Well-defined Polynuclear Iron(II) Complexes Bridged by Back-to-back Ligands

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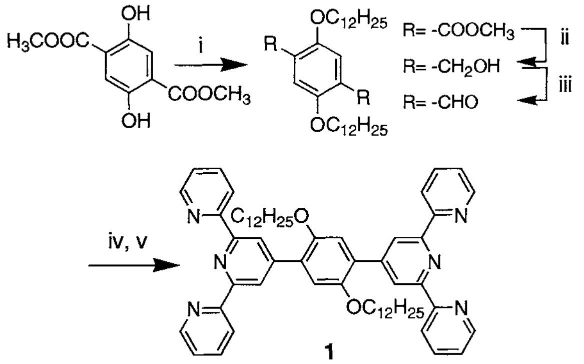
Novel linear high-molecular-weight polynuclear iron (II) complex has been synthesized using a new bridging ligand in which two 2, 2': 6', 2"-terpyridine have connected by a 1, 4-pheneylene spacer having long alkyl chains.

Great attention has been paid to the design and synthesis of oligo and polynuclear metal complexes composed of transition metals and bridging ligands.[1] Controlling the distance and angle within the bridging ligands has enabled spontaneous assemblies of well-defined metallosupramolecular structures through the formation of coordination bonds. The use of 2, 2': 6', 2"-terpyridine (tpy) ligands are convenient for the construction of metallosupramolecular structures.[2] Sauvage et al. have reported directional energy and/or electron transfer in heterodinuclear complexes connected by 1, 4-phenylene spacers.[3] Herein, we describe the synthesis and characterization of highly-soluble dinuclear and polynuclear iron (II) complexes using a novel bridging ligand possessing long alkyl chains. The long alkyl chains in **1** may improve the solubility of polynuclear metal complexes.

New bridging ligand **1** was prepared according to Scheme 1. 2,5-Bis(dodecyloxy)-benzene-1, 4-dialdehyde was prepared from dimethyl-2, 5-dihydroxyterephthalate as a starting material. The bridging ligand **1** was synthesized in an overall yield of 20% from dialdehyde and 1-(2-pyridylcarbonylmethyl)-pyridinium iodide. The purification of **1** was achieved by column chromatography and spectroscopic data were consistent with the proposed structure.[4]

It is well-known that the tpy ligands possess an excellent ability to coordinate metal ions and afford a bistridentate type of octahedral bis(terpyridyl)metal complexes.[5] We selected Fe^{2+} as the metal ion for assembling of bridging ligands because of its formation of thermodynamically stable complexes with tpy. To investigate the possibility of assembly between **1** and Fe^{2+}, the absorption spectra were monitored for varying concentration of Fe^{2+} in $CHCl_3$-methanol solution (1:1 v/v) (Figure 1 A). The spectrum of **1** changed by the addition of Fe^{2+} and a metal-to-ligand charge transfer (MLCT) transition band appeared.[6] The maximum absorbance at the MLCT band was observed to be approximately equal to the bridging ligand concentration (Figure 1B). Furthermore, λ_{max} of the MLCT band was red-shift with increasing of Fe^{2+} concentration. This result shows that the coordination of Fe^{2+} with **1** undergoes stoichiometrically and the bridging ligand **1** is assembled to a linear polynuclear complex.



Scheme 1. Reatgents and conditions: i, $C_{12}H_{25}Br$, Na, EtOH, reflux, 24 h, 47%; ii, $LiAlH_4$, dry ether, 90%; iii, PCC, CH_2Cl_2, 95%; iv, 2-acethylpyridine, KOH, MeOH; v, 1-(2-pyridylcarbonylmethyl)pyridinum iodide, NH_4OAc, MeOH, reflux, 24 h, 23%.

