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A new bis(pyrenyl)azadiene-based probe for the colorimetric and fluorescent sensing of Cu(II) and Hg(II)

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ABSTRACT

A novel colorimetric and fluorescent chemosensor **2**, made up of two pyrene units connected by a 2-aza-1,3-butadiene ionophore, was designed and prepared for the selective detection of Cu^{2+} and Hg^{2+} in the presence of other metal cations. This molecular sensor exhibits substantial colour changes and fluorescence enhancement upon complexation with these metal cations in acetonitrile solutions, with detection limits in the order of 10^{-6} M. Job's plots revealed a 1:1 stoichiometry rationalized by theoretical DFT calculations.

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1. Introduction

The development of chemosensors that are capable of sensing different target species is currently a topic of major interest in supramolecular chemistry.[1] Then, considerable efforts have been made to design new molecular probes able to recognize and sense environmentally and biologically important ionic species. Consequently, the construction of chemosensor molecules with high selectivity and sensitivity for the detection of transition- and heavy-metal cations has received substantial attention, as these ions play important roles in living systems and have an extremely toxic impact on the environment.[2] Within this context, particular interest has been devoted to the detection of copper and mercury.

Copper is one of the essential trace elements of transition metal, which serves as a cofactor by taking an active part in large variety of enzymes. As a consequence, it plays an important role in fundamental physiological processes in organisms.[3] Thus, daily ingestion of copper is indispensable for good health. However, it is also a significant metal pollutant responsible for a number of neurodegenerative diseases. Its toxicity for humans is rather low compared with other heavy metals, although certain microorganisms are affected by submicromolar concentrations. Thus, copper is, on one side, important for life but, on the other side, is highly toxic to organisms: exposure to a high level of copper even for a short period of time can cause gastrointestinal disturbance, while long-term exposure causes deeper damages in the human being.[4]

On the other hand, mercury is one of the most well known toxic elements that exists in metallic, inorganic and organic forms, which is widely distributed in air, water and soil.[5] As a consequence of this pollution, mercury can accumulate in the human body causing a wide variety of diseases, even in a low concentration, such as digestive, kidney and especially neurological disorders. The relative abundance of methylated mercury species is of particular concern since these compounds are highly toxic. They are the major form of mercury that accumulates in fish tissues and they can enter the food chain by direct uptake from solution. However, the mercury problem is not limited to the aquatic food chain since rice has recently been proposed as the major source of methylmercury intake from food in parts of the Chinese population, and the results indicate that this derivative is more prominent in the rice grains than would be expected from the occurrence of methylmercury versus inorganic mercury in the soil.[6]

For these reasons, and keeping in view the roles of Cu^{2+} and Hg^{2+} cations, the past few years have witnessed a number of reports on the design and synthesis of chemosensors for their detection.[7] Most of these receptors are often structurally complicated and require an elaborate and sophisticated synthetic process. Therefore, the development of simple and easy-to-make chemosensor molecules for metal cations is strongly demanded.

The importance of the colorimetric sensors is closely related to their ability to allow the so-called 'naked-eye' detection in a straightforward and inexpensive manner, offering qualitative and

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quantitative information without using expensive equipments. However, fluorescent sensors make the best choice, since they are qualified with high sensitivity, high selectivity, fast response and inexpensive installations, too. As fluorogenic groups, pyrenyl substituents are very attractive because of their strong and well characterized emissions and their chemical stabilities.[8]

From this perspective, here we report the design, synthesis and evaluation of the metal ion binding properties of the novel ligand **2**.

This ligand is based on the coupling of two structural subunits: one ionophore, constituted by a 2-aza-1,3-butadiene unit, for the selective recognition of metal ions, which connects two photoactive pyrene moieties, used for signal transduction. These components are intramolecularly correlated together such that the binding of the target metal ion could cause significant changes to the optical and/or other photophysical properties of the corresponding signalling unit. The binding events involved in these recognitions processes are described, by using UV–vis, fluorescence and ^{1}H NMR spectroscopies as well as by using theoretical calculations at the DFT level.

