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Unusually high cation-induced fluorescence enhancement of a structurally simple intrinsic fluoroionophore with a donor–acceptor–donor constitution†

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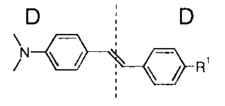
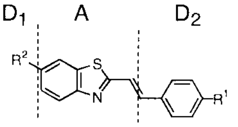
Upon cation complexation, donor–acceptor–donor–substituted intrinsic fluoroionophore 3 shows red-shifted emission spectra accompanied by an extraordinarily high fluorescence enhancement.

Ionically controlling the fluorescence of molecular systems which contain an ion-sensitive receptor as an integral part of their signal generating fluorophore is of particular interest in fluorometric analysis.[1] These so-called intrinsic fluoroionophores usually combine an electron rich donor (D) as the ion-sensitive receptor and an electron acceptor unit (A) in a π-conjugated D–A arrangement.[2] Many such compounds are known including, *e.g.* styryl or stilbene dyes.[3] In highly polar solvents often encountered in sensing applications, the spectroscopic behaviour of such dyes is usually governed by an intramolecular charge transfer (ICT) process which leads to broad, structureless, and largely Stokes-shifted absorption and emission bands.[2,3] Upon cation binding to the receptor (= donor, R_D), strong hypsochromic shifts in absorption are found but the corresponding effects in emission are rather small.[2,3] The latter behaviour has been attributed to a decoordination reaction in the excited complex as a consequence of the ICT process, where a shift of negative charge from R_D to A leads to electrostatic repulsion between cation and formally positively charged donor.[4] Owing to complexation-induced fluorescence intensity changes as well as spectral shifts, these dyes are advantageous in terms of spectral discrimination as compared to PET (photoinduced electron transfer) systems[5] with electronically decoupled fluorophore and receptor. However, besides small shifts in emission the main disadvantage of intrinsic fluoroionophores is the relatively small change in fluorescence intensity (usually factors $\leqslant 5$) upon ion binding.

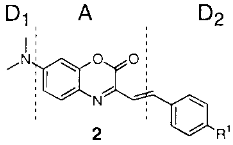
In order to circumvent the problem of cation decoordination in the excited state and thus to achieve stronger shifts in emission, other design concepts were realized including D–D-substituted sensor molecules (*e.g.* **1**) as well as compounds with a D–A–D arrangement (*e.g.* **2**). Unfortunately, cation complexation to **1** resulted in fluorescence quenching[3c] unfavourable in terms of a high signal output and complex specific fluorescence lifetimes and **2** is already moderately fluorescent (ϕ_f = 0.33) in the uncomplexed state.[3a] As was shown in various mechanistical studies of such dyes,[6] the excited state reaction mechanism involves several emissive and non-emissive conformers, closely related to the theory of so-called twisted intramolecular charge transfer (TICT) and biradicaloid states.[7] Upon complexation, the change in fluorescence yield critically depends on the change of the relative energetic positions of the excited species involved and thus on the rate constants of the competing reactions from planar emissive locally excited E* to a highly polar single-bond-twisted species A* or to a non-emissive and weakly polar double-bond-twisted conformer P* of biradicaloid nature (three-state-model, Scheme 1).[6,7] Since for **2**, efficient formation of an emissive A* state is responsible for the moderate fluorescence in the uncomplexed dye in polar solvents,[3a,6a] reducing the acceptor strength promised to decrease the energy gap between emissive A* and quenching P* state and thus promised to lead to higher cation-induced fluorescence enhancement. With this in mind we designed the D–A–D fluoroionophore **3**.



1

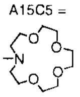


3-5



2

A15C5 =



1: R^1 = A15C5

2: R^1 = A15C5

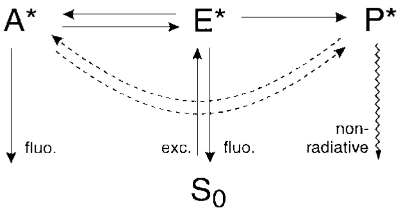
3: R^1 = A15C5, R^2 = NMe_2

4: R^1, R^2 = NMe_2

5: R^1 = NMe_2, R^2 = H

Introduction of the electron donating dimethylamino group to the benzothiazole acceptor leads to slight shifts in both absorption (bathochromic) and emission (hypsochromic) accompanied by an increase in fluorescence quantum yield and lifetime (**4** *cf.* **5**, Table 1). A similar behaviour has been previously found for 4,4′-bis(dimethylamino)stilbene[6b] and corresponding 4-(dimethylamino)stilbene[6c] and quantum chemical calculations performed in analogy to those reported in ref. 6(*b*) support the validity of this model for **4** and **5**.[8] Based on the differences in bulkiness and donor strength of the two alkylated amino substituents, **3** and **4** show very similar spectroscopic properties and a slightly higher fluorescence yield in the case of **3** (Table 1).