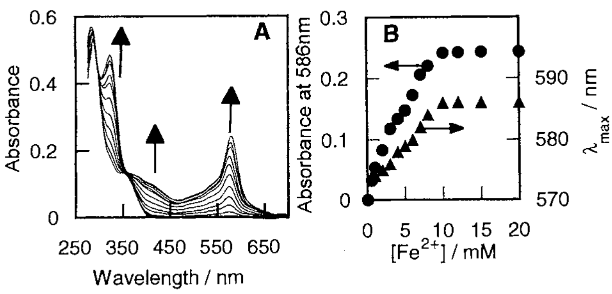
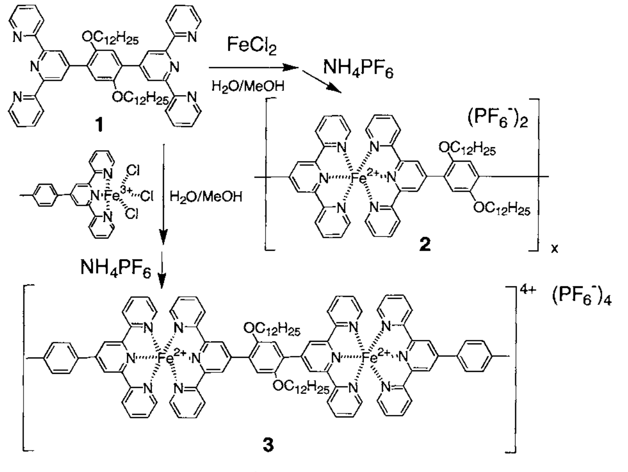


Figure 1. (A) Effect of Fe^{2+} concentration on the absorption spectrum of **1** (10 mM) in $CHCl_3$/MeOH: $[Fe^{2+}]$ = 0, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 10.0 mM. (B) Absorbance and λ_{max} change with increasing of Fe^{2+} concentration.

The bridging ligand **1** reacted with exact equimolar amount $FeCl_2$ in water-methanol (1:1 v/v) solution to give a purple solution. Subsequently, polynuclear complex **2** was precipitated by the addition of $[NH_4][PF_6]$. Exhaustive extraction with methanol to remove low-molecular-weight oligomers, followed by fraction precipitation from acetone and methanol, afford an 89% yield (Scheme 2). Polynuclear complex **2** was soluble in acetonitrile, acetone, and DMF. Dinuclear complex **3** was also prepared from 4'-(*p*-tolyl)-2, 2': 6', 2" – terpyridyliron (III) trichloride[7] and **1**.[8] The degree of polymerization was determined by gel permeation chromatography (GPC), ^{1}H NMR,



Scheme 2.

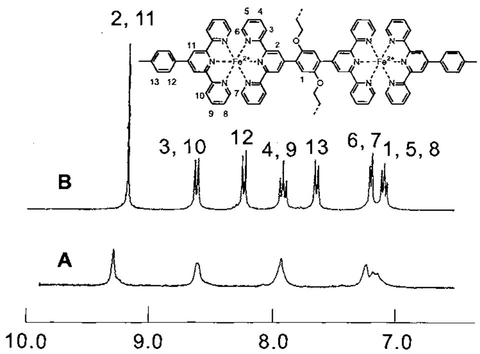


Figure 2. ^1H NMR at 400 MHz in CD_3CN (aromatic region) of (A) **2** and (B) **3**.

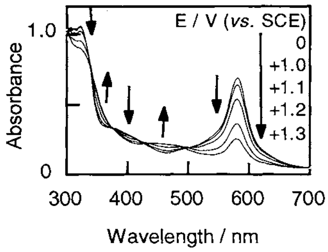


Figure 3. Spectroelectrochemical analysis of **2** film on an ITO electrode in KPF_6 aqueous solution.

and solution viscosity studies. The molecular weight of **2** was estimated to be 1.01×10^5 g/mol by GPC analysis (0.01 M NH_4PF_6/DMF, polystyrene standard). Figure 2 shows ^1H NMR spectra of **2** and **3** in CD_3CN. The observed ^1H NMR signals for **2** can be assigned to bis(terpyridyl) iron(II) complex, and the spectra of **2** did not contain any peaks of the iron-free ligands as end groups. The intrinsic viscosity [η] of **2** was 2.59 in 0.01 M NH_4PF_6/acetonitrile at 25 °C. ^1H NMR and viscosity studies of **2** also implied a high degree of polymerization.[9] The matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-Ms) gave only the fragment $[Fe(\mathbf{1})_2](PF_6)_2$, in which no peak corresponding to the oligonuclear complex was detected.

