



Synthesis and characterization of d^{10} metal complexes of 3-Me-5-FcPz: Structural, theoretical and third order nonlinear optical properties



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ABSTRACT

The d^{10} metal complexes based on 3-methyl-5-ferrocenyl-1H-pyrazole (**L** = 3-Me-5-FcPz) ligand $[M(L)_4(NO_3)_2]$ Zn=(**1**) and Cd=(**2**), $[Hg(L)_4(NO_3)_2].dmf$ (**3**) have been synthesized and characterized by FT-IR, NMR, UV–Vis and elemental analysis. The molecular structure of compound **2** and its crystal packing were determined by single crystal X-ray diffraction. The nitrate anions are also involved in intermolecular hydrogen bonding with adjacent ferrocene units and it forms zig-zag one-dimensional polymeric structure. UV–Vis investigations on the positive solvatochromic behavior of **1–3** revealed that the solvation of the push–pull character increases with increasing polarity. The third-order nonlinear optical (NLO) properties of **1–3** have been determined by Z-scan technique and the results indicate that compounds **1–3** exhibits the strong self-defocusing effect. The nonlinear susceptibility $\chi^{(3)}$ values are calculated in the order of 10^{-6} esu.

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1. Introduction

Materials with nonlinear optical (NLO) responses have a promising future in the optical field. They can be used in the fields of telecommunications, lasers, processing optical information and optical transferring, etc [1,2]. Whereas organic compounds have most attention, molecules containing transition metals are also of considerable interest due to definitive advantages such as tenability of the polarizability by changing the oxidation state of the metal atoms or by varying the ligands [3]. Recent interest has been generated by studying organometallic and inorganic compounds [4,5]. Complexes of the popular group 8 metals such as iron and ruthenium provide wide spectrum for optical investigations [6,7]. Modern research based on ferrocenyl conjugated system offers the possibility of electronic communication between terminal sub-units, which is further being of particular interest in nonlinear optics [8]. Also, the ferrocenyl group is an excellent π -donor

system, it can donate electron in the push-pull fashion. In fact, ferrocenyl group and transition metal ions are responsible for the excellent NLO behavior of their corresponding compounds. Therefore, ferrocene containing transition metal coordination compounds may exhibit stronger NLO effects [8]. NLO chromophores most often have simple dipolar, octupolar (T_d , D_{2d}) and guanidinium type (D_{3h} , D_3) electronic structures, whereas very little about octahedral (D_{4h}) symmetric metal complexes are known in the literature [9,10]. Miller et al. reported pyrazole N-arylated molecules with large second harmonic NLO activity ($\beta = 31.4 \times 10^{30}$ esu) [11]. Pyrazole-containing ferrocenyl complexes consist of two parts: which is ferrocenyl ligands and metal ions. Both parts possibly will make an important contribution to the optical nonlinearity of ferrocenyl complexes. Mochida et al. have demonstrated supramolecular aggregation of 5-ferrocenylpyrazole based late transition metal complexes [12]. Based on ferrocenyl heterocycles, Hou and co-workers have studied some novel third-order NLO active ferrocenyl d^{10} complexes $[Zn(4-PFA)_2(NO_3)_2](H_2O)$ ($\gamma = 2.46 \times 10^{-28}$ esu), $[Hg_2(OAc)_4(4-BPFA)_2](CH_3OH)$ ($\gamma = 3.12 \times 10^{-28}$ esu) and $[Cd_2(OAc)_4(4-BPFA)_2]$ ($\gamma = 3.10 \times 10^{-28}$ esu),

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[4-PFA = (4-pyridylamino)carbonyl]ferrocene and 4-BPFA = 1,1'-bis[(4-pyridylamino)carbonyl]ferrocene with consisting of hydrogen bonds N – H...O and O – H...O forming one-dimensional chains [13]. Recently Meyer et al. described the coordination chemistry of a ferrocene unit decorated with one pyrazolyl unit on each ring, which copper(I) and silver(I) generates a structural motif, the ferrocene units act as the linker between two triangular metal environments with bridging pyrazole moieties [14]. Quite surprisingly, the well-established chemistry of pyrazole and ferrocene, only a few reports about 3-methyl-5-ferrocenyl-1H-pyrazole have appeared in the literature, and its potential to serve as a ligand toward d^{10} /group 12 metal ions seems unexplored so far [15].

