

Bis(4'-dibutylaminostyryl)benzene: Spectroscopic Behavior upon Protonation or Methylation

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Abstract: We have investigated the UV/Vis absorption and emission of 1,4-bis(4'-dibutylaminostyryl)benzene (**1**) upon protonation with trifluoroacetic acid in dichloromethane and in acetonitrile. We find that **1** does not display significantly dynamic acidity in the excited state, that is, it is not a photoacid. Three protonation states of **1** were investigated, all of which, neutral, singly protonated, and bis-protonated, are flu-

orescent. As an isolable model for the mono-protonated species, a methylated derivative of **1** was prepared by reaction with methyl triflate. This species displays redshifted emission but similar

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absorption as the non-quaternized parent, **1**. The strong observed emission of all three protonated states of **1** suggests that the kinetic photoacidity of **1*** is low or absent. We assume that the lifetime of the excited state is too short to allow solvent reorganization and therefore we cannot make a statement on the thermodynamic photoacidity of the protonated forms of **1**.

Introduction

Fluorophores assembled from stilbene and distyrylbenzene π -systems have attracted intense interest due to their potential utility in optoelectronic and sensory applications, including poly(phenylenevinylene)s (PPVs) in organic light-emitting diodes.^[1] Amino-functionalized stilbenes have been examined by Tsien et al.,^[2] Valeur et al.,^[3] and others as potential fluorescent metal ion probes.^[4] Though substantial shifts in the absorption of alkylamino-functionalized stilbenes were observed upon treatment with Mg, Ca, or Ba salts, only minor shifts in emission resulted. Subsequent pump-probe experiments by Valeur et al.^[5] and Lapouyade et al.^[6] established light-induced cation ejection as the putative explanation for the limited excited state sensory responses observed in these stilbenes.

In later experiments, Perry et al. explored the metal-binding capabilities of donor-acceptor substituted distyrylbenzenes as two-photon absorbing fluorophores for the detection of metal ions.^[7] While these authors did not claim excit-

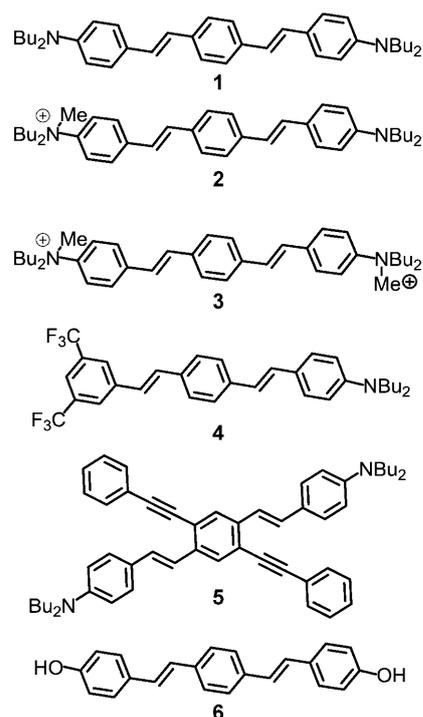
ed state ejection of the bound magnesium cations, they found large blueshifts in absorption but only miniscule shifts in emission upon complexation with magnesium perchlorate in acetonitrile. As a consequence of the apparently unsatisfactory excited state properties of these aminostyryl-based molecules, they have been relegated to the sidelines and are not considered as viable cores for advanced sensor design.

In contrast, most 1,4-bis(aminostyryl)-2,5-diarylethynylbenzenes (cruciforms, XFs) exhibit spectacular shifts in absorption and emission upon treatment with trifluoroacetic acid (TFA) or metal cations.^[8] This is a somewhat surprising result, as XFs such as **5** are in effect distyrylbenzene derivatives; however, XFs as well as their tetraalkynyl analogues reported by Haley et al.^[9] seem to be unhampered by "excited state decomplexation", which has thus far plagued other stilbene- and distyrylbenzene-based fluorophores, requiring us to reconsider the assumption that excited state decomplexation will impede sensory dyes assembled from a distyrylbenzene scaffold.