2. Results and discussion

2.1. Synthesis

Compound **2** was prepared by two-step reaction following the recently method described for the synthesis of 1,4-disubstituted 2-aza-1,3-butadienes[9] (Scheme 1). Firstly, diethyl aminomethylphosphonate[10] was condensed with 1-pyrenylcarboxaldehyde to give the corresponding *N*-pyrenyl substituted diethyl aminomethylphosphonate **1** in almost quantitative yield. Secondly, generation of the metalloenamine by reaction with *n*-BuLi at −78 °C and subsequent reaction with 1 equiv of the same aldehyde provided the 1,4-bis(1-pyrenyl)-2-aza-1,3-butadiene **2**, which was recrystallized from CH$_2$Cl$_2$/diethyl ether (1/10) and thoroughly characterized by using standard techniques: ^{1}H and ^{13}C NMR spectroscopies, EIMS spectroscopy as well as elemental analyses.
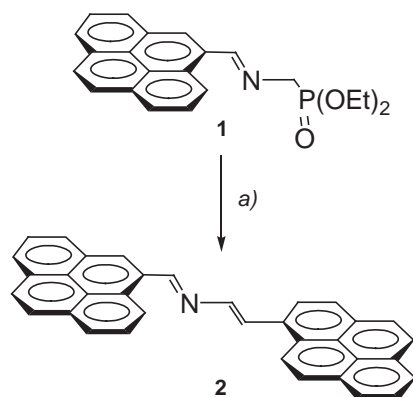
Scheme 1. Synthetic route for ligand **2**. Reaction conditions: (a) (i) *n*-BuLi, −78 °C; (ii) 1-pyrenecarboxaldehyde.

Assignment of the (*E*,*E*)-configuration of the double bonds present in receptor **2** was achieved by inspection of the ^{1}H NMR spectroscopic data. It is well established that the condensation reaction between a primary amine and an aldehyde is not stereoselective, hence both (*E*) and (*Z*)-aldimine isomers are generally present in the reaction product. However, it must be emphasized that the condensation reaction between the *N*-pyrenyl substituted diethyl aminomethylphosphonates and 1-pyrenylcarboxaldehyde takes place stereoselectively to give exclusively the (*E*)-isomer, as ascertained by NOE experiments. Indeed, an NOE effect is observed to the methylene group on irradiation of the aldiminic proton present in **1**. On the other hand, reaction of the deprotonated

N-substituted diethyl aminophosphonates with 1-pyrenylcarboxaldehyde gives only the trans configured carbon–carbon double bond, as is expected in a Horner–Wadsworth–Emmons olefination reaction,[11] which is confirmed by the characteristic vicinal coupling constants obtained.

2.2. Cation-sensing properties

The chemosensor behaviour of receptor **2** with several metal cations (Li$^+$, Na$^+$, K$^+$, Mg^{2+}, Ca^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Sm^{3+}, Eu^{3+}, Yb^{3+} and Lu^{3+}) in CH$_3$CN was investigated by UV–vis and fluorescence measurements, because this small system display not only absorption but also emission variations depending on the metal ion present. All titration experiments were analyzed using a computer program.[12]

