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Synthesis of a New Phenanthroline Derived Ligand with Acceptor Properties

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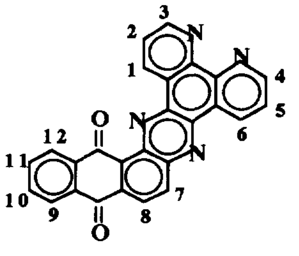
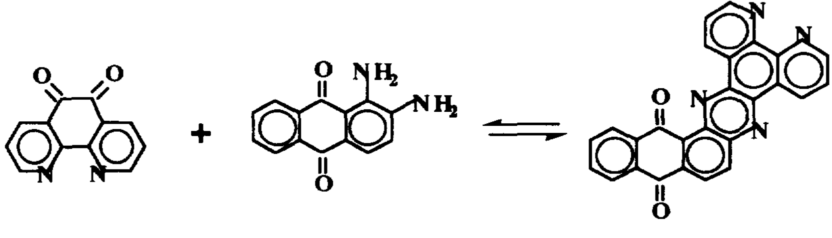
Abstract: By a condensation of 1,10-phenanthroline-5,6-dione and 1,2-diamino antraquinone, the new acceptor polypiridine ligand, 10,11-[1,4 naphtalendione]dipyrido[3,2-a;2',3'-c]phenazine, was obtained. A new synthetic route for the 1,10phenanthroline-5,6-dione precursor is also reported.

The interconversion among different forms of energy based on molecular assemblies is a major scientific and technological goal. One objective is converting solar into chemical energy,[1] and a series of polypiridine Ru(II), Os(II) and Re(I) complexes have been synthesized which have relevant properties as light absorbers.[2] These compounds can absorb light throughout the visible due to metal-to-ligand charge transfers (MLCT) transitions, and light absorption and excited state properties can be tuned systematically by changing the electronic properties of the ligands bound to the metal.[3] Commonly used polypiridine ligands include 2,2'bipyridine (**bpy**), 1,10-phenanthroline (**phen**) and 2,2':6',2"-terpyridine (**terpy**), which by appropiate derivatization can behave as electron donors or acceptors.[4,5,6] Owing to their carbonyl groups, quinones are good acceptors. Some N-monocoordinating derivatives, as benz[g]isoquinoline-5,10 dione (**BIQD**), have been coordinated to metals like Ru or Re.[7]

With the aim of designing a ligand that could simultaneously coordinate in a bidentate chelating form (as **bpy**[8] or **phen**[6]) and show the acceptor behaviour of quinones, the new ligand,10,11-[1,4 naphtalendione]dipyrido[3,2-a;2',3'-c]phenazine, **I**, (**Aqphen**) was designed:



The synthesis of **Aqphen** was conducted by a condensation of 1,10-phenanthroline-5,6-dione, **II**,[9,10] and 1,2-diamino-anthraquinone, **III**, (Aldrich):



Elemental Analysis for **I** gave satisfactory results. By IR spectroscopy, the dissapearance of the carbonyl absorptions of **II** (1691cm^{-1}) and NH absorptions of **III** (3200-3400cm^{-1}) gave further evidence for the coupling. The UV-Vis spectrum shows two main bands of equal intensity (396 and 410nm in DCE, $\varepsilon \approx 15000$) characteristic of anthraquinone derivatives.[11] The bands in this spectrum are blue shifted in regard to the amino precursor **III**, and in comparable positions respect to nitro-anthraquinones.[11] The low solubility of **I** in most common solvents made its characterization by NMR difficult and deuterated acetic acid was required. Nevertheless, it was possible to acquire the ^{1}H-NMR spectrum of the complex (Aqphen)Re(CO)$_3$Cl, where the only ^{1}H-NMR resonances correspond to the Aqphen ligand. The assignement of the spectrum was made with the aid of double irradiation techniques.[12]

The acceptor capacity of the new ligand here reported was implied by cyclic voltammetry: Ep(red) = -0.5V and -0.8V vs.SCE, DCE. Preliminar photophysical studies confirm this perception. No apreciable emission was detected for the (Aqphen)Re(CO)$_3$Cl complex. On the other hand, Transient Absorbance experiments show a very short lived excited state ($\tau < 20$ns), and a deactivation path through the quinonic part of the molecule. This means that the MLCT excitation to the phenanthroline fragment of Aqphen is quenched, probably by electron transfer, to the quinonic residue of the ligand. Work is in progress in this field.

