

Dual Purpose Br-Containing Schiff Base Cu(II) Complexes for DSSC Dyes and Polymer Flame Retardants

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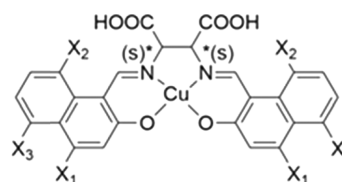
INTRODUCTION

In recent years, as increasing much attention of dye sensitized solar cell (DSSC) to overcome energy and environmental problems, new arguments about safety or fire issues have been widely discussed for materials used solar cells or buildings equipping with them.¹ At present, DSSC is not used industrially, in future frame retardant functional materials for DSSC modules will be necessary from the viewpoint of safety of building potentially.

In order to develop low-cost dyes for DSSC, we have designed² or prepared³ several new Schiff base Cu(II) complexes as dyes. In the theoretical design guidelines, electron withdrawing substituent effect resulted in long-wavelength light absorption and stabilizing LUMO band, and we have prepared Br-containing Schiff base complexes expecting light harvesting and investigated both computational and experimental UV-Vis-NIR spectra and measured conversion efficiency as DSSC cells.

By the way, Br-containing organic compounds was also one of the typical components of flame retardants for polymers such as polymethyl methacrylate (PMMA) as many patents were reported. Indeed, Br-containing organic flame retardants caused serious environmental damages in the past.⁴ The first generation flame retardants of a representative bromine compounds were called PBB. Accidentally drinking PBB (prohibited at present) by cows resulted in damage against human health through milk and environmental damage in wide area. Previously, we have reported patents of several bis(bidentate) Schiff base Cu(II) complexes incorporating various substituent groups (not organic compounds) as flame retardants for PMMA.

Herein, we report on structure, DSSC performance, and



Scheme 1. Chemical structure of **1-3** ($X_1, X_2, X_3 = \text{Br, H, H}$ for **1**; Br, Br, H for **2**; Br, Br, Br for **3**).

thermal behavior of three Br-containing Schiff base Cu(II) complexes **1-3** incorporating extended π -conjugated ligands (Scheme 1), exhibiting long-wavelength shift of the intense π - π^* bands (255, 264, and 272 nm, respectively) as introducing many Br-groups.⁵

EXPERIMENTAL

Materials and Synthesis

Samples of **1-3**⁵ (checked by IR) and their DSSC cells³ were prepared according to the literature procedures.

Physical Measurements

IR spectra were obtained with KBr pellets using a JASCO 460 plus series FT-IR spectrometer. TG-DTA was obtained using a Bruker AXS MS9610/DSC3200A/TG-DTA2010SA supported on alumina. Performance as DSSC was measured in the methods of literature.³

Powder of complexes was packed in the 0.5 mm diameter (wall thickness is 0.01 mm) capillary and the diffraction data measured transparency as Debye-Scherrer at 298 K respectively, with the 100 mm of detector distance in 10 sec exposure with synchrotron radiation ($\lambda = 1.20007 \text{ \AA}$) on an ADSC Quantum-210 detector at 2D SMC with a sil-

Table 1. Crystallographic data for **1**

CCDC	1536362
Empirical formula	C ₂₆ H ₁₆ Br ₂ CuN ₂ O ₆
Formula weight	675.77
Crystal system	Monoclinic
Space group	P2 ₁ (#4)
<i>a</i> (Å)	11.851 (4)
<i>b</i> (Å)	7.8368 (14)
<i>c</i> (Å)	22.026 (6)
β (°)	99.34 (2)
<i>V</i> (Å ³)	2018.5 (10)
<i>Z</i>	2
R _{wp} (%)	12.36

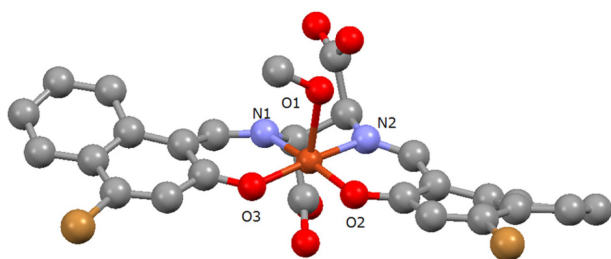
icon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Korea. The PAL BL2D-SMDC program⁶ was used for data collection, and Fit2D program⁷ was used converted 2D to 1D pattern and wavelength and detector distance refinement. Powder crystal structure analysis could be carried out only for **1** (Table 1) with a Rigaku PDXL2, commercially available program package.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as CCDC 1536362. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

