Water-Soluble Distyrylbenzenes: One Core with Two Sensory Responses— Turn-On and Ratiometric

Juan Tolosa,^[a] Jonathan J. Bryant,^[a] Kyril M. Solntsev,^[b] Kerstin Brödner,^[a] Laren M. Tolbert,^[b] and Uwe H. F. Bunz^{*[a, b]}

Abstract: The synthesis of four watersoluble distyrylbenzenes (compounds 1–4) is reported. Their acidochromicity in aqueous media was investigated. Blue shifts and increases in the quantum yields were observed as a general response. The pH-dependent photophysics of 1b–3b in water reveal unexpected protonation sequences upon titration: compound 1b is green-yellow fluorescent at high pH (10) but becomes very weakly fluorescent between pH 5 and pH 3, whereas below pH 2 strong blue fluorescence is observed. This behavior can be explained in terms of the interplay in the protonation of aniline and of the carboxylate

Keywords: acidochromicity • amines • distyrylbenzene • fluorescence • photophysics groups. In compound **4**, a higher basicity of the amino group is observed and ratiometric fluorescence change takes place upon protonation or on reaction with zinc salts in water. Compound **4** can therefore act as a weak ratiometric zinc ligand in water, even though it has only a dimethylamino unit as a binding motif.

Introduction

Distyrylbenzenes (DSBs)^[1] find widespread applications as paper whiteners, as fluorophores for light-emitting diodes,^[2] as competent two-photon absorbers.^[3] and as β-amyloid binding ligands.^[4] DSBs are oligomers of poly(*para*-phenylenevinylene) (PPV)^[5-7] but also styryl-stilbenes.^[8] Their optical properties, though, are more PPV-like and do not resemble those of the stilbenes, as evidenced by the 10 times higher quantum yield of DSB relative to that of (E)-stilbene.^[9] DSBs have not (yet) been found to be useful as sensory cores for the detection of pH changes in aqueous solutions or as metal sensors, even though one of the first calcium ion sensors, developed by Tsien et al., was stilbene based.^[10] Tsien's apparent lack of success with this specific molecule was attributed to excited-state decomplexation^[11] of the aminostyryl-coordinated metal cation. In the case of similar azacrown-substituted DSBs, carefully investigated by Perry et al.,^[3] the lack of fluorescence response upon exposure to metal cations is probably due to a conformational

 [a] Dr. J. Tolosa, J. J. Bryant, K. Brödner, Prof. U. H. F. Bunz Organisch-Chemisches Institut Ruprecht-Karls-Universität Heidelberg Im Neuenheimer Feld 270, 69120 Heidelberg (Germany) E-mail: uwe.bunz@oci.uniso-heidelberg.de

[b] Dr. K. M. Solntsev, Prof. L. M. Tolbert, Prof. U. H. F. Bunz School of Chemistry and Biochemistry Georgia Institute of Technology 901 Atlantic Drive, Atlanta, GA 30332 (USA)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201102402. Experimental details for the synthesis of DSBs **1–4** are provided, as well as the corresponding photophysical experiments performed with these compounds. effect.^[12] However, dialkylamino-DSBs act in acetonitrile as successful ratiometric ligands for divalent manganese and calcium cations.^[13]

New metal-coordinating and acid-sensing fluoroionophores are potentially important for biological applications (cell staining etc.), so it would be attractive to develop DSBs to this end.^[14,15] We have recently synthesized watersoluble X-shaped^[16] DSB derivatives incorporating aminobisacetic acid structures.^[17] In aqueous solution these compounds did not show the expected acidochromic properties, that is, blue shifts in absorption and emission, but formed excimers that were broken up by the addition of protons or metal salts.^[17] Their unexpected behavior was probably due to the electronegative effects of the two attached CH₂CO₂R (R = H, Na, Et) groups, which greatly reduce the basicity of the aniline groups. To remove the inductive electronic influence of the carboxylate groups, we envisioned a second generation of DSBs, compounds 1-3 (Scheme 1), in which the aniline nitrogen atoms each bear two CH2CH2CH2CO2-(H,Na) units as auxiliary metal chelating appendages. These insulate the electron-withdrawing carboxylate groups from the aniline nitrogen much more strongly than the CH₂CO₂-(H,Na) groups do. Here we describe the water-soluble DSBs 1-4, which display either turn-on or ratiometric behavior upon protonation in water.