Based on the above consideration, we have currently involved in the search of new potential third-order NLO materials with d^{10} transition metal complexes which possess donor and acceptor moieties distributed in octahedral (D_4h) complex system (Fig. S1). In this manuscript, we report the synthesis, spectroscopic characterization, electrochemical and linear optical properties of ferrocenylpyrazole based d^{10} metal complexes $[M(L)_4(NO_3)_2]$ $M = Zn(1)$ and $Cd(2)$, $[Hg(L)_4(NO_3)_2].DMF(3)$ as given in Scheme 1. In addition, the values of the nonlinear susceptibility, $\chi^{(3)}$ are obtained by the Z-scan technique.

2. Experimental section

2.1. Instruments and methods

All starting materials and products were found to be stable in moisture and air, and hence no specific precautions were taken to rigorously exclude air during the manipulation. Commercially available starting materials, Ferrocene (Sigma-Aldrich), Zinc nitrate (S.D.Fine), Cadmium nitrate (S.D.Fine), Mercuric nitrate (S.D.Fine) were used as received. Elemental analyses were performed on a Perkin-Elmer 2400 Series Elemental Analyzer. Infrared spectra were recorded on a Perkin Shimadzu spectrometer spectrum One as KBr diluted discs. UV–Visible spectra were recorded using JASCO UV–Vis NIR with methanol as solvent. 3-methyl-5-ferrocenyl-1H-pyrazole (3-Me-5-FcPz = L) were prepared and purified by literature procedures [16].

2.2. Preparation of $[Zn(L)_4(NO_3)_2]$ (1)

Methanol solution (10 mL) of L (133 mg, 0.5 mmol) was added to a methanol solution of $Zn(NO_3)_2 \cdot 6H_2O$ (74 mg, 0.25 mmol). The reaction mixture was stirred for 1 h and left to stand at room

temperature. Dark orange plate crystals were formed in a week. (47% yield). mp. 181 °C. Anal. Calc. For $C_{56}H_{56}Fe_4N_{10}O_6Zn$: C, 53.64; H, 4.50; N, 11.17. Found: C, 53.95; H, 4.18; N, 11.09; IR (KBr disc, cm^{-1}): 3523 m, 3230 m, 3107 m, 3045 m, 2927 m, 1600 s, 1496 s, 1450 s, 1384 s, 1292 s, 1217 s, 1169 s, 1105 s, 1053 s, 1001 s, 972 m, 827 s, 707 m, 684 m; 1H NMR (400 MHz, $CDCl_3$) δ 6.10 (s, 1H, pz), 4.66 (s, 2H, -Cp), 4.33 (s, 2H, -Cp), 4.10 (s, 5H, -Cp), 2.27 (s, 3H, -CH₃) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 103.20 (s), 77.34 (s), 77.02 (s), 76.70 (s), 72.58 (s), 69.82 (s), 69.47 (s), 66.91 (s), 12.48 (s) ppm; UV–Vis (CH_3CN , nm): 208, 228(s), 275, 342(s), 447.

