

## Crystal Growth

## Novel method for the fabrication of a charge transfer complex crystal by photoirradiation

Masaki Matsuda,<sup>\*,[a]</sup> Miki Nishi,<sup>[a]</sup> Shoko Koga,<sup>[a]</sup> Mika Fujishima,<sup>[a]</sup> Norihisa Hoshino,<sup>[b]</sup> Tomoyuki Akutagawa,<sup>[b]</sup> and Hiroyuki Hasegawa<sup>[c]</sup>

**Abstract:** A novel method for the fabrication of a charge transfer complex crystal was developed. Photoirradiation of a solution of TPP[Co(tbp)(CN)<sub>2</sub>] and TPP[Co(Pc)(CN)<sub>2</sub>] (tbp = tetrabenzoporphyrin, Pc = phthalocyanine, TPP = tetraphenylphosphonium) gives a molecular conducting crystal of a charge transfer complex TPP[Co(tbp)(CN)<sub>2</sub>]<sub>2</sub>, which was produced via the process in which the photoexcited electron in tbp was transferred from the LUMO of tbp to that of Pc.

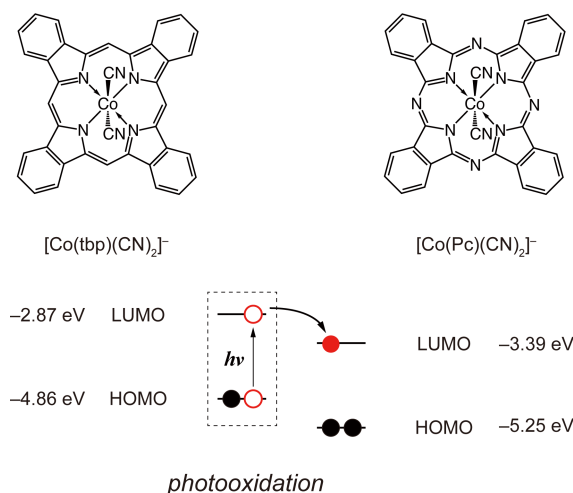
The charge transfer (CT) interaction between an electron donor and an acceptor attracts much interest and plays an important role in various field of chemistry.<sup>1–4</sup> Furthermore, CT complexes afford many functions, including electrical conductivity, electrical switching and/or memory phenomena, etc.<sup>5–8</sup> CT complex crystals are typically fabricated either by an electrolysis method which produces the salt of a radical cation or anion, or by the direct mixing of donor and acceptor molecules. In the latter method, only when the HOMO of the donor and the LUMO of the acceptor are of similar energy levels, a portion or all of the electrons in the HOMO of the donor molecule can transfer to the LUMO of the acceptor molecule,<sup>9</sup> resulting in radical species and the formation of a CT complex. Such electron transfers also play an important role in organic photovoltaic cells (OPVCs) where the charge separation of the exciton into a free electron and a hole occurs at the interface between the donor and acceptor molecules.<sup>10</sup> When

an electron excited by photoirradiation transfers from the LUMO of a donor molecule (D) to that of an acceptor molecule (A), D<sup>•+</sup> and A<sup>•–</sup> are produced. In other words, D and A are photooxidized and photoreduced respectively, in the OPVC. Therefore, we reasoned that it might be possible to use the photooxidation and photoreduction processes for the fabrication of CT complex crystals as opposed to the conventional methods including electrolysis or mixing.

