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Cu^{2+}-Induced Blue Shift of the Pyrene Excimer Emission: A New Signal Transduction Mode of Pyrene Probes

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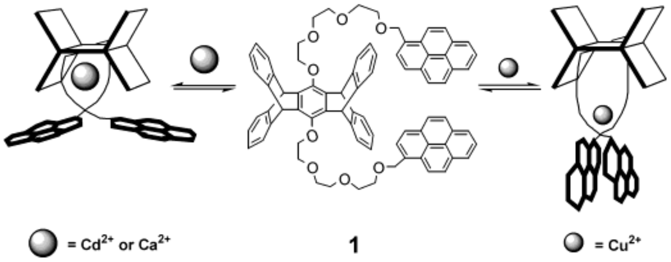
ABSTRACT



A pentiptycene-bispyrenyl system (1) has been synthesized and investigated as a fluorescent chemosensor for metal ions. A novel blue shift along with an intensity enhancement of the pyrene excimer emission is observed for 1 in the presence of Cu^{2+}. Such a new signal transduction mode of pyrene probes results from the formation of a static pyrene excimer that has very different characteristics from its dynamic counterpart.

A key feature rendering pyrene so attractive and useful as a fluorescent probe is its relatively efficient excimer formation and emission in comparison to other polyaromatic fluorophores.[1] Two informative parameters associated with the pyrene excimer are the intensity ratio of the excimer to the monomer emission (I_E/I_M) and the wavelength corresponding to the maximum of excimer emission (λ_E). While the I_E/I_M parameter is sensitive to the structure of pyrene-labeled systems and thus has been very useful in the biological, polymeric, and sensory materials chemistry,[2−4] the corresponding pyrene λ_E is much less variable and generally locates at 475−485 nm. We report herein a pentiptycene-derived bispyrenyl system (**1**) that displays not only the I_E/I_M but also the λ_E variations depending on the metal ion present: namely, Ca^{2+} and Cd^{2+} decrease the I_E/I_M ratio without changing the λ_E, whereas Cu^{2+} shifts the λ_E toward blue ($\lambda_E = 440$ nm) along with an enhanced I_E/I_M. Excitation spectra suggest that the mechanisms of the initial and the blue-shifted excimer formation are dynamic and static, respectively. In conjunction with the results from the corresponding investigation of compound **2**, molecular models that might account for our observations are proposed.

Compound **1** was designed by following our continued interests in the supramolecular chemistry of iptycene derivatives[5,6] to investigate its interactions with metal ions by the

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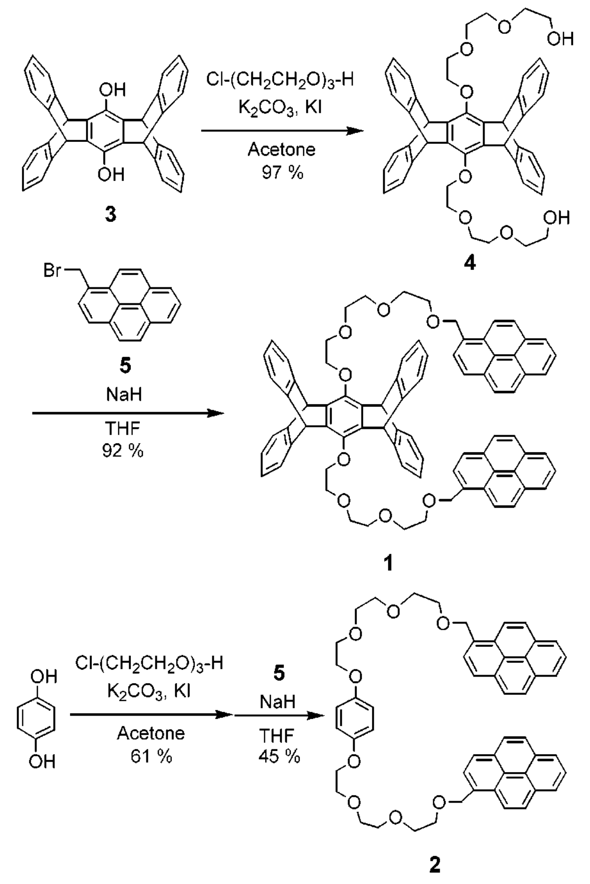
fluorescent probe of pyrenes. We reasoned that a hybrid of the potential noncyclic polyether ligand[4d] and the three-dimensional aromatic pentiptycene group[5−7] might form a selective ionophore, where the cation−π interactions[8] might contribute to the ion recognition of **1**. The synthesis of compound **1** was performed starting with the precursors of pentiptycene hydroquinone[5] **3** and 1-bromomethylpyrene[9] **5** based on the route shown in Scheme 1. The same procedures were also employed in the formation of compound **2** from hydroquinone.

