1740 Bull. Chem. Soc. Jpn. Vol. 80, No. 9, 1740–1745 (2007)

Spectroelectrochemical Study of the Reversible Adduct Formation of Bis(phthalocyaninato)neodymate(III) Complex with CO_2 in a DMF Solution

Qiqige Wulan and Fusao Kitamura*

Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering,
Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502

Received January 26, 2007; E-mail: kitamura@echem.titech.ac.jp

The reaction between CO_2 and electrochemically reduced bis(phthalocyaninato)neodymate(III) complex in a dimethylformamide solution was investigated by cyclic voltammetry and in situ visible spectroscopy. The introduction of gaseous CO_2 into the phthalocyanine solution caused a considerable increase in the first reduction peak current of the complex and a shift in the second reduction peak to more positive potentials. In addition, new anodic current peaks appeared in the reverse sweep at potentials different from those of the complex. These observations were explained in terms of the formation of a CO_2-adduct. The formation and decomposition of the CO_2-adducts occurred reversibly with the applied potential, which was confirmed by in situ visible spectroscopy.

Electrochemical reduction of CO_2 to useful compounds is one of the most important topics in electrochemistry. A number of reduction products at various metal electrodes in both protic and aprotic solvents have been identified.[1–5] In addition, electrochemical reduction of CO_2 using transition-metal complexes as an electrocatalyst has been extensively investigated, since CO_2 reduction proceeds with these complexes in potentials lower than at metal electrodes. Several metallo-phthalocyanines have been reported to be active toward the electrochemical reduction of CO_2.[6–19] As has been pointed out by many authors, the coordination of CO_2 molecule to the metallo-phthalocyanine complex is the first stage of the reaction pathway. In many studies concerning the transition-metal complexes, the CO_2 molecule is considered to favorably be coordinated at the central metal ion. For instance, Eggins et al. have studied the catalytic activity of tetrasulfonated phthalocyaninatocobalt and tetrasulfonated phthalocyaninatonickel toward electrochemical CO_2 reduction in dimethyl sulfoxide (DMSO) solutions by cyclic voltammetry.[13] They reported a positive shift in reduction potential and also the appearance of additional anodic waves in the reverse potential sweep, which have been explained in terms of a chemical reaction, following the electrochemical reduction of the complex (adduct formation). However, the presence of such an intermediate has not yet been detected by in situ measurements other than the electrochemical techniques.

On the other hand, bisphthalocyanines that bear double-decker ring structures are another type of promising electrocatalysts, since they exhibit a larger number of reversible electron-transfer processes than the mono-phthalocyanines in an accessible potential range. We have already reported the physicochemical properties of a series of lanthanide–bisphthalocyanines ($Ln(Pc)_2$, where Ln is a rare-earth metal).[20–23] Regarding studies using bisphthalocyanines as a catalyst, however, only few researches have been reported. Magdesieva et al. have reported the catalytic behavior of bisphthalocyanines toward electrochemical CO_2 reduction in acetonitrile[24] and aqueous media.[25,26] They have proposed a molecular structure of CO_2 adduct based on the molecular mechanics calculation, and concluded that the CO_2 molecule favorably coordinates on the nitrogen atom of the meso-position in the Pc ring rather than the central rare-earth metal. To our knowledge, however, no experimental evidence for such CO_2-adducts for rare-earth phthalocyanines has been reported.

In the course of our electrochemical study on the rare-earth bisphthalocyanines in organic solvents, we found that the voltammograms were largely influenced by the presence of CO_2 in the solution; a voltammogram similar to that reported by Eggins et al.[13] was observed, and it can be interpreted in terms of an adduct formation mechanism. In this paper, we report spectroelectrochemical evidence for the reaction intermediate formed in the early steps of the electroreduction of CO_2 in DMF solution containing lanthanide–bisphthalocyanine complex ($Nd(Pc)_2$).

