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Synthesis, crystal structures and third-order nonlinear optical properties in the near-IR range of two novel Ni(II) complexes

Yanqiu Liu [a], Hui Wang [a], Jun Zhang [a], Shengli Li [a], Chuankui Wang [c], Hongjuan Ding [c], Jieying Wu [a,*], Yupeng Tian [a,b,*]

[a] Department of Chemistry, Key Laboratory of Functional Inorganic Materials Chemistry of Anhui Province, Anhui University, Hefei 230039, PR China
[b] State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, PR China
[c] Department of Physics, Shandong Normal University, Jinan 250014, PR China

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ABSTRACT

Two novel Nickel(II) complexes (NiL^1_2 and NiL^2_2) with remarkable two-photon absorption (TPA) and optical power limiting (OPL) properties were synthesized and fully characterized. Single crystals were obtained and solved by X-ray diffraction analysis. Their photophysical properties had been further investigated both experimentally and theoretically. The third-order nonlinear optical (NLO) properties (TPA and OPL) were investigated by open/closed aperture Z-scan measurements using femtosecond pulse laser in the range from 680 to 1080 nm. The results revealed that the two Nickel(II) complexes exhibited strong two-photon absorption and superior optical power limiting properties, which are much better than that of the free ligands.

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1. Introduction

Materials exhibiting strong third-order nonlinear optical (NLO) absorptions have attracted considerable interest because of their potential applications in optical switching [1,2], three-dimensional (3D) fluorescence imaging [3], 3D optical data storage [4], 3D lithographic microfabrication [5,6] and optical power limiting [7–12]. A promising approach to develop such materials with improved NLO effects is to incorporate metal centers into organic materials. Metal ions, being powerful 3D templates, can assemble simple organic ligands in a variety of multipolar arrangements showing interesting electronic and optical properties and tunable by virtue of the coordinated metal center. This can induce a strong intraligand charge-transfer (ILCT) transition as well as a low-energy metal–ligand charge-transfer transition (MLCT). Compared with traditional NLO materials, the incorporation of metal atoms in coordination complexes introduces more sublevels into the energy hierarchy, which permits more allowed electronic transition to take place and hence a larger NLO effect [13–17]. In addition, coordination complexes have high damage threshold and fast response time that are important from the perspective of applications.

Spurred by this, we first rationally designed two novel ligands (HL^1 and HL^2) and their Ni(II) complexes (NiL^1_2 and NiL^2_2) (Scheme 1). This idea is based on the following considerations: (i) carbazole compound is well known to exhibit good hole transporting properties and their charge transfer (CT) complexes can create free carriers in the visible region through the photocarrier generation process [18–20]. (ii) Flexible polyether chains as a substituted unit was introduced into carbazole ring to enhance their solubility [21]. (iii) Thiosemicarbazone or S-benzyldithiocarbazate units can coordinate readily with transition metals to give stable complexes, forming a long π-conjugated system by deprotonation [22,23]. (iv) Nickel(II) complex was selected because of its good coordination planarity further to form extended π-conjugated system. Therefore, the nickel complexes should exhibit large NLO response as expected (as shown in Scheme 2). In this article, synthesis, crystal structures and third-order NLO properties in the near-IR range of two novel Ni(II) complexes were investigated systematically.

2. Experimental section

2.1. Materials and apparatus

All chemicals and solvents were dried and purified by usual methods. Elemental analysis data were obtained using a Perkin–Elmer 240 analyzer. IR spectra (4000–400 cm^{-1}), as KBr pellets, were recorded on a Nicolet FT-IR 170 SX spectrophotometer. Mass spec-

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* Corresponding authors. Address: Department of Chemistry, Key Laboratory of Functional Inorganic Materials Chemistry of Anhui Province, Anhui University, Hefei 230039, PR China (Y. Tian). Tel.: +86 551 5108151; fax: +86 551 5107342.
E-mail addresses: jywu1957@163.com (J. Wu), yptian@ahu.edu.cn (Y. Tian).