Surprisingly, and in spite of the intense interest in the photophysical properties and sensory potential of styryl-derived fluorophores,^[10] no study has been performed detailing the response of simple bis(alkylaminostyryl)benzenes such as **1** upon *protonation*. This is of significant interest as it provides an opportunity for the careful spectroscopic examination of the cation-induced responses of **1**.^[11] TFA serves as a representative model analyte for alkylamino-functionalized dyes, since it shares a mode of interaction (i.e. nitrogen co-

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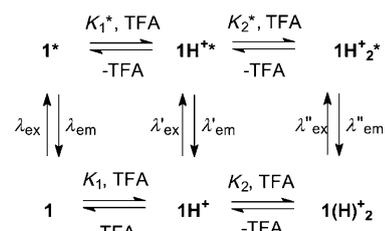


ordination) with metal cations. This permits simulation of the response observed upon exposure of distyrylbenzenes to metal ions. However, the higher binding constant, greater solubility, and lack of coordination-induced assembly in protonation experiments are advantageous; simplicity matters. To a first approximation, the basicity of the chromophore might be expected to mirror the binding affinity, both in the ground and excited states. Thus, a detailed study of the acidochromicity in both states should shed light on whether 'excited state decomplexation' expressed as enhanced photoacidity might be a favorable process in **1** and related compounds. If excited state effects do not diminish analyte interactions in the excited state, one would expect concomitant spectral changes in absorption and emission upon addition of TFA. However, if these distyrylbenzenes are prone to excited state deprotonation,^[12] one might anticipate excited-state decomplexation as well.^[13] The thermodynamics of proton transfer in the excited state is provided by the Förster cycle [Eq. (1)], where R is the gas constant, T is the absolute temperature, N is Avogadro's number, h is Planck's constant, c is the speed of light, and ν_F is the respective emission in wavenumbers.

$$\Delta pK_a = pK_a - pK_a^* = \frac{E_{HA} - E_{A^-}}{2.3RT} \quad (1)$$

$$E_i = Nhc(\nu_F)$$

Thus the comparison of the ground and excited-state acidities of $1H^+$ and $1(H^+)_2$ (see Scheme 1), may provide clues to their metallochromic behavior. In this case, we would expect to observe either shifts exclusively in the absorption or a lagging change in emission relative to absorption upon



Scheme 1. Summary of ground- and excited-state equilibria following protonation of **1**.

addition of TFA. In this fashion, TFA can function as a simple proxy for metal cations, should 'excited state decomplexation' inhibit the sensory response of a dye. In the event, we would observe a rich and complex photophysical behavior for these fluorescent dyes upon protonation.

Results and Discussion

Target **1** was synthesized by a Horner reaction of 4-dibutylaminobenzaldehyde with tetraethyl *para*-xylenediphosphate and obtained as a yellow crystalline solid (see the Supporting Information).^[14] The distyrylbenzene derivative **1** displays a vibrant blue emission in toluene solution ($\lambda_{max} = 457$ nm). While limited solvatochromic shifts are observed in the absorption of **1**, substantial solvent dependence is observed in emission, ranging from a structured emission of 457 nm in toluene to a broadened emission of 517 nm in a 2:1 mixture of methanol and water (Figure 1).

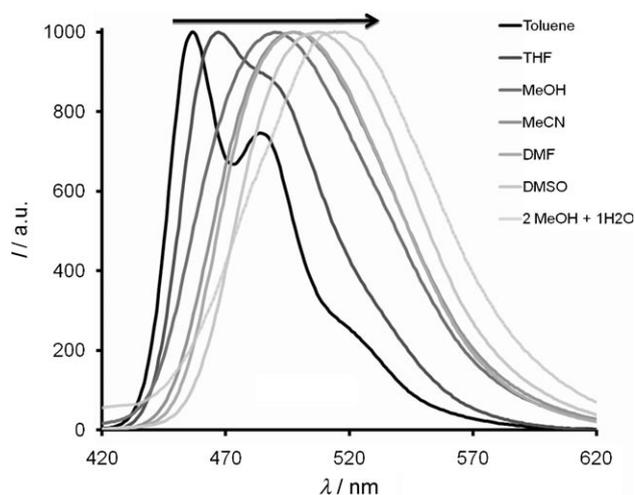


Figure 1. Normalized emission spectra of **1** in different solvents.