Experimental

Materials. Neodymium(III) acetate (Wako Chemicals), *o*-dicyanobenzene (Tokyo Chemical Industry Co., Ltd.) and Na_2CO_3 (Fluka), tetrabutylammonium bromide (Tokyo Chemical Industry Co., Ltd.), tetrabutylammonium perchlorate (TBAP) (>99% in purity, Fluka) were used without further purification. *N*,*N*-Dimethylformamide (99.5%, maximum water content 0.005%), sodium methoxide, methanol were purchased from Kanto Chemical Co., Inc. Gaseous Ar (99.999%) and CO_2 (99.9%) were used as received.

Synthesis of Tetrabutylammonium Bis(phthalocyaninato)neodymate(III). A mixture of neodymium(III) acetate, *o*-dicyanobenzene, and Na_2CO_3 (1:8:0.5 in mole ratio, respectively) was placed in a glass tube and heated at 280 °C for 20 min. After cooling, the crude product was dissolved in small amount of DMF and

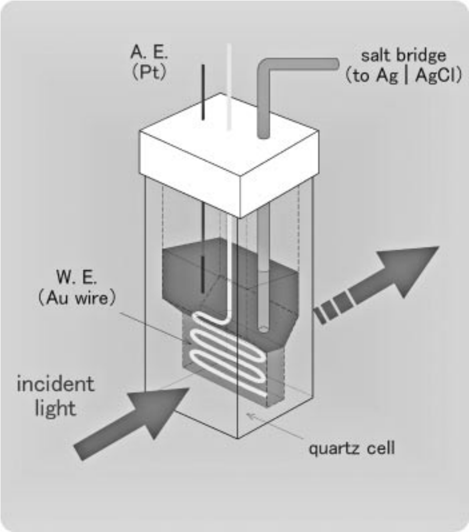


Fig. 1. Schematic illustration of the spectro-electrochemical cell used in this study.

filtered. The filtrate was then passed through 200-mesh alumina column using sodium methoxide-saturated methanol as an eluent, and the blue-colored band was collected. After an excess amount of tetrabutylammonium bromide was added, the solution was allowed to stand in a refrigerator overnight. Purple crystals of TBA[$NdPc_2$] deposited.

Cyclic Voltammetry. Cyclic voltammetry was carried out in DMF solutions containing 0.5 mM of TBA[$Nd(Pc)_2$] and 0.1 M TBAP as an electrolyte. A conventional three-electrode system consisting of a glassy carbon working electrode (3 mm in diameter), a platinum wire auxiliary electrode, and a silver–silver chloride (Ag|AgCl) reference electrode was used. A fine glass tube filled with KCl saturated aqueous agar was used as the salt bridge. Voltammograms were recorded on an ALS Model 900B electrochemical analyzer (BAS Inc.).

In Situ Visible Absorption Spectroscopy. In situ visible absorption spectroscopy was carried out on a system composed of a KTX-100R halogen lamp (Kenko Co., Ltd.) and a PMA-11 multichannel detector (Hamamatsu Photonics K. K.). A quartz spectroelectrochemical cell was used, and its structure is depicted in Fig. 1. The optical pathlength was 1 mm, and a gold serpentine wire (0.5 mm in diameter) was used as the working electrode. A platinum wire was placed outside of the thin solution compartment and was used as the auxiliary electrode. A fine salt bridge was used as the junction between the cell and the Ag|AgCl (KCl sat.) reference electrode. The electrode potential was controlled with a PS-07 potentiostat (Toho Technical Research Co., Ltd.). The spectral measurement was performed in two different modes, i.e., transient mode and steady-state mode. In the former measurement, the spectral acquisition was started immediately after the potential was stepped to the destination potential. In the latter mode, the spectral accumulation was done after a steady state of the electrolytic system at the potential was established. All measurements were carried out at room temperature (25 °C ± 1).

