that sulfophthalocyanine and its copper(II) and zinc(II) complexes, as well as a positively charged magnesium(II) phthalocyanine do not act as the photosensitizer in a water solution due to efficient reverse electron transfer,10) showing a sharp contrast to the high photocatalytic capabilities of the HPcLnPc complexes. By solubilizing the HPcLnPc complexes into the aqueous solution by means of detergents, the photocatalysis of the complexes will be further performed in our laboratory.

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7)The yield of the $\dot{MV}^+$ radical cation after irradiation for 30 min was obtained by measuring the absorbance increase at 603 nm. The RQY is estimated as a relative value to the largest one in runs of the metal effect.
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9)The methanol solution containing the complexes showed very weak fluorescences around 700 nm at room temperature. Quenching experiments by MV^{+2} could not be performed in the present conditions.
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