Here, we focus on the dicyano cobalt tetrabenzoporphyrin anion ([Co<sup>III</sup>(tbp)(CN)<sub>2</sub>]<sup>–</sup>) and the dicyano cobalt phthalocyanine anion ([Co<sup>III</sup>(Pc)(CN)<sub>2</sub>]<sup>–</sup>). Highly conducting CT complex crystals TPP[Co(tbp)(CN)<sub>2</sub>]<sub>2</sub> and TPP[Co(Pc)(CN)<sub>2</sub>]<sub>2</sub> (TPP = tetraphenylphosphonium) can be obtained by the electrolysis of each anion in the presence of TPP cations.<sup>11, 12</sup> Although the molecular structure of tbp and Pc are similar to each other, the oxidation potential of TBA[Co(tbp)(CN)<sub>2</sub>] (TBA = tetrabutylammonium) is about 0.4 V smaller than that of Na[Co(Pc)(CN)<sub>2</sub>],<sup>13</sup> meaning the HOMO of [Co(tbp)(CN)<sub>2</sub>]<sup>–</sup> is higher than that of [Co(Pc)(CN)<sub>2</sub>]<sup>–</sup>. By measuring the oxidation potentials against ferrocene/ferrocenium,<sup>14</sup> we estimated the HOMO levels of TPP[Co(tbp)(CN)<sub>2</sub>] and TPP[Co(Pc)(CN)<sub>2</sub>] to be –4.86 eV and –5.25 eV, respectively. Furthermore, the LUMO levels of TPP[Co(tbp)(CN)<sub>2</sub>] and TPP[Co(Pc)(CN)<sub>2</sub>] were also estimated to be –2.87 eV and –3.39 eV by the energy gap values determined from the electronic absorption spectra. Therefore, if an excited electron in the LUMO of [Co(tbp)(CN)<sub>2</sub>]<sup>–</sup> can transfer to that of [Co(Pc)(CN)<sub>2</sub>]<sup>–</sup> in a mixed solution of the two anions, we can produce an oxidized [Co(tbp)(CN)<sub>2</sub>]<sup>•+</sup> unit with a  $\pi$ -radical on

- [a] Prof. M. Matsuda, M. Nishi, S. Koga, M. Fujishima  
Graduate School of Science and Technology  
Kumamoto University  
Kurokami 2-39-1, Kumamoto 860-8555 (Japan)  
Fax: (+81)-96-342-3372  
E-mail: masaki@sci.kumamoto-u.ac.jp
- [b] Dr. N. Hoshino, Prof. T. Akutagawa  
Institute of Multidisciplinary Research for Advanced Materials  
Tohoku University  
Katahira 2-1-1, Sendai 980-8577 (Japan)
- [c] Dr. H. Hasegawa  
Division of Chemistry, Faculty of Science  
Hokkaido University  
Kita 10 Nishi 8, Sapporo 060-0810 (Japan)

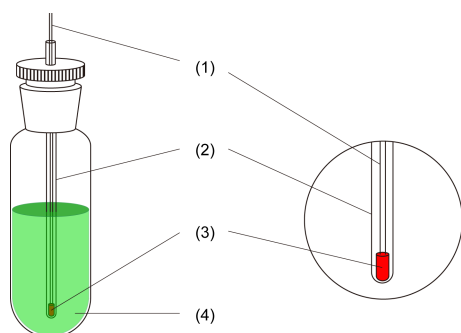
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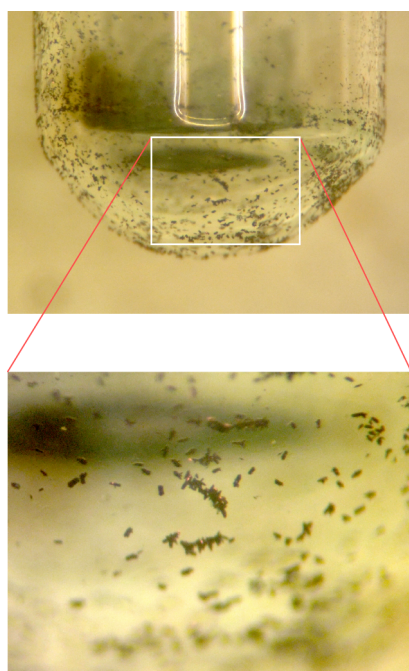
**Scheme 1.** Formation of a [Co(tbp)(CN)<sub>2</sub>]<sup>•+</sup> radical by photooxidation.

the *tbp* ligand (Scheme 1). This situation is similar to what occurs in electrochemical oxidation by which a CT complex crystal of  $\text{TPP}[\text{Co}(\text{tbp})(\text{CN})_2]_2$  can be fabricated. In this paper, fabrication of a CT complex crystal by photoirradiation through the HOMO and LUMO excitation of *tbp* is reported, in addition to the electrical properties and structure of the obtained crystal.

The synthesis of simple salts  $\text{TPP}[\text{Co}(\text{tbp})(\text{CN})_2]$  and  $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]$  were reported elsewhere.<sup>11, 12</sup> The photocrystallization was carried out at room temperature in the dark with the use of a custom-built cell equipped with a slender round bottom tube for the insertion of a light emitting diode (LED) with a  $\lambda_{\text{max}}$  at 660 nm corresponding to the HOMO–LUMO excitation of the *tbp* and *Pc* ligands. The image of the custom-built cell is depicted in Figure 1. A saturated solution of  $\text{TPP}[\text{Co}(\text{tbp})(\text{CN})_2]$  and  $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]$  in acetonitrile was added to the cell. With irradiation by the LED, tiny crystals (typically less than  $0.05 \times 0.01 \times 0.01 \text{ mm}^3$ ) grew at the tip of the round bottom tube as shown in Figure 2.