We chose TFA in acetonitrile to probe the excited state acidochromicity (i.e. photoacidity) of **1** as a proxy for its metallochromicity. Although acetonitrile does not support fast proton transfer,^[15] the solubility of our dyes is limited in water and the proton transfer kinetics are complex, having

been the subject of numerous investigations.^[13a] Addition of an excess (50 equivalents) of TFA to **1** elicits a blueshift in both absorption (411 \rightarrow 343 nm) and emission (496 \rightarrow 414 nm). This result is significant, as related aminostyryl fluorophores have not been shown to exhibit large emission responses upon cation binding. To understand this effect, we performed a titration of **1** with TFA in acetonitrile (Figure 2); we observe a decrease in the absorption of **1** at 411 nm accompanied by the development of a blueshifted

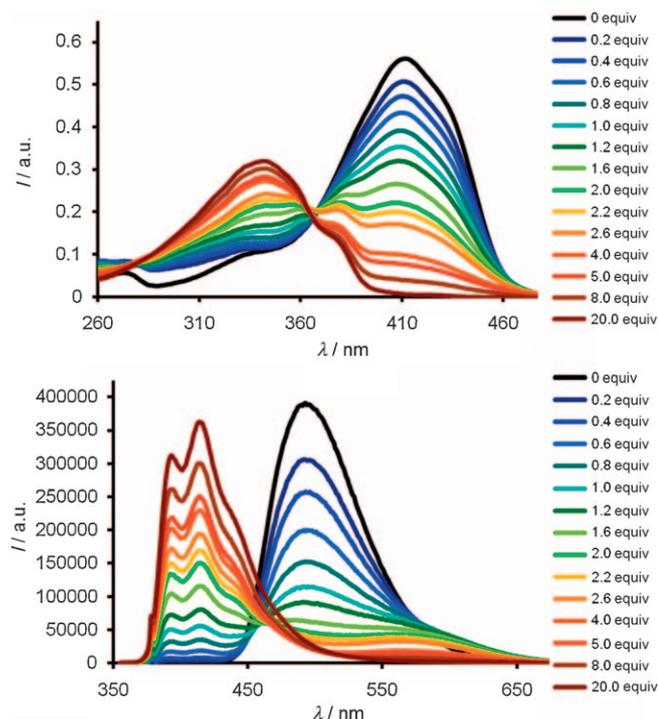


Figure 2. Spectrophotometric titration of **1** with TFA in CH₃CN. Selected absorption (top) and emission (bottom) traces are shown here for clarity. To ensure constant absorptivity during the course of the titration, excitation occurred near the isosbestic point (367 nm). Complete data sets used for SPECIFIT analysis are included in the Supporting Information.

absorption at 343 nm. As TFA is added, a decrease in the intensity of the emission at 496 nm is observed. A strong blue emission at 414 nm develops; in addition, a small shoulder at approximately 585 nm is visible. Significantly, a qualitative assessment of the shifts in absorption and emission observed upon treatment of **1** with TFA suggests that the *responses occur concomitantly*.

We employed SPECIFIT^[16] to deconvolute the binding data independently from the absorption and emission spectra using a complexation model which assumed two distinct, spectroscopically distinguishable binding events. Table 1 highlights the results of this analysis. The β values obtained from the absorption and emission spectra are in close agreement, suggesting the absence of excited-state prototropism. Through SPECIFIT, we obtained the relative abundance of **1**, **1H⁺**, and diprotonated **1(H⁺)₂** as the titration progresses (Figure 3). Plots detailing the solution composition obtained

Table 1. Binding data obtained from a SPECIFIT analysis of the absorption and emission spectra.