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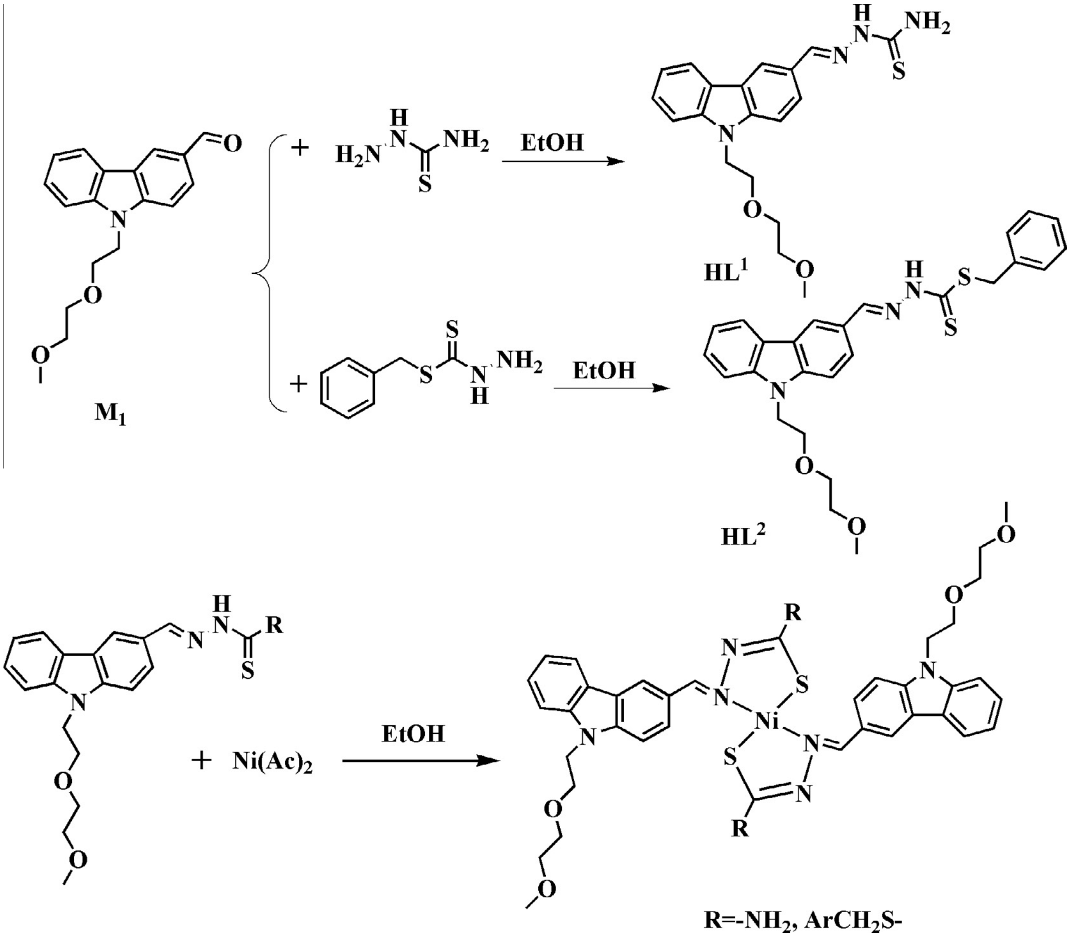
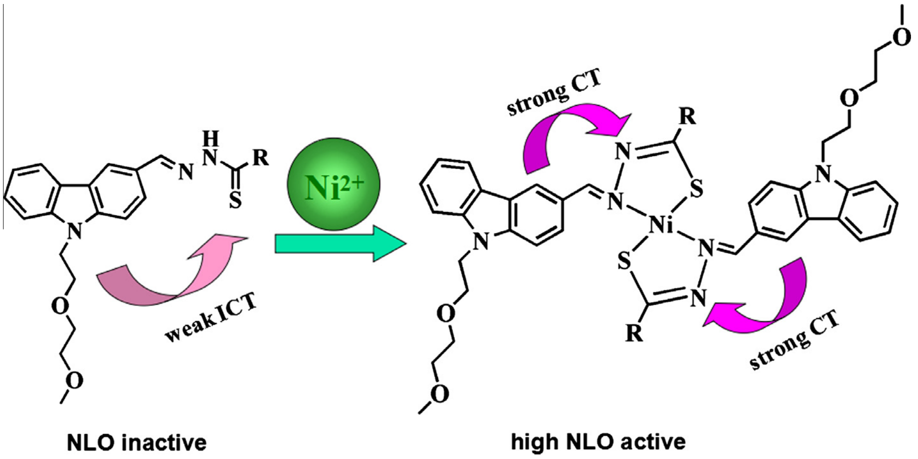


Scheme 1. Synthetic route for the title complexes.



Scheme 2. Plan for metal-mediated third-order nonlinear optical response in Schiff base ligand.

tra were obtained on a Micromass MALDI-TOF-MS. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 400 spectrometer with TMS as internal standard.

2.2. Optical measurements

Electronic absorption spectra were obtained on a UV-3600 spectrophotometer in THF solution (5.0×10^{-6} mol L^{-1}). Fluorescence measurements were performed using a Hitachi F-2500 fluorescence spectrophotometer. The fluorescence quantum yields (Φ) were determined by using quinine sulfate as the reference according to the literature method [24]. For time-resolved fluorescence measurements, the fluorescence signals were collimated and focused onto the entrance slit of a monochromator with the output plane equipped with a photomultiplier tube (HORIBA HuoroMax-4P). The decays were analyzed by 'least-squares'. The quality of the exponential fits was evaluated by the goodness of fit (χ^2).

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