X-ray Crystallography

The complex **1** crystallized in the monoclinic space group P2₁ with *Z* = 2. It consists of a mononuclear Cu(II) complex with a nearly twisted conformation of planar moieties (Fig. 1). It affords a five-coordinated square pyramidal coordination environment with the four donor atoms of the tetradentate Schiff base ligand forming the equatorial plane and methanol ligand occupying an axial site. For convenience, a perspective drawing together with the atomic

**Figure 1.** Molecular structure of **1**.**Table 2.** Table selected bond lengths [Å] and angles [°] for **1**

Cu-N1	1.9845(6)	O1-Cu1-N1	99.49(2)
Cu-N2	1.9763(4)	O1-Cu1-N2	89.74(18)
Cu-O1	2.2698(5)	O2-Cu1-N1	172.54(3)
Cu-O2	1.9305(6)	O2-Cu1-N2	91.85(18)
Cu-O3	1.9377(4)	O3-Cu1-N1	91.36(18)
O1-Cu1-O2	87.65(2)	O3-Cu1-N2	174.09(4)
O1-Cu1-O3	95.94(18)	N1-Cu1-N2	86.08(18)
O2-Cu1-O3	90.02(17)		

labeling is depicted in Fig. 1. It is found that the Cu(II) ion is coordinated by five *O*- or *N*- donor atoms with *O*- bond lengths ranging from 1.9377(4) to 1.9305(6) Å of the basal plane, while slightly long axial bond length of 2.2698(5) Å. *Trans*-bond angles of the basal plane are in the range of 172.54(3)° – 174.09(4)°. Thus all geometrical parameters (Table 2) were common values among the analogous complexes known.

Measurements as DSSC Cells

To be suitable dyes for an electronic cycle of DSSC, dye complexes are required to have both lower HOMO level than reduction potential of iodine (acting as mediator) and higher LUMO level than conduction band level of TiO₂.^{8–11} It seemed to be not necessarily good to have many Br-groups, in contrast to long-wavelength shift of optical absorption bands. As DSSC cells consist of SLG, ITO, carbon, and TiO₂ (Scheme 2) conversion efficiency (*h*) based on I-V curves was evaluated to be 0, 3.4 × 10⁻⁴, and 6.9 × 10⁻⁵ % for **1-3**, respectively. Thus **2** was the best dye among **1-3**, and inconsistency of *h* and HOMO-LUMO levels may be attributed to complicated reasons besides light absorbing layers such as the carbon component.

TG-DTA

Thermolysis temperature was measured using TG-DTA for PMMA cast films containing **1-3**. Testing samples were prepared by drying 3% complexes in PMMA acetone solu-

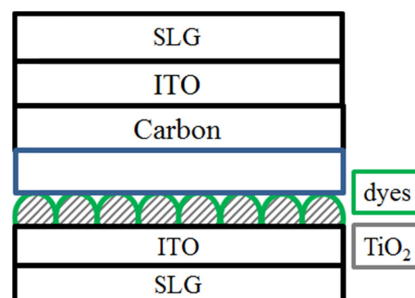
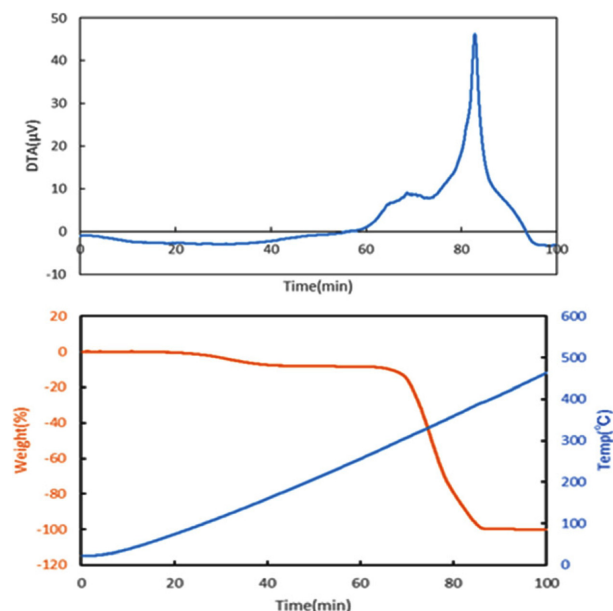
**Scheme 2.** Layered structures of DSSC cells composed.³

