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Excimer-Based On-Off Bis(pyreneamide) Macrocyclic Chemosensors

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A series of bis(pyreneamide) macrocycles, synthesized in two steps from THF, THP, oxepane and 1,4-dioxane, are tested as chemosensors for a large range of mono-, di- and trivalent cations. In their native states, these macrocycles exhibit a strong excimer fluorescence that is quenched upon the addition of the metal ions (alkaline, alkaline earth, *p*-, *d*-, and *f*-block metals). UV-Vis spectrophotometric titrations, cyclic voltammetry, excimer fluorescence quenching and transient absorption spectroscopy experiments helped characterize the On-Off changes occurring upon binding and demonstrate that the highest stability constants are obtained with divalent cations Ca²⁺ and Ba²⁺ specifically.

Keywords: Cation sensing • Conformations • Excimer • Macrocycle • Pyrene

Introduction

Detection and sensing of alkali, alkali earth and other metallic cationic elements is essential to the analysis of biological, chemical and environmental processes. Fluorescence techniques,^[1-7] which present the advantage of being highly sensitive (nanomolar detection),^[8, 9] are particularly used for this purpose. One of the most popular fluorophore is the pyrene moiety, which exhibits a characteristic emission band at *ca.* 380-400 nm. In case of spatial proximity between pyrenes, a tell-
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excimer fluorescence centered at 500 nm occurs that depends strongly upon the distance and orientation of the aromatic moieties.^[10] This sensitivity of the pyrene emission to the environment has been perceived as an opportunity for the construction of cation sensors.^{1, [11-14]} Systems were designed with (i) podand,^[15] crown ether^[16-18] or calixarene-based^[19-22] fragments for cation binding, (ii) covalently linked pyrenes acting as fluorophores and, upon the presence or absence of metal cations, (iii) sufficiently different conformations to modulate the fluorescence.^{2, [23-28]} For instance, Nakamura *et al.* reported the synthesis of an alkaline and alkaline earth metal cation sensor composed of a non-cyclic polyether and two terminal pyrenyl units (Figure 1, left).^[15] Kim *et al.* showed that calix[4]arene-based chemosensors with two possible binding sites (the polyether ring and the amide moieties) demonstrate a quench of the excimeric fluorescence upon addition of several cations (Figure 1, center).^[29, 30] Métivier and co-workers have described a sugar-derived azamacrocycle which is an efficient molecular sensor for Cu(II) (Figure 1, right).^[31]

In our group, a series of bis(pyreneamide) macrocycles was also prepared, namely compounds 16C4-Pyr₂, 18C4-Pyr₂, 20C4-Pyr₂ and 18C6-Pyr₂ (Figure 2, Pyr = 1-pyrenyl).^[32] These derivatives are synthesized in two steps from THF, THP, oxepane and 1,4-dioxane, respectively.^[33-36] The macrocycles are globally planar and act as a platform; the amide units being oriented perpendicularly to the mean plane.

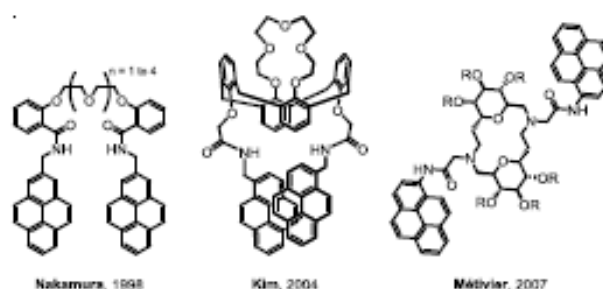


Figure 1. Examples of previously reported bis(pyrene)-based cation sensors.

The two aromatic pyrenes then face each other and a strong excimer fluorescence is observed (eg. 18C6-Pyr₂, Figure 2, bottom left). In the presence of potassium ions, a conformational change is however observed.^[32] It has been proposed that the amide C=O bonds turn inwards. Consequently, the environment of the aromatic units is modified and the excimer fluorescence is (partially) quenched (Figure 2, bottom right).^[37]

¹ These properties have been exploited to design chemical sensors, showing variations in their fluorescence spectra in response to external stimuli, such as temperature variations, light irradiation, cation/anion complexation or supramolecular interactions; see references 11-14.

² For other examples of cation sensors based on non-polyether structures, see references 23-28.