Upon cation addition, the absorption band is slightly blue-shifted (Fig. 1) and the isosbestic points found in a titration indicate the formation of 1 : 1 complexes. This is supported by the fits of the titration data yielding complex stability constants in a range characteristic for neutral ICT fluoroionophores.[2,3] Concerning the cation-induced effects in fluorescence, **3** combines a red shift of the emission spectrum (Fig. 1) with extraordinarily high fluorescence enhancement factors (FEF),



Scheme 1 Three-state-model involving multiple emissive states (A*, E*). E* is the planar conformer, A* corresponds to the different single-bond-twisted conformers and P* to the double-bond-twisted conformers.

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† Electronic supplementary information (ESI) available: experimental details including synthesis of **3**–**5**, optical spectroscopy and the determination of complex stability constants. See http://www.rsc.org/suppdata/cc/a9/a909899b/

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Table 1 Spectroscopic data for **3** and its cation complexes **4** and **5** in acetonitrile at room temperature[a]

	λ_{abs}/nm	λ_{em}/nm	FEF[b]	τ_f/ns	log K_s[c]
3	409	502	1	0.19	—
3 $\subset$ Li^{I}	399	517	4.4	1.12	2.96
3 $\subset$ Na^{I}	396	522	9.6	1.98	2.43
3 $\subset$ K^{I}	405	511	2.6	1.48	n.d.[d]
3 $\subset$ Mg^{II}	395	541	26.7	2.87	2.98
3 $\subset$ Ca^{II}	397	537	31.8	3.20	4.52
3 $\subset$ Sr^{II}	397	534	26.7	3.12	3.67
3 $\subset$ Ba^{II}	396	532	28.5	3.03	3.71
4	406	505	0.67	0.14	—
5	395	511	0.22	0.06	—

[a] *Experimental conditions*: see caption to Fig. 1, λ_{exc} = 425 nm for time-resolved fluorometry. [b] FEF relative to **3** (ϕ_f = 0.027). [c] K_s = Complex stability constant (dm^3 mol^{-1}). [d] Not determined.

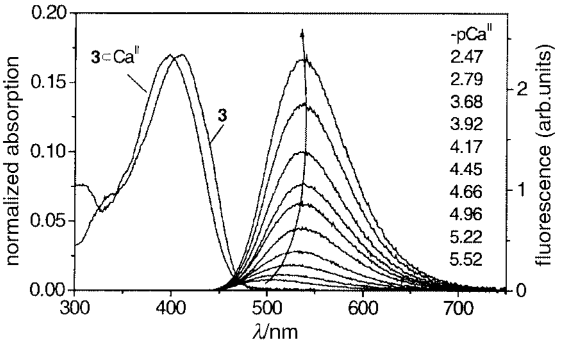
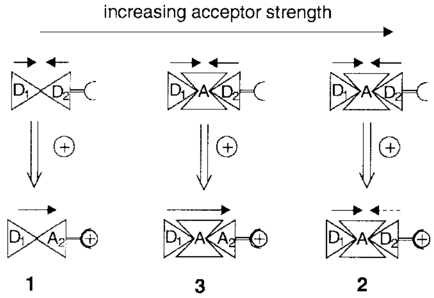


Fig. 1 Absorption spectra of **3** and **3** $\subset$ Ca^{II} and fluorometric titration spectra of **3** and Ca(ClO$_4$)$_2$ in acetonitrile (c_{probe} = 1 × 10^{-6} M; λ_{exc} = 406 nm; $-$pCa^{II} = $-$log c_{Ca} of the titration steps indicated in the plot).

normally only found for electronically decoupled PET systems,[5] and cation specific fluorescence lifetimes (Table 1).