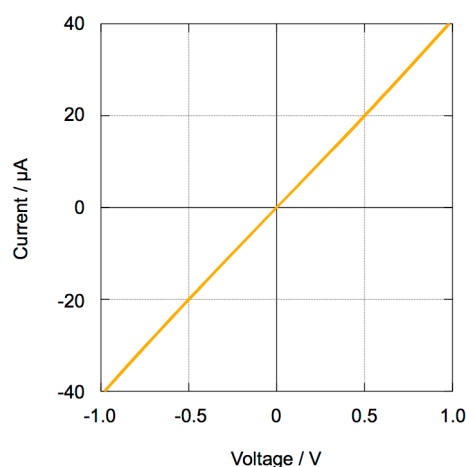


**Figure 1.** Custom-built cell for fabricating the CT complex crystal by photoirradiation. The cell consists of the following components: (1) LED electrode, (2) round bottom tube, (3) LED, and (4) solution of starting materials.



**Figure 2.** Crystals grown at the tip of the round bottom tube for the insertion of the LED.

Figure 3 shows the current–voltage characteristics of the compressed pellet of the obtained crystals at room temperature. The current was proportional to the applied voltage, following Ohm's law. The estimated resistivity of the compressed pellet measured was  $75 \Omega \text{ cm}$ . The relatively low resistivity suggested that the crystal obtained by photoirradiation is the same CT complex of  $\text{TPP}[\text{Co}(\text{tbp})(\text{CN})_2]_2$  or  $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]_2$ , although the resistivity is two or three orders of magnitude higher than that of the single crystal of  $\text{TPP}[\text{Co}(\text{tbp})(\text{CN})_2]_2$  or  $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]_2$ , respectively. The discrepancy between the data of the compressed pellet and the single crystal might be due to the highly one-dimensional electronic system and the effect of the grain boundary.



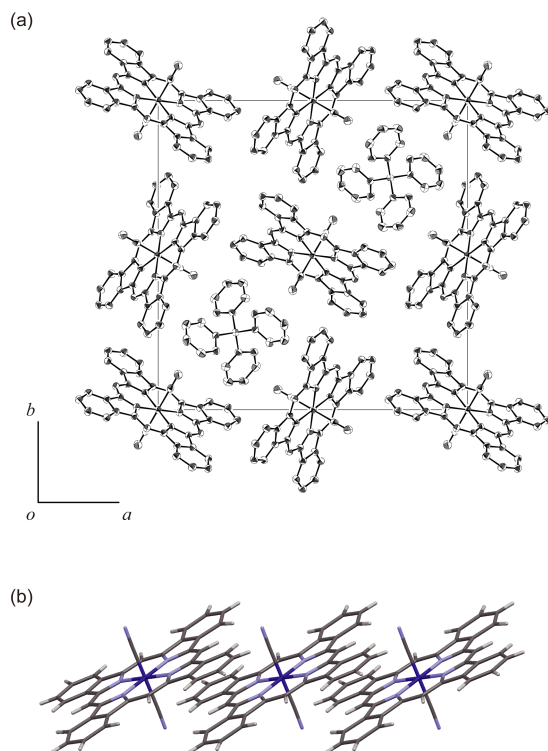
**Figure 3.** Current-voltage characteristics of the compressed pellet of the obtained crystals by photoirradiation.

Figure 4 shows the crystal structure of a crystal obtained by the photocrystallization.<sup>15</sup> The difference in the molecular structure of *tbp* and *Pc* is only the atoms in the *meso* positions bridging the four pyrrole rings; substitution of the bridging nitrogen atoms of *Pc* with less electronegative methine groups forms *tbp*. Therefore, it is difficult to distinguish  $\text{TPP}[\text{Co}(\text{tbp})(\text{CN})_2]_2$  and  $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]_2$  at a glance. As such, here we represent the chemical formula of the obtained crystal as  $\text{TPP}[\text{Co}(\text{Mc})(\text{CN})_2]_2$ , where *Mc* is the macrocyclic ligand. The structure, in which  $\text{Co}(\text{Mc})(\text{CN})_2$  forms a one-dimensional chain along the *c*-axis, is isostructural to both  $\text{TPP}[\text{Co}(\text{tbp})(\text{CN})_2]_2$  and  $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]_2$  fabricated by electrooxidation. Furthermore, the 1:2 ratio of cation: $\text{Co}(\text{Mc})(\text{CN})_2$  units gives an effective charge of  $-0.5$  for one  $\text{Co}(\text{Mc})(\text{CN})_2$  unit. Each *Mc* ligand is formally oxidized by  $0.5e$  from the initial closed-shell  $\text{Mc}^{2-}$ , indicating that the oxidation of the macrocyclic ligand by the photoirradiation was surely achieved.