	Absorption	Emission
log (β 1)	3.4	3.7
σ (β 1)	0.039	0.032
log (β 2)	7.0	7.4
σ (β 2)	0.063	0.031
σ (fit)	3.4×10^{-3}	3.5×10^{-3}
relative error of fit	2.1 %	3.6 %

independently from the absorption and emission spectra suggest a similar solution composition as the titration proceeds. This offers further confirmation that excited state effects do not significantly inhibit the fluorescent response of **1** upon protonation.

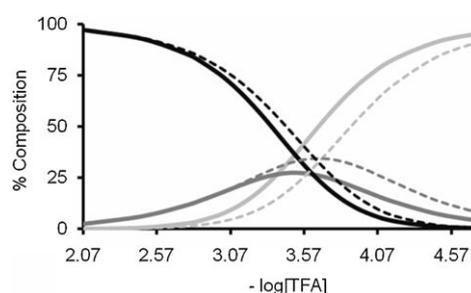


Figure 3. SPECIFIT plots derived from the absorption (solid traces) and emission (dashed traces) describing the solution composition as the TFA titration progresses. Here, the percent composition of **1** (light gray), monoprotonated **1H⁺** (dark gray), and diprotonated **1(H⁺)₂** (black) are plotted as a function of TFA concentration. Similar profiles are obtained independently from the absorption and emission spectra.

The term β 1 represents the equilibrium K_1 for proton transfer between TFA and **1** in MeCN (see Scheme 1), which means that **1H⁺** is less acidic than TFA by $-\log K_1$, or 3.4 pK_a units. TFA has a pK_a of 0.52 in water^[17] and 3.45 in DMSO;^[18] thus, the pK_a of **1H⁺** is roughly 3.9 anchored to water and 6.9 anchored to DMSO. To our knowledge, the pK_a of TFA in CH₃CN has not been reported; as a rough approximation for the purposes of discussion, we will assume the pK_a of TFA in CH₃CN is similar to its pK_a in DMSO. We note that the pK_a of dibutylaniline is about 6 in DMSO,^[19] which should be slightly less basic than **1**. Similarly, β 2 represents K_1K_2 , so $-\log K_2 = 7 - 3.4 = 3.6$, making **1(H⁺)₂**, pK_a = 3.6 + 3.5 = 7.1 slightly less acidic than **1H⁺**. Thus the binding affinity of the second nitrogen is relatively little affected by protonation of the first.

The quality of this fit and the residual analysis performed confirm two sequential protonation events. Because of the closeness of the two complexation constants, a superficial evaluation of the acetonitrile titration does not reveal an intermediate species which could be unambiguously assigned to the monoprotonated intermediate. Deconvolution of the titration using SPECIFIT was unable to adequately resolve the emission spectra of **1H⁺**; however, it does suggest the

presence of an emission at lower energy (ca. 585 nm). We suspected that the shoulder appearing in the emission spectra at 580 nm during the course of the titration might be the emission of 1H^+ . The minimal intensity of this feature is readily explained by the low abundance of monoprotonated 1H^+ during the course of the titration in acetonitrile (<30% at maximum). However, addition of TFA performed in dichloromethane reveals a yellow-emissive intermediate visible both by the naked eye and by visible spectroscopy (Figure 4).

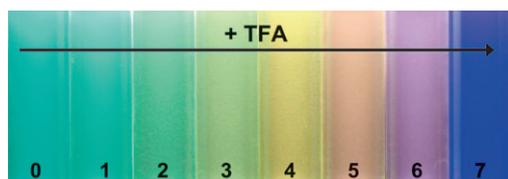


Figure 4. Fluorescence color of **1** after addition of TFA in dichloromethane. Samples contain increasing amounts of TFA and are illuminated under blacklight ($\lambda_{\text{ex}}=365$ nm). Solutions were photographed using a Canon EOS Digital Camera equipped with an EFS 18-55 mm lens. Spectra of solutions 0–7 are available in the Supporting Information.

