Fluorescence Switches Triggered by Metal Ions

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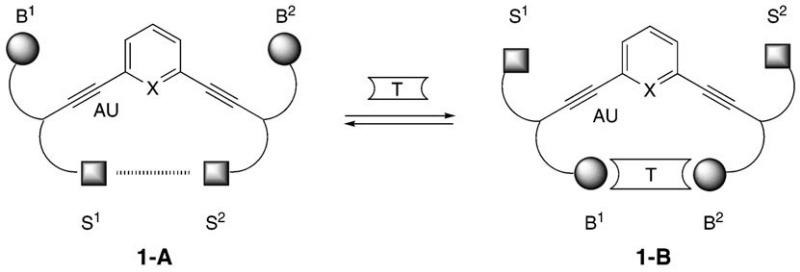
Molecular switches **1** with a modular architecture whose functional principle is based on conformational changes around two acetylene axes were developed. By systematic screening of various metal ions, it was found that especially Pb^{2+} ions effectively trigger the switching event. The reporting of this event takes place by the change of the ratio between excimer and monomer fluorescence emission of two pyrene moieties.

Introduction. – The development of functional units with nanoscopic dimensions or even at molecular level is of permanently growing interest, and much impressive progress has been achieved in recent years. In this context, molecular switches, molecules that can change between two distinct states by action of an external stimulus, play a very important role [1], not least due to potential applications as logical elements in nanoelectronics [2]. The functional principle of most molecular switches is based on conformational changes triggered by light [3], temperature [4], changes of pH [5], or redox potential [6], by anions [7], or by complexation of metal ions [8]. An essential requirement for the applications mentioned above is that the conformational change (the switching event) is readable, *i.e.*, the switch must generate an unambiguous signal for each conformational state. Owing to their outstanding sensitivity and the relatively simple technical equipment, the fluorescence spectroscopy is the method of choice for signal generation of molecular switches. Herein, we report on a conformational switch with novel architecture and dual-mode fluorescence signal generation, which are triggered by particular metal ions.

Results and Discussion. – Recently, we developed a new class of compounds **1** with modular composition that can be used both as molecular probes and as molecular switches [9]. *Scheme 1* shows the construction and the functional principle of compounds **1**. Two signal-emitting groups, S^1 and S^2, and two binding groups, B^1 and B^2, are linked to an aromatic core (where X can be an N-atom as well) *via* an acetylene unit (AU), which serves for signal transduction. In the initial state **1-A**, a signal is generated (or inhibited) by the spatial proximity between S^1 and S^2. The specific interaction between the trigger (T) and the binding groups B^1 and B^2 causes a conformational change that leads to state **1-B**, in which S^1 and S^2 are separated from each other, and the original signal is changed[1]).

[1]) Fluorescence probes with 'pin-wheel' architecture bearing also C≡C bonds, but whose signal generation is based on cooperative interactions, were recently reported by *Glass* and co-workers, see [10].

Scheme 1. *Construction and Functional Principle of Switches* **1** (S^1 and S^2 = signal-emitting groups; B^1 and B^2 = binding groups; AU = acetylene unit; T = trigger)



As signal-generating principle, we chose the change between monomer and excimer fluorescence of pyrene because this system had proven its value in many other molecular probes[2]) and switches[3]) and is well examined. Another important advantage of the pyrene system is the occurrence of two oppositional signals (monomer and excimer fluorescence), which facilitates their distinction from unspecific quenching effects, as well as the outstandingly long fluorescence lifetime of the pyrene fluorophore, a property especially important for biochemical applications [13].

As a potential trigger, we chose metal cations, and carboxylic groups as binding groups B. The synthesis of switches **1** is shown in *Scheme 2*. Starting from pyrene-1-carboxaldehyde (**2**), a chain elongation is carried out affording pyrene-1-propanoic acid [14], esterification of which leads to **3**. By alkylation of the lithium enolate with propargyl bromide, ester **4** is obtained as racemate. Compounds **1a**–**1c** contain two of the chiral centers originating from **4**, which leads to two diastereoisomers of these compounds. To suppress the formation of excimers between the two pyrene moieties and to obtain an optimal signal generation, the distance between these moieties in the state of the trigger binding should be as large as possible. This is the case with the pseudo-C_2-symmetrical isomers **1a** and **1b** but not with the pseudo-C_S-symmetrical **1c**. To verify this thesis, we were interested in both isomers and consequently required both enantiomers of ester **4**. After several attempts for the asymmetric synthesis of **4** had failed[4]), racemic resolution was finally successful[5]). Starting with the pure enantiomers of **4**, compounds **1a**–**1c** were easily accessible *via Sonogashira* coupling with 1,3-diiodobenzene or 2,6-dibromopyridine, respectively, and subsequent saponification of the ester groups.

