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A modular ligand design for cation sensors: phosphorus-supported pyrene-containing ligands as efficient Cu(II) and Mg(II) sensors

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ABSTRACT

A modular ligand design allowed the assembly of four phosphorus-supported pyrene-containing ligands. The number of pyrene arms could be varied from 1 to 6 depending on the phosphorus support. While ligands containing one and three pyrene arms are excellent fluorescence-based sensors of Cu^{2+}, the ligand containing two pyrene arms shows a high specificity for Mg^{2+}.

1. Introduction

In recent years there has been considerable research interest in the area of molecular sensors, which can detect cations (or anions) with a high degree of specificity even at low concentrations.[1–5] Detection techniques based on optical spectroscopic methods have been favoured in view of the simplicity of the technique as well as rapid nature of detection. In general the design of ligands is carried out with a view to induce absorption spectral changes or fluorescence emission changes upon interaction with cations.[6–8] Fluorescence-based methods are more sensitive than the corresponding absorption techniques and hence there has been considerable interest in the design of new ligands that would show significant changes in their fluorescence output upon interaction with a cation input.[9–15] We have been interested in phosphorus-based ligands for some time in view of their modular design and also because the latter allows ready assembly of a wide choice of ligands with varying properties. For example, using (*S*)P[N(Me)N=CH–C_6H_4–2-OH]$_3$ we were able to assemble neutral trinuclear derivatives (L_2M_3) whereas by the use of (*S*)P[N(Me)N=CHC_6H_4–2-OH–3-OMe]$_3$ we could prepare ionic 3d–4f assemblies possessing interesting magnetic properties including single molecule magnet behaviour.[16,17] In view of this versatility it was of interest to probe if this design allowed the preparation of ligands whose fluorescence properties could be affected by metalation. Our particular interest was the possibility of finding an effective fluorescence-based sensor for Cu^{2+} in view of the fact that paramagnetic ions quench fluorescence[18–21] and only in some instances a fluorescence enhancement has been observed.[22–26] Accordingly, we report herein, the design, assembly and structural characterization of a family of phosphorus-supported pyrene containing ligands $Ph_2P(O)[N(Me)N{=}CH(Py)]$ (**1**), PhP(O)[N(Me)N=CH(Py)]$_2$ (**2**), (*S*)P[N(Me)N=CH-Py]$_3$ (**3**) and N_3P_3[N(Me)N=CH-Py]$_6$ (**4**) (Py=1-pyrenyl). While **1** and **3** are excellent sensors of Cu^{2+}, **2** is specific for Mg^{2+}.

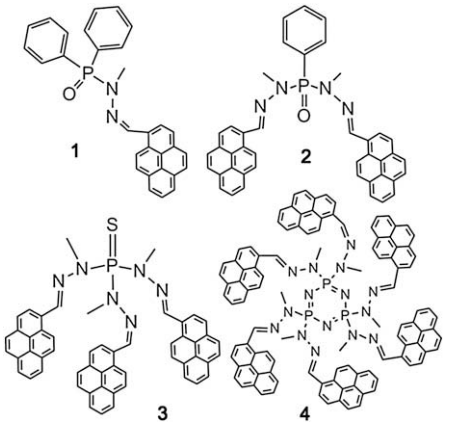

Figure 1. Phosphorus-supported pyrene-containing ligands **1**–**4**.

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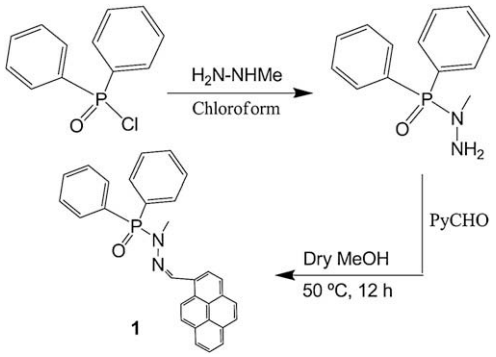

Scheme 1. Synthesis of **1**.

