Solvatochromism and Fluorescence Response of a Halogen Bonding Anion Receptor

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Solvatochromism and fluorescence response of a halogen bonding anion receptor

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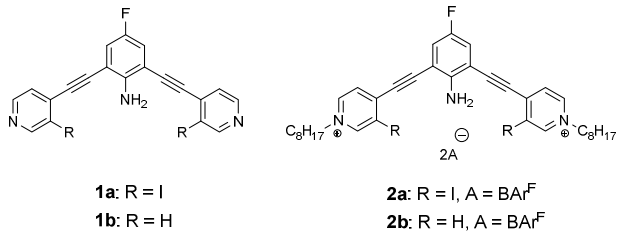
Herein, we present on two 2,6-bis(4-ethynylpyridinyl)-4-fluoroaniline receptors that display solvatochromic absorption and emission. Neutral derivatives displayed opposite solvatochromic behavior as compared to the alkylated receptors. Adding anions induced changes in the absorption and emission spectra. In general, the fluorescence of the halogen bonding receptor was quenched less efficiently when compared to the hydrogen bonding receptor.

A halogen bond (XB) is an attractive noncovalent interaction between an electron-deficient halogen atom and a Lewis base. XBs are more directional and display different solvent dependencies[1] compared to hydrogen bonds (HB), and can be applied in anion recognition and sensing.[2] Recently, Beer's macrocycles, rotaxanes and catenanes; Molina and Alkorta's halotriazolium; and Taylor's urea were reported as leading examples of fluorescent and colorimetric anion sensors that employ XBs.[3] However, there are still relatively few spectroscopic studies devoted to XBing anion receptors. Herein we report a new UV-Vis/fluorescence responsive XB receptor that explores how XBing influences spectrophotometric properties in this system.

Building on previous studies conducted in our laboratory,[4] we designed and synthesized a pair of 2,6-bis(4-ethynylpyridinyl)-4-fluoroaniline receptors (**2a** and **2b**). Solution studies, crystal structures and computations supported our hypothesis that the intramolecular HB between the electron-deficient aniline and the two XB donor iodine atoms enhance the electrophilicity of the XB donors and preorganizes the bidentate XBing conformation.[5] We refer to this new preorganization strategy as intramolecular HB-XB. Receptor **2b**, lacks XB donors and was prepared to quantify C–H HBing and serve as a control. While synthesizing and characterizing the receptors, solvent dependent color changes were observed, especially under ultraviolet light. To better understand this solvatochromism, UV-Visible absorption and fluorescence emission studies were conducted for **1a**, **1b** and octyl derivatives **2a** and **2b** (Fig. 1).



1a: R = I
1b: R = H

2a: R = I, A = BAr^F
2b: R = H, A = BAr^F

Fig 1. Structures of 2,6-bis(4-ethynylpyridinyl)-4-fluoroaniline XB donor **1a**, HB donor **1b** and octyl derivatives **2a**, **2b**.

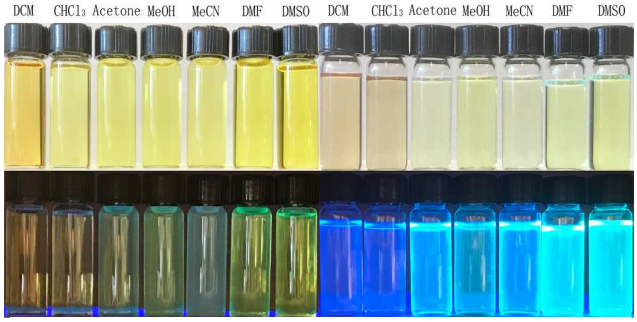


Fig 2. Solvatochromism of 1mM **1a** (top left: under sunlight; bottom left: under 365nm UV light) and **1b** (top right: under sunlight; bottom right: under 365nm UV light) in a set of solvents.