Scheme 1



Compound **1** in dichloromethane displays selective and sensitive fluorescence responses to metal ions.[10] As is shown in Figure 1, a decrease of the excimer with an increase of the monomer emission of **1** is selectively induced by Ca^{2+} among six alkali and alkaline earth metal ions. Selectivity is also found for **1** among nine transition metal ions, where only Cd^{2+} leads to a reduced I_E/I_M in a manner similar to that shown in Figure 1. Binding constants, expressed as log K, determined by either fluorimetry or absorption spectroscopy[11] assuming 1:1 complex formation are consistent, and the values are 4.6 and 4.8 for Ca^{2+} and Cd^{2+}, respectively.

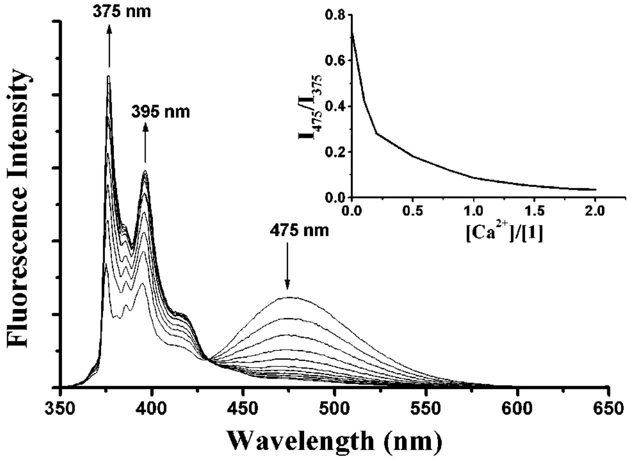


Figure 1. Fluorescence spectra of **1** in CH_2Cl_2 (1×10^{-5} M, excitation at 335 nm) in the presence of 0, 0.1, 0.2, 0.5, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, and 2.0 equiv of $Ca(ClO_4)_2 \cdot 4H_2O$ predissolved in MeCN (0.005 M) and the corresponding change in the I_E/I_M ratio represented by the intensities at 475 (I_{475}) and 375 (I_{375}) nm (inset).

Surprisingly, a pronounced blue shift along with an intensity enhancement of the pyrene excimer emission was observed for **1** in the presence of Cu^{2+} (Figure 2A). An intensity maximum is reached at $[Cu^{2+}]/[\mathbf{1}] = 10-13$, where the λ_E shifts as much as 35 nm (from 475 to 440 nm). The corresponding absorption spectra are not shifted but broadening, resulting in isosbestic points at 325, 331, 339, and 348 nm (Figure 2B), and suggest a binding constant of log K = 4.4 for the formation of 1:1 complexes of **1** and Cu^{2+}.[11] Further introduction of Cu^{2+} does not result in a larger shift of the λ_E but decreases the intensity of the 440 nm emission. The reduced intensity could be attributed to the increased content of acetonitrile that competes with **1** for Cu^{2+} and/or the nature of Cu^{2+} as a moderate fluorescence quencher[12,13] (vide infra).

Although dichloromethane is such a poor solvent in solvating ionic species that one might expect many metal ions will interact with **1**, the other 12 metal ions[10] studied in this work cause little or no fluorescence changes. When

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[10] Fifteen metal ions (perchlorate salts unless otherwise noted) were studied in this work, including Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Mn^{2+}(acetate), Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Y^{3+}(nitrate), Ag^+, Cd^{2+}(chloride), and Hg^{2+}(acetate).

