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Synthesis of the New 1,2-Dithiolene Metal Complexes[M(BDDT)₂⁻] (M=Ni, Cu) and Their Electronic Structures

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The new 1,2-dithiolene, 1,4-butanediyldithioethylene-1,2-dithiolate ($BDDT^{2-}$), has been isolated. In addition, new monoanionic bis-complexes with nickel and copper have been prepared and characterized. In order to investigate the detailed electronic structure of the metal complexes of the new ligand, $BDDT^{2-}$, in terms of the oxidation state of the central metal ions, we have carried out molecular orbital (MO) calculations of $Ni(BDDT)_2^-$ and $Cu(BDDT)_2^-$ utilizing an Extended Hückel method. Cyclic voltammetry data for both complexes were obtained with a potentiostat. We have also compared these results to the previously synthesized $Ni(PDDT)_2^-$, $Ni(DDDT)_2^-$, $Cu(PDDT)_2^-$, and $Cu(DDDT)_2^-$.

Introduction

Over the past 30 years, there has been a great deal of interest in the coordination chemistry of 1,2-dichalcogenolenes. Unsaturated sulfur donors have been particularly well characterized. These ligands first came into prominence in the mid 1930's when they were utilized as analytical reagents.[1,2] However, it was not until 1957 that any really serious efforts were made to characterize some of the metal complexes of these unsaturated 1,2-dithiols.[3]

There have been several important reviews of metal sulfur chemistry. Discussions by Harris and Livingstone,[4] Livingstone,[5] and Jorgenson[6] deal with sulfur ligands in general. Holm and O'Conner[7] discuss the stereochemistry of [M(II)-S₄] complexes along with other bischelate metal(II) complexes in their review. Many authors[8~13] have reviewed the chemistry of 1,2-dithiolene complexes. Electronic spectral studies of bidentate sulfur containing ligands have been reviewed in detail by Coucouvanis.[14] Systematic examinations of the crystal and molecular structures of 1,2-dithiolene complexes have been carried out by Eisenberg[15] and Mahadevan.[16] Exchange interactions in some low dimensional metal dithiolene complexes have been the subject of a review by Monoharan and co-workers.[17]

Bis(dithiolene) complexes of metals are possible candidates for counteranions in conducting molecular solids.[18~20] Recently (TTF)[Ni(dmit)₂]₂ has been shown to be superconducting
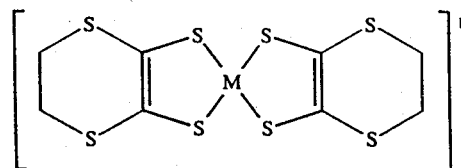

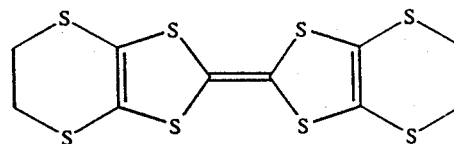**Figure 1.** Lewis Structure of $[M(DDDT)_2]^n$.

Figure 2. Lewis Structure of BEDT-TTF or ET.

at 1.62 K under a hydrostatic pressure of 7 Kbar.[18b] A good deal of interest has been shown recently in 5,6-dihydro-1,4-dithiin-2,3-dithiolate (DDDT) since its metal complexes [M(DDDT)₂]ⁿ (Figure 1) are similar in structure to bis(ethylenedithio)tetrathia-fulvalene (BEDT-TTF or ET, Figure 2) which have led to the ambient-pressure superconductors β-$(ET)_2X$ ($X^- = I_3^-$, AuI_2^-, IBr_2^-).[21]

