Communication

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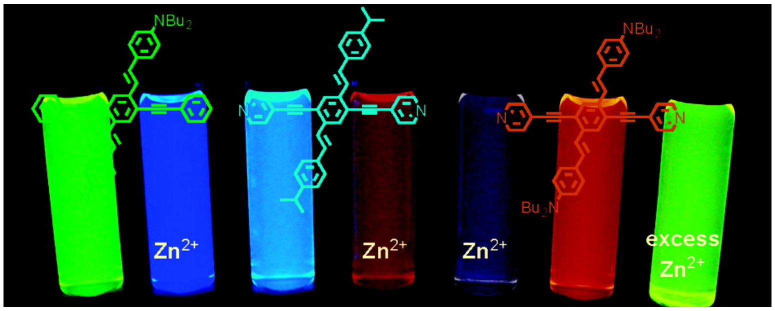

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Switching of Intramolecular Charge Transfer in Cruciforms: Metal Ion Sensing

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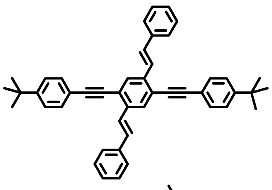
In most, but not all, chromophores, HOMO and LUMO are spatially superimposed. However, adding donor and/or acceptor substituents to *cross-shaped* chromophores at suitable positions can lead to *independent* electronic shifts in HOMO and LUMO into opposite directions.[1−4] In the cruciforms **2**−**4**, the HOMO is located on the distyrylbenzene branch, while the LUMO is situated on the bisarylethynyl axis of the molecule.[4] As a consequence, the intramolecular charge-transfer emission and absorption of such cruciforms is dependent upon solvent polarity, etc. Herein, we demonstrate dramatic blue and/or red shifts of emission and absorption upon coordination of metal cations to cruciforms **2**−**4**; the cruciforms should be valuable functional scaffolds for differential metal sensor arrays.[5−7]

The synthesis of **1** and **2** is described elsewhere,[4] while details of the preparation of **3** and **4** are presented in the Supporting Information. The general route to **1**−**4** starts from 1,4-bis(diethyloxyphosphonylmethyl)-2,5-diiodobenzene, which is subjected to a Wittig−Horner reaction[8] followed by a Sonogashira coupling to an arylalkyne[9] to give the desired cruciforms in good yields and purity after crystallization. In a first experiment, **4** was exposed to Zn^{2+} ions in dichloromethane. We selected Zn^{2+} due to its importance as an active ion in biological systems.[10,11] Upon coordination of 0.81 equiv of Zn^{2+}, the emission of **4** (Figure 1, 570 nm) is blue shifted (420 nm). Upon addition of a total of 4 equiv of Zn^{2+}, the emission red shifts back again to 530 nm. This behavior was surprising and needed explanation. Compounds **2** and **3** are similar to **4** but are lacking either the pyridine (**2**) or the dibutylamino (**3**) groups. Their emission spectra in dichloromethane and upon addition of zinc triflate are likewise shown in Figure 1. Addition of zinc ions to **2** leads to a blue shift (527 → 430 nm), while addition of zinc to **3** leads to a red shift (457 → 564 nm) of the observed emission. Addition of more Zn^{2+} ions to either **2** or **3** does not lead to any further spectral changes.



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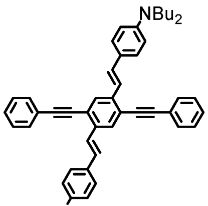

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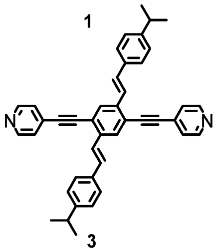

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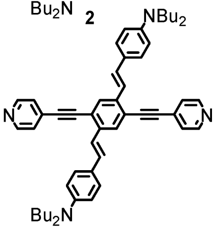

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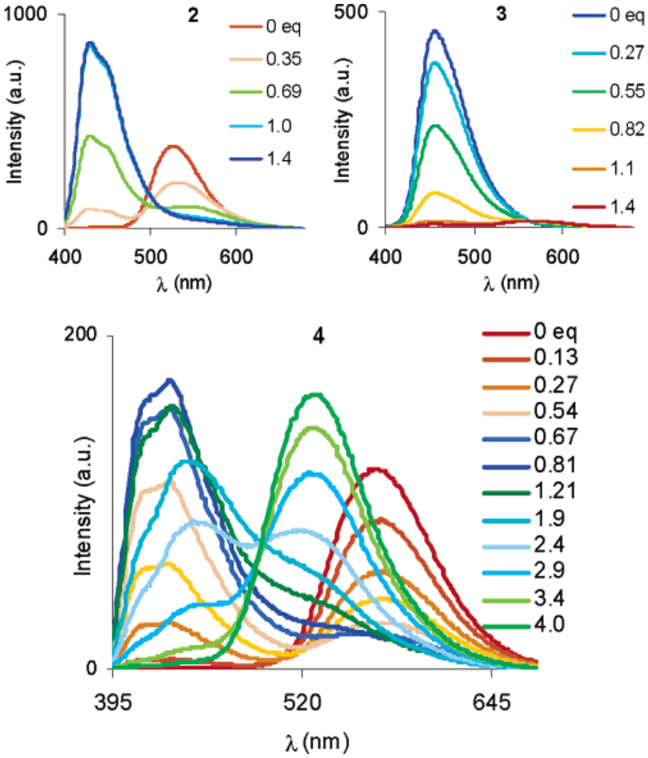

Figure 1. Emission spectra of **2**, **3**, and **4** upon addition of zinc trifluoromethylsulfonate in dichloromethane.

