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# A charge transfer-type fluorescent molecular sensor that “lights up” in the visible upon hydrogen bond-assisted complexation of anions†

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**A charge transfer-type fluorescent molecular sensor consisting of a bisamidopyridine receptor and two styryl base chromophores shows $H_2PO_4^-$ and acetate-enhanced fluorescence due to the conversion of weak intramolecular hydrogen bonds into strong ones in the host–guest ensemble.**

The selective detection of chemical species by redox- or photoactive sensor molecules is a challenging area of supramolecular chemistry.[1] Over the past decade, anions in particular have received increasing attention as target analytes.[2] A variety of approaches has been realized, basically utilizing electrochemical, colorimetric or, as the most sensitive of these, fluorimetric techniques.[1,2] Within the latter field, alternative concepts such as competitive binding assays or sensory polymers have been introduced lately.[3] However, for many small in-/organic anions, the design of fluorescent molecular sensors still is the most versatile and widespread approach. The major strategies followed here are the development of systems operating *via* photoinduced electron transfer (PET)[4] or the modulation of luminescence processes involving metal ions.[5] Frequent disadvantages of many PET probes however are that they emit in the UV range and often indicate anions *via* fluorescence quenching, a counterproductive effect in terms of specificity and sensitivity.[6] Probes with metal ion centers on the other hand generally emit in the visible region, but often lack a straightforward tunability of their output frequencies over a broad spectral range. In this respect, it would be very interesting to have donor–acceptor (D–A) substituted molecules available that show broad intramolecular charge transfer (ICT) absorption and fluorescence bands.[7] Such architectures are usually modular in nature and allow facile equipping of a system with very different donor and acceptor units for purpose-fit wavelength ranges or target species.[8]

The lack of ICT sensor molecules for anions that exists so far is on the one hand related to the generally weaker binding forces of these guests, which would entail only weak spectroscopic effects upon complexation.[9] On the other hand, binding of a negatively charged species at an electron-deficient acceptor’s receptor site of a D–A system would harbor the disadvantage that a D–A would be turned into a D–D constitution. Such a change would reduce the CT character, which is often manifested in blue-shifted spectra and quenched emission. To obtain a system that combines the advantages of analyte-enhanced fluorescence with the spectral features of ICT chromophores, we pursued a different strategy in the design of sensor molecule **1** (Chart 1) and opted for a tandem-type $D^1$–$A^2$–$A^3$ structure that can be modularly assembled by a facile synthetic route.† Targeting hydrogen bonding anions such as acetate ($AcO^-$) and $H_2PO_4^-$, a bisamidopyridine receptor[10] was employed and a hydrogen bond-mediated quenching process was installed for signal generation in the $A^3$ receptor moiety.

Table 1 collects the spectroscopic properties of **1–3** in the DMSO–water mixture employed for the present studies. The virtual identity of the absorption spectra of **1** and **2** and the favorable, two-fold higher molar absorptivity of the sensor dye suggest that the two chromophoric subunits or “arms” in **1** are not conjugated and do not interact in the ground state. Comparison with the absorption data of model **3**, with a phenyl ring as $A^3$, indicates that $A^3$ acts only as a considerably weak tandem acceptor in **1** and **2**. These less pronounced differences in D–A character are reflected by the spectral fluorescence data. Again, the emission maximum varies only within ±10 nm for **1–3**. As can be deduced from Fig. 1, the emission as well as the absorption bands show the typical broad and structureless CT features and are largely Stokes shifted. The ICT processes responsible for the optical transitions thus seem to be similar for the three dyes. Furthermore, the high fluorescence quantum yield of **3** points to a strongly allowed, radiative $S_1 \rightarrow S_0$ CT transition, most probably involving planar species.[11] From Table 1 it is obvious that the analytically important difference