Schultz *et al.*[22] recently reported that the $[Au(DDDT)_2]^0$ molecule and the $[Ni(DDDT)_2]^-$ ion are isoelectronic in terms of their valence electrons. The metal coordination geometry is square planar in both molecules. They are described
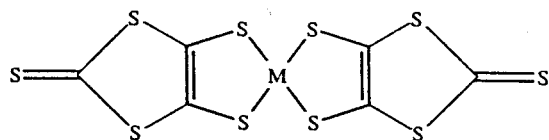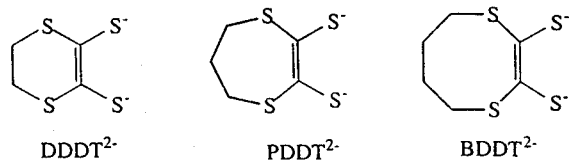
Figure 3. Lewis Structure of [M(dmit)$_2$]^n.

DDDT^{2-} PDDT^{2-} BDDT^{2-}

Figure 4. Lewis Structures of DDDT^{2-}, PDDT^{2-}, and BDDT^{2-}.

as d^8 ions with the unpaired electron in each molecule located in the π^* orbitals of DDDT ligand which contains only a small contribution from the metal d_{yz} orbital.[23]

Very recently, Doublet *et al.*[24] reported a detailed study of the structural and electronic factors controlling the metallic or semiconducting properties of the β-type charge transfer salts containing the [M(DDDT)$_2$]$^{2-}$ and [M(dmit)$_2$]$^{2-}$ (M = Pd, Pt) (Figure 3) dimer unit. This work showed that the partially filled band of the both salts is derived either from the HOMO for [M(dmit)$_2$]$^{2-}$ or from the LUMO for [M (DDDT)$_2$]$^{2-}$ of their monomer unit, depending on the extent of dimerization. They reported that good electrical conductivity is expected for strongly dimerized M(dmit)$_2$ systems and for weakly dimerized M(DDDT)$_2$ systems.

In the view point of superconducting property, partially oxidized properties have prompted many laboratories to explore new complexes in this area. Earlier, we have designed a scheme to combine the properties of the "TTF type" organosulfur molecules and the inorganic systems that have been recently studied. Since it is apparently the tetrathioethylene unit of TTF that is fundamentally important to that of the class of molecules, therefore we have undertaken a synthetic program to investigate inorganic complexes of new ligands containing this subunit. In an attempt to gain a better understanding of the electronic structure and partial oxidation property, a knowledge of the molecular orbital ordering and cyclic voltammetry data is important.[25]

In order to investigate the detailed electronic structure of the metal complexes of a newly reported ligand, BDDT^{2-} (Figure 4), in terms of the oxidation state of the central metal ions, we have carried out molecular orbital (MO) calculations of Ni(BDDT)$_2^-$ and Cu(BDDT)$_2^-$ utilizing an Extended Hückel method.[23] We have also compared these results to the previously synthesized Ni(PDDT)$_2^-$, Ni(DDDT)$_2^-$, Cu(PDDT)$_2^-$, and Cu(DDDT)$_2^-$.

Experimental

Reagents. 2,7,9,11-tetrathiabicyclo[6.3.0]undec-1(8)-en-10-thione (TTUET) and its derivative, 2,7,9,11-tetrathiabicyclo [6.3.0]undec-1(8)-en-10-one, were prepared by literature methods[26] with some modifications and characterized by IR, NMR, elemental analysis and melting point (mp.). Nickel chloride hexahydrate was purchased from Matheson, Coleman

and Bell, Inc. Cupric chloride dihydrate was purchased from J. T. Baker Chemical Co. Tetraethylammonium bromide and potassium metal were obtained from Aldrich Chemical Company, Inc. Argon was purchased from Air Products, Inc. All chemicals were used without further purification. THF was freshly distilled from Na/benzophenone prior to use. Methyl alcohol and acetonitrile were purchased from Fisher Chemical Company and stored over 4 Å sieves for more than 24 h before use. Ethyl alcohol was purchased from Aaper Alcohol and Chemical Company. Ethyl alcohol and water used in the syntheses of the complexes were degassed with argon for 30 min prior to use.