2.3. Preparation of $[Cd(L)_4(NO_3)_2]$ (2)

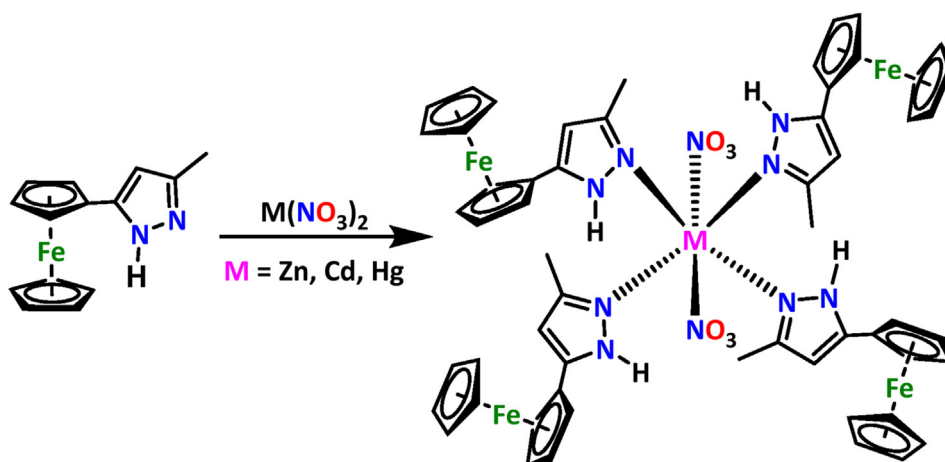
Compound 2 was prepared in a manner analogous to that used to prepare compound 1. The reaction of $Cd(NO_3)_2 \cdot 2H_2O$ (59 mg, 0.25 mmol) with L gave 2 as red-orange single crystals. Crystals 2 is stable in air. (52% yield). mp. 178–179 °C. Anal. Calc. For $C_{56}H_{56}CdFe_4N_{10}O_6$: C, 51.70; H, 4.34; N, 10.77. Found: C, 52.11; H, 4.38; N, 10.70%. IR (KBr disc, cm^{-1}): 3562 m, 3282 m, 3082 m, 2924 m, 2858 m, 1597 s, 1489 m, 1436 s, 1384 s, 1294 s, 1280 s, 1203 s, 1151 s, 1103 s, 1035 m, 999 s, 873 s, 819 s, 704 m, 505 s; 1H NMR (400 MHz, $CDCl_3$) δ 6.13 (s, 1H, -pz), 4.60 (s, 2H, -Cp), 4.27 (s, 2H, -Cp), 4.08 (s, 5H, -Cp), 2.33 (s, 3H, -CH₃) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 103.73 (s), 77.34 (s), 77.02 (s), 76.70 (s), 69.92 (s), 67.19 (s), 12.44 (s) ppm; UV–Vis (CH_3CN , nm): 209, 226(s), 277, 339(s), 448.

2.4. Preparation of $[Hg(L)_4(NO_3)_2].DMF(3)$

Methanol solution (0.5 mL) of L (133 mg, 0.5 mmol) is added to dimethylformamide (DMF) solution $Hg(NO_3)_2 \cdot 6H_2O$ (85 mg, 0.25 mmol) and stirred for 3 h. The reaction mixture was filtered off and dried under high vacuum, and then re-dissolved with methanol and DMF solvent for recrystallization. The solid product was obtained (31% yield). mp. 232–235 °C Anal. Calc. For $C_{59}H_{63}Fe_4HgN_{11}O_7$: C, 48.42; H, 4.06; N, 10.08. Found: C, 48.71; H, 4.73; N, 10.65%. IR (KBr disc, cm^{-1}): 3558 m, 3178 m, 3078 m, 3043 m, 2951 m, 2856 m, 2835 w, 1585 s, 1475 m, 1431 s, 1398 s, 1384 s, 1290 s, 1219 w, 1205 s, 1145 s, 1105 s, 1028 s, 1001 s, 875 m, 812 s, 717 m, 680 m, 515 s; UV–Vis (DMF, nm): 211, 226(s), 275, 336(s), 445.

2.5. Crystal structure determination

Crystal measurement was made on a BRUKER APEX 2 X-ray (three-circle) diffractometer coupled with a CCD area detector with graphite-monochromated with radiation type of Mo K α and the



Scheme 1. Synthesis of complexes 1–3.

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