In the fluorescence spectra of **1a**–**1c**, measured in MeCN/H_2O 1:1, a broad unstructured band dominates at *ca.* 470 nm, which can be assigned to the intramolecular excimer emission of the pyrene residues (see, *e.g.*, *Fig. 1*). Moreover, a weak

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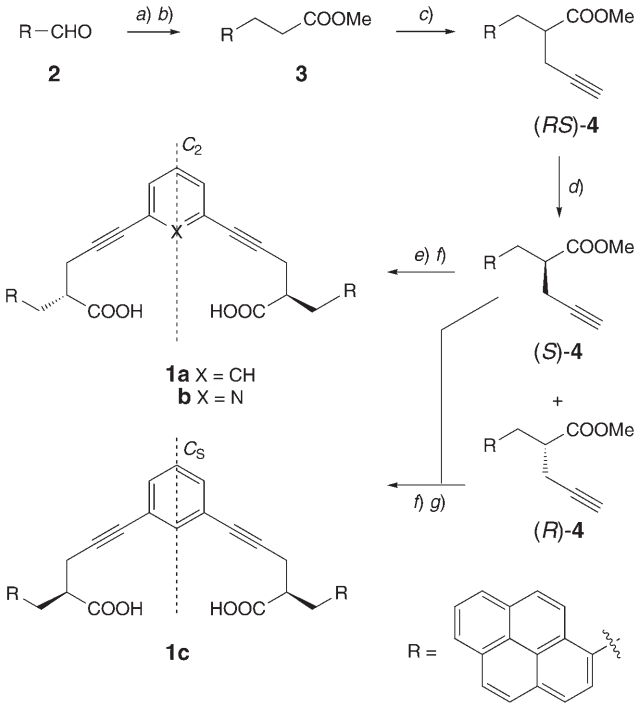
[2]) For molecular probes with pyrene as signalling unit, see [11].

[3]) For molecular switches with pyrene as signalling unit, see [12].

[4]) Alkylation of (*R*)-binol ester of pyrene-1-propanoic acid [15a] and of (4*S*)-4-isopropyl-5,5-diphenyl-3-[3-(pyren-1-yl)propanoyl]oxazolidin-2-one [15b] with propargyl bromide gave the corresponding products only with moderate *de* values.

[5]) Resolution of the enantiomers of **4** was achieved by HPLC separation of the corresponding esters with (+)-(*R*)-1,1′-binaphthalene-2,2′-diol; see *Exper. Part.*

Scheme 2. *Synthesis of* **1a**–**1c**



a) *Meldrum*'s acid, $HCOOH/Et_3N$ 5:2, 100°, 1 h; 100%. *b*) $MeOH/SOCl_2$; 84%. *c*) Lithium diisopropylamide (LDA), propargyl bromide (= 3-bromoprop-1-yne); 78%. *d*) HPLC Resolution of racemates. *e*) 1,3-Diiodobenzene, $[Pd(PPh_3)_2Cl_2]$ (4 mol-%), CuI (2 mol-%), Et_3N; 87% of **1a**; or 2,6-dibromopyridine, $[Pd(PPh_3)_4]$ (5 mol-%), $^iPr_2NH$; 45% of **1b**. *f*) LiOH; 78% of **1a**, 56% of **1b**, and 58% of **1c**, resp. *g*) 1. (*S*)-**4**, 1,3-diiodobenzene, $[Pd(PPh_3)_2Cl_2]$ (10 mol-%), CuI (2 mol-%), Et_3N; 33% 2. (*R*)-**4**, $[Pd(PPh_3)_2Cl_2]$ (1 mol-%), CuI (2 mol-%), Et_3N; 55%.

emission with two bands at *ca.* 375 and 395 nm can be detected, which originates from the monomer emission of individual pyrene residues. We first examined the changes of the fluorescence spectra of **1a** ($5 \cdot 10^{-7}$ mol/l) on addition of 17 different metal cations, *i.e.*, of Na^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Pb^{2+}, Mn^{2+}, Co^{2+}, Tl^+, Ni^{2+}, Ag^+, Cr^{3+}, Hg^{2+}, and Fe^{3+}, to find the most effective trigger. Most of these cations only cause marginal changes in the fluorescence spectrum of **1a**. Pb^{2+}, Cd^{2+}, and Zn^{2+} on the other hand lead, even in micromolar dilutions, to a significant decrease of the excimer emission, whereupon isoemissive points are detectable with Cd^{2+} ($K \approx 40000$ l/mol) and Zn^{2+} ($K \approx 5000$ l/mol) [16], while with Pb^{2+} at the same time also the monomer emission decreases, albeit to a minor degree (*Fig. 1,a*). Apparently, Pb^{2+} ions act as fluorescence quenchers, a well known phenomenon for many heavy-metal cations [17] and especially for Pb^{2+} [18]. The regression of the measured data $\Delta F = F - F_o = f(c[M^{n+}])$ with $F = I_E/I_M$ for the determination of the binding constants unambiguously establishes the presence of 1:1 complexes for these cations.