General Procedure. All reactions were carried out under a static atmosphere of argon using standard Schlenk techniques. Transfers of liquid solvents and/or reagents were made using argon purged ground glass syringes with Luerlock type stainless steel needles.

Syntheses. [C$_7$H$_8$S$_5$ (TTUET)]: To a stirred solution (0 ℃) of 200 mL CS$_2$ in 400 mL of DMF, 10 g of sliced potassium metal was added very slowly and carefully. After stirring for 1 h, 10 g of potassium metal and 30 mL of CS$_2$ were added to the solution. This same addition was again repeated one hour later. To this solution, 50 mL of CS$_2$ was added and stirred for 3-4 h. To the reaction mixture, 100 mL of DMF and 1,4-dibromobutane (46 mL) were added slowly. The solution was allowed to warm to room temperature and stirred overnight. To destroy any unreacted potassium metal, approximately 20 mL of MeOH, followed by H$_2$O (200 mL) were added. To remove any by-product, the solution was filtered, extracted with chloroform and washed with H$_2$O. Organic extracts were dried over K$_2$CO$_3$ and concentrated to give orange-brown solid. The crude product was recrystallized from ethanol to give orange crystals.: mp 107-108 ℃; ^{1}H NMR (CDCl$_3$) δ 3.005 (t, 4H), 2.024 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 212.2, 140.2, 38.4, 27.4; IR (KBr pellet) 2920 (m), 2900 (s), 1440 (s), 1400 (s), 1288 (s), 1055 (vs), 1020 (s), 880 (m), 855 (s), 800 (m), 765 (m), 505 (m), 445 (m) cm^{-1}; Anal. calcd. for C$_7$H$_8$S$_5$: C, 33.31; H, 3.19; S, 63.50. Found: C, 33.45; H, 3.13; S, 63.26.

[C$_7$H$_8$S$_4$O (TTUEO)]. To a solution of 2.50 g (1.0×10^{-2} mol) of TTUET in 30 mL CHCl$_3$, 3.2 g of Hg(OAc)$_2$ in 50 mL HOAc was added. The solution was refluxed for about 6 h and the color changed to black. Approximately 8 g of anhydrous Na$_2$SO$_4$ was added and the reaction mixture was filtered to remove any by-product. To the filtrate, a saturated Na$_2$CO$_3$ aqueous solution was added slowly. Extraction with CH$_2$Cl$_2$, drying over MgSO$_4$ and concentration gave a yellow solid. The crude product was recrystallized from ethanol to yield light yellow crystals.: mp 78-80 ℃; ^{1}H NMR (CDCl$_3$) δ 3.00 (t, 4H), 2.02 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 189.7, 131.6, 38.6, 27.5; IR (KBr pellet) 2950 (m), 2930 (m), 2910 (s), 1755 (m), 1750 (vs), 1600 (vs), 1440 (m), 1420 (s), 1408 (s), 1295 (s), 1275 (m), 1170 (m), 1005 (m), 990 (s), 880 (vs), 805 (s), 765 (s), 730 (s), 550 (m), 455 (m), 380 (m) cm^{-1}; Anal. calcd. for C$_7$H$_8$S$_4$O: C, 35.57; H, 3.41; S, 54.25. Found: C, 35.52; H, 3.37; S, 54.13.

[K$_2$(BDDT)]. Potassium ethoxide was prepared by adding 3.2 g (8×10^{-2} mol) of sliced potassium metal to 8 mL (excess) of absolute ethanol under argon. After approximately 200 mL of freshly distilled THF was added to this solution,

614 *Bull. Korean Chem. Soc.* **1996**, Vol. 17, No. 7

Geewon Chung and Robert D. Bereman

4.73 g (2×10^{-2} mol) TTUEO was added. A light-cream colored precipitate formed after a few minutes. The mixture was stirred for about 15 h, filtered, washed with ethyl ether, dried and stored in a Schlenk tube for further use.

