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Synthesis and properties of multi-nuclear ruthenium (II) complexes of bis(2,2'-bibenzimidazole)

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Abstract

Conjugated metallopolymers in which metal sites are in electronic communication through a conjugated organic backbone have been attracting growing interest. Bis(2,2'-bibenzimidazole) has been prepared as the conjugated backbone. The multinuclear Ru complexes were synthesized by the complexation of the conjugated bis(2,2'-bibenzimidazole) with $Ru(bpy)_2Cl_2$. The deprotonation form of the dinuclear Ru complexes may show enhanced electron transport ability between metal centers through the conjugated bibenzimidazole backbones. Deprotonation also allows the synthesis of tetranuclear Ru complexes. The preparations, spectroscopic and electrochemical properties of these multinuclear Ru complexes were investigated.

Keywords: Heterocycle synthesis, Organic semiconductors based on conjugated molecules, UV-Vis-NIR absorption, Electrochemical methods.

1. Introduction

Current interest in the design of materials for applications in molecular electronics has focused in large part on the identification of molecules having spatially remote, redox-active centers in good electronic communication [1-5]. Within the past few years, many conjugated linear oligomers and polymers containing bound redox-active metal ions have been prepared and investigated. The most studied systems contain ruthenium (II) bipyridine segments in their backbone structures owing to the known photophysics and redox properties of these groups. In these one-dimensional systems, photoconductivity (excited state electron transport) of the conjugated polymer was shown to be strongly enhanced by metal complexation owing to metal-ligand charge transfer (MLCT) interactions [6].

It has been demonstrated that polybenzimidazoles are attractive choices for the synthesis of conjugated metallopolymers for a number of reasons. They tend to be very robust, remaining stable under considerable thermal and chemical stress. Studies of binuclear benzimidazole complexes have shown that they possess notable electronic coupling between two metals [7]. In addition, removal of the imidazole proton allows pH control of the electron density along the polymer backbone. It is also known that the redox potential of the ruthenium (II) complexes containing 2,2'-bibenzimidazole ($BiBzImH_2$) and the related ligands can be tuned by deprotonation [8]. Our current interest is focused on synthesizing a series of metal complexed π conjugated polymer based on bibenzimidazoles and exploring their optical and electronic properties. Here we report the synthesis and properties of bis(2,2'-bibenzimidazole) and the related ruthenium complexes.

2. Experimental

2.1 Reagents and materials

All reagents were used without further purification. 1,2-Phenylenediamine (98%), 3,3'-diaminobenzidine (99%), methyl 2,2,2-trichloroacetimidate (98%) and ammonium hexafluorophosphate (95+%) were purchased from Aldrich. Acetonitrile was distilled over CaH_2 before use.

2.2 Measurement

NMR spectra were obtained on a JEOL Eclipse+ 500 MHz spectrometer. UV-Vis spectra were obtained using a Varian Cary 500 UV-Vis-NIR spectrophotometer. Elemental analysis was performed by Quantitative Technologies Inc. (QTI). Mass analysis was performed by Scripps Research

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Institute (ESI-MS spectra were obtained on a Waters-Micromass LCT mass spectrometer; MALDI-TOF spectra were obtained on Applied Biosystems Voyager-STR Mass spectrometer). Cyclic Voltammogram experiments were performed at 20 °C using a PC-controlled potentiostat (CH Instruments, electroanalytical analyzer). The working electrode was a 1.5 mm glassy carbon electrode and the auxiliary electrode was a platinum wire. The reference electrode was a no leak Ag/AgCl reference electrode. They were purchased from Cypress Systems, Inc.

2.3 Synthesis

The synthesis of the 2,2'-bibenzimidazole ($BiBzImH_2$) [9], $Ru(bpy)_2Cl_2{\cdot}2H_2O$ [10], 2-trichloromethylbenzimidazole [9], $[Ru(bpy)_2(BiBzImH_2)](PF_6)_2$ [8], $[Ru(bpy)_2(BiBzIm)]$ [8], and $[(Ru(bpy)_2)_2(BiBzIm)](PF_6)_2$ [11] followed previously published procedures.

Bis(2,2'-bibenzimidazole)·$1.5H_2O$ (**5**). To a suspension of 3,3'-diaminobenzidine (**4**) (1.24 g, 5.8 mmol), 2-trichloro-methylbenzimidazole (**3**) (3.00 g, 12.7 mmol) and absolute ethanol (50 mL), triethylamine (5.86 g, 58 mmol) was added dropwise. The suspension was stirred at room temperature for 12 hrs and then refluxed under nitrogen for 36 hrs. The precipitated bis(2,2'-bibenzimidazole) ([Bis-($BiBzImH_2$)]) was washed with hot glacial acetic acid and filtered to collect the solid. Then it was stirred in diluted ammonium hydroxide solution to neutralize the acid residue. The final product was yellow powder. Yield 70%. ^{1}H NMR (500 MHz, CF_3COOD): δ = 8.43 (s, 2H), 8.29 (d, J = 8.8 Hz, 2H), 8.26 (d, J = 8.8 Hz, 2H), 8.12 (dd, J = 6.6, 3.3 Hz, 4H), 7.94 (dd, J = 6.6, 3.3 Hz, 4H); ^{13}C NMR (125 MHz, CF_3COOD): δ = 144.0, 135.3, 134.8, 134.3, 134.1, 133.7, 132.5, 132.3, 118.2, 117.0, 116.1. ESI-MS (m/z): 467.2 $[M+H]^+$. Anal. Calcd for $C_{28}H_{18}N_8{\cdot}1.5H_2O$: C, 68.14; H, 4.29; N, 22.71. Found: C, 67.60; H, 3.79; N, 22.27.