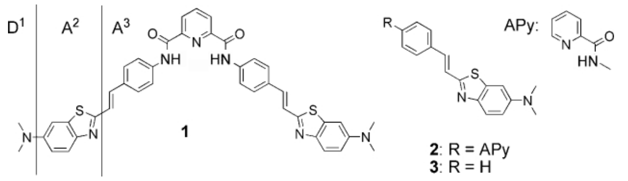

**Chart 1**

**Table 1** Spectroscopic properties of **1–3** in DMSO : $H_2O$ (95 : 5 vol%)[a]

| | $\lambda_{abs}$/nm | $\varepsilon_{max}{}^{b}$/$M^{-1}$ $cm^{-1}$ | $\lambda_{em}$/nm | $\phi_f{}^{c}$ | $\tau_f{}^{d}$/ns |
|---|---|---|---|---|---|
| **1** | 415 | 76 930 | 551 | 0.004 | 0.02 |
| **2** | 414 | 38 730 | 555 | 0.032 | 0.17 |
| **3** | 403 | 27 820 | 547 | 0.65 | 3.47 |

[a] At 298 K. [b] $\varepsilon_{max}$ from $N = 4$ measurements, ± 3%. [c] Relative to coumarin 102 in EtOH ($\phi_f = 0.60$; ref. 18), ± 20, 10 and 5% for **1**, **2** and **3**. [d] ± 0.005 ns.

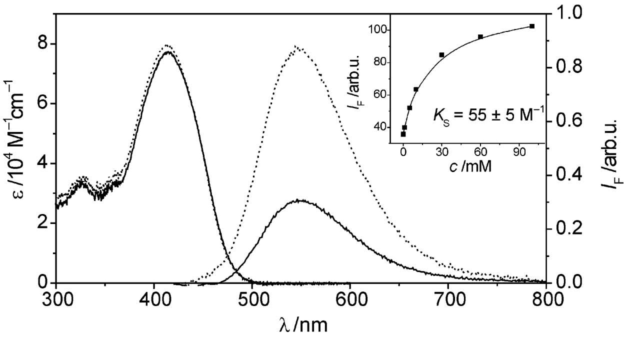

**Fig. 1** Optical spectra of **1** (—) and **1**–$AcO^-$ ( . .) in DMSO : $H_2O$. Inset: representative titration curve and fit of KS to a 1 : 1 binding model.

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† Electronic Supplementary Information (ESI) available: details on synthesis, X-ray structure analysis, NMR and competition studies. See http://www.rsc.org/suppdata/cc/b4/b405207b/

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between the three compounds is manifested in the strongly quenched emission of the amido derivatives **2** and especially **1**. The concurrent reduction in fluorescence quantum yield and lifetime suggests that the emitting state remains largely unchanged, but an efficiently competing, radiationless deactivation channel is activated.[12] This process most probably is a fast hydrogen bond shift in the excited state, involving the amido group hydrogen(s) and either a solvent molecule[13] or the pyridino nitrogen atom.

In the case of probe molecules that are capable of forming intramolecular hydrogen bonds, X-ray structure analysis can provide important insights and can help to better understand the active mechanisms. Here, we were able to obtain crystals of the two solvates **1** × **DMF**† and **1** × **DMSO** (Fig. 2). In both species, the solvent molecules are hydrogen bound to the receptor's amido hydrogens *via* the solvent's oxygen atom, the molecular conformations being largely similar. In both cases, one styryl base arm is coplanar with the bisamidopyridine group, while the other arm is significantly tilted.[14] The tilt is a result of the torsion around the single bonds N6′–C8′ and C11′–C14′, the largest one being around the bond next to the amido group (C5′–N6′–C8′–C9′ torsion angles are 28.5°/−27.1° for **1** × **DMF/1** × **DMSO**). Such a conformation seems to be required for the best spatial fit of receptor and solvent to give a four-fold stabilization with two intra- and two intermolecular hydrogen bonds (Fig. 2).[15]

