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Synthesis, spectral, electrochemical, crystal structures and nonlinear optical properties of unsymmetrical Ni(II) and Cu(II) Schiff base complexes

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ABSTRACT

This paper explores the synthesis, spectroscopic and structural characterization, linear and nonlinear optical properties, as well as the electrochemical behavior of two series of robust neutral Ni(II)- and Cu(II)-centered organometallic macroacyclic salen-type Schiff base complexes, namely, the 5-nitrosubstituted derivatives M[Fc-C(O)CH = C(CH_3)N-*o*-C_6H_4-N = CH-(2-O,5-NO_2-C_6H_3)] (M = Ni (**2**), Cu (**3**)), and their 3,5-difluorosubstituted analogues M[Fc-C(O)CH = C(CH_3)N-*o*-C_6H_4-N = CH-(2-O-3,5-F_2-C_6H_2)] (M = Ni (**4**), Cu (**5**); Fc = ferrocenyl = (η^5-C_5H_5)Fe(η^5-C_5H_4))). Compounds **2**–**5** were synthesized in good yields (75–87%) in refluxing ethanol for 4 h, *via* template reaction by condensation of the tridentate half-unit metalloligand Fc-C(O)CH = C(CH_3)-N(H)-*o*-$C_6H_4NH_2$ (**1**) with 5-nitrosalicylaldehyde and 3,5-difluorosalicylaldehyde, respectively, in the presence of hydrated nickel(II) and copper(II) acetate salts, respectively. Their composition and identity were inferred from elemental analysis, FT-IR, UV–Vis, and multinuclear NMR spectroscopy. Single crystal X-ray diffraction analysis of the two 3,5-difluorosubstituted compounds **4** and **5** indicates a slightly bowed structure of the unsymmetrical Schiff base scaffold. Both Ni^{2+} and Cu^{2+} ions are tetracoordinated in a distorted square planar environment, with two nitrogen atoms and two oxygen atoms as donors. The electrochemical behavior of the four binuclear complexes was investigated by cyclic voltammetry, showing greater anodic shifts of the reversible redox process ascribed to the Fe^{II}/Fe^{III} couple of the ferrocenyl donor fragment of the 5-nitrosubstituted derivatives compared to their 3,5-difluorosubstituted counterparts. Harmonic Light Scattering measurements showed that compounds **2**–**5** exhibited rather high second-order nonlinear responses, found between 200 and 267 $\times$ 10^{-30} esu, establishing a good correlation between redox potentials and the hyperpolarizability $\beta_{1.91}$ values.

1. Introduction

Rational design and synthesis of cyclic or acyclic Schiff bases metal complexes are of continuing interest [1,2], not only as synthetic intermediates but also as polytopic ligands in coordination chemistry [3]. Interests for these complexes is mainly due to their use in numerous fields of applications varying from catalysis [4] to pharmaceuticals [5], including new functional molecular-based materials [6,7] with second-order nonlinear optical (NLO) properties [8]. In particular, tetradentate N_2O_2 salen-type Schiff base complexes[1] that are well-established for all first-row transition metals have appeared to be a promising class of efficient chromophores exhibiting large NLO responses [8a,9]. Among them, various unsymmetrical acyclic Schiff base complexes possessing strong electron donor (D) and electron acceptor (A) groups bound to a planar metal-containing π-conjugated Schiff base M(ONNO) framework have been extensively investigated [10–15]. Such D-π-A systems,

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[1] Traditionally, the term salen refers to ligands prepared via the condensation of salicylaldehyde and ethylenediamine, but has come to include dianionic N_2O_2 ligands with varying carbonyl-containing substituents and diamine backbones.

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obtained by the 1:1:1 stepwise condensation of β-diketone, salicylaldehyde and a primary alkyl- or aryldiamine in the presence of a metal salt, have gained considerable attention for nonlinear optics due to their facile syntheses, thermal stability, and versatility in ligand design providing for the straightforward modulation of the sterics, electronics, and chirality at the central metal ion. In addition, coordination compounds that can be either neutral or ionic, exhibit low energy electronic charge transfer excitations tunable by virtue of the nature, oxidation state, and coordination sphere of the metal center and thus should be promising candidates as second-order NLO materials [8,16].