Results and Discussion

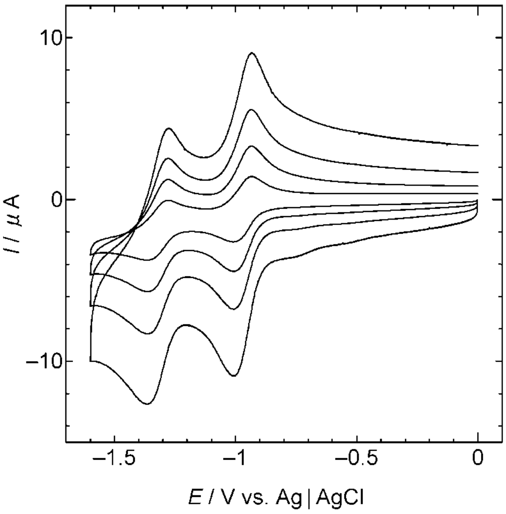


Fig. 2. Typical cyclic voltammogram for GC electrode measured in Ar-saturated DMF solution containing 0.5 mM TBA[$Nd(Pc)_2$] and 0.1 M TBAP. Sweep rate was 20, 50, 100, and 200 mV s^{-1}.

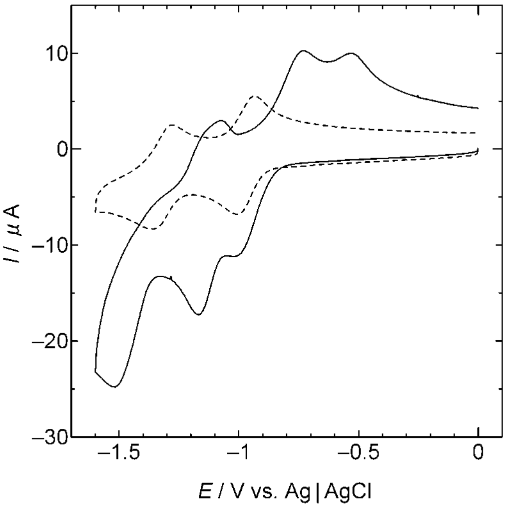


Fig. 3. Cyclic voltammograms for GC electrode measured in CO_2-saturated DMF solution containing 0.5 mM TBA-[$Nd(Pc)_2$] and 0.1 M TBAP. Broken curve was obtained in Ar saturated solution. Sweep rate was 100 mV s^{-1}.

Figure 2 shows typical CVs for $Nd(Pc)_2$ complex obtained at a GC electrode in deaerated DMF solution. Two couples of well-defined redox waves were observed with midpoint potentials of −0.97 and −1.32 V. They were ascribabed to one-electron-transfer processes of $[Nd(Pc)_2]^{1-/2-}$ and $[Nd(Pc)_2]^{2-/3-}$ couples, respectively.[20,22]

$$[Nd(Pc)_2]^{1-} + e^- \rightleftharpoons [Nd(Pc)_2]^{2-}, \quad (1)$$

$$[Nd(Pc)_2]^{2-} + e^- \rightleftharpoons [Nd(Pc)_2]^{3-}. \quad (2)$$

Since the peak potentials showed almost no shift with sweep rates and the peak currents were in proportion to the square root of the sweep rate, both processes are diffusion-controlled reversible process.

The CV pattern was markedly changed when gaseous CO_2 was introduced into the solution. The solid curve in Fig. 3 shows the CV obtained in the same solution, but saturated with gaseous CO_2. The current intensity at the first reduction peak at −0.97 V increased substantially, while the second reduction peak shifted significantly in the positive direction. Moreover,

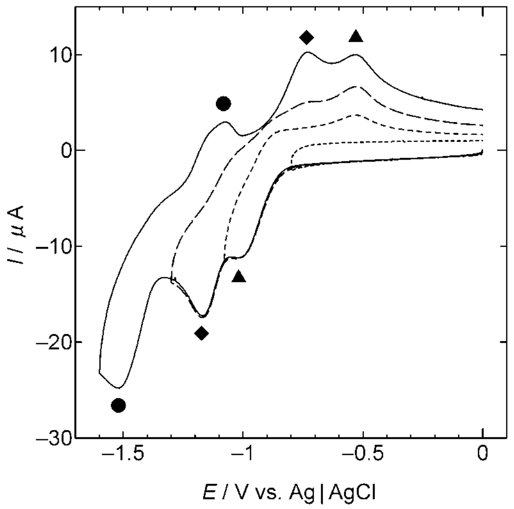


Fig. 4. Cyclic voltammograms under the same conditions as in Fig. 3, but with different negative limit potentials.

