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Triarylmethane dye-conjugated hexanuclear zinc complexes: Photophysical properties and cyanide anion-binding behavior

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ABSTRACT

Hexanuclear zinc complexes conjugated with a triarylmethane (TAM) dye were prepared by chemically oxidizing the corresponding leuco-form complexes. The dye-form complexes exhibited an intense absorption band around 542 nm, which is typical of TAM dyes. The molecular structures of the leuco- and dye-form complexes were compared on the basis of X-ray crystal structure data. Adding a stoichiometric amount of cyanide anion to a solution of one of the dye-form complexes resulted in discoloration, suggesting the formation of a leuconitrile. Halide anions showed similar discoloration activity, but the stoichiometry was not simple for Cl^-, Br^-, and I^-. The formation of covalent bond between cyanide anion and the dye moiety was also confirmed by cyclic voltammetry.

1. Introduction

Triarylmethane (TAM) dyes, which have three aromatic groups attached to a carbon atom, are an industrially important family of synthetic dyes [1–3]. Over the course of the last two decades, TAMs with various aryl groups, including heteroaromatic rings, have been developed [4] and used for a variety of purposes, including as indicator reagents [5,6], nonlinear optical materials [7–9], and near-infrared dyes [10,11]. TAM derivatives have also been used in supramolecular complexes [12,13], nanoscale fibers [14], self-assembled monolayers [15], and liquid crystals [16]. Combinations of TAMs with various inorganic materials can be expected to lead to new functions based on the intrinsic electronic properties of TAMs and related dyes [17–20]. However, there have been few studies on well-defined metal complexes with a TAM core.

Recently, we developed a series of hexanuclear zinc complexes conjugated with 4,4′,4″-trihydroxytriphenylmethane, the leuco form of aurin, a representative TAM dye [21,22]. As prepared, the complexes are colorless and exhibit blue photoluminescence; prolonged UV irradiation of the complexes induces a color change and a bimodal emission profile (blue and red) with orthogonal polarization planes [21]. The blue emission originates in the zinc complex moiety. Although the red emission was attributed to the dye form generated by photooxidation, we were unable to determine its structure because of the low efficiency of the photooxidation reaction. In this paper, we describe our attempt to isolate the complexes in their dye form by means of chemical oxidation. In addition, we report that the complexes had cyanide-selective anion-sensing behavior, as determined by means of spectroscopic and electrochemical characterization of the complexes.

2. Experimental

2.1. General

Zinc acetate dihydrate purchased from Koso Kagaku, and all the other chemicals purchased from Tokyo Kasei Kogyo (TCI) were used without further purification. FT-IR spectra were recorded with a JASCO FT/IR 420 transmission-type spectrometer. ^1H and ^{13}C NMR spectra were obtained with a JEOL ECS-400 spectrometer with field gradient amplifier (400 MHz for ^1H) for ca. 10 mM solution with tetramethylsilane as internal standard (0 ppm) of chemical shift.

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Solution UV–vis spectra were measured with a JASCO V-630 spectrophotometer at the ambient temperature (25 °C).

2.2. Measurements

Spectrophotometric titration was performed for 1×10^{-5} M solution of **2c** in spectrograde dichloromethane, by stepwise addition of 1×10^{-2} M solutions of tetrabutylammonium (*n*-Bu_4N^+) salts (cyanide, fluoride, chloride, bromide, iodide) in the same solvent. The spectra were recorded immediately after each addition of the salt's solution.

Solid-thin-film absorption spectra were measured for samples smeared onto glass slides at a sample thickness that yielded a maximum absorbance of about 1. Each sample was placed on the stage of an Olympus BX-51 optical microscope equipped with a UV-transmitting objective lens and an Ocean Optics USB4000 portable fiber optic spectrophotometer. Light from a xenon lamp was guided into the condenser lens through a quartz optical fiber and was focused on a selected 50-mm-diameter area of the sample. Solid-state photoluminescence spectra of crystalline samples on glass slides were measured by using the same equipment as described above. Light from a high-pressure Hg lamp (output 100 W) was guided onto the specimen plate (a band-pass filter was employed to select the 330–380 nm wavelength range), and emission with wavelengths >420 nm was detected.

Electrochemical measurements were performed by using a conventional three-electrode cell with a glassy carbon working electrode, a platinum wire electrode, and an Ag^+/Ag reference electrode. The samples were prepared as 2 mM solutions in dry dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Cyclic voltammograms were run by using a BAS 100B/W system. Solutions were purged with nitrogen gas before each run, and measured at ambient temperature (25 °C).