Results and Discussion

Synthesis and spectroscopic properties of the distyrylbenzenes 1–4: Direct or consecutive Horner reactions of A (Scheme 1) gave rise to the formation of the DSBs 1a, 3a, and 4 in 24–56% yields (see the Supporting Information).



Scheme 1. Synthesis of compounds 1–4. SW=branched oligoethyleneglycol substituent.

Treatment of an excess of **1a** with methyl triflate smoothly afforded **2a** after chromatography. Saponification of **1a–3a** with equimolar amounts of sodium hydroxide in methanol/ water mixtures furnished **1b–3b** in quantitative yields after lyophilization as yellow, powdery solids. The electrolytes dissolve well in water and to lesser extents in methanol or acetonitrile but are insoluble in CH₂Cl₂ or THF. We investigated the optical properties of **1a–3a** and **4** before and after addition of trifluoroacetic acid (TFA) in excess in acetonitrile (Table 1, Figure 1). The absorption spectra of the DSBs are all similar (Figure 1, left, λ_{max} from **1a**=406 nm to **4**= 387 nm) to one another. Surprisingly, the donor–acceptor DSB **2a** does not display a red-shifted absorption maximum, although in its emission spectrum **2a** displays, as anticipated,

Table 1. Spectroscopic data for compounds 1-4 in acetonitrile and water.

	CH ₃ CN				H_2O		
	$\lambda_{ m abs}/\lambda_{ m em}$ [nm]	ε [Lmol ⁻¹ cm ⁻¹]	Φ		$\lambda_{ m abs}/\lambda_{ m em}$ [nm]	ε [L mol ⁻¹ cm ⁻¹]	Φ
1a	406/499	33400	0.31	1b	407/545	43 400	0.09
1a+TFA	356/415	25800	0.48	1b+HCl	343/438	21 500	0.18
2 a	401/571	27100	0.04	2b	411/578	19900	< 0.01
2a+TFA	356/416	34600	0.45	2b+HCl	342/440	38700	0.16
3a	391/524	31100	0.19	3b	388/570	34 500	0.04
3a+TFA	354/424	32300	0.41	3b+HCl	319/437	15200	0.09
4	387/520	30 500	0.31	4	377/526	33100	0.13
4+TFA	363/477	29000	0.47	4+HCl	361/478	38400	0.35

the most red-shifted spectral feature. On exposure to trifluoroacetic acid, all DSBs feature blue shifts in absorption and in emission, coupled with increases in quantum yields (see Table 1, Figure 1).^[18,19]

The UV/Vis absorption and emission spectra of 1b-3b (saponified) and 4 were recorded in water before and after addition of HCl in excess (Table 1, pH 0). The absorption spectra do not change much on going from acetonitrile (1a-3a) to water (1b-3b), but some of the emission features, particularly those of 1b and 3b, display red shifts in emission with the change in solvent to water. The similarity in the emission wavelengths of all four different DBSs in water is surprising. In the cases of 2b and 4 the emission wavelengths do not change significantly on going from acetonitrile (2a, 4) to water (2b, 4). The quantum yields for 1-3 are all reduced to 20–30% of their values in acetonitrile $(\mathbf{a} \rightarrow \mathbf{b})$ on going to the charged species in water at pH 7, but in the case of 4 the fluorescence intensity only drops to 42% of its value reported in acetonitrile with the change to water (see below). Upon protonation the formed cationic species 1b-**3b** (prot, pH 0) have quantum yields that are 20-40% of those of 1a-3a (prot, addition of TFA (0.2 mL) to a 16 mL drum vial of fluorophore solution) in acetonitrile, whereas compound 4 in its protonated form experiences only a small reduction in its quantum yield with the change from acetonitrile to water.^[12] Under these conditions we assume that both nitrogen atoms (1-4) as well as all of the carboxylate groups (1b-3b) are protonated, because increasing the amount of acid does not lead to any further spectral changes. The reason for the differing behavior of 1b-3b with regard to 4 in water is probably due to the presence of the branched oligoethylene glycol groups (swallowtail, SW), which are well known for increasing fluorescence quantum yields.^[20] The carboxylate groups in **1b-3b** might also have an additional negative effect on the quantum yields, allowing charge-transfer quenching, potentially through a water molecule inserted between the carboxylate and the aniline as a conduit.