[(C_2H_5)$_4$N][Ni($C_6H_8S_4$)$_2$]. A solution of 0.25 g (1.1×10^{-3} mol) of NiCl$_2$·6H$_2$O in 20 mL CH$_3$OH was added dropwise to 0.58 g (2.0×10^{-3} mol) of K$_2$BDDT in 20 mL CH$_3$OH. The solution color changed from amber to dark brown as the reaction proceeded. The solution mixture was stirred for 3 h at room temperature and filtered to remove any by-product. To the filtrate, 0.25 g (1.1×10^{-3} mol) of tetraethylammonium bromide was added, and stirred for 30 min. A brown precipitate formed which was collected by filtration. Brown crystals suitable for X-ray analysis were obtained by careful recrystallization from dry acetonitrile.[27] The product yield was 0.201 g (33%): mp 187-189 °C; ^{1}H NMR (DMSO-d$_6$) δ 3.33 (d, 8H), 3.20 (br. s, 8H), 1.17 (br. s, 12H); IR (KBr pellet) 2970 (m), 2905 (s), 2840 (m), 1470 (s), 1440 (s), 1402 (s), 1380 (vs), 1285 (s), 1165 (s), 995 (m), 880 (m), 860 (m), 800 (s), 740 (m), 445 (m), 385 (m) cm^{-1}; Anal. calcd. for NiC$_{20}$H$_{36}$NS$_8$: C, 39.66; H, 5.99; N, 2.31. Found: C, 39.70; H, 5.97; N, 2.37.

[(C_2H_5)$_4$N][Cu($C_6H_8S_4$)$_2$]. A solution of 0.20 g (1.2×10^{-3} mol) of CuCl$_2$·2H$_2$O in 10 mL H$_2$O was added dropwise to 0.58 g (2.0×10^{-3} mol) of K$_2$BDDT in 20 mL 1 : 1 ethanol/water solution made basic with KOH. The color changed from amber to dark purple immediately. The solution was stirred for 1 h at room temperature and then filtered to remove by-product. A solution of 0.25 g (1.1×10^{-3} mol) of tetraethylammonium bromide in 5 mL of water was added, and stirred 20 min. A dark purple precipitate was formed and collected by filtration. The yield was 0.13 g (21%). Single crystals were obtained by careful recrystallization from acetonitrile /isopropanol[27]: mp 196-197 °C; ^{1}H NMR (DMSO-d$_6$) δ 3.20 (d, 8H), 2.68 (br. s, 8H), 1.70 (br. s, 8H) 1.15 (dt, 12H); IR (KBr pellet) 2980 (m), 2920 (m), 2840 (m), 1480 (s), 1450 (s), 1450 (s), 1428 (s), 1410 (s), 1390 (s), 1170 (s), 1005 (s), 955 (s), 890 (s), 870 (s), 805 (s), 780 (s), 430 (m), 380 (m) cm^{-1}; Anal. calcd. for CuC$_{20}$H$_{36}$NS$_8$: C, 39.35; H, 5.94; N, 2.29. Found: C, 39.46; H, 6.08; N, 2.30.

Physical Measurements. Melting points were taken on a Thomas Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1430 spectrophotometer over the range 4000-200 cm^{-1}. Electrochemical data were obtained with a BAS CV-27 potentiostat. A platinum wire was used for both the working and auxiliary electrode and a Ag/AgCl electrode was used as the reference electrode. The solution contained 0.1 M tetraethylammonium perchlorate as the supporting electrolyte in DMF with the metal complex concentration of 10^{-3} M. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA. Nuclear magnetic resonance spectra were obtained with a G.E. GN 300 (300 MHz) spectrometer. Chemical shifts are in δ units (ppm) with TMS (0.0 ppm) used as an internal standard for ^{1}H NMR.