*2.3. Synthesis of **1d** ($[Zn_6L_{re}(OCOCH_3)_6](CF_3SO_3)_3$)*

The ligand (**1**H3) [21] of 31.2 mg (0.02 mmol) was dissolved in methanol (0.2 mL), to which methanol solution (0.4 mL) of zinc acetate dihydrate (26.3 mg, 0.12 mmol) was added. Subsequently, a methanol solution (0.45 mL) of mixture of trifluoromethanesulfonic acid (0.02 mL, 0.23 mmol) and triethyl amine (0.03 mL, 0.28 mmol) was added to the former solution, which was left for 24 h at ambient temperature to afford crystalline precipitate. The product was collected by filtration and dried under reduced pressure. Yield 42 mg (23%); colorless needles; IR(KBr): 1604 (s, $\nu_{C=O}$), 1206 (m, $\nu_{S\text{-}O}$), 1159 (m, $\nu_{S\text{-}O}$), 1031 (s, $\nu_{S\text{-}O}$), 639 (m, $\nu_{S\text{-}O}$) cm^{-1}; FAB(+) MS *m/z* not detected; Elemental Analysis Calcd for $C_{112}H_{109}F_9N_{18}O_{24}S_3Zn_6 \cdot 8H_2O$:C, 46.5; H, 4.4; N, 8.7% Found C, 46.7; H, 4.3; N, 8.4%; ^1H NMR ($CDCl_3$, 294 K): δ 2.05 (18H, s, CO_2CH_3), 3.32 (12H, br d, $ArCH_2$), 3.70–4.10 (12H, br m, $ArCH_2$), 4.51 (6H, d, $ArCH_2$), 5.04 (1H, s, Ar_3CH), 6.40 (6H, br s, $ArCH$), 6.90 (6H, br s, Py*H*), 7.00 (6H, br m, Py*H*), 7.38 (12H, d, Py*H*), 7.84 (6H, t, Py*H*), 8.26 (6H, s, Py*H*), 8.89 (6H, d, Py*H*).

*2.4. Synthesis of **2a** ($[Zn_6L_{ox}(OCOC_7H_{15})_6](PF_6)_4$)*

$[Zn_6L_{re}(OCOC_7H_{15})_6](PF_6)_3$ (**1a**) was synthesized according to the reported procedure [22] **1a** (32 mg, 0.01 mmol) was dissolved in acetone (3 mL), to which a methanolic solution (1 mL) of potassium hexafluorophosphate (1.8 mg, 0.01 mmol), and a methanol solution (2 mL) of ceric ammonium nitrate (11 mg, 0.02 mmol) was successively added. The solution was left for 24 h at ambient temperature, to afford red precipitate. To this mixture, dichloromethane was added until the precipitate was dissolved, and then left under open air, resulting in red needle crystal. Yield 22 mg (65%); red needles; IR(KBr): 2927 (m, ν_{CH3}), 2854 (m, ν_{CH2}), 1602 (s, $\nu_{C=O}$), 1443 (m), 1344 (s), 1308 (m), 1204 (m), 1043 (m), 844 (s, $\nu_{P\text{-}F}$), 768 (m), 557 (m, $\nu_{F\text{-}P\text{-}F}$) cm^{-1}; FAB(+) MS *m/z* not detected; Elemental Analysis Calcd for $C_{145}H_{180}F_{24}N_{18}O_{15}P_4Zn_6 \cdot 3(C_2H_6CO)$: C, 51.9; H, 5.6; N, 7.1% Found C, 52.3; H, 5.3; N, 7.1%; ^1H NMR(acetone-d_6, 298 K): δ 0.92 (18H, t, *J* = 7 Hz, $CO_2C_6H_{12}CH_3$), 1.1–1.6 (60H, m, $CO_2CH_2C_5H_{10}CH_3$), 2.41 (12H, t, *J* = 7, $C_6H_{13}CH_2CO_2$), 3.34 (6H, d, *J* = 12, $ArCH_2$), 3.62 (6H, d, *J* = 17, $ArCH_2$), 3.97 (6H, d, *J* = 18, $ArCH_2$), 4.26 (6H, d, *J* = 12, $ArCH_2$), 4.46 (6H, d, *J* = 15, $ArCH_2$), 4.64 (6H, d, *J* = 15, $ArCH_2$), 6.41 (6H, s, Ar*H*), 7.43 (6H, br s, Py*H*), 7.62 (6H, t, *J* = 6, Py*H*), 7.68 (6H, d, *J* = 8, Py*H*), 7.83 (6H, t, *J* = 7, Py*H*), 8.11 (6H, t, *J* = 9, Py*H*), 8.48 (6H, br d, *J* = 6, Py*H*), 8.92 (6H, d, *J* = 4, Py*H*);^{13}C NMR ($CDCl_3$) not detected.