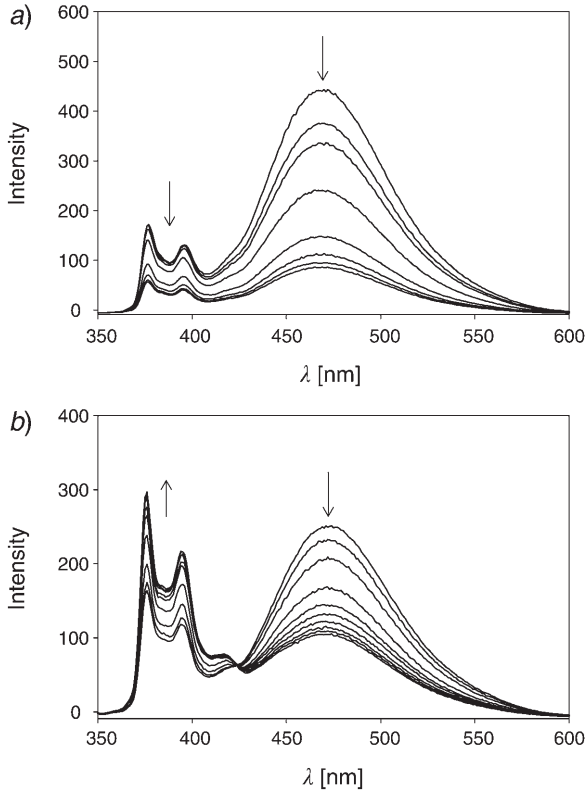


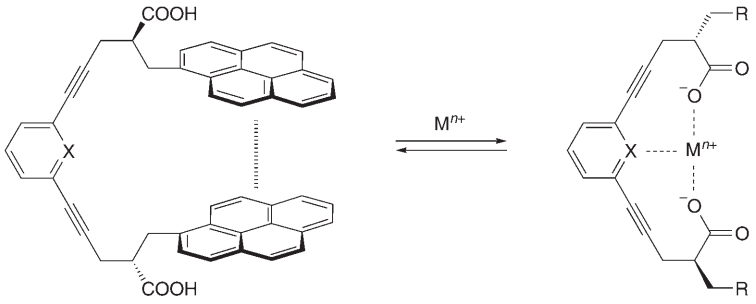
Fig. 1. *Fluorescence spectra of* a) **1a** ($5 \cdot 10^{-7}$ M), *and* b) **1b** ($5 \cdot 10^{-7}$ M) *in the presence of* Pb^{2+} *ions. a*) $c = 5 \cdot 10^{-6} - 6 \cdot 10^{-5}$ M, λ_{ex} 340 nm; *b*) $c = 5 \cdot 10^{-7} - 8 \cdot 10^{-6}$ M, λ_{ex} 342 nm) in $MeCN/H_2O$ 1:1 (*v*/*v*).

Cr^{3+} Ions, and markedly less distinctly also Hg^{2+}, Cu^{2+}, and Ag^{+}, cause an increase in the excimer emission. In the case of Cr^{3+}, this behavior could originate from the well-known kinetic stability of the corresponding aqua complexes of the chromium salts [19a]. Therefore, we presume that second-sphere complexes [19b] are formed between Cr^{3+} and **1a**, which have a substantially other geometry. The origin of the differing behavior of Hg^{2+}, Cu^{2+}, and Ag^{+} is still unknown, but the formation of 2:1 complexes cannot be ruled out. The *meso*-compound **1c** responds to Cd^{2+} and Zn^{2+} ions in a similar way as **1a** but to a considerably lesser degree, verifying the validity of the functional principle shown in *Scheme 1*.