Receptor **2** shows a UV/vis absorption spectrum in CH$_3$CN (c=2.5×10^{-5} M), which is dominated by the typical pyrene absorption bands[7] appearing in the region 233–393 nm. Its chemosensor behaviour in the presence of the above-mentioned set of metal ions indicated that only Cu^{2+} and Hg^{2+} ions promoted a notable response in its absorption spectra, while the other metal ions tested induced negligible responses. Notably, stepwise addition of Cu^{2+} and Hg^{2+} ions induced the appearance of a new low energy (LE) absorption band at λ=528 nm reaching its maximum in intensity when 1 equiv of such metal ions was added. At the same time, a decrease in intensity of the bands at λ=233–393 nm (Fig. 1 and Supplementary data). In each case, well-defined isosbestic points were also observed during the titration experiments, indicating the presence of a unique complex in equilibrium with the neutral ligand. The simultaneous change of colour of the solution from yellowish to deep pink can be used for a 'naked-eye' detection of Cu^{2+} and Hg^{2+} ions.
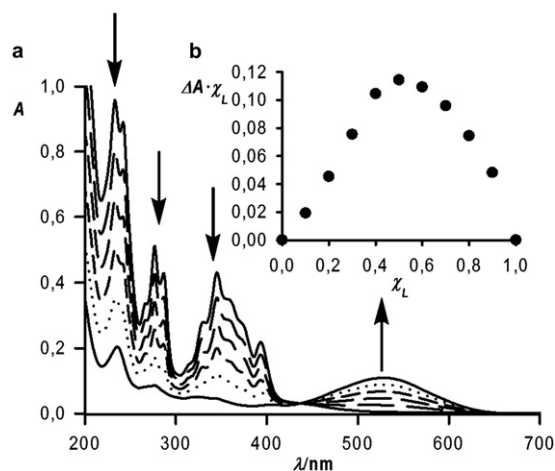
Figure 1. (a) Changes in the absorption spectra of compound **2** (c=2.5×10^{-5} M) in CH$_3$CN upon addition from 0 to 1 equiv of Hg^{2+} ion. Arrows indicate absorptions that increase or decrease during the experiment. (b) Job's plot for **2** titrated with Hg^{2+} illustrating the 1:1 stoichiometry of the complexed formed; the total [L]+[Hg^{2+}]=1×10^{-4} M.

When these titration experiments where carried out in CH$_3$CH/H$_2$O (7/3) solutions, similar results to those obtained in the pure organic solvent were observed although the recognition of Cu^{2+} and Hg^{2+} metal cations was only accompanied by slight changes in the UV–vis of the free ligand and, as a consequence, in the colour of its solution.

Analysis by Job's law plot (see Supplementary data) gave a 1:1 stoichiometry for the complexes formed, in both cases. By using the titration curve data and the stoichiometry of the complexes the corresponding binding constants were calculated (K_a=1.3×10^6 M^{-1}

and $K_a=1.2\times10^6$ M^{-1} for Cu^{2+} and Hg^{2+}, respectively), the magnitude of the resulting detection limits[13] being 3.7×10^{-6} M, in both cases.

For the reported constant to be taken with confidence, we have proved the reversibility of the complexation process. If the sensing system is reversible, depletion of the cation that coordinates **2** must produce a change of the absorption spectrum, causing it to revert to the original spectrum. Formation of the complexes **2**·Cu^{2+} or **2**·Hg^{2+} and the subsequent decomplexation by extraction of the metal cation with EDTA were carried out over several cycles. The optical spectra were recorded after each step and found to be fully recovered on completion of the step, thus demonstrating the high degree of reversibility of the sensing process (see Supplementary data).