The polynuclear complex **2** exhibits a substantial red-shift of the MLCT band relative to that of **3** (**2**: λ_{max}=586 nm, **3**: λ_{max}=568 nm).[6] Cyclic voltammetry was carried out in degassed acetonitrile solution containing $[Bu_4N][PF_6]$ as the supporting electrolyte at a platinum working electrode. The dinuclear complex **3** shows one reversible oxidation – reduction couple at $E_{1/2}$ = +0.99V (*vs.* SCE), which is assign to metal centered $Fe^{II/III}$ couple. On the other hand, the oxidation potential of the iron centers in **2** ($E_{1/2}$ = 1.04 V) is slightly higher than that of the dinuclear complex **3** and the redox peaks are broadened. This red-shift of the MLCT band and electrochemical results suggest the electronic interaction among iron centers in the polynuclear complex **2**.[10]

A solid film of **2**, formed by evaporating **2** solution onto indium/tin oxide (ITO) glass electrode, exhibited reversible color change in 0.1 M KPF_6 aqueous solution (Figure 3). The film of **2** overlaid on the electrode was stable in aqueous solution. The film shows a well-defined reversible oxidation – reduction couple at +1.05 V. Both currents for oxidation and reduction peaks are roughly proportional to the potential scan rate, indicating that the electrode supported with an electroactive film. The film displays the MLCT band at 586 nm at +0 V. As the polynuclear complex was oxidized, the absorbance at the MLCT band decreases above +1.00 V and a new absorption band appeared at 465 nm. This absorbance change results in the oxidation of Fe^{II} to Fe^{III}. The color of the coated electrode with **2** changed from purple to pale yellow according to the oxidation of iron centers in **2**.

In conclusion, we have demonstrated the spontaneous assembly of the high-molecular-weight linear polynuclear metal complex by using the new bridging ligand **1**. The introduction of long alkyl chains into the bridging ligand resulted in a high degree of polymerization. The solubility and steric control of bridging ligands are the important factors for the constructions of high-molecular-weight polynuclear complexes. The absorption and electrochemical studies of **2** indicated an electronic interaction among iron centers through the 1, 4-phenylene-bridged ligand.

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4 **1**: Pale-yellow needle. mp 153 °C. ^1H-NMR ($CDCl_3$): δ = 8.62-8.75 (m, 8H, pyridine), 7.86 (m, 4H, pyridine), 7.36 (d, 4H, pyridine, *J* = 8.1 Hz), 7.23 (s, 2H, Ph), 4.03 (br, 4H, $-OCH_2(CH_2)_{10}CH_3$), 1.20-1.90 (m, 40H, $-OCH_2(CH_2)_{10}CH_3$), 0.86 (s, 6H, $-OCH_2(CH_2)_{10}CH_3$). Anal. Calcd for $C_{60}H_{72}O_2N_6$: C, 79.3; H, 8.0; N, 9.2 %. Found: C, 79.1; H, 8.0; N, 9.2 %.

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8 **3**: Yield 90%. ES-MS: *m/z* = 2102.0 [M-PF_6 (calc. 2101.62)]. ^1H-NMR (CD_3CN): δ = 9.17(s, 8H, pyridine), 8.60(d, 8H, pyridine, *J* = 8.1 Hz), 8.22 (d, 4H, Ph, *J* = 8.2 Hz), 7.92 (d, d, d, 8H, pyridine, *J* = 1.3, 1.5, and 1.3 Hz), 7.63 (d, 4H, Ph, *J* = 7.9 Hz), 7.19 (d, 8H, pyridine, *J* = 4.8 Hz), 7.06-7.10 (10H, pyridine and Ph), 4.03 (br, 4H, $-OCH_2(CH_2)_{10}CH_3$), 2.57 (s, 6H, CH_3), 1.30-2.18 (m, 40H, $-OCH_2(CH_2)_{10}CH_3$), 0.86 (s, 6H, $-OCH_2(CH_2)_{10}CH_3$); Anal. Calcd for $C_{104}H_{106}O_2N_{12}Fe_2P_4F_{24}$: C, 55.6; H, 4.8; N, 7.5 %. Found: C, 55.2; H, 4.5; N, 7.8 %.

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