Despite the promising response of **1a** towards Pb^{2+} ions, as shown in *Fig. 1*,*a*, the competing fluorescence quenching is of course a disadvantage with regard to the signal generation of the switch. In the following, we hypothesized that the fluorescence quenching was not triggered by the complexed but by the excess Pb^{2+} ions in the solution [17], due to the relatively large distance between the pyrene residues and the complexed Pb^{2+} ions (*Scheme 3*). Hence, a suppression of this quenching effect should be possible by stronger complexation. We hoped to achieve this by introduction of an N-atom in the benzene ring of probe **1a**. To our delight, the thus obtained compound **1b**

(*Scheme 2*) exhibited a considerably higher affinity towards most of the cations, whereas by far the highest sensitivity is once again observed for Pb^{2+} ions ($K \approx$ 690000 l/mol; *Fig. 1,b*).

Scheme 3. *Complexation of Cations* M^{n+} *by Switches* **1a** *and* **1b** (R = pyren-1-yl)



In contrast to **1a**, in **1b**, the undesirable fluorescence quenching does not occur anymore, but over a wide range of concentrations, a continuous decrease of excimer emission and an increase of monomer emission can be observed (*Fig. 1,b*). Here too, a moderate reaction is noticeable on addition of Cd^{2+} and Zn^{2+}, while most other cations cause considerably weaker effects on **1b**. In *Fig. 2* the corresponding binding constants are graphically displayed. For **1b** too, we can observe the opposite behavior for the ions Cr^{3+}, Hg^{2+}, Ni^{2+}, and Ag^{+}, where again, as for **1a**, this effect is most distinct for Cr^{3+}. Furthermore, upon addition of Fe^{3+} ions to **1b**, the whole fluorescence is very effectively quenched.

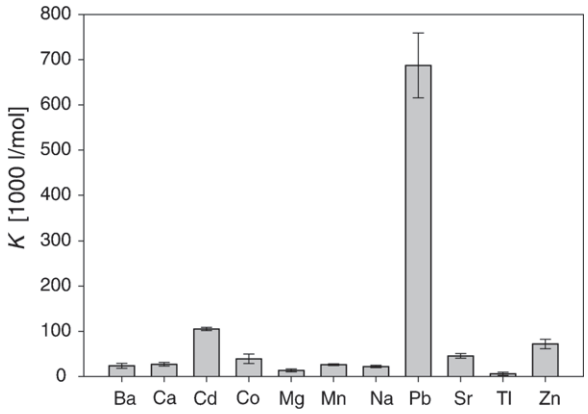


Fig. 2. *Binding constants of various cations with* **1b**

It should be noted that compound **1b** may also be used as probe for the detection of Pb^{2+} ions in view of the very high binding constants. Lead compounds are, especially due to anthropogenic influences, widespread in nature. Particularly the decade-long use of Et_4Pb as antiknock additive has substantially contributed to this fact. Lead poisoning worldwide still represents the most abundant environmental disease [20], and

especially the filial organism is very susceptible to it. Viewed from this point, there is a great demand for highly sensitive but easily practicable analytical methods for the detection of Pb^{2+} ions. On the other hand, we realized that the sensitivity of **1b** toward many other ions could prevent the practical utilization of this compound as a lead probe[6]).

Conclusion. – In summary, we have developed a conformational switch whose functional principle is based on two opposite rotations around two acetylene units. By systematic screening of a variety of metal ions, we found that this conformational change can be effectively caused by the addition of Pb^{2+} ions. Because Pb^{2+} ions work as strong fluorescence quenchers, the introduction of a third ligand in the form of a pyridine moiety (see **1b**) is mandatory for a clean signal generation. The latter one is based on the change between excimer and monomer fluorescence emission of pyrene residues. The opposite changes in the fluorescence spectra at two clearly separated wavelengths during the switching event (*Fig. 1,b*; dual-mode fluorescence switch) is of great advantage compared with single-mode fluorescence switches. The modular construction of compounds **1** puts us now in the position to develop switches with other binding site – trigger pairs for a variety of applications.

Experimental Part

General. The following reagents were commercially available: pyrene-1-carboxaldehyde, 2,6-dibromopyridine, 1,3-diiodobenzene, (+)-(*R*)-1,1′-binaphthalene-2,2′-diol, 2,2-dimethyl-1,3-dioxan-4,6-dione (= *Meldrum*'s acid). THF was dried over Na in the presence of benzophenone as an indicator of dryness and distilled under atmospheric pressure and Ar. All moisture-sensitive reagents were transferred *via* syringe under N_2 or Ar, and moisture-sensitive reactions were carried out under N_2 or Ar. Anal. TLC: precoated *Merck* SiO_2 *60* F_{254} plates; detection by UV light. Flash column chromatography (FC): silica gel (SiO_2), 230–400 mesh (*Fluka*). M.p.: *Büchi 530*; uncorrected. ^{1}H- and ^{13}C-NMR Spectra: *Bruker DPX300* equipment; in $CDCl_3$ or (D_6)DMSO solns., with Me_4Si or solvent signals as an internal standard; δ in ppm.