Cation affinities were also determined through the extent to which the fluorescence intensity of receptor **2** was affected in the presence of cations. Compound **2** exhibits a very weak fluorescence in CH$_3$CN ($c=2.5\times10^{-5}$ M) when excited at $\lambda_{exc}=350$ nm ($\Phi=0.014$). The emission spectrum shows typical bands at 388 and 409 nm, attributed to the pyrene monomeric emission. The low fluorescence show by the free ligand results from the efficient photoinduced electron transfer (PET) quenching of the excited estate of the pyrene moiety by the lone pair of electrons on the nitrogen atom in the 2-azadiene bridge. The fluorescence behaviour of **2** in CH$_3$CN in the presence of the previously mentioned set of metal ions was also examined and a sizable chelation enhanced fluorescence (CHEF) was specifically observed only upon addition of Cu^{2+} (CHEF=27) (Fig. 2) and Hg^{2+} (CHEF=12) (see Supplementary data).
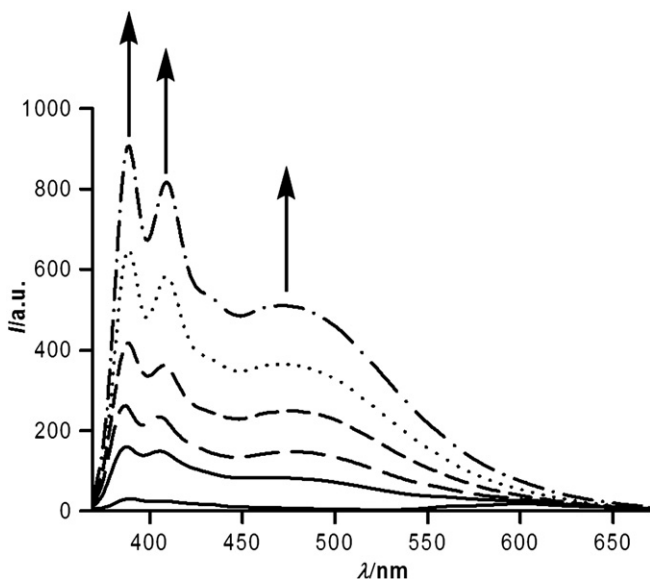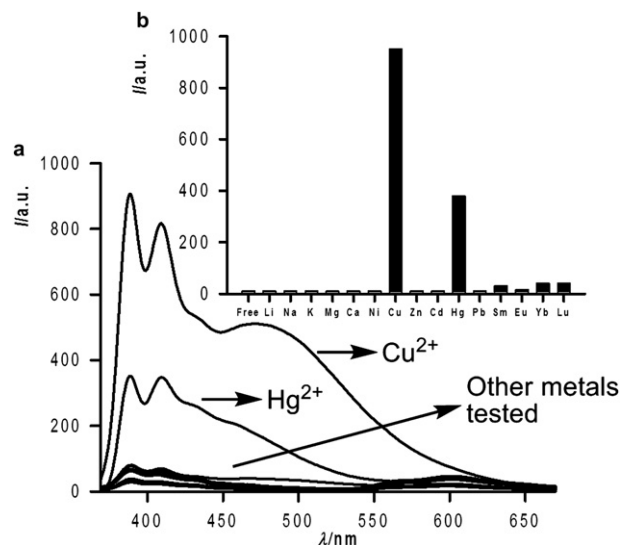

Figure 3. (a) Changes in the fluorescence emission spectrum of **2** ($c=2.5\times10^{-5}$ M) in CH$_3$CN upon addition of several metal cations (Li$^+$, Na$^+$, K$^+$, Mg^{2+}, Ca^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Sm^{3+}, Eu^{3+}, Yb^{3+} and Lu^{3+}). (b) Fluorescence intensity increase of ligand **2**, in CH$_3$CN, in relation to the free ligand, after addition of 3 equiv of several cations. Emission is monitored at $\lambda_{exc}=350$ nm.

stoichiometry (see Supplementary data). The values of the detection limits[13] were also calculated and are 2.5×10^{-6} M and 4.5×10^{-6} M, for Hg^{2+} and Cu^{2+}, respectively.

The other metal ions studied exhibited basically no discernible changes at all even when they are present in high concentrations (i.e., 100-fold excess). So, this fluorescence change can be possibly utilized in devices for the measurement of Cu^{2+} and Hg^{2+} concentrations, even in the presence of other cations.