Table 3. Thermolysis temperature (T) of PMMA films

	T (K)
PMMA	541
PMMA + 1	570
PMMA + 2	579
PMMA + 3	581

**Figure 2.** DTA [above] and TG [below] (blue: temperature; orange: weight) data for PMMA+3.

tions (w/w) for 4 hours at room temperature. As listed in Table 3, as increasing thermolysis temperature ascribes to incombustible improvement for PMMA by adding many Br-atoms in the samples straightforwardly. One can see the weight of materials reduced as burning time passed in TG chart above and positive peak in DTA chart. This feature means combustion of materials typically. As depicted in Fig. 2 (only for PMMA+3 as an example), terminal temperature of combustions is almost same and similar phenomenon were around combustion temperature range.

The thermal degradation of PMMA happened in the main chain scission, side group scission and depolymerisation. The chain scission results in the radical formation and depolymerisation regenerates the monomer. The side chain scission evolves methane and carbon dioxide. The degradation occurs at 573 to 773 K. In our case PMMA decompose at 814 K while the Br-containing complexes filled PMMA decompose at higher temperature.

Kandare *et al.*,¹² investigated thermal decomposition of PMMA filled with copper hydroxy methacrylate and found out that the degradation of the PMMA is delayed by 45 K. He also observed that T50 temperature at which 50% of

original polymeric mass is lost is also increased by 30 K. In our studies too, the decomposition temperature is increased.

CONCLUSIONS

Aiming at dual purpose materials, three Br-containing Schiff base Cu(II) complexes were composed as DSSC cells and PMMA films and investigated conversion efficiency as DSSC and the improvement of incombustibility for PMMA films. Although adding many Br-atoms in complexes resulted in better incombustible for PMMA, introducing appropriate number of Br-groups in complexes must be important to realize better conversion efficiency as DSSC dyes. In this way, metal complex with halogen atom may be better flame retardant materials at least.

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REFERENCES

1. National Research Institute of Fire and Disaster, Japan, <http://nriofd.fdma.go.jp/publication/gijutsushiryo/index.html>. **2014**.
2. Yamaguchi, M.; Takahashi, K.; Akitsu, T. *J. Indian Chem. Soc.* **2016**, *93*, 921.
3. Shoji, R.; Ikenomoto, S.; Sunaga, N.; Sugiyama, M.; Akitsu, T. *J. Appl. Sol. Chem. Model.* **2016**, *5*, 48.
4. Venier, M.; Salamove, A.; Hites, R. A. *Acc. Chem. Res.* **2015**, *48*, 1853.
5. Akitsu, T.; Takahashi, K.; Yamaguchi, M.; Tanaka, S.; Sugiyama, M.; Soni, R. K.; Mizuno, M.; Matsuyama, K.; Takakura, K.; Endo, K.; Ida, T.; Palafox, M. A. *Hybrid materials*, in press; Nova Science Publisher: USA.
6. Shin, J. W.; Eom, K.; Moon, D. *J. Synchrotron Rad.* **2016**, *23*, 369.
7. Fit2D program: Andy Hammersley (E-mail: hammersley@esrf.fr), ESRF; 6 RUE JULES HOROWITZ BP 220 38043 GRENOBLE CEDEX 9 FRANCE.
8. Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Muller, E.; Liska, P.; Vlachopoulos, N.; Gratzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6595.
9. He, M.; Ji, Z.; Huang, Z. *J. Phys. Chem. C.* **2014**, *118*, 16518.
10. Baviskar, P. K. *et al.*, *J. Solid. State. Electrochem.* **2017**, *3*, 3507.
11. Yu, K.; Sung, E.; Kang H.; Tack, I.; Choi, I. *RSC. Adv.* **2015**, *5*, 80859.
12. Kandare, E.; Deng, H.; Wang, D.; Hossenlopp, J. M. *Polymers for Adv. Tech.* **2006**, *17*, 312.