NMR studies† carried out on **1** and **2** in DMSO-$d_6$ and $CDCl_3$ suggest that the unique features of **1** are basically preserved in solution. In DMSO, the NH signals of both compounds appear at lower field as compared to chloroform solution, presumably due to N–H···O=S hydrogen bond formation. Moreover, the magnitude of these shifts, $\Delta\delta = 1.62$ *vs*. 0.68 for **1** *vs*. **2**, clearly indicates that the effect is much more pronounced for the sensor dye **1**. Concerning the different quenching rates in **1** and **2**, these results let us assume that both intramolecular and solvent-assisted hydrogen bond deactivation pathways contribute to the extremely low $\phi_f$ of **1**. In **2**, where the probability of the dye existing in an *anti*-conformation of amido-H and pyridino-N is much higher and the stabilization modes are less efficient, quenching mainly occurs *via* solvent interaction.

In the presence of anions in DMSO–water mixtures, **1** shows modulated fluorescence signals only for $AcO^-$ and $H_2PO_4^-$,† the anions which are known to be most effectively bound by the present receptor unit.[10,16] Fig. 1 reveals that the spectral band positions of **1**–$AcO^-$ are virtually unchanged,[17] and only amplified fluorescence is observed. The latter is manifested in a 3.5- and 6.5-fold enhanced emission for **1**–$AcO^-$ and **1**–$H_2PO_4^-$, and reflected in the occurrence of complex-specific $\tau_f$ of 0.11 and 0.20 ns, respectively. For both anions, complex formation follows a 1 : 1 stoichiometry with complex stability constants of 55 ± 5 and 74 ± 7 $M^{-1}$ for **1**–$AcO^-$ and **1**–$H_2PO_4^-$. In particular the latter fact, *i.e.* that the presence of water does not interfere with the sensing process, is encouraging with respect to the demand for sensors capable of anion signaling in aqueous media. **2** and **3** by contrast are entirely silent toward the anions studied here.† Based on the results obtained for **1** and its complexes, the key step of the signaling reaction is the replacement of a neutral solvent molecule from the cavity by the anion upon complexation, forming considerably tighter bonds as verified by NMR studies.† The conversion of weak into strong hydrogen bonds thus blocks the major quenching channel and leads to enhanced output signals. Closer contacts between anions such as $AcO^-$ and $H_2PO_4^-$ and the aromatic *o*-hydrogens are possible, thus allowing for the formation of more planar conformations. Larger anions like $Cl^-$ are most probably too bulky to form a coplanar complex with the bisamidopyridine moiety so that even in the case of binding, the anion would be positioned considerably out of the plane and hydrogen bonding would be weaker; no interference is observed.

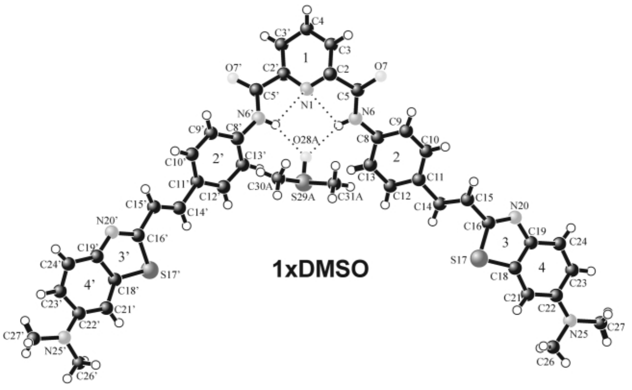

**Fig. 2** Crystal structure of the DMSO solvate of **1**.‡

In conclusion, the anion-sensitive ICT sensor molecule introduced here combines the advantages of modularity, facile synthesis and, by invoking hydrogen bond-mediated signaling, the favorable spectroscopic features of intramolecular charge transfer transitions with fluorescence between 500 and 600 nm. Furthermore, this design with two different yet coupled processes allows to gain increased signal outputs with analyte-specific fluorescence lifetimes upon anion binding. The present results let us assume that such architectures present a promising route toward long-wavelength optical sensor molecules for anions.

## Notes and references

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