Results and Discussion

The formal electronic charges in Ni(BDDT)$^{2-}$ could be written as either [Ni^{3+}(d^7)] (BDDT^{2-})$_2$ or [Ni^{2+} (d^8)] (BDDT)$_2^{3-}$. Likewise, the formal oxidation state of Cu(BDDT)$_2^-$ could
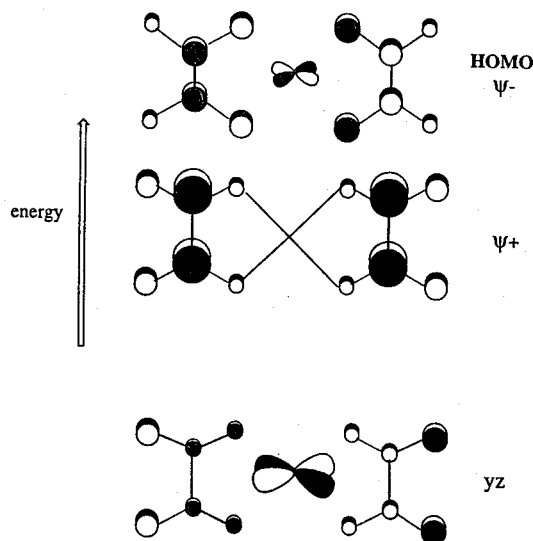

Figure 5. Some MO's of M(BDDT)$_2^-$.

be expressed as either [Cu^{3+}(d^8)] (BDDT^{2-})$_2$ or [Cu^{2+}(d^9)] (BDDT)$_2^{3-}$. Like the earlier report[22] that square planar geometry in M(DDDT)$_2^-$ type complex is more likely to be the d^8 oxidation formalism, we presume that the metal coordination geometry of Ni(BDDT)$_2^-$ and Cu(BDDT)$_2^-$ is square planar and more consistent with the d8 oxidation formalism for both complexes.

The atomic orbitals employed in our calculations are as follows: Hii, the negative of valence orbital ionization potentials and the exponent ζ_i of the Slater-type atomic orbital χ_i are respectively -20.0 and 2.122 for S 3s, -13.3 and 1.827 for S 3p, -21.4 and 1.625 for C 2s, -11.4 and 1.625 for C 2p, -13.6 and 1.3 for H 1s, -9.17 and 1.825 for Ni 4s, -5.15 and 1.125 for Ni 4p, -11.4 and 2.20 for Cu 4s, and -6.06 and 2.20 for Cu 4p. The d orbitals of Ni and Cu are represented by a linear combination of two Slater-type orbitals of exponents ζ_i and $\bar{\zeta}_i$ with weighting factor c_i and $\bar{c}_i$, respectively. The Hii(ev), ζ_i, c_i, $\bar{\zeta}_i$, and $\bar{c}_i$ values are respectively -13.49, 5.75, 0.5683, 2.00 and 0.6292 for Ni 3d, and -14.00, 5.95, 0.59332, 2.30 and 0.57442 for Cu 3d. The off-diagonal Hamiltonian matrix elements Hij were obtained by a modified Wolfsberg-Helmholz formula.[28] Supplementary materials are available for detailed results of the MO calculations.

According to our MO calculations on Ni(BDDT)$_2^-$, Ni(PDDT)$_2^-$, and Ni(DDDT)$_2^-$, the highest two filled MO's are mainly represented by the π* orbitals of each of the ligands. These MO's are shown as Ψ$^-$ and Ψ$^+$ of Figure 5. The MO calculation data of the series of nickel dithiolene complexes (Figure 4) are shown in Table 1. Each complex has the LUMO lying at a considerably higher energy than the HOMO Ψ$^-$ (by ~3 eV) and the LUMO levels have mostly metal d-orbital character. The HOMO levels are singly occupied and are predominantly ligand located as can be seen by the metal d AO coefficients of Table 1. Several MO's below the HOMO have metal d AO coefficients around 0.5 indicative of high M-S covalency.