The blue shift in **2** and the red shift in **3** upon addition of zinc ions can be explained. In **2**, addition of the zinc ions will lead to a lowering of the HOMO due to the electron-withdrawing effect of the positive charge brought about by the zinc coordination to the dibutylamino groups. The LUMO will not be greatly affected because it is situated at the noncoordinating alkyne branch of the cruciform. The reverse is true for **3**. Upon coordination of the pyridine nitrogen to a metal cation, the LUMO and, therefore, the excited state of **3**, should be stabilized, while the HOMO should be virtually unaffected. Quantum chemical calculations (B3LYP, 6-31G**) on donor-acceptor cruciforms (−NMe$_2$ instead of −NBu$_2$ groups) supported the intuitive notion of an intramolecular charge-transfer band.[4b,d] A ZINDO computation using B3LYP-6-31G** geometry with (correctly) planarized −NMe$_2$ groups demonstrates that the observed lowest energy transitions, indeed, involve the branch-wise separated HOMO and LUMO.[12,13] The exposure of **4** to trifluoroacetic acid was investigated. The results of protonation were similar to those obtained for the complexation of **4** with Zn^{2+} (Table 1). The emission spectra of **2**−**4** show large shifts upon protonation or complexation, and the absorption spectra of **2** and **4** show blue shifts. In **3**, the changes in absorption upon zinc coordination are somewhat more difficult to assess because the lowest absorption maximum in the complexed and free **3** are only weak shoulders, probably forbidden CT transitions. The donor−acceptor system **4** shows the largest *overall* ratiometric shifts upon

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Table 1. Optical Data for Metal Coordination of Compounds **1**−**4** (**1** is included as a reference)

	1	2	3	4
abs, λ_{max}	330	340, 446	328 373 sh	335, 440
$+Zn^{2+}$ CH_2Cl_2	nd^a	331	353 456 sh	350
$+H^+$ MeOH	nd^a	nd^a	nd^a	342 (pH 0.34)
ϵ, CH_2Cl_2	92000	48000	83700	53800
E_m, λ_{max}	421, 442	530	456	571
$+Zn^{2+}$	nd^a	430	564	418 (1 equiv) 530 (4 equiv)
$+H^+$ MeOH	nd^a	nd^a	nd^a	435 pH 2.7 543 pH 0.34
Φ CH_2Cl_2	0.83	0.31	0.49	0.08
Φ Zn^{2+}	nd^a	0.66	0.01	0.10 (1 equiv) 0.10 (4 equiv)

[a] Not determined (nd).

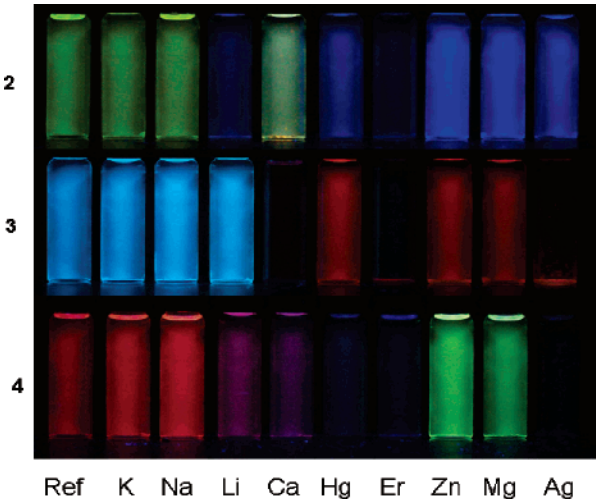

Figure 2. Emission of **2**, **3**, and **4** upon addition of different metal salts in dichloromethane.

complexation with zinc. A noteworthy conclusion that we draw is that the aniline units in **4** are better ligands for zinc cations than the pyridine ones.

With these results in hand, we examined the influence of other metal cations on the emission of **2**−**4** in dichloromethane. Three different responses can occur: (a) no change in emission, (b) bathochromic or hypsochromic shift (i.e., a ratiometric response), and (c) quenching of fluorescence. Figure 2 shows that **2**−**4** are nonresponsive to Na^+ and K^+. However, Li^+ shows a blue shift with **2** and **4**, but it does not influence the emission of **3**. Ca^{2+}, Hg^{2+}, and Zn^{2+} can be distinguished from each other, but Mg^{2+} and Zn^{2+} give identical results with all three cruciforms. For eventual biological applications, it is interesting to note that Ca^{2+} and Mg^{2+} give different results for all three dyes *and are, therefore, easily discerned by the cruciforms*. Ag^+ seems to quench fluorescence when coordinated to the pyridine end of the cruciform, but not to the aniline moiety. Overall, the observed capability of these sensing platforms to differentially discern different metal cations is impressive.

Cruciforms **2**−**4** can be seen as members of a differential sensor array.[5−7] Single members of such an array do not recognize a specific analyte, but an ensemble of different ones will; the modular assembly of the cruciforms by standard organic synthesis is facile. The addition of recognition elements such as crown ethers linked onto the aniline groups and/or electron acceptors or bipyridine motifs onto the bis(pyridinylethynyl)benzene unit will lead to cruciforms with further differentiated response capabilities. Such cruciforms could be made by adding different aldehydes and alkyne building blocks to the central bisphosphonate core. The creation of potent sensory platform arrays that can perform ratiometric sensing of two or more metal cations at the same time is a winning proposition with this versatile system.

In conclusion, two new cruciform chromophores, **3** and **4**, have been synthesized, and the set of **2**−**4** has been investigated with respect to the change of their optical properties upon metal ion binding. Depending upon the binding preference of the metal, the optical properties of the cruciforms change via switching of the intramolecular charge-transfer band. The almost complete spatial separation of HOMO and LUMO makes it possible to address desired spectral features independently.

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Supporting Information Available: Synthesis and characterization of **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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