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The effect of spin–orbit coupling on selenadiazolo- and thiadiazolo-fused 1,10-phenanthrolines

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ABSTRACT

Phenanthroline derivatives have been widely studied for many practical applications, and when fused with either a selenadiazole or a thiadiazole unit and used as ligands to produce metal complexes such complexes present unique photochemical and magnetic properties. In this work, a detailed theoretical description (using computational methods) of the electronic structure of these ligands is presented to explain their different photochemical and photophysical properties. In particular, the heavy atom effect on the spin–orbit coupling has a major influence on transitions between the excited states of [1,2,5]selenadiazolo[3,4-*f*][1,10]phenanthroline and the appearance of phosphorescence under inert argon atmosphere at room temperature. Photocurrent experiments demonstrated that these specific properties of the [1,2,5]selenadiazolo[3,4-*f*][1,10]phenanthroline are promising for photovoltaic applications.

1. Introduction

Phenanthroline (Phen) is a versatile building block for the construction of ligands for various purposes with a wide range of properties [1,2]. Phen is a classic chelating bidentate ligand with different coordination sites, forming transition metal complexes of an N2 type ligand, and its derivatives have played an important role in the development of coordination chemistry as well as molecular scaffolds for supramolecular assemblies [3–5], molecular switches [6,7] and artificial nucleases [8–12] (DNA,cleavers).

Amongst many classes of molecules studied for their photophysical and photochemical properties, fused pyridines and their derivatives are one of the most thoroughly investigated, with 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen) and 2,2′; 6′2″-terpyridine (terpy) being the major examples [13–16]. Either metal free or in the form of metal complexes, compounds of the Phen type find applications in various fields such as sensing [17,18], luminescence [19,20], magnetics [21], photocatalysis [22], electrochemical devices [23,24], photodynamic therapy [25,26] and solar energy production [27].

The simplest phenanthroline does not present significant properties, but as it is readily available and easy to react, many different compounds with a wide range of properties were synthesized from it (Fig. 1).

Phen also forms very stable complexes with transition metals, which can present interesting electrochemical and photochemical properties. Complexes of Ru(II), as an example, present long excited state lifetimes and have been proposed as dyes for solar cells [29,30] and optical sensors [31].

A recent development in terms of modifications of Phen was the synthesis by our group of a Phenanthroline (Phen) fused at the 3,4 positions with a thiodiazole unit [2] (TDZP) or a selenodiazole (PhenSe) (Fig. 2). These derivatives were used as ligands in the synthesis of metal complexes of Fe(II) [32,33], V(IV) [34], Ru(II) [35], Eu(III) [36], Tb(III) [37] and they presented unique photochemical and magnetic properties. In particular, the iron complex with TDZP has one of the highest photonuclease activities reported so far [32].

When studying the reasons behind such a high activity, we found out that the selenadiazole analogue had significantly different properties to Phen. In this work we present a study of the physicochemical properties of TDZP and PhenSe in comparison to their parent molecule. A detailed description of the electronic structure of these systems was obtained via CASSCF calculations and it is shown that the spin–orbit coupling has a major influence

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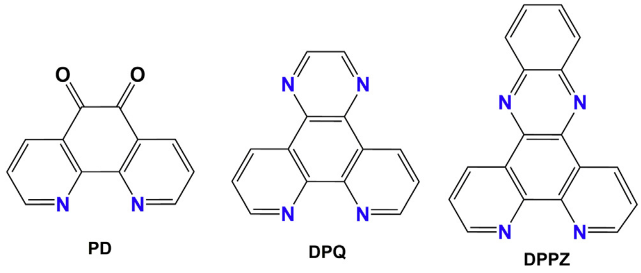

Fig. 1. Some important phenantroline derivatives: PD [28] (1,10-phenanthroline-5,6-dione), DPQ [25] (dipyridoquinoxaline) and DPPZ [25] (dipyridophenazine).

when describing transitions between the excited states, thus explaining the different photochemical and photophysical properties of these molecules, in particular that of the PhenSe. The longer lifetime of the excited state of PhenSe is then exploited in a simple photocurrent experiment to demonstrate the applicability of the spin–orbit coupling effect in photovoltaics.

2. Experimental

2.1. Materials and characterization

All solvents and reagents were purchased from commercial sources and used as received. 5,6-Diamino-1,10-phenanthroline was prepared according to the literature [2].

Proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained at 200 MHz on a Bruker AC-200 NMR spectrometer. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$ or tetramethylsilane (TMS) as the external reference. Data are reported as follows: chemical shift (δ), multiplicity, coupling constant (J) in Hertz and integrated intensity. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained at 50 MHz on a Bruker AC-200 NMR spectrometer. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$. The following abbreviations were used to designate multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet) and m (multiplet). Selenium-77 nuclear magnetic resonance spectra (^{77}Se NMR) were recorded at 38.14 MHz on a Bruker AC-200 NMR spectrometer. Chemical shifts are referenced to diphenyl diselenide as the internal reference (464 ppm). High resolution mass spectra were recorded on a Bruker microTOF-Q II ESI mass spectrometer equipped with an automatic syringe pump for sample injection. FT-IR spectra were recorded on a Perkin–Elmer model FTIR-2000 spectrometer, using KBr pellets, in the range of 4000–400 cm^{-1}. Melting points were obtained using an Olympus BX50 microscope (Tokyo, Japan) equipped with a Mettler Toledo FP-82 hot stage and a PM-30 exposure control unit. A Cary Bio 50 spectrophotometer was used for UV and visible absorption measurements. The lifetime of single state was measured using Edinburg FLS980 Fluorescence Lifetime Spectrometer with Nanosecond H_2 flashlamp and a single photon counting detector. Triplet state lifetime was detected using Luzchem LFP101 Laser flash photolysis, Excitation Surelite II Nd-YAG 3rd hamonic Laser (366 nm). The fluorescence spectra in solution were recorded on a Varian Cary Eclipse Fluorescence Spectrophotometer. Cyclic voltammetry (CV) measurements were carried out using a system of three electrodes: Vitreous Glassy Carbon as the working electrode, a platinum wire as auxiliary and an Ag/Ag + reference electrode. Supporting electrolyte: 0.1 mol.L^{-1} n-Bu_4NPF_6.