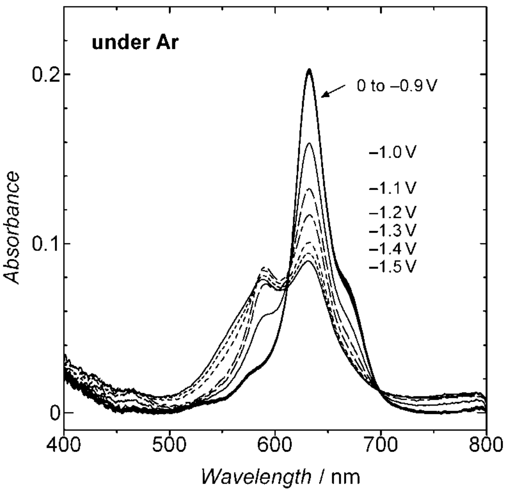


Fig. 5. Potential dependence of in situ visible spectra obtained in Ar-saturated DMF solution containing 10 μM TBA[Nd(Pc)$_2$] and 0.1 M TBAP.

an additional reduction peak appeared at −1.52 V. On the reverse potential sweep, the original two anodic current peaks of the Nd(Pc)$_2$ complex diminished, and a new anodic peaks appeared at −1.07, −0.73, and −0.53 V. Since CO$_2$ does not undergo any electro-reduction at the bare GC electrode in the potential region indicated here, this irreversible voltammetric feature strongly suggests the presence of homogeneous chemical reactions between the reduced forms of Nd(Pc)$_2$ and CO$_2$.

A current increase in the first reduction wave of the rare-earth bisphthalocyanines (i.e., the [Ln(Pc)$_2$]$^{1-/2-}$ couple) in the presence of CO$_2$ was first reported by Magdesieva et al. in acetonitrile solution.[24] Since they have not observed any irreversible voltammetric feature except for the lack of the re-oxidation peak of the [Ln(Pc)$_2$]$^{2-}$ form on the reverse sweep, they ascribed the enhancement in the reduction current solely to the phthalocyanine-catalyzed electroreduction of CO$_2$. In the DMF solvent, in contrast, we observed rather complicated behavior as shown in Fig. 3 (similar voltammograms were also observed in DMSO solvent).

On the other hand, Eggins et al. have reported voltammograms similar to Fig. 3 for tetrasulfonated cobalt and nickel phthalocyanines, and also disulfonated copper phthalocyanine in DMSO solution in the presence of CO$_2$.[13] They have concluded that the electrochemical reduction process of phthalocyanines includes follow-up chemical reactions with CO$_2$ (i.e., intermolecular electron transfer between the phthalocyanine and the CO$_2$ ligand). In addition, they have ascribed the additional current peak (−1.52 V in this study) to the reduction of a CO$_2$-adduct. In order to clarify the relationships between reduction and oxidation peaks, we performed CV measurements with different potential limits.

Figure 4 shows the resulting CVs. When the electrode potential was swept back in the positive direction from the negative of the first reduction peak (−1.1 V), an anodic wave was observed at −0.53 V. If the switching potential was set to the negative of the second reduction peak (−1.3 V), another anodic peak started to appear at −0.73 V in the reverse sweep. Finally, an oxidation peak was observed at −1.08 V when the forward potential sweep was reversed just after the appearance of the third reduction peak. Accordingly, it can be concluded that each oxidation peak corresponds to the re-oxidation process of the reduction products of the related reduction peak.

It should be noted at this point that if a simple catalytic electron-transfer via the reduced form of the Ln(Pc)$_2$ occurs, the mono-anionic form should be reproduced after the electron donation to the CO$_2$ molecules. As far as the electron-transfer process is facile enough, the mono-anionic form will be reproduced quickly and the resulting optical absorption spectrum of the solution should not change, as has already been reported by Abe et al. for phthalocyaninatocobalts in pyridine solutions.[27,28] In order to clarify this point, we carried out in situ visible spectroscopic measurements using a thin-layer electrochemical cell.