The minimal change in the absorptive nature of this monoprotonated intermediate 1H^+ when compared to **1** make its study problematic. To better understand the system, we prepared the mono- (**2**) and dimethylated (**3**) analogues of **1**, which should serve as stable, isolable, and isoelectronic models of the protonated compounds formed upon treatment of **1** with TFA. Reaction of **1** with 0.3 equivalents of methyl triflate in dichloromethane results in a mixture of **1**–**3** separable by column chromatography (see the Supporting Information). The absorption and emission spectra of **2** and **3** are shown in Figure 5 (see also Table 2).

As expected, **3** closely resembles the diprotonated endpoint of the titration of **1** with TFA, displaying an absorption of 340 nm and a structured blue emission at 416 nm in acetonitrile (see Table 2). Cation **2**, our model for 1H^+ , possesses an absorption at 406 nm as well as at 317 nm and a broad emission at 582 nm. The emission of **2** corresponds to the shoulder visible upon titration of **1** with TFA. The similarity of the long wavelength absorptions of **1** and **2** and the short wavelength absorption of **2** and **3** suggests that this is a localized π – π^* absorption, with components in the aniline end and the anilinium end, and explains the lack of a visible monoprotonated intermediate in the titration absorption spectra. The absorption and emission of **2** are similar to that of an asymmetrically donor–acceptor substituted distyrylbenzene **4**, resulting in a charge-transfer excited state.

The absorption and emission spectra of **1**–**3** were recorded in a variety of solvents (see the Supporting Information) to construct Lippert–Mataga plots, where Δf , the Lippert–Mataga solvent parameter, is defined by Equation (2).^[20] The slope of the best fit provides a relative assessment of the degree of charge transfer present in **1**–**3** (Figure 6). Distyrylbenzene **1**, which is donor substituted and possesses

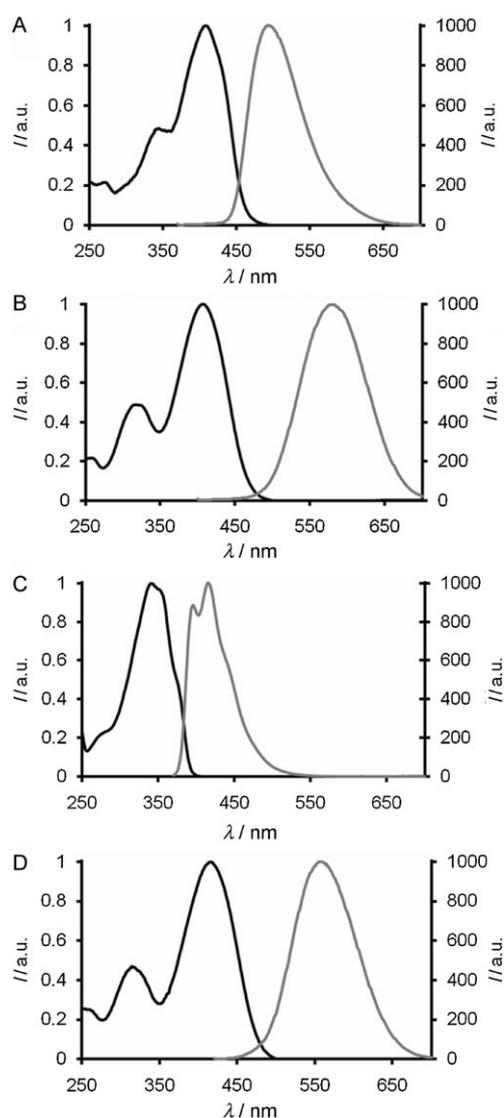


Figure 5. Normalized absorption and emission spectra of **1** (A), **2** (B), **3** (C), and **4** (D) in acetonitrile.

Table 2. Selected spectroscopic data for compounds **1**–**4**, 1H^+ , and $1(\text{H}^+)_2$. pK_a values were calculated by using SPECFIT and anchored to DMSO as an approximation for CH_3CN ; pK_a^* values were calculated by using the Förster equation. For the purposes of Förster cycle calculations, λ_{max} values for 1H^+ were estimated by using the values for mono-methylated **2**, whereas λ_{max} values for $1(\text{H}^+)_2$ were obtained from the titration endpoint (Figure 2).