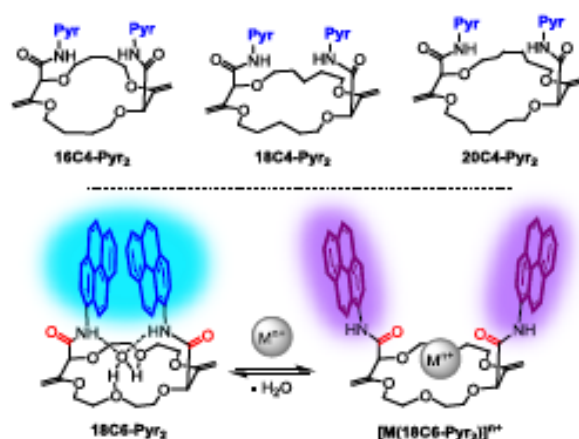


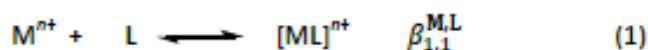
Figure 2. Top: Structure of polyether macrocycles (Pyr = 1-pyrenyl); Bottom: Conformational change upon cation binding responsible for the excimer fluorescence quenching.

This study was however limited to the detection of potassium cations in reversed lipophilic micelles.^[32] The ability of scaffolds 16C4-Pyr₂, 18C4-Pyr₂, 20C4-Pyr₂ and 18C6-Pyr₂ to act as general sensors towards a wide range of cations was therefore debatable. Herein, the binding abilities of different cations (alkaline, alkaline earth, *p*-, *d*-, and *f*-block metals) towards these polyether macrocycles are presented using UV-Vis spectrophotometric titrations, cyclic voltammetry, excimer fluorescence quenching and transient absorption spectroscopy experiments.

Results and Discussion

Absorbance

Initial experiments were aimed at determining the binding abilities of various metal ions by spectrophotometric titrations. Care was taken to select compound 18C6-Pyr₂ for these preliminary experiments as the crown ether-like nature was ensuring – in principle – a higher affinity towards cations than derivatives 16C4-Pyr₂, 18C4-Pyr₂, 20C4-Pyr₂ that possess aliphatic chains between the polar branches. Experiments were performed in acetonitrile and perchlorate salts were selected due to the weakly coordinating nature of this anion. Table 1 collects the stability constants of the complexes fitted with eqn (1).³ Using the HySS program, speciations were calculated for 3.3 equivalents of Mⁿ⁺ per receptor L ($C_M = 6.6 \cdot 10^{-6}$ M, $C_{18C6-Pyr_2} = 2.0 \cdot 10^{-6}$ M).^{4, [38]}



³ See Figures S1 to S65 in Supporting Information for experimental spectra.

⁴ Spectrophotometric titrations were performed from 0 to 3 equivalents of metal at $C_{18C6-Pyr_2} = 1 \cdot 10^{-4}$ M. Fluorescence spectra were recorded at $C_{18C6-Pyr_2} = 2 \cdot 10^{-4}$

M for 3.3 equivalents of metal to maximize formation of the complex.

Table 1. Effective ionic radii for six-coordinate metal cations, binding constant ($\log \beta$) and ligand speciation (at 3.3 equivalents of M^{n+} ; $C_M = 6.6 \cdot 10^{-6}$ M, $C_{18C6-Pyr_2} = 2.0 \cdot 10^{-8}$ M) of $[M(18C6-Pyr_2)]^{n+}$ complexes (acetonitrile, 293 K)

Entry	M^{n+}	r [Å]	$\log(\beta_{1:1}^{M:L})$	% complex ^a
1	Li^+	0.76	<2 ^b	<0.1
2	Na^+	1.02	3.815(6)	4.2
3	K^+	1.38	3.781(2)	3.8
4	Cs^+	1.67	2.60(1)	0.3
5	Ag^+	1.15	<2 ^b	<0.1
6	Ca^{2+}	1.00	5.753(6)	74.4
7	Mg^{2+}	0.72	3.553(1)	2.3
8	Ni^{2+}	0.69	<2 ^b	<0.1
9	Zn^{2+}	0.74	2.987(9)	0.6
10	Cd^{2+}	0.95	2.724(6)	0.4
11	Ba^{2+}	1.35	6.281(7)	90.2
12	Pb^{2+}	1.19	7.57(7)	99.5
13	La^{3+}	1.216	5.51(2)	63.6

^a Speciation for 3.3 equivalents of metal; ^b Formation of the complex was not observed under the experimental conditions used; the stability constants were estimated to be <2. ^c Nine-coordinate ionic radius.