The changes in fluorescence emission of **2** in CH$_3$CN/H$_2$O (7/3) ($c=2.5\times10^{-5}$ M) upon addition of the above cited set of metal cations were also studied. Compound **2** displays three very weak emission
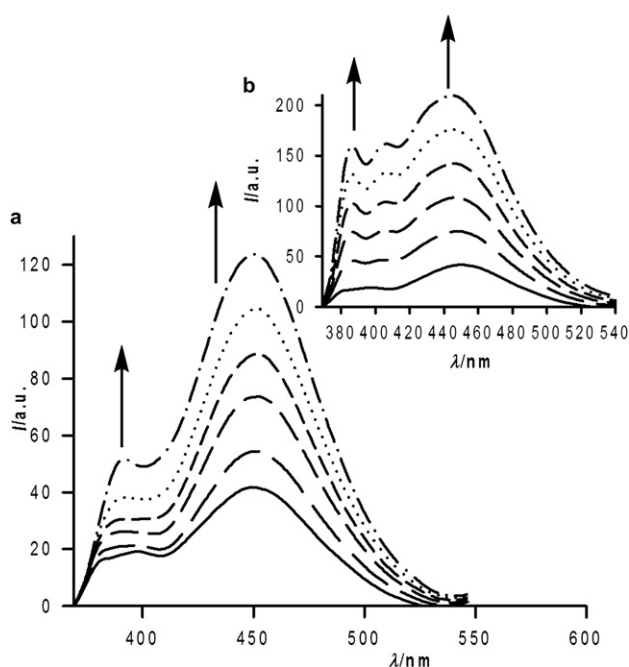

Figure 2. Changes in the fluorescence emission spectrum of **2** ($c=2.5\times10^{-5}$ M) in CH$_3$CN upon addition of Cu^{2+}, from 0 to 1 equiv ($\lambda_{exc}=350$ nm).

During the titration process, not only an increase of the pyrene monomeric emission bands was observed but also the appearance of the typical pyrene excimer emission.[7] However, it is note worthy that the pyrene excimer emission wavelength was dependent on the metal cation used: $\lambda=473$ nm for the case of Cu^{2+} and $\lambda=430$ nm, for Hg^{2+} (Fig. 3).

The stoichiometry of the complexed systems was also determined by the changes in the fluorogenic response of **2** in the presence of varying concentrations of Cu^{2+} and Hg^{2+} and the results obtained indicate the formation of a 1:1 complex, giving association constants of 7.74×10^6 M^{-1} and 8.40×10^6 M^{-1}, for Cu^{2+} and Hg^{2+}, respectively. It is worth mentioning that electrospray mass spectra of the complex [**2**·Cu(OTf)$_2$] formed also confirmed the 1:1

Figure 4. Changes in the fluorescence emission spectrum of **2** ($c=2.5\times10^{-5}$ M) in CH$_3$CN/H$_2$O (7/3), $\lambda_{exc}=350$ nm, upon addition, from 0 to 1 equiv, of (a) Cu^{2+} and (b) Hg^{2+}.

bands, at 382, 398 and 450 nm, in this aqueous solution when excited at λ_{exc}=350 nm (Φ=0.033). The only noticeable spectral changes observed upon titration with these ions are those derived from the addition of Cu^{2+} and Hg^{2+}. In both cases, a significant increase of the emission bands was observed (λ=391 and 450 nm for $\mathbf{2}\cdot Cu^{2+}$ and λ=391, 410 and 450 nm for $\mathbf{2}\cdot Hg^{2+}$) (Fig. 4). Nevertheless, the fluorescence emission increase associated to the complexation process is produced in a considerably lesser extent than that observed in the pure acetonitrile medium. In fact, the CHEF values obtained were of 2.7 for the case of $\mathbf{2}\cdot Cu^{2+}$ (Φ=0.066) and 3.6 for $\mathbf{2}\cdot Hg^{2+}$ (Φ=0.121). The stoichiometry of the complexes formed was also determined by the changes in the fluorogenic responses of $\mathbf{2}$ in the presence of varying concentrations of Cu^{2+} and Hg^{2+} metal cations, the results indicating the formation of 1:1 complexes with lower values for the association constants (K_a=2.81×10^5 M^{-1} for $\mathbf{2}\cdot Cu^{2+}$ and 2.63×10^5 M^{-1} for $\mathbf{2}\cdot Hg^{2+}$) than those obtained in CH$_3$CN. On the other hand, the detection limits calculated under these conditions were 4.0×10^{-6} M and 5.3×10^{-6} M for $\mathbf{2}\cdot Cu^{2+}$ and $\mathbf{2}\cdot Hg^{2+}$, respectively.