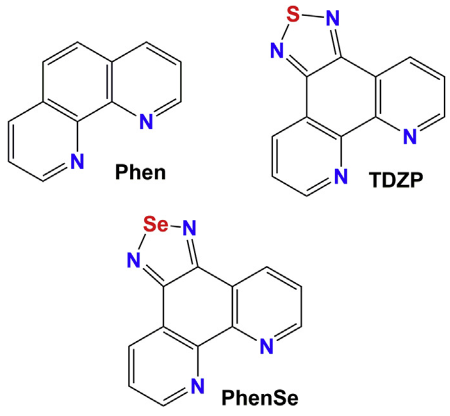

Fig. 2. Molecules studied in this work.

2.2. Procedure for the synthesis of chalcogenated ligands

2.2.1. Synthesis of [1,2,5]thiadiazolo[3,4-f][1,10]phenanthroline (TDZP) [2]

m.p. 230.8-231.9°C; **FT-IR (KBr)** : 3068, 3045, 1970, 1947, 1632, 1590, 1552, 1485, 1400,1080, 849, 807, 740 cm^{-1}; **^{1}HNMR (200 MHz, $CDCl_3$, 25 °C, TMS):** $\delta = 7.77$ (dd, ^3J (H,H) = 8.0 Hz ^3J (H,H) = 4.5 Hz, 1H; CH), 9.04 (dd, ^3J (H,H) = 8.0 Hz ^4J (H,H) = 1.8 Hz, 1H; CH), 9.26 (dd, ^3J (H,H) = 4.5 Hz ^4J (H,H) = 1.8 Hz, 1H; CH) ppm; **^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS):** $\delta = 123.3$ (s,C), 124.4 (s; CH), 135.5 (s, CH), 147.7 (s, C), 151.9 (s, C), 152.2 (s, CH) ppm; **ESI HRMS:** calcd for $[C_{12}H_6N_4S + H]^+$ 239.0386, found 239.0386.

2.2.2. Synthesis of [1,2,5]selenadiazolo[3,4-f][1,10]phenanthroline (PhenSe)

To a refluxing solution of 5,6-diamino-1,10-phenanthroline (210 mg, 1 mmol) in ethanol (10 mL), a hot solution of selenium dioxide (111 mg, 1 mmol) in water (1 mL) was added dropwise and the mixture was refluxed for 1 h. The reaction was monitored by TLC ($CHCl_3$–MeOH, 8:2). The solvent was removed under vacuum and the residue was dissolved in cloroform and purified on a chromatographic column (silica gel; $CHCl_3$) to give PhenSe as a pink solid. Yield 257 mg (90%). **m.p.** 292.5–295.5 °C with decomposition; **FT-IR (KBr):** 3051, 3014, 1571, 1549, 1471, 1430, 1399, 1341, 1125, 1078, 803, 738 cm^{-1}; **^{1}HNMR (200 MHz, $CDCl_3$, 25 °C, TMS):** $\delta = 7.69$ (dd, ^3J (H,H) = 8.0 Hz ^3J (H,H) = 4.5 Hz, 1H; CH), 8.99 (dd, ^3J (H,H) = 8.1 Hz ^4J (H,H) = 1.8 Hz, 1H; CH), 9.20 (dd, ^3J (H,H) = 4.5 Hz ^4J (H,H) = 1.8 Hz, 1H; CH) ppm; **^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS):** $\delta = 124.4$ (s,CH), 125.3 (s; C), 134.2 (s, CH), 148.0 (s, C), 152.2 (s, CH), 156.6 (s, C) ppm; **^{77}Se NMR (38.14 MHz, $CDCl_3$, 25 °C, TMS):** $\delta = 1528.6$ ppm; **ESI HRMS:** calcd for $[C_{12}H_6N_4Se + H]^+$ 286.9831, found 286.9832.

2.3. X-ray crystallographic analysis

The crystallographic analysis of compound PhenSe was performed with a Kappa APEX II DUO diffractometer with graphite-monochromated Mo-Kα radiation. The temperature was set at 200(2) K using an Oxford cryostream 700 device. A total of 3159 frames were collected by a φ and ω scan procedure. The frames were integrated with the Bruker SAINT software package [38]. All data were corrected for Lorentz and polarization effects. The data were also corrected for absorption effects using the multi-scan method (SADABS) [39]. The structure was solved by direct methods and refined by full-matrix least-squares methods using SHELXS and SHELXL97 programs [40]. All non-hydrogen atoms