Figure 5 shows a series of spectra obtained for Ar-saturated DMF solution containing 10 μM Nd(Pc)$_2$ complex as a function of applied potential. The spectrum observed at 0 V is consistent with that of the [Nd(Pc)$_2$]$^{1-}$ solution. The spectral pattern gradually changed with negative potential alternation, which is in accordance with the current response observed in the CV; the absorption peak at 632 nm gradually decreased, and a peak at 597 nm developed with the potential change across the first reduction wave down to −1.2 V, which is indicative of the formation of [Nd(Pc)$_2$]$^{2-}$. Another shoulder band due to the electrogenerated [Nd(Pc)$_2$]$^{3-}$ appeared around 550 nm with further negative potential excursion. These spectral features are consistent with our previous results obtained in *o*-dichlorobenzene solutions.[22]

On the other hand, Figure 6 shows a series of spectra obtained in the solution saturated with CO$_2$. One can see that the spectral pattern was completely different from those depicted in Fig. 5. The band at 632 nm diminished promptly with the negative potential change down to −1.0 V, at which the first reduction current peak was observed in the CV (see Fig. 3). Concomitant with this, a new absorption peak developed at 564 nm, which was located closer to the band ascribed to [Nd(Pc)$_2$]$^{3-}$ in Fig. 5. Further potential change in the negative direction brought about a blue shift and simultaneous broadening of the band. It is obvious that neither spectral pattern seen in Fig. 6 coincides with those obtained during the reduction process of the complex under Ar atmosphere, which may be a result of strong electronic interactions between the $Nd(Pc)_2$ complex and CO_2 molecule. Similar spectral changes were also observed with other lanthanide complexes, and the results are summarized in Table 1. One can see that the band position observed at -1.0 V in the presence of CO_2 almost coincided with each other irrespective of the nature of the central rare-earth metals.

Although CO_2 molecule is apt to coordinate to the central metal ion in a number of transition metallo-phthalocyanines, scarce is known about the structure of CO_2 adducts for the bisphthalocyanines. In order to identify the molecular structure, we tried to isolate the adducts from the solution. Unfortunately, it was found that the adduct was unstable and quickly re-oxydized to decompose into the CO_2-free complex in the presence of a trace amount of oxygen. On the other hand, Magdesieva et al. have performed molecular mechanics calculation on a model bisphthalocyanine complex in order to estimate the structure of CO_2-adducts.[24] Various modes of CO_2 coordination with the metal center are considered; however, they finally conclude that the coordination of the CO_2 molecule to the metal center in the complex is unfavorable. Instead, CO_2 molecule is thought to be coordinated at the nitrogen atom in the macrocyclic ring, i.e., the nitrogen atoms at the meso-position, forming a carbamic acid fragment. Although to the best of our knowledge theoretical and experimental evidence supporting such a molecular structure have not been reported, it is reasonable to consider that the CO_2 coordination to the reduced complex significantly changes its original electronic structure, i.e., the electronic states associated with the central 18π-electron system of the macrocycles, which are responsible for the strong optical absorption characteristics of phthalocyanines. In any case, a rigorous theoretical study by ab initio molecular orbital calculations on reduced forms of the bisphthalocyanine is necessary to obtain structural information about the coordination configuration.

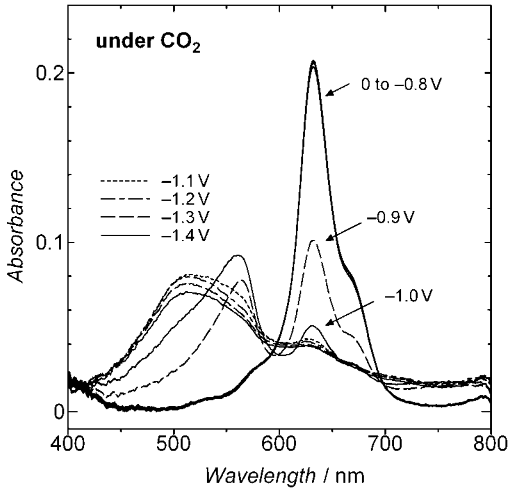


Fig. 6. Potential dependence of in situ visible spectra obtained in CO_2-saturated DMF solution containing 10 μM TBA[$Nd(Pc)_2$] and 0.1 M TBAP.