While the differences in the cell parameters between  $\text{TPP}[\text{Co}(\text{tbp})(\text{CN})_2]_2$  and  $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]_2$  are small at room temperature, one can notice some significant differences in bond lengths and angles in the molecular structures of *tbp* and *Pc* including:<sup>11</sup>

- Distances between the pyrroles and the atoms in the *meso* position are longer in the *tbp* complex.
- Angles between the pyrroles and the atoms in the *meso* position are larger in the *tbp* complex.

- (iii) The Co–C≡N angle in the tbp complex is more linear than that of the Pc complex.



**Figure 4.** (a) Crystal structure of TPP[Co(tbp)(CN)<sub>2</sub>]<sub>2</sub> obtained by photocrystallization; view along the c-axis. H atoms are omitted for clarity. (b) Molecular arrangement along the c-axis (neighboring molecules are related by a unit translation along the c-axis). We concluded that the macrocyclic ligand in the obtained crystal was tbp (see main text).

To investigate the molecular structure, crystal structure analyses of the obtained TPP[Co(Mc)(CN)<sub>2</sub>]<sub>2</sub> as well as TPP[Co(tbp)(CN)<sub>2</sub>]<sub>2</sub> and TPP[Co(Pc)(CN)<sub>2</sub>]<sub>2</sub> prepared by electrolysis were carried out at a low temperature (120 K),<sup>15</sup> and the selected distances and angles are summarized in Table 1. The distances and angles between the pyrroles and the atoms in the *meso* position in the obtained crystal were longer and larger than those in TPP[Co(Pc)(CN)<sub>2</sub>]<sub>2</sub>, and similar to those in TPP[Co(tbp)(CN)<sub>2</sub>]<sub>2</sub>. The Co–C≡N angle in the obtained crystal was 177.5°, which was consistent with that of TPP[Co(tbp)(CN)<sub>2</sub>]<sub>2</sub>.<sup>11</sup> Therefore, the bond lengths and angles suggested that the Mc in the obtained crystal was tbp, and that the obtained crystal was TPP[Co(tbp)(CN)<sub>2</sub>]<sub>2</sub>. This was supported by the fact that during the X-ray crystal structure analysis of the obtained crystal, we found reflections attributable to H atoms attached to the *meso* positions, and the obtained *R* factor of 7.64 was smaller than that calculated under the assumption the Mc was not tbp but Pc where *R* was 7.81.

We also estimated the overlap integral along the c-axis, signifying the effectiveness of the intermolecular interaction along the conduction path, by the extended Hückel calculation. It is reported that the overlap integral at room temperature for TPP[Co(tbp)(CN)<sub>2</sub>]<sub>2</sub> is 12% smaller than that for TPP[Co(Pc)(CN)<sub>2</sub>]<sub>2</sub>.<sup>11</sup> The estimated value at 120 K is  $8.2 \times 10^{-3}$ ,

**Table 1.** Selected bond lengths and angles, and overlap integral (*s*) along the c-axis of TPP[Co(Mc)(CN)<sub>2</sub>]<sub>2</sub>, TPP[Co(tbp)(CN)<sub>2</sub>]<sub>2</sub> and TPP[Co(Pc)(CN)<sub>2</sub>]<sub>2</sub> at 120 K.