2. Results and discussion

The synthesis of the ligands **1**–**4** was carried out by a two-step protocol and involved the conversion of the chloro precursors into the corresponding phosphorus hydrazides by a regiospecific reaction with *N*-methylhydrazine. Condensation of the hydrazides with pyrene-1-carboxaldehyde afforded **1**–**4** in excellent yields (Fig. 1). A representative synthetic protocol is shown in Scheme 1. The conversion of the chloro precursors into the products is readily monitored by $^{31}P\{H\}$ NMR [cf. δ (^{31}P); (*S*)PCl_3 31.7 (s); (*S*)$P[N(Me)NH_2]_3$, 84.5 (s); **3**, 75.1 (s)]. Compounds **1**–**4** are soluble in a wide range of organic solvents. The chemical integrity of these compounds is retained in solution as evidenced by the presence of strong $[M+H]^+$ peaks in their ESI-MS spectra recorded under positive ion mode (see Supplementary data). Finally, **1**–**3** were also characterized by solid state X-ray crystallography. Compound **2** crystallized in two modifications, one as a methanol solvate and the other without any solvent of crystallization. The perspective views

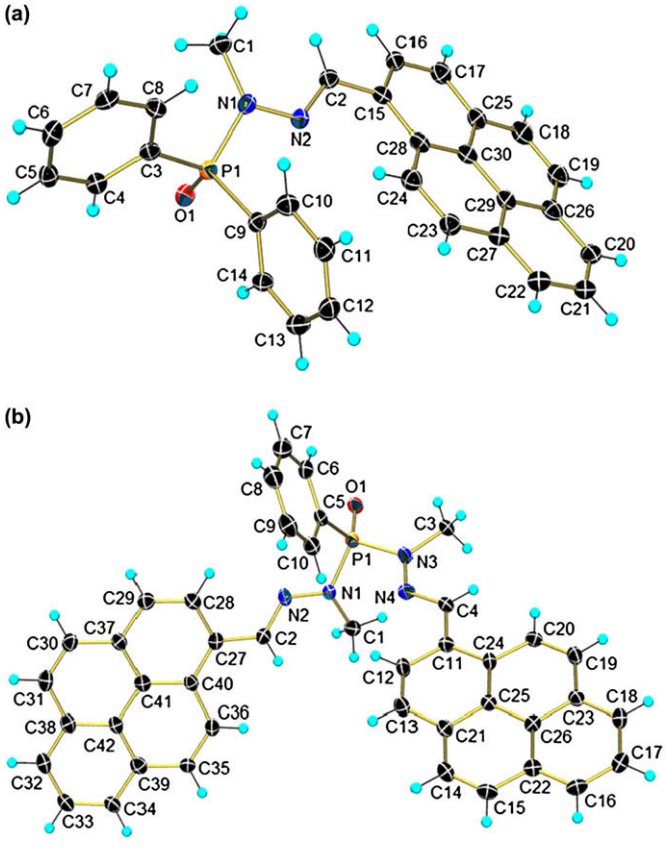

Figure 2. ORTEP diagrams of **1** (a) and **2**·MeOH (b) with 50% thermal ellipsoids (solvent molecules are omitted for clarity). Selected bond distances (Å) and angles (°) are as follows: **1**: C(3)–P(1), 1.803(3); C(9)–P(1), 1.800(2); N(1)–P(1), 1.687(2); P(1)–O(1), 1.4797(19); O(1)–P(1)–N(1), 116.69(11); O(1)–P(1)–C(9), 113.36(11); N(1)–P(1)–C(9), 103.21(11); O(1)–P(1)–C(3), 110.99(11); N(1)–P(1)–C(3), 104.47(11); C(9)–P(1)–C(3), 107.27(11). **2**·MeOH: C(5)–P(1), 1.787(3); N(1)–P(1), 1.663(3); N(3)–P(1), 1.669(2); O(1)–P(1), 1.472(2); O(1)–P(1)–N(1), 116.56(12); O(1)–P(1)–N(3), 108.88(12); N(1)–P(1)–N(3), 102.65(12); O(1)–P(1)–C(5), 112.49(13); N(1)–P(1)–C(5), 105.63(13); N(3)–P(1)–C(5), 110.12(13).