Experimental

Synthesis of 1,10-phenanthroline-5,6-dione, **II**:

A modification of the synthesis reported in literature[9,10] was used. This new synthesis is straightforward and has a considerable better yield: 50 ml of comercial bleach at pH = 8.6 was added to a solution of 2 g (11.11mmol) of 1,10-phenanthroline in 15 ml chloroform. 1.8 g (5.30 mmol) of tetra-n-butylammonium hydrogensulphate was added,[13] and the mixture agitated vigorously at RT for 30 minutes. Two phases separated. The product present in the aqueous phase was extracted by washing three times with ca.15 ml of chloroform, and all the extractions added to the organic phase. This mixture was dried over anhydrous sodium sulphate, filtered and taken to dryness under vacuum. To the yellow solid residue was added 10 ml of a 6:3:1 (v:v:v) mixture of H_2SO_4(conc): HNO_3(conc): H_2O. The mixture was heated at reflux at 90 °C until disappearance of the red-brown vapour. The solution was neutralized with Na_2CO_3 and the product extracted with $CHCl_3$. The organic phase was dried over anhydrous Na_2SO_4 and evaporated to dryness. Finally, the product was recrystallized from methanol. (Yield: 1.23 g, 53%).

Synthesis of 10,11-[1,4 naphtalendione]dipyrido[3,2-a;2',3'-c]phenazine, **I** *(Aqphen)*:

0.260 g (1.24 mmol) 1,10-phenanthroline-5,6-dione and 0.284 g (1.24 mmol) 1,2-diamino-anthraquinone were heated at reflux for eight hours, in a mixture of 30 ml ethyleneglycol and 20 ml ethanol. After evaporating the ethanol, the suspenssion was filtered and the dark brown residue dissolved in 500 ml of hot chloroform in the presence of charcoal. After filtering, the orange solution was concentrated to aproximately 50 ml, and a yellow solid formed. Diethyl ether was added to complete precipitation. The product was filtered, washed with ether and taken to dryness under high vacuum giving 0.453 g of a golden yellow solid (Yield:89%).

Synthesis of (Aqphen)Re(CO)$_3$Cl: [8]

0.3 g (0.728 mmol) of Aqphen and 0.262 g (0.725 mmol) of Re(CO)$_5$Cl (Aldrich) were refluxed in toluene during two hours. The solid obtained was filtered, dissolved in chloroform, and precipitated with cold ethyl ether, giving 0.46 g of product (Yield:88%). Elemental analysis gave satisfactory results. For ^{1}H-NMR see Note 12. UV-Vis: 403nm and 380nm in DCE, assigned to Aqphen intraligand bands. By taking the difference absorption spectrum (complex vs. free Aqphen ligand) two MLCT were evidenced: 368nm and ≈ 415nm. Cyclic Voltammetry: Ep(red) = -0.4V and -0.86V ; Ep(ox) = +1.52V in DCE.

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12. ^{1}H-NMR for (Aqphen)Re(CO)$_3$Cl: 10.10 ppm (dd, **H(1)**); 9.87 ppm (dd, **H(6)**); 9.53 ppm (dd, **H(3)**,**H(4)**); 8.95 ppm (d, **H(8)**); 8.79 ppm (d, **H(7)**); 8.35 ppm (m, **H(9)**,**H(12)**); 8.12 ppm (m, **H(2)**); 8.07 ppm (m, **H(5)**);7.9 ppm (m, **H(10)**,**H(11)**).
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