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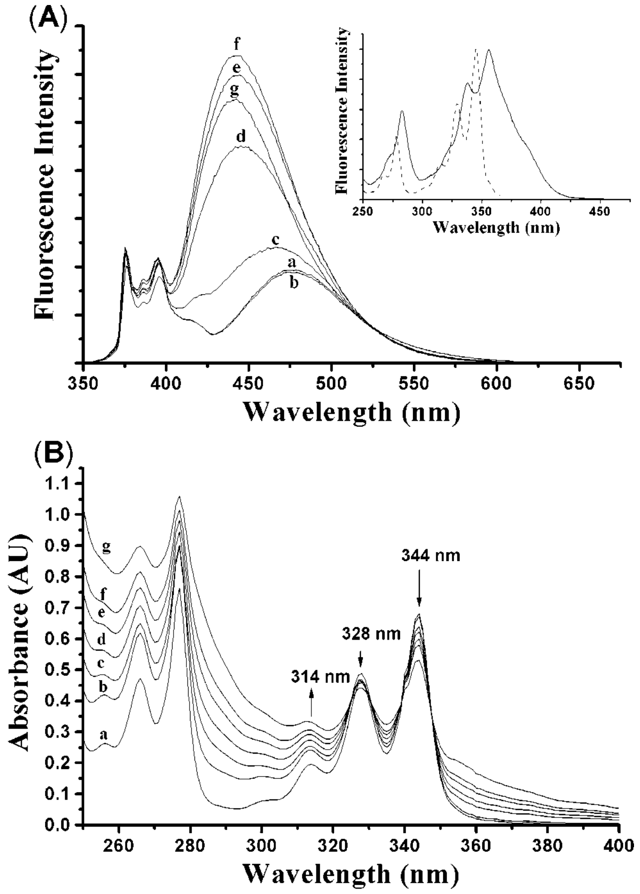

Figure 2. (A) Fluorescence and (B) absorption spectra of **1** in CH_2Cl_2 (1×10^{-5} M, excitation at 335 nm) in the presence of (a) 0, (b) 1.0, (c) 5.0, (d) 7.0, (e) 9.0, (f) 11.0, and (g) 15 equiv of $Cu(ClO_4)_2\cdot 6H_2O$ predissolved in MeCN (0.005 M) and the corresponding change in the excitation spectra (normalized) monitored at 375 (dash) and 440 (full) nm (inset).

dichloromethane is replaced by the more polar acetonitrile, no more fluorescence variations could be induced by Ca^{2+} or Cd^{2+}, whereas the spectral features of blue-shifted and intensity-enhanced pyrene excimer emission are retained, albeit to a lesser extent and requiring a higher $[Cu^{2+}]/[\mathbf{1}]$ ratio ($\log K = 3.6$), in the presence of Cu^{2+}.[14] An intensity maximum also occurs, where the $[Cu^{2+}]/[\mathbf{1}]$ ratio is ~60 and the λ_E is 449 nm. Unlike the case in dichloromethane, the λ_E continues to shift toward blue upon further addition of Cu^{2+} (e.g., $\lambda_E = 444$ nm at $[Cu^{2+}]/[\mathbf{1}] \sim 180$). Apparently, the interactions between **1** and metal ions are weak, and this might be related to its high ion selectivity even in dichloromethane solutions.

To understand the different fluorescence responses of **1** in dichloromethane to Ca^{2+} or Cd^{2+} vs Cu^{2+}, the nature of the blue-shifted 440 nm emission vs the normal 475 nm excimer should be characterized. One of the powerful methods for the differentiation of a dynamic excimer from a static one is the excitation spectrum.[2] Excitation spectra recorded at both the monomer (375 nm) and the excimer (475 nm) regions for **1** in metal-free solutions are the same, indicating a dynamic nature for the 475 nm emission. In the presence of Ca^{2+} or Cd^{2+}, the dynamic character is maintained for the residual pyrene excimer. Thus, the decrease of I_E/I_M in Figure 1 simply suggests that the pyrene groups in the ion-bound complexes cannot adopt an overlapping geometry. On the other hand, the excitation spectrum of the Cu^{2+}-induced 440 nm emission is broadened and largely red-shifted (e.g., 11 nm for the 0−0 band) in comparison to that recorded at 375 nm (Figure 2A, inset). Evidently, the 440 nm emission is from a static excimer. The same conclusions can be drawn on the basis of the fluorescence decay times.[2,15] In metal-free solutions, both the pyrene monomer (294 ns, 65%) and excimer (102 ns, 100%) emissions have long decay times (τ and preexponential). In addition, a rising time of 36 ns was determined for the 475 nm excimer emission, corresponding to the short component of monomer emission (32 ns, 35%). By contrast, the Cu^{2+}-induced 440 nm emission has a relatively short lifetime (6.3 ns, 96%; 46.5 ns, 4%) and shows no rising component. The 16-fold reduction in fluorescence lifetime for the 440 nm vs 475 nm excimer emission suggests a larger radiative decay rate constant for the static than the dynamic pyrene excimers.[16]