Methyl Pyrene-1-propanoate (**3**). A mixture of pyrene-1-carboxaldehyde (5 g, 21.7 mmol), *Meldrum*'s acid (3.13 g, 21.7 mmol), and Et_3N/HCOOH (molar ratio 2:5, 20 ml) was put in an oil bath preheated to 100° (→vigorous gas evolution and foaming). After gas evolution had ceased, additional *Meldrum*'s acid (1.6 g) was added. The mixture was stirred until the gas evolution had again ceased. Then the soln. was poured into ice-H_2O (100 ml). The mixture was acidified to pH 1 and the solid filtered off and dissolved in THF (100 ml). The soln. was dried ($MgSO_4$) and concentrated and the residue dried under high vacuum at 50°: 5.9 g (100%) of pyrene-1-propanoic acid, which was directly used in the next step without further purification.

MeOH (100 ml) was cooled to −10° under N_2, and $SOCl_2$ (13 ml) was added carefully. Then, pyrene-1-propanoic acid was added, and the mixture was stirred overnight. After removal of the solvent, the residue was purified by FC (CH_2Cl_2): **3** (3.54 g, 84%). TLC (CH_2Cl_2): R_f 0.7. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.90 (*t*, *J* = 8.1, 2 H); 3.72 (*t*, *J* = 8.1, 2 H); 3.74 (*s*, 3 H); 7.89–8.30 (*m*, 9 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 28.6; 35.8; 51.7; 122.8; 124.8; 125.0; 125.8; 126.8; 126.9; 127.4; 127.6; 128.5; 130.1; 130.8; 131.3; 134.4; 173.3.

*Methyl (α*RS*)-α-(Prop-2-ynyl)pyrene-1-propanoate* ((*RS*)-**4**). A soln. of **3** (3.5 g, 12.1 mmol) in THF (40 ml) was slowly added dropwise to a soln. of LDA (14.5 mmol) in THF (120 ml) at −78° under N_2. After the addition, the soln. was stirred for 30 min, and a propargyl bromide soln. in toluene (4.3 ml, 4

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6) For recently developed fluorescence sensors for Pb^{II}, see [21].

equiv., 80%) was added during 10 min. The mixture was stirred for 30 min at $-78°$ and then allowed to warm to r.t. H_2O (100 ml) was added, and the mixture extracted with Et_2O (2 × 100 ml). The combined org. phase was dried ($MgSO_4$) and concentrated, and the residue purified by FC (petroleum ether/AcOEt 10:1): (*RS*)-**4** (3.08 g, 78%). TLC (CH_2Cl_2): R_f 0.7. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.17 (*t*, *J* = 2.6, 1 H); 2.57 (*dd*, *J* = 6.6, 2.6, 2 H); 3.19 (*m*, 1 H); 3.65 (*s*, 3 H); 3.69–3.83 (*m*, 2 H); 7.89–8.34 (*m*, 9 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 21.0; 34.5; 46.2; 51.9; 70.6; 82.2; 122.9; 124.7; 124.8; 124.9; 125.1; 125.9; 127.0; 127.4; 127.7; 128.0; 128.9; 130.4; 130.7; 131.3; 132.5; 174.2.

*Resolution of (*RS*)-***4**. (*RS*)-**4** was saponified with LiOH (3 equiv.) and esterified with (+)-(*R*)-1,1′-binaphthalene-2,2′-diol in the presence of *N*,*N*-dicyclohexylcarbodiimide (DCCI; 1 equiv.) and *N*,*N*-dimethylpyridin-4-amine (DMAP; 0.12 equiv.) as catalyst. The diastereoisomeric binol esters were separated by prep. HPLC (*Knauer*, *Eurospher 100*, 5 μm, 250 × 32 mm, CH_2Cl_2/hexane 3:1, 50 ml/min). Finally, (*R*)-**4** and (*S*)-**4** were obtained by treatment of the corresponding binol ester with MeONa. (*S*)-**4**: $[\alpha]_D^{20} = -18$ (*c* = 0.148, $CHCl_3$).