Protonation studies in water: Because water is essential for the study of biological processes or for operation in living systems, biosensory fluorophores need to function under aqueous conditions. Figure 3, below, displays titration studies of **1b**, **2b**, **3b**, and **4** in aqueous media. From the starting

> point at pH 10, acidification to pH 5 leads to a significant quenching of the fluorescence of **1b** and a partial decrease in the absorption band at 400 nm. Between pH 5 and pH 3, a red-shifted feature, visible as a shoulder at 480 nm, appears in the absorption spectrum of **1b**, whereas the intensity of the fluorescence spectrum remains close to zero. Below pH 3, a fluorescent species appears, with bands that would be expected both in absorption and in emission. As a result of the relatively small differences in the pK_a values of the carboxylic acids and the aniline nitrogen atoms in **1b**, protonation apparently leads to a nonfluorescent double zwitterion at

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Figure 1. Normalized absorption and emission spectra a) of 1a-3a and 4 in acetonitrile, and b) of 1b-3b and 4 in water. a), b) Before and c) d) after the addition of c) trifluoroacetic acid (TFA, excess) or d) HCl (pH 0). Excitation wavelength was at 390 nm for the neutral species and at 350 nm for the protonated species (1=--; 2=---; 3=---).

pH 7 (Scheme 2). *N*,*N*-Dimethylaniline has a pK_a value of 5.2, whereas carboxylic acid functionalities, such as in butanoic acid, have pK_a values around 4.8. Upon protonation of the aniline units, they might form strongly hydrogen-bonded non-fluorescent complexes with the carboxylate groups. The CO_2^- groups could then induce efficient fluorescence quenching.

Upon further protonation, these complexes are disrupted and the negatively charged carboxylate groups are transformed into carboxylic acids, which neither interact with the anilinium group nor are capable of performing excited-state



Scheme 2. Proposed protonation sequence for 1b-3b.

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the later stages of the titration of 1b, but is also an attractive turn-on fluorophore in its own right. From pH 10 to pH 4, solutions of **2b** are non-fluorescent. The pK_a values of the carboxylic acids are around 4.5, so most of the carboxylate groups and the aniline unit are protonated at pH<4. When all sites are fully protonated we find a turn-on of the fluorescence as in 1b. This effect is accompanied in the absorption spectrum of 2b by an isosbestic point suggesting two spectroscopically different states that are in equilibrium at pH values between 4.3 and 3.2, which would correspond to the pK_a of the carboxylic acids (!). The interpretation of the UV/Vis absorption spectra suggests that although the aniline group must be protonated, it is also strongly hydrogen-bonded to one of the carboxylate groups. The electronic consequences of the protonation are only manifested when the carboxylate is likewise protonated and the full positive charge is localized on the aniline unit. The close presence of the carboxylate groups might lessen the effective charge of the anilinium ion to such a point that its effect is spectroscopically not detectable: only when the carboxylate groups are fully protonated does the expected blue fluorescence appear, but not before pH 1 is reached.^[22]

electron transfer.^[21] Compound **2b** aids the understanding of

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Figure 2. Quantum chemical calculation (B3LYP 6–311+G**) of a simplified model system representing **1b–3b** (left) and calculation of a protonated dimethylaniline as perchlorate salt (right). Salient features are the almost tetrahedral symmetry of the aniline nitrogen but also the N–H–O interatomic distances, which are considerably longer for the N–H bond than for the O–H bond (left). Bond lengths for the O–H and the N–H bonds are given.

To test this hypothesis further we calculated (Spartan Windows, B3LYP 6-311+G**, Figure 2) the structure of a simplified hydrogen-bonded complex that is formally uncharged. To our surprise, the aniline nitrogen is already tetrahedral, but the N-H bond length is 1.74 Å, whereas the CO-H bond is 1.0 Å, much shorter than the N-H bond. To provide a reference point, we also calculated the structure of N,N-dimethylaniline•HClO₄, in which the proton is now much closer to the nitrogen, as expected. These calculations are gasphase species, but it is still surprising that the single-bonded carboxylic acid oxygen wins out over the nitrogen in the model structures, yet this is exactly what we conclude when we interpret our experimental data.

During the titration of 4, in contrast, neither donor-acceptor intermediates nor zwitterions are formed; as a consequence, the emission spectra do not show any non-fluorescent pHdependent intermediates (Figure 3), just the expected blue shift in absorption and emission, with an isosbestic point at 377 nm in the UV/Vis absorption spectrum. Compound 4, lacking the carboxylate groups, therefore starts to fluoresce at pH 3.1. This is still somewhat puzzling, though, because one would expect the full blue fluorescence to be found at around pH 4 (pK_a of dimethylaniline 5.15), at which most of the aniline units should be protonated. From our UV/Vis absorption spectroscopic measurements for **4**, we can estimate the pK_a of the anilinium ion from the isosbestic point to be 3.6, a bit lower than expected. However, changes in absorption and emission are almost concomitant, so we conclude that **4** does not display enhanced kinetic photoacidity.