Over the last decade, we designed and constructed novel neutral binuclear and ionic trinuclear three-dimensional Schiff base architectures featuring a planar metallo-salen framework that connects through its π-electron system a ferrocene donor unit and the cationic 12-electron [(η^5-C_5Me_5)Ru^+] acceptor moiety, η^6-coordinated to the salicylidene ring [17,18]. Those organometallic donor–acceptor substituted unsymmetrical Ni(II)- and Cu(II)-centered Schiff base complexes exhibited large second-order NLO responses that increased with the nuclearity of the compounds [14,15]. As an extension of this work and in order to further enhance the second-order NLO responses, we were interested in reacting the metalloligand Fc-C(=O)CH = C(CH_3)N(H)-*o*-C_6H_4-NH_2 (**1**, Fc = (η^5-C_5H_5)Fe(η^5-C_5H_4)) [19] with strong electron-withdrawing salicylaldehydes bearing fluorine and nitro groups to generate, via template synthesis, new D-π-A organometallic-inorganic hybrids and to study their electronic and NLO properties. Herein, we wish to report on the thorough investigation, including synthesis, analytical and spectroscopic characterization, and electrochemical behavior of a family of four neutral metal(II)-centered organometallic macroacyclic salen-type Schiff base complexes, namely, the binuclear 5-nitro derivatives M[Fc-C(O)CH = C(CH_3)N-*o*-C_6H_4-N = CH-(2-O,5-NO_2-C_6H_3)] (**2**: M = Ni, **3**: M = Cu), and their 3,5-difluoro analogues M[Fc-C(O)CH = C(CH_3)N-*o*-C_6H_4-N = CH-(2-O-3,5-F_2-C_6H_2)] (**4**: M = Ni, **5**: M = Cu) (see formulas on Scheme 1). The X-ray crystal structures of these two latter difluorinated compounds **4** and **5** are also described. In addition, we disclose the first hyperpolarizability (β) values of the neutral binuclear unsymmetrical Schiff base complexes **2**–**5** obtained in this work from Harmonic Light Scattering (HLS) experiments.

2. Experimental

2.1. Materials and general procedures

Reactions were performed under dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and distilled according to standard procedures [20]. 5-nitrosalicylaldehyde, 3,5-difluorosalicylaldehyde, nickel(II) acetate tetrahydrate, and copper(II) acetate monohydrate were purchased from Aldrich and used without further purification. The organometallic tridentate "half unit" Fc-C(O)CH = C(CH_3)N(H)-*o*-$C_6H_4NH_2$ (**1**), was synthesized according to published procedure [19].

2.2. Characterization

Solid-state FT-IR spectra were recorded on a Perkin-Elmer Model 1600 FT-IR spectrophotometer with KBr disks in the 4000 to 450 cm^{-1} range. Electronic spectra were obtained with a SHIMADZU UV-1800 spectrophotometer. NMR spectra were recorded with a Bruker Avance III 400 spectrometer. All NMR spectra are reported in parts per million (ppm, δ) relative to tetramethylsilane (Me_4Si) for ^{1}H and ^{13}C NMR spectra, with the residual solvent proton and carbon resonances used as internal standards. Chemical shifts of ^{19}F NMR spectra are referenced against external $CFCl_3$. Coupling constants (J) are reported in Hertz (Hz), and integrations are reported as number of protons. The following abbreviations are used to describe peak patterns: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. ^{1}H and ^{13}C NMR chemical shift assignments are supported by data obtained from ^{1}H–^{1}H COSY, ^{1}H–^{13}C HMQC, and ^{1}H–^{13}C HMBC NMR experiments, and are given according to the numbering scheme of Fig. 1. Elemental analyses were conducted on a Thermo-FINNIGAN Flash EA 1112 CHNS/O analyzer by the Microanalytical Service of the Centre Regional de Mesures Physiques de l'Ouest (CRMPO) at the University of Rennes 1, France. Cyclic voltammetry (CV) measurements were performed using a Radiometer Analytical model PGZ 100 all-in one potentiostat, using a standard three-electrode setup with a vitreous carbon working electrode, platinum wire auxiliary electrode, and Ag/AgCl as the reference electrode. Dichlor omethane solutions were 1.0 mM in the compound under study and 0.1 M in the supporting electrolyte n-$Bu_4N^+PF_6^-$ with voltage scan rate = 100 mV s^{-1}. The ferrocene/ferricenium redox couple (Cp_2Fe/Cp_2Fe^+) was used as internal reference for the potential measurements. Melting points were determined in evacuated capillaries on a Kofler Bristoline melting point apparatus and were not corrected.