Li^+ , Ag^+ and Ni^{2+} evidenced no measurable interaction with 18C6-Pyr₂ within our limit of detection ($\beta < 10^2$),⁵ whereas the other tested monovalent and divalent cations showed the formation of a 1:1 complex, the association free energy of which are scattered with respect to the electrostatic Born factor z^2/R (Figure 3, z is the charge of the cation in electrostatic units and R its ionic radius). Such behavior is diagnostic for the operation of some specific size recognition by the receptor, which is magnified by the increasing charge borne by the cation (see trendlines in Figure 3). A focus on the divalent cations reveals a marked preference for the larger member of the series (Ca^{2+} , Ba^{2+} and Pb^{2+}) despite their reduced electrostatic factors.⁶ The anomalously small thermodynamic constant recorded for the triply charged La^{3+} confirms the preeminence of structural factors over simple electrostatic associations. Cu^{2+} and Hg^{2+} were also investigated, but redox reactions involving the pyrene-containing macrocycles and these metal ions prevent the determination of stability constants.

⁵ The reconstructed spectra of the complexes are identical to 18C6-Pyr₂ alone.

⁶ See Table S1 in Supporting Information.

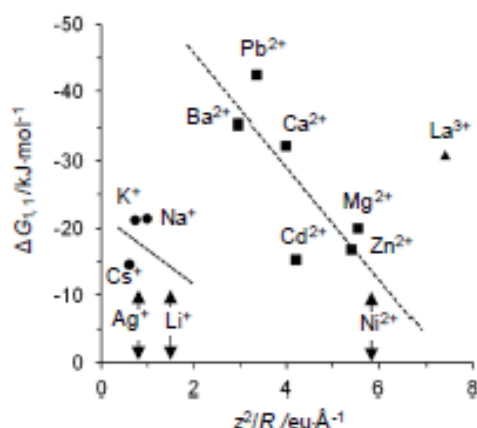


Figure 3. Stability constants of $[M(18C6-Pyr_2)]^{2+}$ complexes vs electrostatic Born factors (acetonitrile, 293 K).

Cyclic Voltammetry

To support the claim for redox processes between Cu^{2+} or Hg^{2+} and the substituted crown ethers, cyclic voltammograms of separated partners were recorded in anhydrous acetonitrile. In line with previous detailed investigation,^[39] Cu^{2+} salts are strongly oxidizing in pure acetonitrile, which leads to two successive quasi-reversible one-electron reduction processes corresponding to Cu^{2+}/Cu^+ ($E_{pc/2} = 1.15$ V vs SHE) and Cu^+/Cu^0 ($E_{pc/2} = -0.24$ V vs SHE including some adsorption on the electrode surface, Figure S68). The voltammogram recorded for Hg^{2+} (Figure S69) displays closely related characteristics with a first dimerization-coupled reduction $2Hg^{2+}/Hg_2^{2+}$ ($E_{pc/2} = 0.80$ V vs SHE) followed by additional electron transfer leading to elemental mercury $Hg_2^{2+}/2Hg^0$ ($E_{pc/2} = -0.64$ V vs SHE). On the other hand, the voltammogram of the 18C6-Pyr₂ ligand shows essentially irreversible redox processes, from which a one electron reduction $18C6-Pyr_2/18C6-Pyr_2^-$ occurs around $E_{pc/2} = -1.85$ V vs SHE (Figures S66-S67). The oxidative counterpart reveals a succession of stepwise oxidation processes within the 1.08 to 1.61 V vs SHE range, a behavior confirmed by voltammetric data recorded for 18C4-Pyr₂ (Figures S70-S71). Comparing these potentials with those of the metal-centered reduction processes, there is no doubt that Cu^{2+} is a sufficiently strong oxidant in acetonitrile for extracting electrons from the ligands, thus preventing standard complexation reactions. In the case of Hg^{2+} , the situation is less clear and only the large excess of metal required for pushing the limit of complexation may explain a thermodynamically-driven oxidation reaction due to the virtue of the Nernst equation, which models the electrochemical potentials in non-standard conditions.