2.5. Synthesis of $[Zn_6L_{ox}(OCOC_9H_{19})_6](PF_6)_4$

$[Zn_6\mathbf{1}(OCOC_9H_{19})_6](PF_6)_3$ (**1b**) was synthesized according to the reported procedure [22]. **1b** (34 mg, 0.01 mmol) was dissolved in acetone (3 mL), to which a methanolic solution (2 mL) of potassium hexafluorophosphate (1.8 mg, 0.01 mmol), and a methanol solution (2 mL) of ceric ammonium nitrate (11 mg, 0.02 mmol) was successively added. The solution was left for 24 h at ambient temperature, resulting in a turbid suspension. The suspensoid was removed by filtration with continuous washing with methanol, and the filtrate was left under open air to afford red amorphous solid. The solid was collected and recrystallized from dichloromethane, to afford red needle crystal. Yield 21 mg (58%); red needles; IR(KBr): 2925 (m, ν_{CH3}), 2853 (m, ν_{CH2}), 1603 (s, $\nu_{C=O}$), 1444 (m), 1344 (s), 1308 (m), 1204 (m), 1043 (m), 844 (s, $\nu_{P\text{-}F}$), 768 (m), 557 (m, $\nu_{F\text{-}P\text{-}F}$) cm^{-1}; FAB(+) MS *m/z* not detected; Elemental Analysis Calcd for $C_{157}H_{204}F_{24}N_{18}O_{15}P_4Zn_6 \cdot 4(C_2H_6CO)$: C, 53.6; H, 6.1; N, 6.7% Found C, 54.0; H, 5.8; N, 6.5%; ^1H NMR (acetone-d_6, 298 K): δ 0.91 (18H, t, *J* = 7 Hz, $CO_2C_8H_{16}CH_3$), 1.1–1.6 (84H, m, $CO_2CH_2C_7H_{14}CH_3$), 2.41 (12H, t, *J* = 7, $C_8H_{17}CH_2CO_2$), 3.33 (6H, d, *J* = 10, $ArCH_2$), 3.58 (6H, d, *J* = 16, $ArCH_2$), 4.05 (6H, d, *J* = 16, $ArCH_2$), 4.24 (6H, d, *J* = 11, $ArCH_2$), 4.44 (6H, d, *J* = 15, $ArCH_2$), 4.69 (6H, d, *J* = 15, $ArCH_2$), 6.42 (6H, s, Ar*H*), 7.41 (6H, br s, Py*H*), 7.62 (6H, t, *J* = 7, Py*H*), 7.69 (6H, d, *J* = 8, Py*H*), 7.84 (6H, d, *J* = 15, Py*H*), 8.11 (6H, t, *J* = 8, Py*H*), 8.47 (6H, br s, Py*H*), 8.93 (6H, d, *J* = 5, Py*H*); ^{13}C NMR ($CDCl_3$) not detected.

*2.6. Synthesis of **2c** ($[Zn_6L_{ox}(OCOCH(C_6H_{13})C_8H_{17})_6](PF_6)_4$)*

$[Zn_6L_{re}(OCOCH(C_6H_{13})C_8H_{17})_6]$ $(PF_6)_3$ (**1c**) was synthesized according to the reported procedure [22]. **1c** (196 mg, 0.05 mmol) was dissolved in acetone (10 mL), to which an acetonic solution (10 mL) of potassium hexafluorophosphate (9 mg, 0.05 mmol), and an acetone solution (10 mL) of ceric ammonium nitrate (55 mg, 0.10 mmol) was successively added. This solution was left for 24 h at ambient temperature under open air, resulting in red needle crystal. Yield 145 mg (71%); red needles; IR(KBr): 2927 (s, ν_{CH3}), 2854 (s, ν_{CH2}), 1599 (s, $\nu_{C=O}$), 1444 (m), 1346 (s), 1309 (m), 1204 (m), 1042 (m), 845 (s, $\nu_{P\text{-}F}$), 766 (m), 558 (m, $\nu_{F\text{-}P\text{-}F}$) cm^{-1}; FAB(+) MS *m/z* not detected; Elemental Analysis Calcd for $C_{193}H_{280}F_{24}N_{18}O_{17}P_4Zn_6 \cdot 2H_2O$: C, 56.6; H, 6.9; N, 6.2% Found C, 56.5; H, 6.7; N, 6.4%; ^1H NMR (acetone-d_6, 298 K): δ 0.94 (36H, m, $CO_2CH(C_5H_{12}CH_3)C_7H_{15}CH_3$), 1.1–1.7 (144H, m, $CO_2CH(C_5H_{12}CH_3)$ $C_7H_{15}CH_3$), 2.42 (6H, br s, $C_8H_{17}(C_6H_{13})CHCO_2$), 3.31 (6H, br s, $ArCH_2$), 3.60 (6H, br s, $ArCH_2$), 4.04 (6H, br s, $ArCH_2$), 4.22 (6H, br s, $ArCH_2$), 4.47 (6H, d, *J* = 15 Hz, $ArCH_2$), 4.64 (6H, br s, $ArCH_2$), 6.36 (6H, br s, Ar*H*), 7.37 (6H, br s, Py*H*), 7.62 (6H, t, *J* = 6, Py*H*), 7.70 (6H,