*(*αS,α′S*)-α,α′-(1,3-Phenylenediprop-2-yne-3,1-diyl)bis[pyrene-1-propanoic Acid]* (**1a**). (*S*)-**4** (1.175 g, 3.6 mmol), 1,3-diiodobenzene (0.54 g, 1.63 mmol), [$PdCl_2(PPh_3)_2$] (0.11 g, 4 mol-%), and CuI (14 mg, 2 mol-%) were added to Et_3N (30 ml), and the mixture was stirred overnight. The solvent was evaporated, petroleum ether (50 ml) was added, and the mixture was stirred for 10 min and filtered. After evaporation, the product was purified by FC (petroleum ether/CH_2Cl_2 1:2): 1.13 g (87%) of diester, which was dissolved in THF (30 ml). Then, $LiOH \cdot H_2O$ (0.7 g, 8 equiv.) and H_2O (20 ml) were added, and the mixture was refluxed for 4 h (TLC monitoring). After completion of the reaction, THF was evaporated and the remaining aq. soln. acidified to pH 1. The product was extracted with AcOEt, the org. phase dried ($MgSO_4$) and concentrated, and the residue purified by FC (MeOH/CH_2Cl_2 1:10): 0.9 g (78%) of **1a**. TLC (CH_2Cl_2/MeOH 100:4): R_f 0.4. $[\alpha]_D^{20} = -64$ (*c* = 0.21, $CHCl_3$). ^{1}H-NMR (300 MHz, (D_6)DMSO): 2.75–2.78 (*m*, 4 H); 3.05–3.09 (*m*, 2 H); 3.58–3.68 (*m*, 4 H); 7.32–7.37 (*m*, 4 H); 7.91–8.40 (*m*, 18 H). ^{13}C-NMR (75 MHz, (D_6)DMSO): 21.6; 34.2; 46.2; 81.0; 88.8; 123.1; 123.2; 123.9; 124.1; 124.7; 124.8; 125.0; 126.1; 126.7; 127.3; 128.0; 128.3; 129.0; 129.6; 130.2; 130.7; 130.8; 131.6; 133.2; 133.7; 174.5.

*(*αS,α′S*)-α,α′-(Pyridine-2,6-diyldiprop-2-yne-3,1-diyl)bis[pyrene-1-propanoic Acid]* (**1b**). A soln. of (*S*)-**4** (0.215 g, 0.66 mol), 2,6-dibromopyridine (0.078 g, 0.33 mol), [$Pd(PPh_3)_4$] (0.038 g, 5 mol-%), CuI (0.0063 g, 5 mol-%) in toluene (3 ml) in the presence of $^iPr_2NH$ (0.15 ml) was stirred at r.t. for 6 h. The mixture was poured into aq. NH_4Cl soln. and extracted with CH_2Cl_2. The extract was washed with brine, dried ($MgSO_4$), and concentrated and the residue purified by FC (CH_2Cl_2/MeOH 100:5): 0.108 g (45%) of the corresponding diester, which was dissolved in THF (5 ml). Then, $LiOH \cdot H_2O$ (0.05 g) and H_2O (4 ml) were added, and the mixture was refluxed for 2 h. THF was evaporated, H_2O (2 ml) added, and the soln. acidified to pH 1. The aq. layer was extracted with CH_2Cl_2, the org. phase dried ($MgSO_4$) and concentrated, and the residue purified by FC (CH_2Cl_2/MeOH/Et_3N 6:1:0.3): 0.77 g (58%) of **1b**. $[\alpha]_D^{20} = -20$ (*c* = 0.2, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): 2.59–2.78 (*m*, 4 H); 3.07–3.14 (*m*, 2 H); 3.54–3.61 (*m*, 2 H); 3.82–3.89 (*m*, 2 H); 7.11 (*d*, *J* = 7.7, 2 H); 7.37 (*t*, *J* = 7.7, 1 H); 7.89–8.10 (*m*, 16 H); 8.41–8.44 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 123.8; 124.6; 124.7; 124.8; 125.6; 125.8; 126.3; 127.3; 127.4; 128.3; 136.1.

Fluorescence Titration. Seventeen metal ions (as chlorides unless otherwise noted) were studied in this work, including Na^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cr^{3+}, and Fe^{3+}, besides Tl^+, Ag^+, Pb^{2+} (nitrate), Hg^{2+} (trifluoroacetate), and Cu^{2+} (sulfate). Fluorescence measurements were performed on a *Shimadzu RF-5301-PC* spectrofluorophotometer (see *Fig. 3*). The excitation wavelength was always adjusted to 342 nm (**1b**) and 340 nm (**1a**). The switches **1** were dissolved in MeCN/H_2O 1:1 (*v*/*v*, $c = 5 \cdot 10^{-7}$ mol/l).

