

Syntheses, characterization and glass-forming properties of new bis[5-((4-ⁿdodecyloxyphenyl)azo)-*N*-(4-ⁿalkoxyphenyl)-salicylaldiminato]nickel (II) complex homologues

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Abstract

A series of bidentate Schiff base ligands, 5-((4-ⁿdodecyloxyphenyl)azo)-*N*-(4-ⁿalkoxyphenyl)-salicylaldimine (ⁿalkoxy = octyloxy, dodecyloxy, hexadecyloxy) homologues, have been synthesized and characterized by IR, NMR, mass spectroscopy and elemental analyses. Nickel (II) complexes of these ligands were synthesized and characterized by elemental analyses, ¹H NMR and IR spectroscopy. DSC measurements, X-ray powder diffraction experiments and optical polarizing microscopy studies indicated that the Ni complexes have a resistance to crystallization and give an amorphous glassy state but after annealing at room temperature for several days transform to an anisotropic glass.

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1. Introduction

In recent years, amorphous molecular materials or molecular glasses have attracted substantial interest due to their successful application in organic electroluminescent devices as well as photovoltaic, photochromic and resist materials [1]. These kinds of materials have excellent processability, transparency and isotropic properties [1a]. Low molecular weight organic compounds, polymers and molecularly doped polymer systems, which are able to form stable glasses with glass transition temperatures above room temperature have attracted great attention both from the scientific and application point of view [2,3].

Systematic studies on such stable low molecular weight organic compounds that readily form stable

amorphous glasses above room temperature started in 1980 by Shirota [4]. Some molecular glasses based on twin molecules containing caracole, dihydrocarbazole, phenothiazine and naphthalimide have recently been reported by Braun and co-workers [5]. Moreover, Braun et al. [6] have reported low-molecular-weight glassy fulvalenes. Bazan et al. [7] have used the binaphthyl framework to synthesize glass-forming organic chromophores. Shirota et al. [8a] have reported 2,3-tetrakis[4-(*N*-2-naphthyl-*N*-phenyl-amino)phenoxy]-substituted phthalocyanines as a novel class of amorphous molecular materials. McKeown et al. [8b] have described the syntheses and glass-forming properties of phthalocyanine-containing poly(aryl ether) dendrimers.

Azo-containing photochromic materials have been attracting a great deal of attention because of their potential technological applications to optical recording for data storage and optical switching [9]. For example, the azobenzene-based compounds, containing an

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azobenzene chromophore, 4-[di(biphenyl-4-yl)amino]-azobenzene and 4,4'-bis[bis(4-*tert*-butylbiphenyl-4-yl)amino]-azobenzene have been used as photochromic amorphous molecular materials [10]. Other azobenzene-based amorphous molecular materials, with a spiro-linked bifluorene, have been synthesized and their photoinduced behavior such as optically induced birefringence, diffraction efficiency and surface relief gratings (SRGs) were investigated in relation to their unique molecular structures [11].

Based on our knowledge, only a few coordination or organometallic compounds have been reported as amorphous molecular materials. Platinum 5-fluorouridine green sulfate is a typical example of an amorphous coordination compound [12]. A polycrystalline sample of titanyl phthalocyanine was vacuum evaporated at ca. 10^{-5} Torr to form an amorphous thin film. Photovoltaic devices consisting of an amorphous thin film of titanyl phthalocyanine and *N,N*-dimethyl-3,4,9,10-perylenebis(dicarboximide), sandwiched between ITO and Au electrodes, demonstrated a response to light over the whole visible wavelength region from 400 to 900 nm [13]. Shirota and co-workers [8a] have synthesized copper and titanyl phthalocyanines containing triarylamine moieties. These compounds are soluble in common organic solvents and readily form stable amorphous glasses with high glass transition temperatures. Bazan and co-workers [14] have synthesized Iridium complexes with fluorene-modified phenylpyridine ligands that are resistant to crystallization and can be used in the fabrication of single layer light emitting diodes. It is worth mentioning that the introduction of a metal center into organic systems in order to form coordination or organometallic molecular materials can introduce extra parameters such as color, magnetism and birefringence in amorphous molecular materials. Besides the metal center can improve the electroluminescent properties of coordination molecular materials.