On the other hand, we found that the once changed spectral pattern was completely recovered to the original one when the electrode potential was switched back to the region well positive of the anodic peaks observed in the CV (>-0.5 V).

Figure 7 shows a series of spectra acquired during the potential steps from 0 to -1.0 V and then back to 0 V. A continuous spectral change, mentioned above, was observed, and the spectral pattern became the original one with a switch back of the applied potential. In Fig. 8, the change in band intensity of the free $[Nd(Pc)_2]^{1-}$ complex at 632 nm was plotted against time. Although it takes ca. 200 s to gain the original band intensity (probably due to the cell constant), we can see that the process is completely reversible against the applied potential. It is noteworthy that such a complete recovery in band intensity was only observed when the reverse step potential was set in a region well positive of the anodic peak at -0.5 V in the CV (Fig. 2). Similar reversibility in spectral band intensity was also observed in the potential step experiment between 0 and -1.2 V, at which the second reduction process takes place. In this case, the spectral pattern developed at -1.2 V was similar to the one shown in Fig. 5.

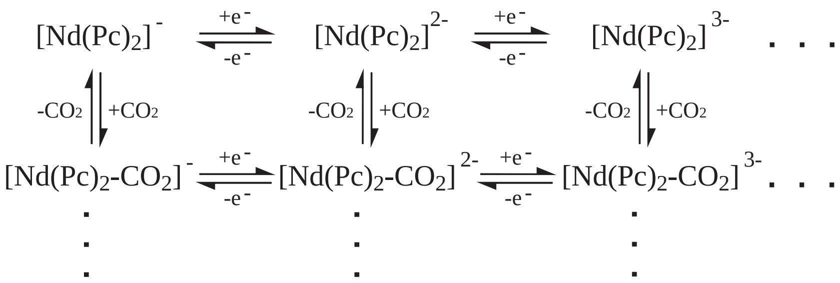
All of these observations strongly suggest that the electroreduction of the $Nd(Pc)_2$ complex proceeds through the formation of a CO_2-adduct. Magdesieva et al. have pointed out that bisphthalocyanines are in equilibrium with the corresponding CO_2-adduct forms in solutions containing CO_2 based on the analogy of metal-free phthalocyane.[24,26] Although they mention nothing about the equilibrium between the adducts in the solution, we describe the initial few stages in Scheme 1.

Thus, the reaction may be a kind of square scheme as a whole. The coordination of CO_2 to the $[Nd(Pc)_2]^{1-}$ form is considered to be unfavorable, since no spectral change was detected when gaseous CO_2 was introduced into the $[Nd(Pc)_2]^{1-}$ contained solution. The spectral changes observed across the first reduction peak are ascribed to the formation of CO_2-ad-

Table 1. Formal Potentials ($E_1^{0\prime}$) and Absorption Maxima of $[Ln(Pc)_2]^z$ Complexes in DMF

	Metal						
	La	Nd	Sm	Eu	Gd	Yb	Lu
$E_1^{0\prime}$/V vs. Ag|AgCl	−0.978	−0.970	−0.968	−0.987	−0.986	−0.987	−0.977
$\lambda_{max}^{a)}$/nm	636	632, 670	627, 675	625, 675	624, 675	616, 693	616, 697
(under Ar)	590	590	592	590	591	589	588
$\lambda_{max}^{b)}$/nm (under CO_2)	563	562	560	563	559	557	559

a) Upper: $z = -1$, lower: $z = -2$. b) Obtained at -1.0 V vs. Ag|AgCl.



Scheme 1.