Fluorescence

The luminescent properties of compounds 16C4-Pyr₂, 18C4-Pyr₂, 20C4-Pyr₂ and 18C6-Pyr₂ were then analyzed along with that of derivative 15C4-Pyr (Figure 4) containing a single pyrene unit and used therefore as reference. The normalized fluorescence spectra presented in Figure 5 were recorded in acetonitrile ($2 \cdot 10^{-6}$ M).

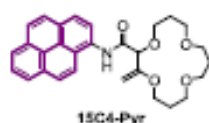


Figure 4. Structure of the monomeric 15C4-Pyr derivative.

As expected, 15C4-Pyr presented the characteristic emission bands of monomeric pyrene with two maxima at 388 nm and 408 nm. In the case of the bis(pyreneamide) polyethers 16C4-Pyr₂, 18C4-Pyr₂, 18C6-Pyr₂ and 20C4-Pyr₂, these emission bands were present along with the specific broad excimer spanning from the blue to the yellow regions (ca. 425-600 nm). To estimate the excimer vs monomer emission ratio, one possibility is a comparison of the intensities of both contributions ($I_{\text{excimer}}/I_{\text{monomer}} = I_{490}/I_{388}$).⁷ This ratio is maximal for macrocycle 18C4-Pyr₂ ($I_{\text{excimer}}/I_{\text{monomer}} = 32$) and sensibly decreases upon replacement of -CH₂- groups by O atoms within macrocycle 18C6-Pyr₂ ($I_{\text{excimer}}/I_{\text{monomer}} = 11$). Interestingly, higher or lower order macrocycles 16C4-Pyr₂ and 20C4-Pyr₂ both exhibit a decrease of this ratio, revealing a weaker overlap of the pyrene moieties ($I_{\text{excimer}}/I_{\text{monomer}} = 4.2$ and 1.6, respectively).

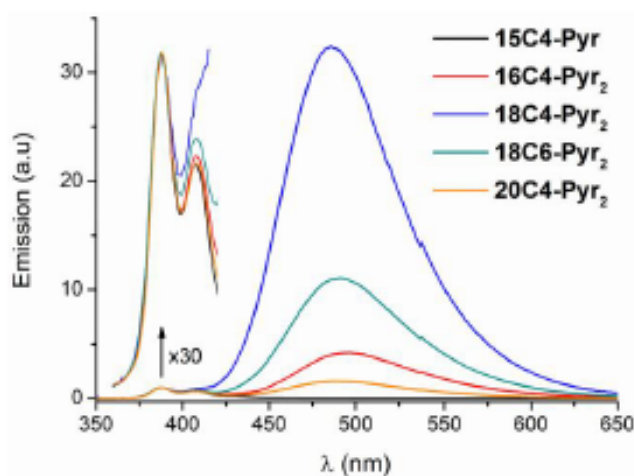


Figure 5. Fluorescence spectra of macrocycles 15C4-Pyr, 16C4-Pyr₂, 18C4-Pyr₂, 18C6-Pyr₂ and 20C4-Pyr₂ in acetonitrile.

The effect on the excimer emission in the presence of 3.3 equivalents of metal perchlorate was then tested. In the case of 15C4-Pyr and as expected, no modification of the fluorescence spectra was detected upon addition of the cations and the characteristic pyrene bands were recorded (Figure S72, right). In a general manner, with the various cations, quenching did not occur in acetonitrile for

⁷ Another possibility is a comparison of the excimer intensity to the total fluorescence using mono(pyreneamide) 15C4-Pyr as reference. The excimer intensities of 16C4-Pyr₂, 18C4-Pyr₂, 18C6-Pyr₂ and 20C4-Pyr₂ are then 12 times, 85 times, 30 times and 5 times stronger than that of 15C4-Pyr respectively.

