Photoinduced Color Change of Methylviologen in Polycyano-Polycadmate Host Clathrates

Hirofumi Yoshikawa and Shin-ichi Nishikiori*
Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153-8902

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A series of polycyano-polycadmate host clathrates accommodating a methylviologen dication and an organic molecule has been prepared. Some of them showed a color change from white to blue under UV-VIS light, which comes from the reduction of the methylviologen dication to its monocation radical. This phenomenon depends on the species of the coexistent organic guest and the crystal structure of the clathrates.

From the discovery of inclusion ability of cadmium-cyanide in 1988,[1] many polycyano-polycadmates which have a multi-dimensional framework structure formed with Cd atoms and cyanide bridges have been prepared from the standpoint of supramolecular chemistry.[2,3] In many cases they form clathrates to include a small organic molecule as a guest in their framework structures. X-Ray diffraction studies of the clathrates have revealed an extraordinary variety of their host framework structures.[2,3] However, there have been no works that develop the polycyano-polycadmate host clathrate to a material with an interesting function or property. We here report a trial to prepare photoresponsive polycyano-polycadmate host clathrates.

In most cases, the polycyano-polycadmate host is anionic as known from its general composition of $[Cd_x(CN)y]^{2x-y}$. In order to cancel the negative charge, the host must include a cationic guest, such as $N(CH_3)_4^+$, $S(CH_3)_3^+$, *etc.*[3] besides a proper guest that is a neutral organic compound. Therefore, the clathrates consist of three parts: host, cationic guest and neutral guest. Some trials to enclathrate a chemically active neutral guest had given no good results so far, so that we changed the target from the neutral guest to the cationic guest, and we choose methylviologen dication (1,1'-dimethyl-4,4'-bipyridinium ion, MV^{2+}) as a cationic guest. MV^{2+} has chemically interesting properties[4]: MV^{2+} is easily reduced to $MV^{\bullet+}$ monocation radical whose color is blue, and the radical is widely used in the fields of photochemistry and solar energy conversion; MV^{2+} forms a charge-transfer complex with a donor.

Preparation used here was similar to the previously reported one.[3] The cationic guest was fixed on MV^{2+} and various kinds of organic compounds were tried as a neutral guest. Into water (50 cm^3), $CdCl_2 \cdot 2.5H_2O$ (5 mmol, 1.14 g), $K_2Cd(CN)_4$ (5 mmol, 1.47 g) and methylviologen dichloride (2 mmol, 0.50 g) were dissolved. After the solution was filtered, a neutral guest compound was poured onto/into the filtrate and the mixture was left at room temperature. In several days products were obtained in a crystalline or a powdered state. By a similar procedure, ethylviologen dication (1,1'-diethyl-4,4'-bipyridinium ion, EV^{2+}) clathrates were prepared, too. The existence of the guests and the polycyano-polycadmate host was confirmed by IR spectroscopy. All clathrates were exposed to the light of a low pressure Hg lamp (λ = 366 nm) under air for 90 min, then their color was checked by ocular inspection. The results of the above experiments are listed in Table 1.

Among the listed clathrates, benzene, diethylether, and benzylalchol clathrates were especially sensitive. They were easily irradiated by sunlight in several minutes. As an example of objective data, the diffuse reflectance spectra of the benzene clathrate, $[MV^{2+}][Cd_{3.5}(CN)_9(H_2O)] \cdot C_6H_6$, before and after the irradiation, and their differential spectrum are shown in Figure

Table 1. Properties of MV^{2+} and EV^{2+} polycyano-polycadmate host clathrates

a	neutral guest	b c d	a	neutral guest	b c d	a	neutral guest	b c d
M	No guest(only host)	CW○	M	Benzene	CW◎	E	1,2-Dichloroethane	CW◇
M	Dichloromethane	CW×	M	Toluene	PW○	E	*trans*-1,2-Dichloroethylene	PY×
M	Chloroform	CW○	M	*p*-Xylene	PW○	E	1,2-Dichloropropane	PY×
M	Carbon tetrachloride	PW×	M	Ethylbenzene	PW○	E	1,1,2-Trichloroethane	PY×
M	1,2-Dichloroethane	CW○	M	Chlorobenzene	PW○	E	1,1,2,2-Tetrachloroethane	CY×
M	1,2-Dichloropropane	PW○	M	Phenol	CY×	E	Tetrachloroethylene	CY×
M	Diethyl ether	CW◎	M	Benzylalcohol	PW◎	E	Bromoform	PY○
M	Diisopropyl ether	PW○	M	Benzaldehyde	PW×	E	1,2-Dibromoethane	CW◇
M	Methanol	CW△	M	Benzonitrile	PW○	E	Diethyl ether	CY×
M	Ethanol	CW△	M	Nitrobenzene	PW×	E	Diisopropyl ether	CY△
M	1-Propanol	CW○	M	Aniline	PW×	E	1-Propanol	CY○
M	2-Propanol	CY○	M	*o*-Toluidine	PW×	E	2-Methyl-1-propanol	CY○
M	2-Methyl-1-propanol	CW×	M	Nitromethane	PW×	E	Cyclohexanol	PW△
M	2-Methyl-2-propanol	CW×	M	Acetnitrile	CW×	E	Benzene	PY×
M	1-Butanol	CW△	E	No guest(only host)	CY○	E	1-Chloronaphtaline	PY△
M	2-Butanol	CY○	E	Dichloromethane	PW○	E	Acetnitrile	PY×
M	2-Methyl-2-butanol	PW○	E	Chloroform	PY×	E	Pentane	CY×
M	Acetone	CW○	E	Carbon tetrachloride	PY×			
M	Ethyl acetate	PW×	E	1,1-Dichloroethane	PY×			

[a] Cationic guest; M: MV^{2+}, E: EV^{2+}. [b] State of product; C: crystals, P: powder. [c] Color before irradiation; W: colorless or white, Y: yellow. [d] Color after irradiation, ◎:dark blue, ○: pale blue, △: slightly blue, ×: no change, ◇: pale purple.