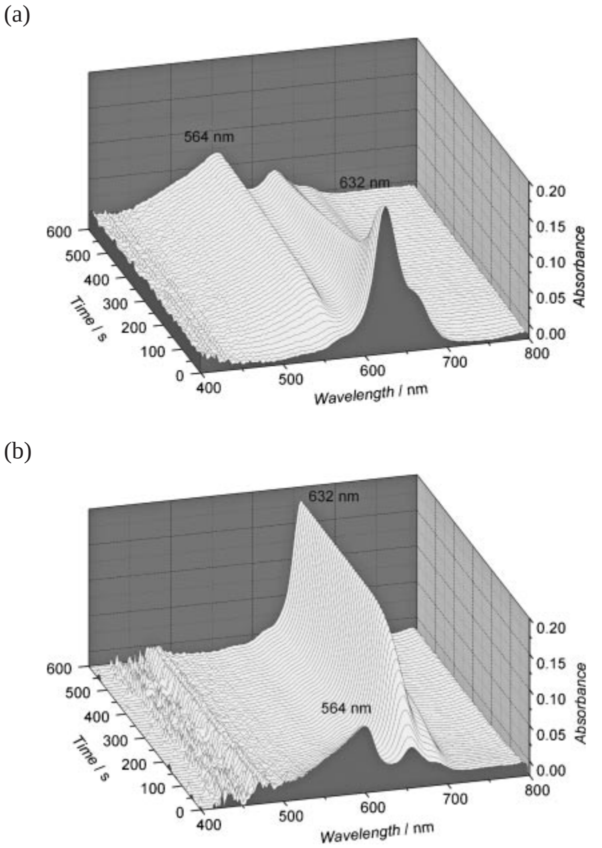


Fig. 7. Time course of the in situ visible spectra obtained in CO_2-saturated DMF solution containing 10 µM TBA-[$Nd(Pc)_2$] and 0.1 M TBAP. Electrode potential was stepped from 0 to −1 V (a), and −1 to 0 V (b).

duct with less oxidized forms of the complex (i.e., $[Nd(Pc)_2–CO_2]^{2-}$). It is suggested that the CO_2-adduct might be further reduced at the applied potential, since it should be reducible more easily compared to the CO_2-free complex. However, we cannot rule out the possible formation of $[Nd(Pc)_2–CO_2]^{3-}$ and successive coordination of the CO_2 molecule to the adduct. In order to clarify the point, further quantitative analysis with the aid of molecular orbital calculation is required and is under way.

Conclusion

We presented a spectroscopic evidence for the reaction between CO_2 and reduced forms of rare-earth bisphthalocyanines in a DMF solution by using potential-step in situ visible spectroscopy. Although the formation of CO_2-adduct has been suggested from electrochemical points of view, this is, to our knowledge, the first spectral observation of such reaction intermediate of bisphthalocyanines. Finally, we think that the reversible CO_2 catch-and-release phenomenon of the complex can be utilized as a CO_2 carrier, which can be controlled by its oxidation states.

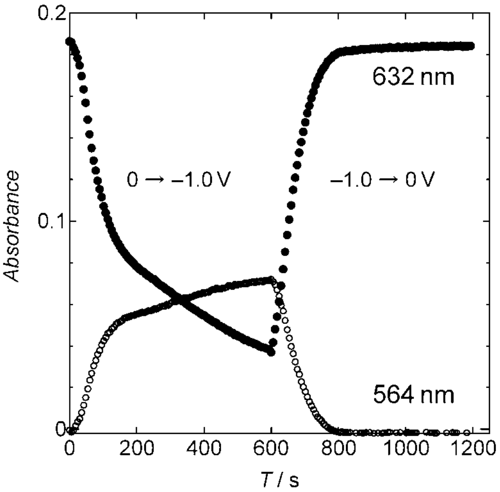


Fig. 8. Change in absorption intensity at 632 nm (●) and 564 nm (○) with the potential step. Data were taken from Fig. 7.