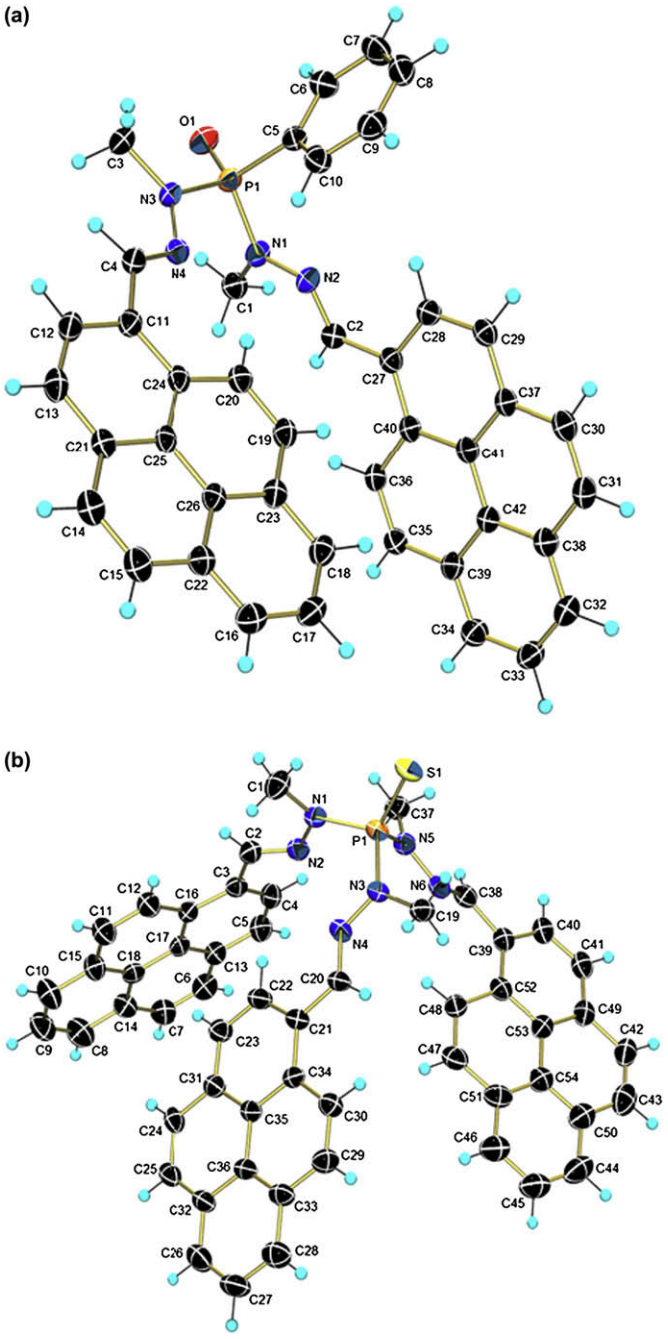

Figure 3. ORTEP diagrams of **2** (a) and **3** (b) with 50% and 30% thermal ellipsoids, respectively. Selected bond distances (Å) and angles (°) are as follows: **2**: C(5)–P(1), 1.788(2); N(1)–P(1), 1.6603(19); N(3)–P(1), 1.678(2); P(1)–O(1), 1.4696(16); O(1)–P(1)–N(1), 112.42(10); O(1)–P(1)–N(3), 108.65(10); N(1)–P(1)–N(3), 107.87(10); O(1)–P(1)–C(5), 113.77(10); N(1)–P(1)–C(5), 105.96(10); N(3)–P(1)–C(5), 107.92(11). **3**: N(1)–P(1), 1.659(4); N(3)–P(1), 1.667(4); N(5)–P(1), 1.672(4); P(1)–S(1), 1.9247(19); N(1)–P(1)–N(3), 107.9(2); N(1)–P(1)–N(5), 101.7(2); N(3)–P(1)–N(5), 106.3(2); N(1)–P(1)–S(1), 112.54(16); N(3)–P(1)–S(1), 110.37(15); N(5)–P(1)–S(1), 117.32(15).