The results of the MO calculations carried out on Cu(BDDT)$_2^-$, Cu(PDDT)$_2^-$, and Cu(DDDT)$_2^-$ are shown in Table 2. Again, the highest two occupied MO's are represented

1,2-Dithiolene Metal Complexes

Bull. Korean Chem. Soc. **1996**, Vol. 17, No. 7   615

Table 1. MO calculation Data for Nickel Dithiolenes (Metal d orbital coefficients)

$Ni(BDDT)_2^-$	HOMO (-10.585 eV)	LUMO (-7.190 eV)
dx^2-y^2	0.0126	-0.7204
dz^2	-0.0010	-0.0006
dxy	-0.0015	-0.0197
dxz	0.1327	0.0369
dyz	0.1088	-0.0304
$Ni(PDDT)_2^-$	HOMO (-10.619 eV)	LUMO (-7.098 eV)
dx^2-y^2	-0.2144	-0.3019
dz^2	-0.1859	0.4743
dxy	0.0538	-0.2914
dxz	0.1741	0.1473
dyz	-0.0558	-0.2458
$Ni(DDDT)_2^-$	HOMO (-10.302 eV)	LUMO (-6.960 eV)
dx^2-y^2	0.0021	-0.7766
dz^2	0.0124	0.0001
dxy	0.0046	-0.0284
dxz	-0.1945	0.0141
dyz	-0.1918	-0.0291

Table 2. MO calculation Data for Copper Dithiolenes (Metal d orbital coefficients)

$Cu(BDDT)_2^-$	HOMO (-11.020 eV)	LUMO (-9.461 eV)
dx^2-y^2	0.0140	0.6285
dz^2	-0.0015	-0.0008
dxy	-0.0160	0.0156
dxz	0.1309	-0.0040
dyz	0.1379	0.0029
$Cu(PDDT)_2^-$	HOMO (-10.950 eV)	LUMO (-9.456 eV)
dx^2-y^2	0.0035	-0.6293
dz^2	-0.0033	-0.0010
dxy	-0.0217	-0.0181
dxz	-0.1261	-0.0066
dyz	-0.1256	-0.0060
$Cu(DDDT)_2^-$	HOMO (-10.597 eV)	LUMO (-9.721 eV)
dx^2-y^2	-0.0045	0.5668
dz^2	-0.0039	0.0031
dxy	0.0042	0.0298
dxz	0.0971	-0.0926
dyz	0.1001	-0.0911

by the ligand orbitals Ψ^- and Ψ^+ shown in Figure 5. The HOMO Ψ^- is doubly occupied and has very low metal orbital character in each complex. As shown in Table 1, 2 and Figure 5, we could reach at the point that 1) the HOMO and some MO's just below the HOMO have very little metal d-orbital character and fully occupied, and 2) below these HOMO's, there should be MO's having mostly metal d-orbital character. 3) The LUMO having mainly metal d-orbital (dx^2-

Table 3. Cyclic Voltammetry Parameters for $[ML_2]^{n-}$ Dithiolene Complexes vs SCE in DMF

Compound	$E_{1/2}$, V		ref.
	$n : 1 \rightleftharpoons 2$	$n : 0 \rightleftharpoons 1$	
$[Ni(BDDT)_2]^-$	-0.70	$+0.29$	This work
$[Ni(PDDT)_2]^-$	-0.60	$+0.30$	30
$[Ni(DDDT)_2]^-$	-0.81	$+0.014$	31
$[Cu(BDDT)_2]^-$	-0.81	$+0.54$	This work
$[Cu(PDDT)_2]^-$	-0.56		30
$[Cu(DDDT)_2]^-$	-0.49	$+0.38$	31

y^2) portion is to be the only one empty d-level. Therefore, in both Ni and Cu complexes central metals are best described as $Ni(II)d^8$ and $Cu(III)d^8$ in nature as their oxidation formalism.