	TPP[Co(Mc)(CN) <sub>2</sub> ] <sub>2</sub>	TPP[Co(tbp)(CN) <sub>2</sub> ] <sub>2</sub>	TPP[Co(Pc)(CN) <sub>2</sub> ] <sub>2</sub>
<i>a</i> / Å	1.366(6)	1.373(4)	1.324(3)
<i>b</i> / Å	1.361(5)	1.379(4)	1.323(3)
<i>c</i> / Å	1.360(6)	1.370(3)	1.328(3)
<i>d</i> / Å	1.356(6)	1.374(4)	1.329(3)
<i>α</i> / °	124.0(4)	124.9(3)	121.6(2)
<i>β</i> / °	124.7(4)	125.3 (3)	121.1(1)
<i>γ</i> / °	177.5(5)	178.2(3)	175.0(2)
<i>s</i>	$8.2 \times 10^{-3}$	$8.2 \times 10^{-3}$	$9.7 \times 10^{-3}$

coinciding with that of TPP[Co(tbp)(CN)<sub>2</sub>]<sub>2</sub> and less than that of TPP[Co(Pc)(CN)<sub>2</sub>]<sub>2</sub>. This result also suggests that the crystal obtained by photocrystallization was TPP[Co(tbp)(CN)<sub>2</sub>]<sub>2</sub>.

In summary, photoirradiation of an acetonitrile solution containing TPP[Co(tbp)(CN)<sub>2</sub>]<sub>2</sub> and TPP[Co(Pc)(CN)<sub>2</sub>]<sub>2</sub> by LED light ( $\lambda_{\text{max}} = 660$  nm) enabled us to fabricate a single crystal of a CT complex by exploiting the electron transfer in the photoexcited state. The X-ray crystal structure analysis revealed that the obtained crystal was TPP[Co(tbp)(CN)<sub>2</sub>]<sub>2</sub>, meaning that the photoexcited electron in tbp can transfer from the LUMO of tbp to the LUMO of Pc. Obtaining a single crystal of the CT complex TPP[Co(tbp)(CN)<sub>2</sub>]<sub>2</sub> is not possible by simply mixing the two components TPP[Co(tbp)(CN)<sub>2</sub>]<sub>2</sub> and TPP[Co(Pc)(CN)<sub>2</sub>]<sub>2</sub>. Therefore, our results using photoirradiation suggest a distinctive method for the fabrication of charge transfer complex crystals, and opens new possibilities for constructing novel materials that cannot be obtained by the conventional electrolysis and mixing methods.

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**Keywords:** Photocrystallization • Crystal growth • Charge transfer complex • Phthalocyanines • Porphyrins

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- [15] Crystal data for TPP[Co(tbp)(CN)<sub>2</sub>]<sub>2</sub> obtained by photocrystallization: tetragonal, *P*4<sub>2</sub>/*n*, *a* = 21.6344(4) Å, *c* = 7.47900(10) Å, *V* = 3500.53(10) Å<sup>3</sup>, *T* = 120 K. Crystal data for TPP[Co(tbp)(CN)<sub>2</sub>]<sub>2</sub> prepared by electrolysis: tetragonal, *P*4<sub>2</sub>/*n*, *a* = 21.6002(3) Å, *c* = 7.49400(10) Å, *V* = 3496.47(8) Å<sup>3</sup>, *T* = 120 K. Crystal data for TPP[Co(Pc)(CN)<sub>2</sub>]<sub>2</sub> prepared by electrolysis: tetragonal, *P*4<sub>2</sub>/*n*, *a* = 21.5342(3) Å, *c* = 7.40200(10) Å, *V* = 3432.47(8) Å<sup>3</sup>, *T* = 120 K. For further details including atomic coordinates, see Supporting Information.

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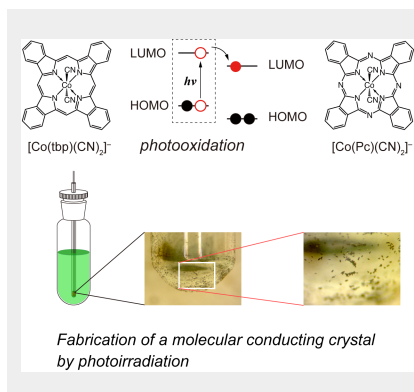
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## Entry for the Table of Contents (Please choose one layout only)

Layout 1:

## COMMUNICATION

Photoirradiation of a solution of  $\text{TPP}[\text{Co}(\text{tbp})(\text{CN})_2]$  and  $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]$  (tbp = tetrabenzoporphyrin, Pc = phthalocyanine, TPP = tetraphenylphosphonium) gives a molecular conducting crystal of a charge transfer complex  $\text{TPP}[\text{Co}(\text{tbp})(\text{CN})_2]_2$ , which was produced via the process in which the photoexcited electron in tbp was transferred from the LUMO of tbp to that of Pc.



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