16C4-Pyr₂ and 18C4-Pyr₂ to the exception of Hg²⁺ and Cu²⁺ (Figure 6). In these latter two cases, the loss of luminescence is linked to a decomposition of the macrocyclic receptors by redox processes (*vide supra*).^{8, [40]}

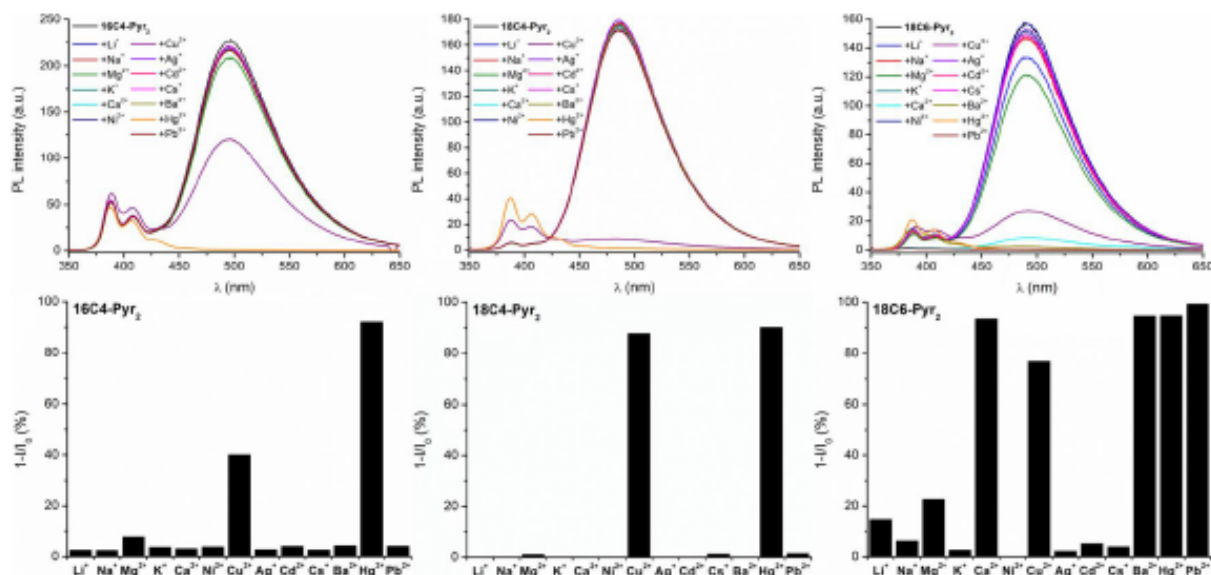


Figure 6. Top: photoluminescence spectra of 16C4-Pyr₂ (left), 18C4-Pyr₂ (center) and 18C6-Pyr₂ (right) ligands in presence of various cations (acetonitrile, C₁ = 2.0·10⁻⁶ M and C_M = 6.6·10⁻⁶ M, 3.33 equivalents). Bottom: percentage of fluorescence quenched (1 - I/I₀) in the presence of various metal cations.

Interestingly, the fluorescence of macrocycle 18C6-Pyr₂ appears to be strongly influenced by the presence of Ca²⁺, Ba²⁺, and Pb²⁺ ions, whereas the other metal ions lead to little or no significant changes in the spectra (Figure 6, right). The two following trends can be differentiated: (i) partial or total quench of the excimer fluorescence with Ca²⁺ (94%) and Ba²⁺ (95%); and (ii) complete quench of both monomer and excimer fluorescence with Pb²⁺ (>99%). Finally, for macrocycle 20C4-Pyr₂, no quenching of the luminescence was monitored in the presence of the metals, the cavity being presumably too large to bind efficiently the cations (Figure S72, left).

Knowing the percentage of [M(18C6-Pyr₂)]ⁿ⁺ for each metal (Table 1), a correlation can be pointed out between the proportion of excimer fluorescence quenching and the amount of metal-ligand complex formed in solution. In fact, for Ca²⁺, Ba²⁺ and Pb²⁺, respectively 74%, 90% and >99% of the

⁸ Métivier et al. already proposed a photoinduced electron transfer (PET) from the excited pyrene to Cu²⁺ as a mechanism that could explain the strong fluorescence quenching. See Ref 31.

ligand are complexed and the quenching of fluorescence is also relatively strong.⁹ However, with the other metals only poor quenching is observed because, under the experimental conditions, only up to 4% of the complex is formed.