Determination of Binding Constants [22]. The binding constants were determined (results see *Table*) by nonlinear regression with the program Sigmaplot 8.0 by using *Eqns. 1–3*, wherein I_E is the fluorescence intensity at 473 nm (**1b**) and 469 nm (**1a**), and I_M is the fluorescence intensity at 376 nm (**1b**) and 377 nm (**1a**).

$$\Delta F = F_0 - F = f(c) \tag{1}$$

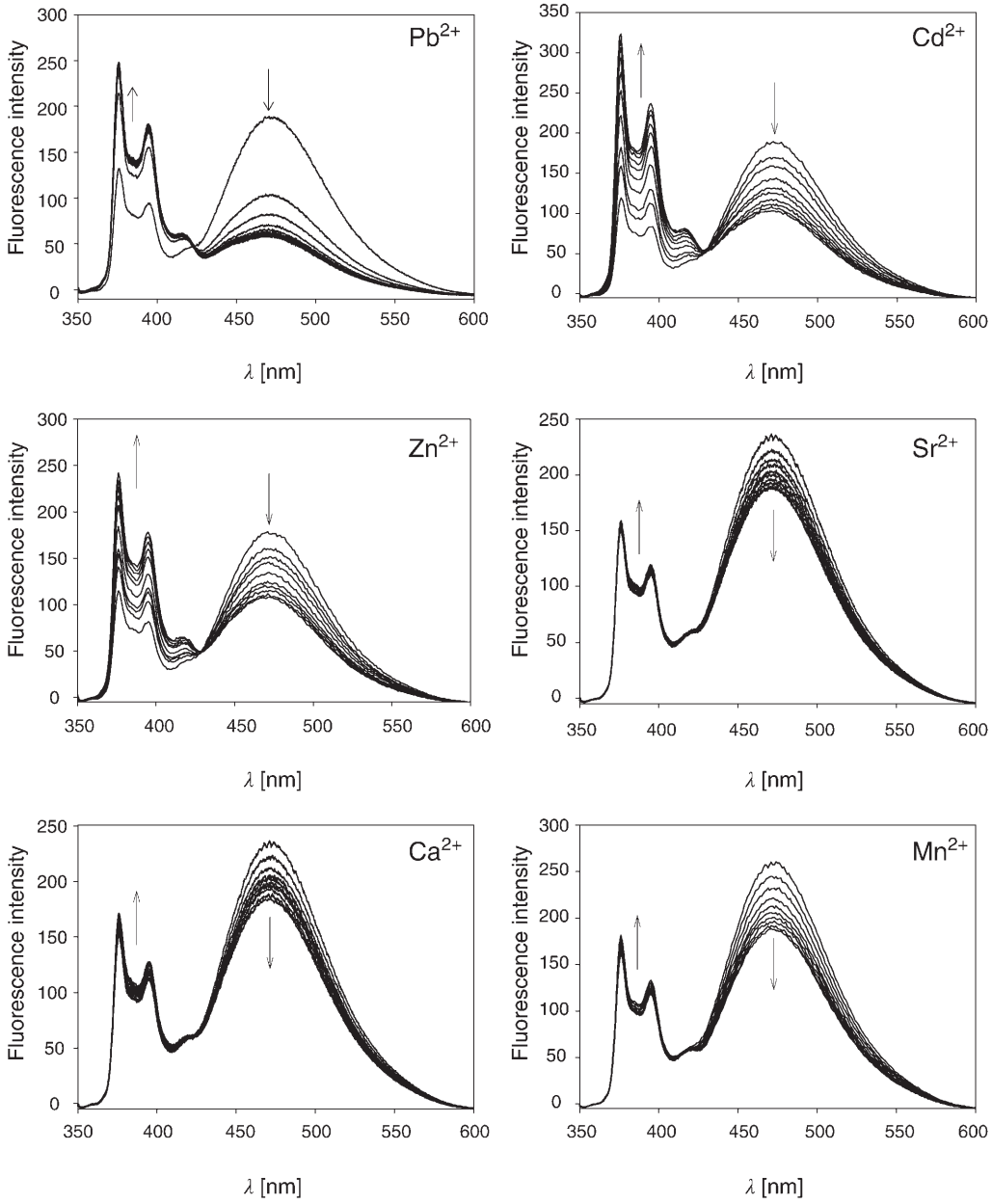

Fig. 3. *Selected fluorescence titration spectra with* **1b**. $c = 10^{-2}$ M (Pb, Cd, Zn, Sr, Ca, Mn, Ba, Na, Mg, and Tl), or $c = 10^{-3}$ M (Cr); added volume each time (μl): 1.5, 1.5, and 7 times 3.0.