The pyrene excimer is proposed to have a symmetrical sandwich-like structure, and the blue-shifted form is generally attributed to partially overlapping pyrene dimers.[2,17] For most pyrenyl systems, emission from the latter is generally weak or negligible and often obscured by the strong emission from the former. As a consequence, methods such as spectral deconvolution analysis and time-resolved spectrometry are required for the identification of the blue-shifted excimer.[2,17] It is known that a locally excited and partially overlapped pyrene dimer can undergo a rapid structural relaxation to the lower energy pyrene excimer,[17c] which might account for the weak emission of blue-shifted pyrene excimers and the poor sensitivity of the pyrene λ_E to the ground-state structures. Accordingly, the binding of Cu^{2+} in **1** not only brings the pyrene groups together in the ground state leading to the formation of static excimers but also prohibits or

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(14) Figures are shown as the Supporting Information.

(15) Decay times were determined at room temperature by means of an Edinburgh photon counting apparatus (OB900-14A) with $\lambda_{ex} = 335$ nm for all measurements. The goodness of fit was judged by the reduced χ^2 value (<1.10 in all cases), the randomness of the residuals, and the autocorrelation function.

(16) (a) On the basis of the deconvolution analysis of emission spectra and the assumption of preexponentials = fraction of emitters (i.e. dynamic excimer = 35% in a metal free dichloromethane solution), the quantum efficiency (Φ_F) of the dynamic excimer of **1** in dichloromethane is estimated to be ca. 0.25.[16b] Due to the complication of monomer excitation and emission and fluorescence quenching by the unbound Cu^{2+}, the determination of the quantum yield of the static pyrene excimer in the presence of Cu^{2+} is difficult. However, an estimation based on Figure 2 suggests a lower limit of 0.26 for the Φ_F value of the Cu^{2+}-bound static excimer in dichloromethane solutions. This would lead to radiative rate constants of $\sim 2.5 \times 10^6$ and 4.1×10^7 s^{-1} for the dynamic and static excimers, respectively. (b) Anthracene ($\Phi_F = 0.27$ in hexane)[1] was used as the actinometer.

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minimizes such a relaxation event in the excited state leading to a blue-shifted excimer emission.

The overall fluorescence enhancement of **1** upon the binding of Cu^{2+} is also interesting, because the opposite is more common in previously reported Cu^{2+} chemosensors.[13] While Cu^{2+}-induced fluorescence enhancement was also observed in a few cases,[18] the mechanism is different from that in **1**: namely, the binding of Cu^{2+} turns off certain nonradiative decay processes (e.g., photoinduced electron transfer) of the fluorophores in earlier cases, but it results in the formation of new emitting species (static excimer) having a stronger fluorescence character than its origins (monomer and dynamic excimer) in **1**. Nonetheless, the unbound Cu^{2+} appears to behave as a fluorescence quencher and to be responsible for the reduced fluorescence at the stages of Cu^{2+} addition at the beginning (low $[Cu^{2+}]/[\mathbf{1}]$ ratio) and after the intensity maximum (high $[Cu^{2+}]/[\mathbf{1}]$ ratio).[19] In both conditions, the net increase of the stronger fluorescent $Cu^{2+}-\mathbf{1}$ complexes is too low to compensate for the fluorescence quenching by the additional unbound Cu^{2+}. Thus, the observed fluorescence enhancement should be considered as a lower limit.[16]