Binding of Cu^{2+} and Hg^{2+} ions by the simple receptor $\mathbf{2}$ has also been investigated by quantum chemical calculations at the DFT level (see Supplementary data). Due to the open-shell nature of the Cu^{2+}-containing complexes, unlikely the Hg^{2+} analogues, the structure for the [$\mathbf{2}\cdot Hg(OTf)_2$] complex was calculated in a first step, following the experimentally observed 1:1 ligand/cation ratio. The 2:2 stoichiometry [$\mathbf{2}_2Hg_2$]$^{4+}$ was also checked but displayed a very endergonic complexation energy. Assuming a qualitative identical behaviour, this 1:1 structure was used as starting point for obtaining the geometry of the—quantitatively—more interesting [$\mathbf{2}\cdot Cu(OTf)_2$] complex. The resulting structure [$\mathbf{2}\cdot Cu(OTf)_2$] (Fig. 5) shows the central Cu^{2+} metal atom essentially hexacoordinated by the azadiene N atom ($d_{N\cdots Cu}$=2.037 Å, WBI$_{N\cdots Cu}$=0.168), four triflate O atoms (two equatorial $d_{O\cdots Cu}$=2.024 and 2.115 Å, WBI$_{O\cdots Cu}$=0.155 and 0.122; and two axial $d_{O\cdots Cu}$=2.534–2.619 Å, WBI$_{O\cdots Cu}$=0.045–0.040) and a weak contact with the C-10 atom belonging to the closest pyrenyl unit ($d_{C\cdots Cu}$=2.350 Å, WBI$_{C\cdots Cu}$=0.104), whose bonding nature was unambiguously proved by localization of the corresponding bond critical point ($\rho(r_c)$=4.04×10^{-2} e/a_0^3 and $\nabla^2\rho(r_c)$=9.64×10^{-2} e/a_0^5).
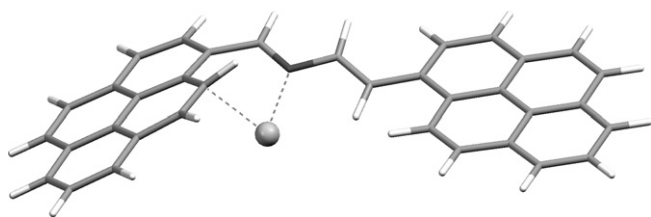

Figure 5. Calculated structure (mPW1B95/aug6-311G** /StRSC-ecp) for the complex [$\mathbf{2}\cdot Cu(OTf)_2$]. Triflate ligands are omitted for clarity.

3. Conclusions

In summary, a new molecular sensor bearing two pyrenyl moieties connected by a 2-aza-1,3-butadiene bridge as the metal-binding group has been synthesized. In terms of selectivity and sensitivity, this ligand showed a good sensing ability towards Cu^{2+} and Hg^{2+} and functions both as a chromogenic (naked-eyed detection) (Fig. 6) and fluorogenic probe for these metal cations. Interestingly, the different emission wavelengths of the pyrene excimer showed by the two different complexes formed with these metal cations could be also used to distinguish both heavy pollutant metals. On the basis of the DFT calculations binding modes between the ligand and the analytes have also been proposed.

Figure 6. Visual changes in the colour of $\mathbf{2}$ (left) after addition of Cu^{2+} metal cation (right).

4. Experimental section

4.1. General

The starting material 1-pyrenecarboxaldehyde was purchased from Sigma–Aldrich and used as received. Solvents were analytic-grade quality and were purified by the standard procedures before use. Counteranion for the Li$^+$, Na$^+$, K$^+$, Mg^{2+}, Ca^{2+}, Ni^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} metal cations was perchlorate, while Cu^{2+}, Zn^{2+}, Sm^{3+}, Eu^{3+}, Yb^{3+} and Lu^{3+} were used as their trifluoromethanesulfonate salts.