References

1 Y. Hori, K. Kikuchi, S. Suzuki, *Chem. Lett.* **1985**, 1695.

2 Y. Hori, A. Murata, K. Kikuchi, S. Suzuki, *J. Chem. Soc., Chem. Commun.* **1987**, 728.

3 M. Azuma, K. Hashimoto, M. Hiramoto, M. Watanabe, S. Sakata, *J. Electrochem. Soc.* **1990**, *137*, 1772.

4 G. Kyriacou, A. Anagnostopoulos, *J. Electroanal. Chem.* **1992**, *328*, 233.

5 T. Saeki, K. Hashimoto, N. Kimura, K. Omata, A. Fujishima, *J. Electroanal. Chem.* **1996**, *404*, 299.

6 S. Meshitsuka, M. Ichikawa, K. Tamaru, *J. Chem. Soc., Chem. Commun.* **1974**, 158.

7 K. Hiratsuka, K. Takahashi, H. Sasaki, S. Toshima, *Chem. Lett.* **1977**, 1137.

8 C. M. Lieber, N. S. Lewis, *J. Am. Chem. Soc.* **1984**, *106*, 5033.

9 S. Kapusta, N. Hackerman, *J. Electrochem. Soc.* **1984**, *131*, 1511.

10 H. Tanabe, K. Ohno, *Electrochim. Acta* **1987**, *32*, 1121.

11 J. P. Collin, J. P. Sauvage, *Coord. Chem. Rev.* **1989**, *93*, 245.

12 N. Furuya, K. Matsui, *J. Electroanal. Chem.* **1989**, *271*, 181.

13 B. Eggins, J. T. S. Irvine, J. Grimshaw, *J. Electroanal. Chem.* **1989**, *266*, 125.

14 T. Yoshida, K. Kamato, M. Tsukamoto, T. Iida, D. Schlettwein, D. Wohrle, M. Kaneko, *J. Electroanal. Chem.* **1995**, *385*, 209.

15 J. Costamagna, G. Ferraudi, J. Canales, J. Vargas, *Coord. Chem. Rev.* **1996**, *148*, 221.

16 H. Aga, A. Aramata, Y. Hisaeda, *J. Electroanal. Chem.* **1997**, *437*, 111.

17 E. R. Savinova, S. A. Yashnik, E. N. Savinov, V. N. Parmon, *React. Kinet. Catal. Lett.* **1992**, *46*, 249.

18 J. Grodkowski, T. Dhanasekaran, P. Neta, P. Hambright, B. S. Brunschwig, K. Shinozaki, E. Fujita, *J. Phys. Chem. A* **2000**, *104*, 11332.

19 T. V. Magdesieva, T. Yamamoto, D. A. Tryk, A. Fujishima, *J. Electrochem. Soc.* **2002**, *149*, D89.

20 C. Harnoode, F. Kitamura, T. Ohsaka, K. Tokuda, A. Iwase, *Electrochemistry* **1993**, *61*, 767.

21 N. Koike, H. Uekusa, Y. Ohashi, C. Harnoode, F. Kitamura, T. Ohsaka, K. Tokuda, *Inorg. Chem.* **1996**, *35*, 5798.

22 C. Harnoode, K. Takamura, H. Kubota, K. Sho, K. Fujisawa, F. Kitamura, T. Ohsaka, K. Tokuda, *Electrochemistry* **1999**, *67*, 832.

23 T. Yonekura, T. Ohsaka, F. Kitamura, K. Tokuda, *J. Porphyrins Phthalocyanines* **2005**, *9*, 54.

24 T. V. Magdesieva, S. V. Milovanov, B. V. Lokshin, Z. S. Klemenkova, L. G. Tomolova, K. P. Butin, N. S. Zefirov, *Russ. Chem. Bull.* **1998**, *47*, 2137.

25 T. V. Magdesieva, I. V. Zhukov, D. N. Kravchuk, O. A. Semenikhin, L. G. Tomolova, K. P. Butin, *Russ. Chem. Bull.* **2002**, *51*, 805.

26 T. V. Magdesieva, K. P. Butin, T. Yamamoto, D. A. Tryk, A. Fujishima, *J. Electrochem. Soc.* **2003**, *150*, E608.

27 T. Abe, T. Yoshida, S. Tokita, F. Taguchi, H. Imaya, M. Kaneko, *J. Electroanal. Chem.* **1996**, *412*, 125.

28 T. Abe, F. Taguchi, T. Yoshida, S. Tokita, G. Schnurpfeil, D. Wohrle, M. Kaneko, *J. Mol. Catal. A: Chem.* **1996**, *112*, 55.