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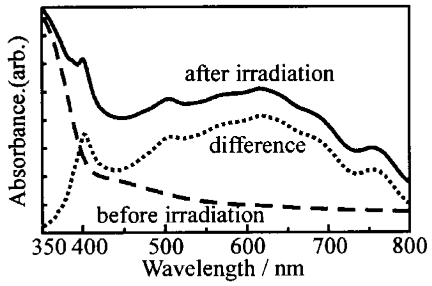

Figure 1. Diffuse reflectance spectra of MV^{2+}-benzene clathrate $[MV^{2+}][Cd_{3.5}(CN)_9(H_2O)]\cdot C_6H_6$.

1. The differential spectrum was similar to that of $MV^{\bullet +}$.[5] The existence of a radical was confirmed by ESR spectroscopy.[6] These data show that the color change comes from the reduction from colorless MV^{2+} to blue $MV^{\bullet +}$. The blue color went back to white gradually within several days under air in dark room. The most interesting observation is that the sensitivity to light depends on the neutral guest species. Broadly speaking, the clathrates including the neutral guest with low ionization potential trend to be sensitive. This finding seems to suggest the existence of an interaction between MV^{2+} and the neutral guest. To confirm this interaction, the information of their crystal structures is essential. First of all, powder X-ray diffraction patterns of the clathrates were measured to survey their crystal structures. The observed patterns were complicated ones, which suggest that their crystal lattices are large and/or in low symmetry. The estimation and the classification of their crystal structures based on the powder patterns were difficult. Therefore, the single crystal X-ray diffraction experiment of each clathrate is indispensable. At this stage, the structure determination of the benzene clathrate, $[MV^{2+}][Cd_{3.5}(CN)_9(H_2O)]\cdot C_6H_6$, has been completed.[7] ORTEP view is shown in Figure 2. There are four independent Cd atoms. Eight cyano groups make bridges between the Cd atoms to form a 3-D framework host. One cyano group and one H_2O molecule work as a monodentate ligand. MV^{2+} and benzene are arrayed alternately along the *a* axis to form a stacking structure, and the shortest distance between them is 3.63(2) Å. This structural situation seems to suggest the existence of a MV^{2+}-benzene interaction. Needless to say, more structural information about other clathrates is necessary to clarify the photochemical behavior of this series of clathrates. The polycyano-polycadmate host clathrate shows a marvelous variety of the host structures depending on the neutral guest,[2,3] so that many cases where the crystal structure influences the MV^{2+}-neutral guest interaction are expected. Detailed studies of the characterization, the photochemical behavior, the crystal structure, and the MV^{2+}-guest interaction are now in progress.

In conclusion, the first photoresponsive polycyano-polycadmate host clathrates have been prepared. Although the sensitivity to light belongs to MV^{2+}, the appearance of the photochemical behavior depends on the coexisting neutral guest species and the crystal structure of the clathrates. Many studies of MV^{2+} trapped in a solid state matrix such as cellulose, zeolite, silica gel, *etc.* were carried out so far.[8] However they were done without structural data. The advantage of the new clathrates is to enable us to discuss about photochemical properties of MV^{2+} based on structural information.

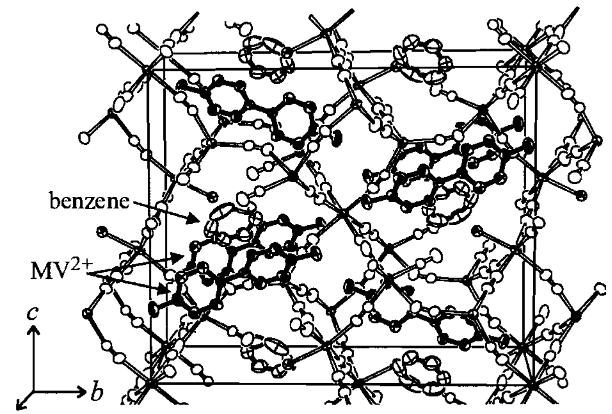

Figure 2. ORTEP view of MV^{2+}-benzene clathrate $[MV^{2+}][Cd_{3.5}(CN)_9(H_2O)]\cdot C_6H_6$.

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6 The authors are indebted to Prof. Tokuko Watanabe, Tokyo University of Fisheries, for measuring ESR spectra.

7 $[MV^{2+}][Cd_{3.5}(CN)_9(H_2O)]\cdot C_6H_6$: monoclinic, $P2_1/n$, a/Å = 8.166(5), b/Å = 22.154(6), c/Å = 18.475(7), β/° = 98.70(5), Z = 4, D_c/gcm^{-3} = 1.83. The structure was refined using SHELXL-93: $wR2$ = 0.1061 and $R1$ = 0.0460 for 5858 reflections.

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