Melting point was determined on a Kofler hot-plate melting point apparatus and is uncorrected. Elemental analyses were carried out on a Carlo-Erba EA-1108 analyzer.

^{1}H and ^{13}C NMR spectra were recorded at 600 MHz and 150 MHz, respectively, on a Brucker AC600 apparatus. Chemical shifts refer to signals of tetramethylsilane in the case of ^{1}H and ^{13}C spectra. The following abbreviations are used to represent the multiplicity of the signals: s (singlet), d (doublet), and q (quaternary carbon atom).

The electron impact and electrospray mass spectra were recorded on a Fisons AUTOSPEC 500 VG spectrometer.

UV–vis spectra were carried out in an UV–vis VARIAN 5000 spectrophotometer using a dissolution cell of 10 mm path. The samples were solved in CH$_3$CN (c=1×10^{-4} M) and the spectra were recorded with the spectra background corrected before and after of the sequential additions of aliquots of 0.1 equiv of M^{2+} in the same solvent (c=2.5×10^{-2} M). To establish the reversibility of the titration process, the following experimental procedure has been carried out: to a solution of $\mathbf{2}$, in CH$_3$CN, 1 equiv of the divalent metal cation (M^{2+}=Cu^{2+} as the triflate salt or Hg^{2+} as the perchlorate salt) was added to obtain the complexed species $\mathbf{2}\cdot M(II)$, and the UV/vis spectrum was recorded. The CH$_3$CN solution of the complex was washed several times with a solution of EDTA until the colour of the solution changed from deep pink to yellowish. The organic layer was dried and the optical spectra were recorded and they were found to be the same than that of the free receptor $\mathbf{2}$. Afterwards, 1 equiv of the divalent metal cation M^{2+} was again added to that solution and the initial UV/vis spectrum of the $\mathbf{2}\cdot M^{2+}$ complex was fully recovered together with its deep pink colour. This experiment was carried out over several cycles. The optical spectrum was recorded after each step and found to be recovered on completion of the step.

Fluorescence spectra were carried out in a VARIAN Carey fluorescence spectrophotometer using a fluorescence cell 10 mm (c=2.5×10^{-5} M), as it is stated in the corresponding figure captions. Before recording the spectra, the samples were deoxygenated, to remove fluorescence quenching via oxygen, by bubbling nitrogen for

at least 10 min All the spectra were recorded before and after the sequential additions of aliquots of 0.1 equiv of a solution of M^{2+} in CH_3CN ($c=2.5\times10^{-3}$ M). Quantum yield values were measured with respect to anthracene as standard ($\Phi=0.27\pm0.01$), using the equation $\Phi_x/\Phi_s=(S_x/S_s)[(1-10^{-As})/(1-10^{-Ax})](n_s^2/n_x^2)$, where x and s indicate the unknown and standard solution, respectively, Φ is the quantum yield, S is the area under the emission curve and A is the absorbance at the excitation wavelength and n is the index of refraction.