To gain an insight into the role of the pentiptycene groups of **1** in ion recognitions, compound **2** was also investigated. Results show that substitution of the pentiptycene group by a phenyl ring no longer leads to fluorescence responses to Ca^{2+} or Cd^{2+} in either dichloromethane or acetonitrile solutions. Fluorescence changes due to the presence of Cu^{2+} can be observed for **2**,[14] but the extent of blue shift and intensity enhancement of pyrene excimer is greatly reduced in both dichloromethane ($\log K = 4.2$) and acetonitrile ($\log K = 1.4$) solutions in comparison to the case of **1**. Apparently, the flanking benzene rings of the pentiptycene groups play an important role in the recognition of Ca^{2+}, Cd^{2+}, and Cu^{2+}. In conjunction with the fact that the radii of Ca^{2+} (1.00 Å) and Cd^{2+} (0.95 Å) ions are comparable and that of Cu^{2+} is smaller (0.57 Å),[20] molecular models[21] that might account for the fluorescence behavior of **1** are proposed in Figure 3. It should be noted that it is the nature rather than the size of metal ions that is responsible for the spectral changes and ion selectivity of **1**, because the sizes of Ca^{2+}, Cd^{2+}, or Cu^{2+} are not unique among the 15 metal ions investigated.[10,20] In addition, the flanking benzene rings of the pentiptycene group in **1** vs **2** not only provide a venue for cation−π interactions but also perturb the conformation of polyether chains. Both effects might contribute to the recognition of Ca^{2+} and Cd^{2+} by **1** in dichloromethane, but their relative contributions cannot be justified, mainly due to the overall weak interactions between **1** and metal ions. Furthermore, the detailed structures of Figure 3, particularly the partially overlapping pyrene dimer, remain to be established. Further studies designed toward a better understanding of these aspects are in progress.

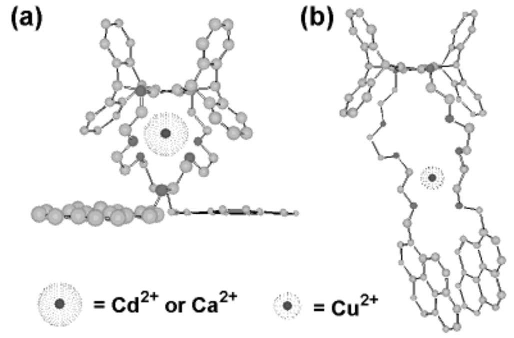

Figure 3. Molecular models showing the proposed structures of **1** in dichloromethane in the presence of (a) Ca^{2+} or $Cd^{2+}$and of (b) Cu^{2+}.

In conclusion, our studies on the pentiptycene-bispyrenyl hybrid **1** have revealed the potential of the three-dimensional pentiptycene group in the formation of new metal ion sensors. In particular, a novel blue shift and intensity enhancement of the pyrene excimer emission has been observed for **1** in the presence of the Cu^{2+} ion. This is attributed to the conversion of a sandwich-like dynamic excimer to a partially overlapping static excimer. Such a new signal transduction mode of pyrene probes might be useful in the design of new pyrene-based sensory materials.

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Supporting Information Available: Experimental procedures and characterization data for compounds **1**, **2**, and **4** and figures of the absorption and/or fluorescence spectra of **1** in acetonitrile and **2** in dichloromethane and acetonitrile in the presence of Cu^{2+}. This material is available free of charge via the Internet at http://pubs.acs.org.

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[19] The little differences of optical density upon the introduction of Cu^{2+} at the wavelengths used for excitation cannot account for the dramatic excimer intensity variations at low and high $[Cu^{2+}]/[\mathbf{1}]$ ratios.

[20] *Handbook of Chemistry and Physics*; Lide, D. R., Ed.; CRC Press: Boca Raton, 1997. The coordination number is assumed to be six for Ca^{2+} and Cd^{2+} and four for Cu^{2+}.

[21] The structures of **1** were optimized in the absence of metal ions using the MM2 force field supplied by Chem 3D Plus, a product of Cambridge Scientific Computing, Inc.