2.3. Synthesis of Ni[CpFe(^{5}-C_5H_4)-C(O)CH = C(CH_3)N-*o*-C_6H_4N = CH-(2-O,5-NO_2-C_6H_3)] (**2**)

To a Schlenk tube containing 200 mg (0.55 mmol) of a solution of CpFe(η^5-C_5H_4)C(O)CH = C(CH_3)N(H)-*o*-$C_6H_4NH_2$ (**1**) in 10 mL of ethanol, a solution of 93 mg (0.55 mmol) of 5-nitrosalicylaldehyde dissolved in 5 mL of ethanol, was added, under stirring. The resulting solution was refluxed for 15 min, cooled to room temperature and a solution of 207.2 mg (0.833 mmol) of nickel(II) acetate tetrahydrate dissolved in 5 mL of ethanol was added. The resulting mixture was refluxed for 4 h affording a dark red solid. The suspension was cooled at −30 °C for 4 h. The dark red material was filtered off and washed with 3 × 4 mL portion of cold ethanol and 3 × 4 mL portion of diethyl ether. The solid was dried under vacuum for 2 h to give 245 mg (78% yield) of **2** as a red powder. M. p. 296–298 °C (dec). *Anal.* Calc. for $C_{27}H_{21}FeN_3NiO_4 \cdot 0.5H_2O$ (574.03 g mol^{-1}): C, 56.44; H, 3.86; N, 7.32. Found: C, 56.51; H, 3.68; N, 7.04%. FT-IR (KBr pellet, cm^{-1}): 3090 (vw), 3070 (vw) ν(C–H aryl), 2968 (vw), 2925 (vw), 2855 (vw) ν(C–H alkyl), 1606 (s) ν(C···O), ν(C···N) and/or ν(C···C), 1544 (s), 1522 (s) ν(C–O), 1377 (vs) $\nu_{asym}(NO_2)$, 1312 (vs) $\nu_{sym}(NO_2)$. ^{1}H NMR (400 MHz, DMSO-d_6, 343 K): 2.47 (s, 3 H, CH_3), 4.23 (s, 5 H, C_5H_5), 4.48 (t, $^3J_{HH}$ = 1.9 Hz, 2 H, H_β C_5H_4), 4.78 (t, $^3J_{HH}$ = 1.9 Hz, 2 H, $H_\alpha C_5H_4$), 5.81 (s, 1 H, CH═C), 6.92 (d, $^3J_{HH}$ = 9.4 Hz, 1 H, H-3), 7.11 (td, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.0 Hz, 1 H, H-11), 7.22 (td, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.0 Hz, 1 H, H-10), 7.50 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.0 Hz, 1 H, H-9), 8.01 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.0 Hz, 1 H, H-12), 8.10 (dd, $^3J_{HH}$ = 9.4 Hz, $^4J_{HH}$ = 3.0 Hz, 1 H, H-4), 8.72 (d, $^4J_{HH}$ = 3.0 Hz, 1 H, H-6), 9.98 (br s, 1 H, N═CH). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 343 K): 26.22 (CH_3), 68.52 (C_α C_5H_4), 69.83 (C_5H_5), 70.76 (C_β C_5H_4), 81.61 (C_{ipso} C_5H_4), 103.01 (*C*H═C), 116.40 (C-12), 120.04 (C-1), 122.51 (C-9), 123.38 (C-11), 123.43 (C-3), 127.77 (C-10), 128.08 (C-4), 131.63 (C-6), 135.95 (C-5), 140.57 (C-7), 144.18 (C-8), 155.95 (N═CH), 163.48 (CH═*C*), 169.10 (C-2), 179.56 (C═O).

2.4. Synthesis of Cu[CpFe(^{5}-C_5H_4)-C(O)CH = C(CH_3)N-*o*-C_6H_4N = CH-(2-O,5-NO_2-C_6H_3)] (**3**)

The synthesis of this complex was carried out following a procedure similar to that described above for complex **2**, using in this case 200 mg (0.55 mmol) of the hemiligand **1** dissolved in 10 mL of ethanol, 93 mg (0.55 mmol) of 5-nitrosalicylaldehyde dissolved in 5 mL of ethanol and 166 mg (0.466 mmol) of copper(II) acetate