We explored the DSBs as metal-binding compounds in polar organic solvents and in water (Figure 4).^[23] Compounds **1a–3a** and **4** all show a distinct response towards addition of Zn^{2+} in acetonitrile. This response is qualitatively identical to that observed towards TFA. We exposed **1b–3b** and **4** to Mg²⁺, Ca²⁺, and Zn²⁺ in aqueous buffered solutions (PIPES, 50 mmolL⁻¹, pH 7.2, Figure 4). Mg²⁺ and Ca²⁺ do not lead to changes in the photophysical properties of the DSBs, but Zn²⁺ ions induce quenching of **1b–3b**,



Figure 3. Absorption and emission of **1b–3b** and **4** in water upon protonation with HCl. The excitation wavelength for each compound was set to the isosbestic or pseudosisosbestic point.

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Figure 4. Photographs of **1–4** (S = reference, A = addition of acid, B = addition of base) upon addition of base, acid, and different metal cations in acetonitrile and in aqueous buffered solutions (piperazine-N,N'-bis(2-ethanesulfonic acid) (PIPES), 0.05 M, pH 7.2).



Figure 5. a) Fluorescence of **4** on exposure to acid and to Zn^{2+} cations in excess. The metalloresponses were measured in buffered solutions of PIPES (0.05 M, pH 7.2).

whereas 4 exhibits blue fluorescence (Figures 4 and 5). The quenching of 1b-3b can be explained by a mechanism similar to that proposed for protonation. Formation of a complex in which the zinc cation serves as a bridge between carboxylate and aniline allows for efficient charge-transfer quenching of the DSBs' fluorescence. In the case of 4, there is no uncoordinated DSB left, but the blue-shifted fluorescence is much weaker. It is currently not clear why this happens, but we plan to investigate this effect in more detail in the future. After the addition of Zn^{2+} , the DSB 4 experiences a decline in quantum yield (Figure 5), but on normalization a blue-shifted band (superimposable on that obtained for 4 in HCl) is produced, suggesting that, in parallel with the quenching, compound 4 presents a true ratiomeric response to a buffered solution of zinc cations, similar to that observed for the reaction of 4 to the presence of zinc in acetonitrile. This is all the more interesting because the DSB 4 does not contain any additional sensory appendages other than the dimethylaniline group. In the future, however, we intend to fine-tune the DSB 4 by using sensory appendages to increase both its selectivity and its sensitivity towards zinc ions.

Conclusion

The water-soluble DSBs **1b–3b** and **4** were prepared.^[24] The acidochromicity of 1b-3b and 4 was investigated in water. Although DSBs and amino-DSBs are long known, this, surprisingly, is the first time that their acidochromicity in water has been investigated. The DSBs 1b-3b display surprisingly complex titration profiles as a result of the formation of hydrogen bonds between the carboxylate groups and the aniline nitrogen atoms (Scheme 2). At high pH values the two carboxylate groups and the unprotonated aniline unit in 3b, for example, give rise to yellow-green fluorescence in water. Upon decreasing the pH to 7 the fluorescence disappeared, only reappearing at a pH of 1, at which apparently all of the carboxylate groups are protonated and the anilinium cation does not show any hydrogen bonding to the carboxylic acid units. Consequently, attempts to build DSB-based pH-sensors through the use of EDTA or similar motifs with negatively charged carboxylate units might be fundamentally problematic, because either ratiometric or turn-on sensing apparently commences only after full protonation has started. Behavior of this type would only be desirable if one wished to investigate extremely acidic compartments in cells or live cultures of stomach epithelial cells.

We successfully observed interaction of **4** with zinc ions in water, but **1b–3b** display quenching under these conditions. The amino-DSB unit is a competent core, but simple carboxylate groups attached to the core at the nitrogen units are not readily compatible with the amino-DSB. One way out would be to maintain long insulating methylene chains between aniline and carboxylate but to increase its acidity, such that it would neither be protonated nor engage in disruptive hydrogen bonding or excited-state electron transfer. Suggested structures include $(CH_2)_3CF_2CO_2H$. In the systems investigated here, fluorescence reports more the protonation/metalation of the carboxylate units than that of the aniline unit that is the designed conduit. None of these surprising properties were known or could reasonably be predicted a priori in these simple yet important systems.

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