In this work, we report the synthesis and investigation of glass-forming properties of new bis[5-((4-*n*-dodecyloxyphenyl)azo)-*N*-(4-*n*-alkoxyphenyl)-salicylaldiminato]nickel (II) complex homologues (see Scheme 1).

2. Experimental

2.1. Reagents

All reagents and solvents used were supplied by Merck chemical company and used without further purification. 4-Alkoxy nitrobenzene homologues were obtained by reaction between 4-nitrophenol with 1-bromooctane or 1-bromododecane in DMF as solvent and K_2CO_3 as base by refluxing for 3 h [15] and then crude 4-alkoxy nitrobenzene homologues were purified by recrystallization from ethanol. 4-Alkoxyaniline

homologues prepared by reduction of the corresponding 4-alkoxy nitrobenzene as described in the literature [16].

2.2. Physical measurements

Elemental (C, H and N) analyses were carried out on a Perkin–Elmer automatic equipment model 240B. Electron impact (70 eV) mass spectra were recorded on a Finnigan-mat GC–MS–DS spectrometer model 8430. Infrared spectra were taken with a Bruker FT-IR spectrometer model vector 22, using KBr pellets in the 400–4000 cm^{-1} range. The DSC thermograms of the compounds were obtained on a Mettler–Toledo DSC 822e module, which was calibrated with indium metal ($T = 156.6 \pm 0.3$, $\Delta H = 28.45 \pm 0.6$ $J g^{-1}$). Samples of 2–5 mg in the solid form were placed in aluminum pans (40 μl) with a pierced lid, and heated or cooled at a scan rate of 10 $^{\circ}C min^{-1}$ under a nitrogen flow. TGA was carried out on a Mettler–Toledo TGA 851e at a heating rate of 10 $^{\circ}C min^{-1}$ under a nitrogen atmosphere. X-ray powder diffraction patterns were recorded on a Bruker D8 powder diffractometer (Cu $K\alpha$: 1.541 Å). The optical observations were made with a Zeiss polarizing microscope equipped with a Linkam THMSG 600 heating and cooling stage and Linkam THMS 93 programmable temperature-controller. 1H NMR spectra were obtained in deuterated chloroform as solvent on a Bruker FT-NMR AC-400 (400 MHz) spectrometer. All chemical shifts are reported in δ (ppm) relative to tetramethylsilane as an internal standard.

2.3. Materials

5-(4-Dodecyloxyphenylazo)salicylaldehyde (**1**). This compound was prepared as described in the literature [17]. Yellow, yield 80%, m.p. 123 $^{\circ}C$. MS m/z (relative intensity): 411.6 (M + 1, 15), 410.6 (M, 45), 242.5 (M – $C_{12}H_{25}$, 25), 121.6 (M – $C_{12}H_{25}OC_6H_4N_2$, 100). Anal. Calc. for $C_{25}H_{34}N_2O_3$: C, 73.15; H, 8.35; N, 6.83. Found: C, 72.73; H, 8.14; N, 6.47%. 1H NMR (400 MHz, $CDCl_3$) δ 11.26 (s, H-9), 10.02 (s, H-8), 8.15 (d, $J = 2.8$ Hz, H-3), 8.13 (dd, $J = 2.9$, 8.2 Hz, H-2), 7.89 (dd, $J = 3.0$, 7.9 Hz, H-4, H-7), 7.11 (d, $J = 8.1$ Hz, H-1), 7.01 (dd, $J = 3.2$, 7.9 Hz, H-5, H-6), 4.04 (t, $J = 6.7$ Hz, H-10), 1.84–0.87 (23H, alkyl chain).

3. Syntheses of the ligands

All homologue materials were prepared similarly. Thus, 0.026 mol of the related amine (4-alkoxy aniline) and 0.026 mol of 5-(4-*n*-dodecyloxyphenylazo)salicylaldehyde were dissolved in 100 ml absolute ethanol with a few drops of glacial acetic acid as a catalyst. The

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