	λ_{max} absorption in CH_3CN [nm]	λ_{max} emission in CH_3CN [nm]	pK_a	pK_a^*	Φ in CH_3CN	τ in CH_3CN [ns]
1	411	496	–	–	0.60	1.3
1H^+	406	582	6.9	13.2	–	–
$1(\text{H}^+)_2$	343	414	7.1	–7.5	0.73	1.1
2	406	582	–	–	0.13	1.0
3	340	416	–	–	0.48	1.3
4	415	558	–	–	–	–

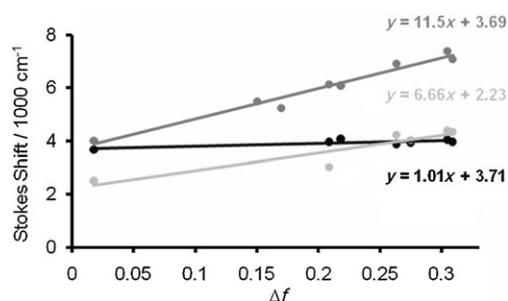


Figure 6. Lippert–Mataga plot of compounds **1** (light gray trace), **2** (dark gray trace), and **3** (black trace). Spectral details of **1–3** in a variety of solvents as well as details of solvent factors for the solvents used are included in the Supporting Information.

two free electron pairs, displays a modest degree of charge transfer.

$$\Delta f = [(\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2(n^2 + 1))] \quad (2)$$

Upon methylation, **2** displays an increased charge transfer character relative to **1**, as indicated by the increased slope. This is readily rationalized as **2** becomes a donor-acceptor substituted distyrylbenzene; the result is a redshifted and broadened emission centered at 582 nm (Figure 5 and Figure 7). The second methylation produces **3**, which dis-

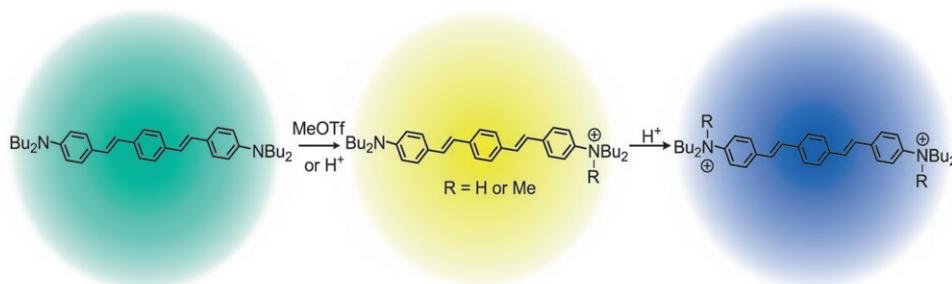


Figure 7. Serial protonation or methylation of **1** and change in its emission color.

plays a decreased charge transfer character; this is expected as **3** no longer possesses available free electron pairs on the alkylamino nitrogen atoms. The resulting dimethylated distyrylbenzene displays a structured, blueshifted emission at 416 nm.

The bathochromic shift upon protonation of **1**, as modeled by the spectra of **2**, suggests that **1H⁺** exhibits increased basicity in the excited state, according to the Förster equation.^[21] Using an approximate pK_a of 6.9 for **1H⁺**, we predict the excited state acidity pK_a^* of **1(H⁺)₂⁺** to be 13.2! Thus the shift in emission maximum from 494 nm to 586 nm corresponds to an *increased* binding affinity for protons in the excited state. This suggests that **1** should, in fact, bind more strongly to metals in the excited state rather than less, since the charge-transfer quality of **2*** would imply in-

creased electron density at the ionic end relative to the ground state. This is in contrast to the previously reported metal sensors,^[5,6] for which excitation produces a charge-transfer state with decreased electron density at the binding site. Conversely, the diprotonated **1(H⁺)₂** is a stronger photoacid by about 14 pK_a units. The fact that no dynamic behavior from **1(H⁺)₂** is observed upon irradiation is not surprising, in keeping with numerous observations that excited-state proton transfer is relatively slow in the absence of a preorganized proton-accepting network.^[13] However, the decreased photoacidity of **1H⁺**, as predicted by the corresponding hypsochromic absorption of **2**, should make properly designed non-symmetrical aminodistyrylbenzenes very powerful sensory cores for the detection and quantitation of transition-metal cations, for which solvent reorganization should play a more modest role, and for which the differences in solvation energies are less dramatic.