These analytically favourable effects can be understood on the basis of the three-state-model introduced above. For **1**, the D–D substitution pattern is turned into a D–A pattern upon ion binding (Scheme 2), exemplified by a red shift in emission, and the decrease in fluorescence yield in the order of **1** > **1** $\subset$ Ca^{II} > 4-dimethylamino-4′-cyanostilbene,[9] correlates with the increase in acceptor strength and should mainly be related to the relative energetic positions of E*, A* and P*.[6b,9] As follows from the blue-shifted emission band of **2** $\subset$ Ca^{II}, complexation to **2** decreases the strength of D$_2$ (Scheme 2) slowing down the formation of (probably less) emissive A* and leads to enhanced emission owing to more efficient formation of an ICT state of planar conformation involving partial charge transfer from D$_1$ to A.[6a] This was also observed for highly fluorescent D–A(–A) benzoxazinone dyes with R^1 = H[6a] or CHO.[10] Accordingly, for **3** $\subset$ M$^{I/II}$ the bathochromic shift in emission suggests the conversion of D$_2$ into an acceptor yielding a D$_1$–A–A$_2$ pattern (Scheme 2) and radiative deactivation of such a highly emissive CT species successfully competes with any quenching channel (P*) restoring the fluorescence as a function of the charge density of the metal ion bound.



Scheme 2 Change of donor and acceptor strength upon complexation (arrows indicate CT interactions).

In summary, we have shown for the first time that efficient complexation-induced ‘switching on’ of the fluorescence can be achieved for simple intrinsic fluoroionophores by careful tuning of the donor–acceptor substitution pattern.

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Notes and references

1 A. W. Czarnik, *Chem. Biol.*, 1995, **2**, 423.
2 B. Valeur, *Probe design and chemical sensing*, ed. J. R. Lakowicz, 1994, Plenum, New York, p. 21.
3 (*a*) S. Fery-Forgues, M.-T. Le Bris, J.-P. Guetté and B. Valeur, *J. Phys. Chem.*, 1988, **92**, 6233; (*b*) J.-F. Létard, R. Lapouyade and W. Rettig, *Pure Appl. Chem.*, 1993, **65**, 1705; (*c*) S. Delmond, J.-F. Létard, R. Lapouyade, R. Mathevet, G. Jonusauskas and C. Rullière, *New J. Chem.*, 1996, **20**, 861; (*d*) I. K. Lednev, T.-Q. Ye, R. E. Hester and J. N. Moore, *J. Phys. Chem. A*, 1997, **101**, 4966; (*e*) S. I. Druzhinin, M. V. Rusalov, B. M. Uzhinov, S. P. Gromov, S. A. Sergeev and M. V. Alfimov, *J. Fluoresc.*, 1999, **9**, 33.
4 M. M. Martin, P. Plaza, Y. H. Meyer, F. Badaoui, J. Bourson, J.-P. Lefèvre and B. Valeur, *J. Phys. Chem.*, 1996, **100**, 6879; R. Mathevet, G. Jonusauskas, C. Rullière, J.-F. Létard and R. Lapouyade, *J. Phys. Chem.*, 1995, **99**, 15709.
5 R. A. Bissell, A. P. de Silva, H. Q. N. Gunaratne, P. L. M. Lynch, G. E. M. Maguire, C. P. McCoy and K. R. A. S. Sandanayake, *Top. Curr. Chem.*, 1993, **168**, 223.
6 (*a*) S. Fery-Forgues, M.-T. Le Bris, J.-C. Mialocq, J. Pouget, W. Rettig and B. Valeur, *J. Phys. Chem.*, 1992, **96**, 701; (*b*) J.-F. Létard, R. Lapouyade and W. Rettig, *Chem. Phys. Lett.*, 1994, **222**, 209; (*c*) J.-F. Létard, R. Lapouyade and W. Rettig, *J. Am. Chem. Soc.*, 1993, **115**, 2441.
7 W. Rettig, *Top. Curr. Chem.*, 1994, **169**, 253.
8 K. Rurack, J. L. Bricks, J. L. Slominskii, U. Resch-Genger and W. Rettig, to be submitted.
9 R. Lapouyade, K. Czeschka, W. Majenz, W. Rettig, E. Gilabert and C. Rullière, *J. Phys. Chem.*, 1992, **96**, 9643.
10 M.-T. Le Bris, J. Mugnier, J. Bourson and B. Valeur, *Chem. Phys. Lett.*, 1994, **106**, 124.

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