$[(Ru(bpy)_2)_2(Bis(BiBzImH_2))](PF_6)_4{\cdot}H_2O$ (**10**). Bis(BiBz-ImH_2) (**5**) (0.30 g, 0.64 mmol) was suspended in 80 mL of ethylene glycol. The mixture was degassed for 30 min under nitrogen, then heated at 120 °C for 3 hrs to dissolve Bis($BiBzImH_2$). $Ru(bpy)_2Cl_2{\cdot}2H_2O$ (0.74 g, 1.42 mmol) was added to the above mixture and heated at 150 °C for 16 hrs. The resulting deep brownish red solution was cooled, diluted with water and filtered to remove the insoluble part. HCl (6 M, 8 mL) was added dropwise to adjust to pH = 2. Then saturated NH_4PF_6 aqueous solution was added dropwise to precipitate the complex. The crude product was directly used in the next deprotonation step without further purification. The pure product was obtained by protonation of the pure deprotonated complex **11** using HCl (6M), then reprecipitation with NH_4PF_6. MALDI-TOF: 1291 $[(M-4HPF_6)+H]^+$. Anal. Calcd for $C_{68}H_{50}F_{24}N_{16}P_4Ru_2{\cdot}H_2O$: C, 43.18; H, 2.77; N, 11.85. Found: C, 43.12; H, 2.70; N, 11.68.

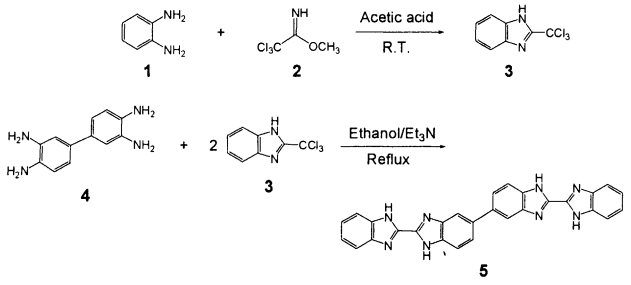
$[(Ru(bpy)_2)_2(Bis(BiBzIm))]$ (**11**). The crude $[(Ru(bpy)_2)_2$-$(Bis(BiBzImH_2))](PF_6)_4$ (**10**) (0.44 g, 0.23 mmol) was added to 50 mL of methanol and the suspension was degassed for 20 min under nitrogen. $NaOCH_3$ (0.20 g, 3.76 mmol) was added to the above mixture. The color of the solution turned from deep brownish red to purple. The solution was refluxed for 5 hrs under nitrogen and then cooled down. The solvent was condensed to a half volume by rotary evaporation. The solid product was collected by filtration and purified by washing with acetone. This complex **11** is not stable in the air, so the purification process and storage should be under nitrogen.

$[(Ru(bpy)_2)_4(Bis(BiBzIm))](PF_6)_4{\cdot}4H_2O$ (**12**). $[(Ru(bpy)_2)_2$-$(Bis(BiBzIm))]$ (**11**) (0.15 g, 0.12 mmol) and $Ru(bpy)_2Cl_2{\cdot}2H_2O$ (0.13 g, 0.26 mmol) were added to ethanol/water (1:1 v/v, 24 mL). The mixture was degassed for 30 min and then refluxed under nitrogen for 18 hrs. The resulting deep brownish red solution was cooled and filtered to remove the insoluble part. Ethanol was removed by rotary evaporation. Then saturated NH_4PF_6 aqueous solution was added dropwise to precipitate the complex. The solid was collected by filtration (approximately 250 mg). Half of the crude product (125 mg) was dissolved in a minimum amount of acetonitrile, and chromatographed over a neutral alumina column (21 cm in length, 17 mm in diameter). The first deep red long band was collected. The eluate was concentrated to around 25 mL by rotary evaporation and then ether was added dropwise to precipitate the desired complex (overall yield 68%). MALDI-TOF: 2551 $[M-1PF_6]^+$, 2406 $[M-2PF_6]^+$, 2261 $[M-3PF_6]^+$, 2116 $[M-4PF_6]^+$. Anal. Calcd for $C_{108}H_{78}F_{24}N_{24}P_4Ru_4{\cdot}4H_2O$: C, 46.86; H, 3.13; N, 12.14. Found: C, 46.37; H, 2.70; N, 11.85.

3. Results and Discussion

3.1 Preparation of the Bis(2,2'-bibenzimidazole)

Holan and coworkers [9] have reported in 1967 that biben-zimidazole can be easily synthesized by the condensation of *o*-phenylenediamine (**1**) with methyl 2,2,2-trichloroaceti-



Scheme 1 Synthesis of Bis(2,2'-bibenzimidazole) **5**

midate (**2**) in methanol. This efficient condensation reaction has been extended to our synthesis of Bis-($BiBzImH_2$) (**5**). 2-Trichloromethylbenzimidazole (**3**) was prepared by