Transient absorption spectroscopy

Transient absorption (TA) measurements on the sub-ns to μ s timescales were performed to obtain deeper insight into the fluorescence quenching mechanism in the presence of Pb^{2+} and Hg^{2+} . Figure 7A and 7B show TA spectra recorded at various time delays after 355 nm excitation of 15C4-Pyr and 18C6-Pyr₂ in acetonitrile. The early-time TA spectra measured with 15C4-Pyr are dominated by several bands at 380, 395, 500 and 565 nm that can be attributed to the chromophore in the S_1 state. Differences with the excited-state absorption spectrum of pyrene^[41] can be explained by the effect of the amide linker. This initial spectrum evolves with a 19 ns time constant to a spectrum with a band around 440 nm that can be assigned to the triplet T_1 state.^[42] Afterwards, this band decays entirely on the μ s timescale. By comparison, the early TA spectra measured with 18C6-Pyr₂ show a single broad band centered at 500 nm, which coincides with the absorption spectrum of the pyrene excimer.^[43] As this excimer band decays in 39 ns, a weak band appears around 440 nm and decays on the μ s timescale. This band is very similar to that observed at long time with 15C4-Pyr, and is assigned to the T_1 state localized on a single pyrene unit.

Then, the TA spectra were recorded with 3.3 equivalents of Pb^{2+} . They reveal an ultrafast decay of the local pyrene S_1 state, whose absorption band is hardly visible with the resolution of the experiment (Figure 7C). The only band observed after less than 1 ns is that of the T_1 state at 440 nm. This very fast decay of the locally excited state of pyrene, which accounts for the absence of fluorescence observed with Pb^{2+} , is attributed to a very efficient non-radiative deactivation of the S_1 state. It could originate from an acceleration of the intersystem crossing due to a heavy atom effect. However, given the small intensity of the T_1 absorption band, a direct ultrafast $S_1 \rightarrow S_0$ non-radiative transition is probably operative as well.

⁹ For Cu^{2+} and Hg^{2+} , strong quenching is observed, but it cannot be related to the stability constant because the latter could not be determined due to redox reactions occurring between the ligand and the metal.

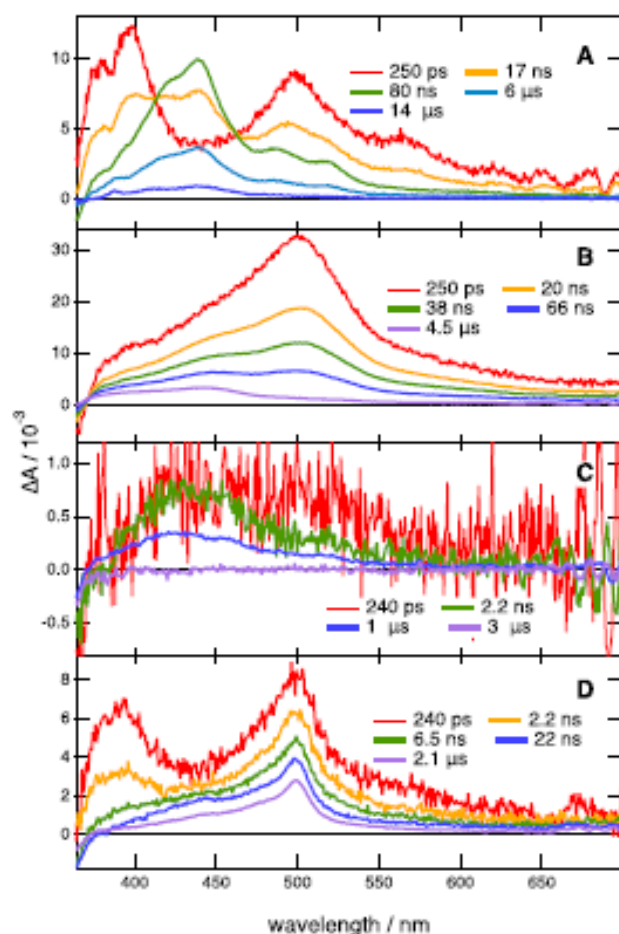


Figure 7. Transient absorption spectra recorded at different time delays after 355 nm excitation of 15C4-Pyr (A), 18C6-Pyr₂ alone (B) and with 3.3 equivalents of Pb²⁺ (C) or of Hg²⁺ (D) in acetonitrile.