A careful examination of the voltammetric data reveals some interesting trends. The cyclic voltammetry parameters for the $[ML_2]^-$ dithiolene complexes are shown in Table 3. For the nickel complexes, the dianionic stability decrease in the order $Ni(PDDT)_2^- > Ni(BDDT)_2^- > Ni(DDDT)_2^-$ according to the cyclic voltammetry results.

It has previously been shown that trends of this type follow the electron withdrawing ability of the dithiolene ligands.[29] From the MO viewpoint, the dianionic stability of the ML_2^- complex is determined by the lowest-lying level that can accept an electron (hereafter referred it as the acceptor level): the dianionic stability increases as the acceptor level is lowered in energy. Table 1 shows that the energy of acceptor level of NiL_2^- (*i.e.*, the singly occupied HOMO) increases in the order $Ni(PDDT)_2^- < Ni(BDDT)_2^- < Ni(DDDT)_2^-$. This predicts that the dianionic stability of NiL_2^- decreases in the order $Ni(PDDT)_2^- > Ni(BDDT)_2^- > Ni(DDDT)_2^-$ in agreement with the cyclovoltametry results.

For the copper complexes of $DDDT^{2-}$, $PDDT^{2-}$, and $BDDT^{2-}$, we find a dianionic stability order of $Cu(DDDT)_2^- > Cu(PDDT)_2^- > Cu(BDDT)_2^-$ based on the cyclic voltammetry. In the case of the CuL_2^- complexes, the acceptor levels are given by the LUMO's. Table 2 shows that the LUMO's of CuL_2^- increase in the order $Cu(DDDT)_2^- < Cu(BDDT)_2^- < Cu(PDDT)_2^-$. This predicts the dianionic stability order of $Cu(DDDT)_2^- > Cu(BDDT)_2^- > Cu(PDDT)_2^-$ in agreement with the cyclovoltametry results.

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616 *Bull. Korean Chem. Soc.* **1996**, Vol. 17, No. 7

Tai Jong Kang et al.

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Transfer of Electronic Excitation Energy in Polystyrene Films Doped with an Intramolecular Proton Transfer Compound

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The transfer of excitation energy from solvent to solute in polystyrene films doped with 2-(2'-hydroxyphenyl)benzothiazole (HBT) which undergoes intramolecular proton transfer in excited electronic state has been studied by employing steady state and time-resolved fluorescence measurements. The degree of Förster overlap between donor and acceptor molecule in this system is estimated to be moderate. Energy transfer efficiency increases with solute concentration at low concentration range and levels off at high concentration. It is observed that the excimer form of polystyrene is largely involved in energy transfer process. Photostability of HBT in polystyrene to UV light is also investigated to get insight into the long wavelength absorption band of HBT which was observed upon electron radiation.

Introduction

Excitation energy transfer is a ubiquitous phenomenon found in many disciplines of chemistry, physics and biology. Excited state reactions, photosynthesis, protein and membrane dynamics proceed *via* a series of excitation energy transfer. Excitation transfer in dye aggregates, biological macromolecules and ordered systems such as molecular and liquid crystals, is an interesting subject in the sense that the excitation transfer pathway could be controlled.[1] Studies on excitation energy transfer have been simply pursued by fluorescence spectroscopy in many cases.[2]

Photoexcitation of an organic molecule normally results in light emission as fluorescence. The fluorescence radiation has been referred to a variety of different terms such as photoluminescence, electroluminescence, chemiluminescence and radioluminescence (scintillation), etc. depending on the mode of excitation. It is common that very similar fluorescence spectra have been observed regardless of the mode of excitation. For example, electroluminescence is very similar to photoluminescence in some molecules, which suggests the same excited state should be responsible for the fluorescence.[3] It is also noted for a large number of organic molecules in condensed phase that fluorescence is usually observed