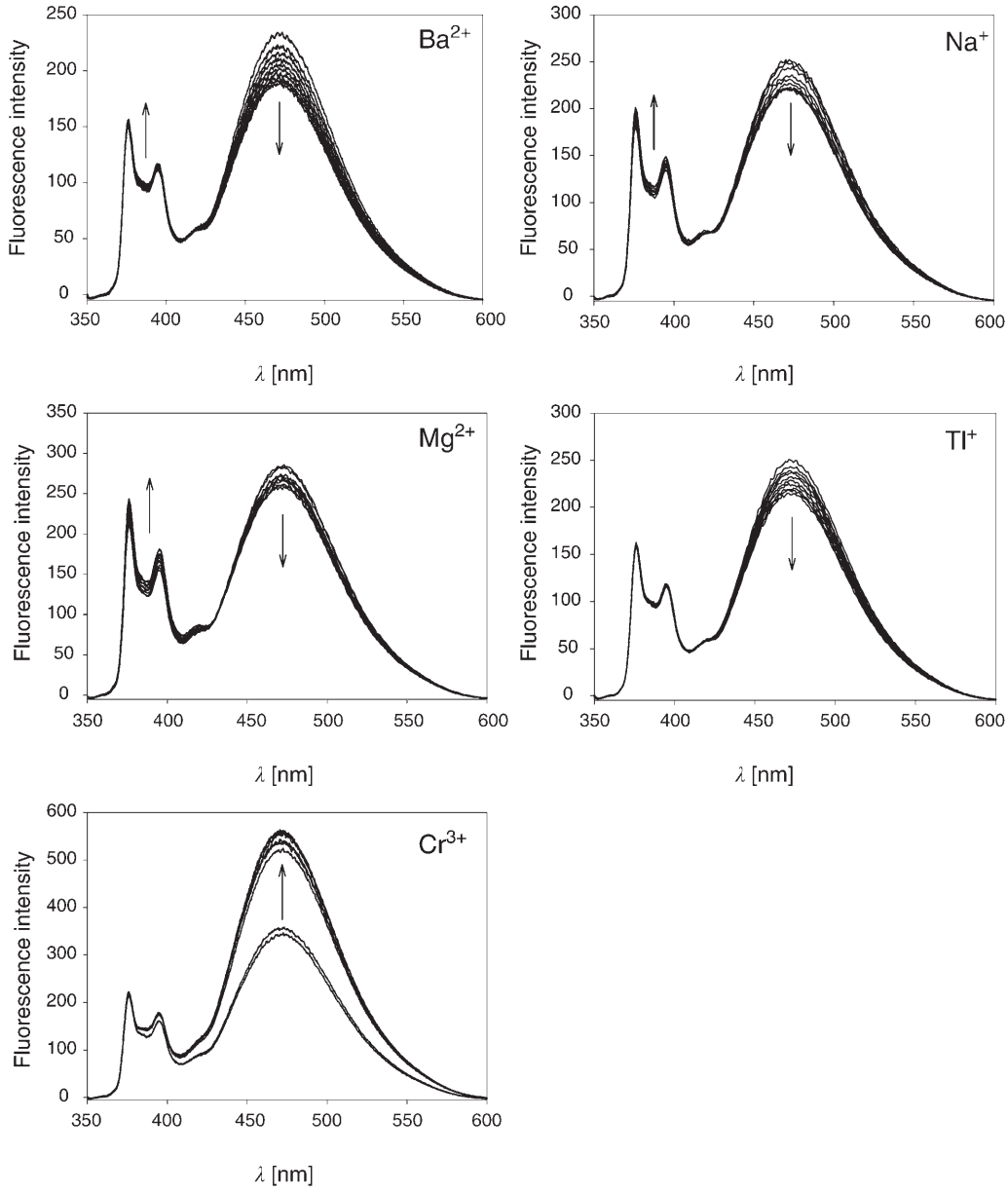

Figure 3 (cont.)

$$F = I_E/I_M \tag{2}$$

$$f(x) = \frac{A \cdot K \cdot x}{1 + K \cdot x} \tag{3}$$

Table 1. *Binding Constants* K *of* **1b** *with Various Cations*

Ion	K [l/mol]	σ[a])	R[b])
Pb^{2+}	687174	71755	0.9986
Cd^{2+}	105124	3655	0.9995
Zn^{2+}	71896	10688	0.9922
Sr^{2+}	45527	5311	0.9959
Ca^{2+}	27015	4149	0.9946
Mn^{2+}	26241	1972	0.9988
Ba^{2+}	23806	5535	0.9884
Na^{+}	22028	2819	0.9968
Mg^{2+}	13391	3184	0.9926
Tl^{+}	6034	3539	0.9866

[a]) Standard deviation. [b]) Regression coefficient.

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