4.2. Computational details

Initial geometries and energies for all complexes and the free ligand were obtained at the semiempirical level of theory by using the PM6 hamiltonian and the Mopac2007 software.[14] Solvent (acetonitrile) effects were taken into account by means of the Conductor-like Screening Model (COSMO) method[15] using 36.64 as relative static permittivity of the solvent and conducting polygonal surfaces around every atom, at the van der Waals' distances, made up of 162 segments each. The reliably accurate description of weak interactions like hydrogen bonds and other found in supramolecular complexes generally requires a treatment of electron correlation. Density functional theory[16] (DFT) has proved quite useful in this regard offering an electron correlation correction frequently comparable to the second-order Møller–Plesset theory (MP2) or in certain cases, and for certain purposes, even superior to MP2, but at considerably lower computational cost. Calculated geometries at the DFT level were fully optimized in the gas-phase with tight convergence criteria using the Gaussian 03 package,[17] employing the hybrid meta functional mPW1B95[18] that has been recommended for general purpose applications and was developed in order to produce a better performance where weak interactions are involved such as those between ligands and heavy metals.[19] Due to the size of the systems investigated in the present study the cost advantage that offers mPW1B95 method in comparison with MP2 was significant. The 6-311G** basis set was used in the optimizations for all atoms and adding diffuse functions on N, O and F atoms (denoted as aug6-311G**), as well as the Stuttgart relativistic small-core basis set (StRSC) with effective core potential (ecp) for mercury and copper.[20] From these gas-phase optimized geometries all reported data were obtained by means of single-point (SP) calculations at the aug6-311G**/StRSC-ecp level. Energy values are uncorrected for the zero-point vibrational energy and were computed considering solvent (acetonitrile) effects by using the Cossi and Barone's CPCM (conductor-like polarizable continuum model) modification[21] of the Tomasi's PCM formalism,[22] and correcting the basis set superposition error (BSSE) by means of the counterpoise approach.[23] Bond orders were characterized by the Wiberg's bond index[24] (WBI) and calculated with the natural bond orbital (NBO) method as the sum of squares of the off-diagonal density matrix elements between atoms. The topological analysis of the electronic charge density was conducted by means of the Bader's AIM methodology[25] using the AIM2000 software[26] and the wavefunction at the working level of theory.

4.3. Preparation of 1,4-bis(1-pyrenyl)-2-aza-1,3-butadiene 2

To a solution of the N-pyrenyl diethyl phosphonate[7g] (4.64 mmol) in dry THF (20 ml), at $-78\,^\circ$C and under nitrogen atmosphere was dropped the adequate amount of n-BuLi (1.6 M in hexane). Then, a solution of the 1-pyrenylcarboxaldehyde (4.64 mmol) in dry THF (10 ml) was added dropwise and the solution was stirred for 1.5 h. The reaction mixture was allowed to reach the room temperature and, afterwards, it was heated under reflux temperature overnight. After the solution was cooled to room temperature, the solvent was evaporated under reduced pressure and the resulting solid was slurried with diethyl ether (25 ml) to

give a crude product, which was recrystallized from dichloromethane/diethyl ether (1/10). Yield: 90%; mp: 297–299 $^\circ$C. ^{1}H NMR (600 MHz; DMSO-d_6; Me$_4$Si) δ: 8.08 (1H, t, $J=7.61$ Hz), 8.12–8.18 (4H, m, $2\times CH+CH=CH-N$), 8.23–8.33 (7H, m), 8.36–8.40 (4H, m), 8.51 (1H, d, $J=8.12$ Hz), 8.65 (1H, d, $J=9.31$ Hz), 8.80 (1H, d, $J=8.12$ Hz), 9.26 (1H, d, $J=9.42$ Hz), 9.69 (1H, s, $1\times CH=N$). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 122.0 (q), 122.4 (q), 122.6 (q), 123.2 (q), 123.4 (q), 124.2 (CH), 124.4 (CH), 124.5 (CH), 124.6 (CH), 124.8 (CH), 125.3 (CH), 125.6 (CH), 125.7 (CH), 125.9 (CH) 126.0 (q), 126.1 (CH), 126.2 (CH), 126.5 (CH), 126.6 (CH), 126.7 (CH), 126.8 (CH), 127.2 (CH), 127.5 (CH), 128.2 (q), 128.3 (CH), 129.5 (q), 129.7 (q), 129.9 ($2\times CH$), 130.0 (q), 130.4 (q), 130.6 (q) 132.4 (q), 145.4 (CH), 160.4 (CH=N). MS EI (70 eV) m/z 455 (M$^+$, 89%), 226 (74), 215 (100). Found: C, 91.99; H, 4.52; N, 3.24. $C_{35}H_{21}N$ requires C, 92.28; H, 4.65; N, 3.07%.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.03.080.

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