Finally, to confirm that an excimer is not formed in the presence of Hg²⁺, the TA spectra were recorded in the presence of 3.3 equivalents of this metal ion. They point to a much more complex dynamics (Figure 7D). The early spectra correspond to the S₁ state localized on a pyrene unit. This spectrum transforms on the ns timescale into one with a single narrow band at 500 nm. Given the results from the cyclic voltammetry, this band is tentatively assigned to the radical cation of a pyrene sub-unit,^[44] which then decays in 65 μs. The excimer is not generated in the presence of Hg²⁺, in agreement with the fluorescence results that only show the local pyrene emission.

Conclusions

To conclude, a series of bis(pyreneamide) macrocycles were synthesized in two steps from THF, THP, oxepane and 1,4-dioxane. 18C6-Pyr₂ is effective as a chemosensor for a large range of mono-, di- and trivalent cations (alkaline, alkaline earth, *p*-, *d*-, and *f*-block metals). UV-Vis spectrophotometric titrations, cyclic voltammetry, excimer fluorescence quenching and transient absorption spectroscopy experiments helped characterize the On-Off changes occurring upon binding and

demonstrate that the highest stability constants are obtained with divalent cations Ca^{2+} , Ba^{2+} specifically. However, Cu^{2+} , Hg^{2+} and Pb^{2+} present different quenching mechanism by redox or heavy atom effects.

Experimental Section

UV-Vis Titration experiments

In a typical experiment, 20 mL of 18C6-Pyr₂ macrocycle in acetonitrile (10^{-4} mol·mL⁻¹) were titrated at 293 K with a solution of metal perchlorate ($2 \cdot 10^{-3}$ mol·mL⁻¹) in acetonitrile under inert atmosphere. After each addition of 0.05 mL, the absorbance was recorded. The titration was pursued till a total of 5.0 equivalents of metal were added to the titration vessel. Mathematical treatment of the spectrometric titration was performed with factor analysis^[43] and with ReactLab™ Equilibria (previously Specfit/32; <http://jplusconsulting.com/products/reactlab-equilibria/>).

Cyclic voltammetry experiments

Cyclic voltammograms were recorded by using a EC Epsilon™ potentiostat (BASi®) connected to a personal computer. A three electrode system consisting of a stationary Pt disc or a glassy carbon working electrode, a Pt counter-electrode and a nonaqueous Ag/AgCl LiCl sat. in EtOH reference electrode was used. (ⁿBu)₄NPF₆ (0.1 M in acetonitrile) served as an inert electrolyte. Potentials were measured against an AgCl/Ag LiCl sat. in EtOH reference electrode and referenced against SHE using the redox couple Fc⁺/Fc (0.624 vs SHE^[46]) as an internal standard.^[47] The scan speed was 100 mVs⁻¹ and voltammograms were analysed according to established procedures.^[48]

Fluorescence experiments

In a typical experiment, steady-state fluorescence spectra of macrocycle were recorded in acetonitrile ($C_L = 2 \cdot 10^{-6}$ M) and with addition of metal perchlorate ($C_M = 6.6 \cdot 10^{-6}$ M, 3.3 equivalents). Excitation was performed at 340 nm for all compounds. All fluorescence spectra were corrected for the wavelength-dependent sensitivity of the detection.

Transient absorption experiments

The transient absorption setup is used to record spectra up to 1 ms with a 350 ps (fwhm) instrument response function as previously described in detail.^[49] Excitation was performed at 355 nm using a passively Q-switched frequency-tripled Nd:YAG laser (Teem Photonics). The pump intensity on the sample was around 0.5 mJ/cm². The sample solutions were located in a 1 mm quartz cell and were continuously stirred by N₂ bubbling. Their absorbance at 355 nm was around 0.15-0.3.

Supplementary Material

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/MS-number>.

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Author Contribution Statement

The syntheses of compounds were carried out by *M.V.*, *A.H.* and *E.B.* under the supervision of *J.L.* *M.V* and *T.L.* performed the absorption and cyclic voltammetry experiments and *T.L.* analyzed the data under the supervision of *C.P.* *M.V* and *S.P.* performed the fluorescence experiments and *S.P.* analyzed the data under the supervision of *J.L.* *O.Y.* performed the transient absorption experiments and analyzed the data under the supervision of *E.V.* All the authors contributed to the redaction of the manuscript.

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