We have cursorily investigated the interaction of **1** with metal salts, to see if the observed trends for protonation are mirrored by the addition of metal triflates in acetonitrile (Figure 8). Addition of zinc triflate or magnesium triflate to the solutions of **1** in acetonitrile lead to emission responses that are qualitatively identical to those observed upon protonation of **1**. If calcium triflate is added, the situation is more complex as apparently only partial binding is observed. Interestingly, a mix of the uncomplexed and the doubly complexed species are seen as envisioned by the emissions at 414 and 596 nm. In addition, a redshifted tail is apparent, perhaps due to the mono-metallated species. Qualitatively, the changes in emission and absorption go hand-in-hand, suggesting that excited state demetallation does not play a significant role in the chosen fluorophore/solvent system; however, when going into water, the situation might

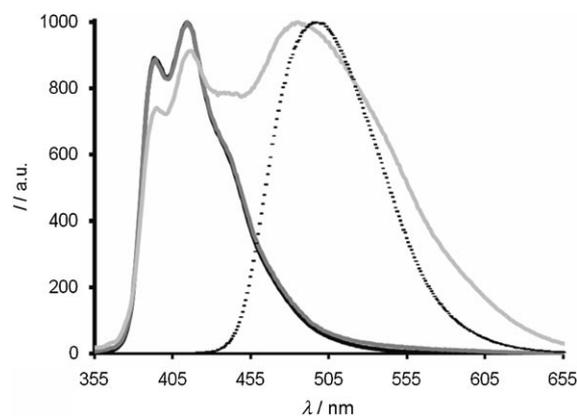


Figure 8. Normalized emission of **1** in CH_3CN (dashed black trace) upon exposure to $\text{Mg}(\text{OTf})_2$ (solid black trace), $\text{Zn}(\text{OTf})_2$ (dark gray trace), and $\text{Ca}(\text{OTf})_2$ (light gray trace).

be very different. As well, in a general vein, the binding of the dialkylanilines to metal cations is weaker than to protons, as the proton's charge density is the highest of all possible cations, particularly in non-protic solvents such as dichloromethane but also acetonitrile.

Conclusions

The results suggest a two-stage response in the absorption and emission of **1** upon exposure to TFA; TFA as a model cation provides a uniquely valuable opportunity to quantitatively assess the sensory responses of **1**. Changes in absorption are accompanied by concomitant changes in emission, suggesting that excited state decomplexation will *not* hinder the performance of all amino-styryl based fluorophores if the charge-transfer nature of the excited-state is properly designed. Surprising is the finding of the enhanced photobasicity (or decreased photoacidity) of the monoprotonated species **1H**⁺, which flies in the face of common chemical reasoning and accentuates the dramatic differences between stilbenes, where according to Valeur et al.^[3,5] cation ejection is observed, and distyrylbenzenes, where other rules seem to apply.

Future studies will more carefully explore the metallochromicity of **1** and related alkylamino-substituted distyrylbenzenes. The proton-induced shifts in **1** are reminiscent of the protonation of the dianions of bis(hydroxystyryl)benzene **6**.^[12a] There, the first protonation of the bisphenolate of **6** results in a significant redshift in emission but only a very small redshift in absorption. Upon full protonation, then into **6**, both a blueshift in absorption as well as a large blueshift in emission is reported. Consequently, **1** and **6** are consanguine and their common distyrylbenzene core dictates their emissive behavior upon protonation or deprotonation. Both **1** and **6** are fundamentally different from stilbene-derived fluorophores as well as the laterally donor-acceptor substituted distyrylbenzenes which have been previously examined.^[6] A number of interesting detection schemes for cationic analytes is therefore envisioned by using either **1** and **2**, attaching attractive sensory appendages to this powerful core.

Acknowledgements

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