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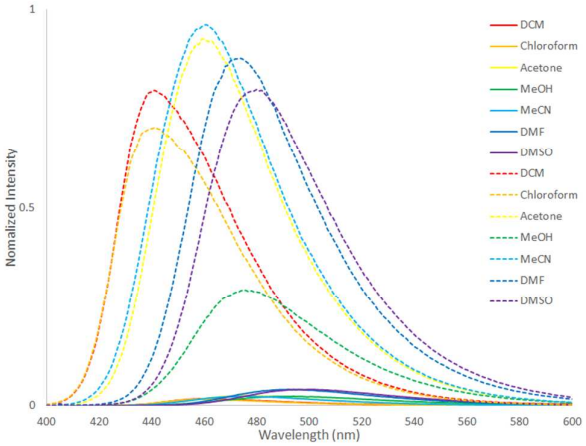

Fig 3. Normalized fluorescence emission spectra of **1a** (20 μM, solid line) and **1b** (20 μM, dashed line) in various solvents.

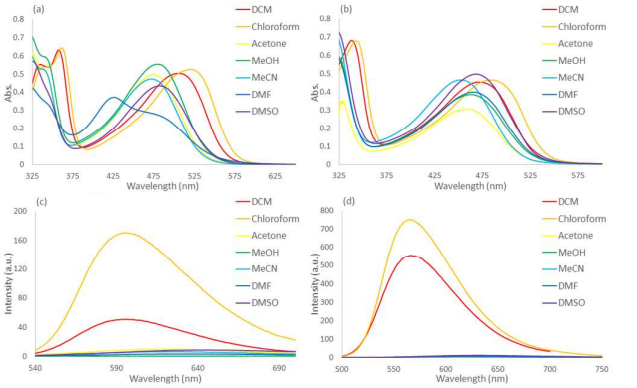

Fig 4. Absorption spectra of **2a** (a) and **2b** (b) in various solvents. Fluorescence emission spectra of **2a** (c) and **2b** (d) in various solvents (for excitation wavelengths and details see SI). All spectra were recorded at 20 μM of receptor.

Solvent dependence of both the absorption and emission spectra was observed for **1a** and **1b** (Fig. 2). Receptors **1a** and **1b** exhibited a major absorbance band in the range of 300-600 nm (Fig. S1 and S3). The absorption band of **1a** is red shifted from 405 nm to 416 nm as the dielectric constant of the solvent is increased with the exception of MeCN (Fig. S9). A similar roughly linear correlation of bathochromic shift with increasing solvent dielectric constant was obtained for **1b** (Fig. S3). Soret bands from π–π* transitions exhibit significant charge-transfer character resulting from the electron-deficient pyridine and electron donating aniline.[6] Other solvent parameters[7] (dipole moment, $E_T(30)$ and π* scale) were also analysed for both the neutral and charged receptors. However, no clear correlation between dipole moment, $E_T(30)$ or π*scale and absorbance ν_{max} (Fig. S10-S12) was observed suggesting that nonspecific solvent polarity effects are not strong determinants of the HOMO and LUMO energy levels. This lack of correlation and solvents that deviate from the trend may be due to the Lewis acidic nature of the studied receptors. Taken together, these results suggest that the dielectric constant of the solvent most influences the HOMO and LUMO energy levels of the receptors. High dielectric solvents stabilize the excited state more than the ground state of the receptor. As a result, the energy for the HOMO to LUMO electron transition is lowered producing a bathochromic shift of the spectra with increasing solvent dielectric constant. The λ_{max} of **1a** is always red shifted when compared to **1b** in the same solvent, a result of the auxochrome iodine groups in **1a**.[8]

The solvatochromic effect on fluorescence was also investigated for **1a** and **1b**. The iodine atoms of **1a** produce a "heavy atom effect" that enhances the probability of intersystem crossing leading to reduced fluorescence of **1a** compared to **1b** (Fig. 3).[9] The emission spectra of **1a** and **1b** obey the same direct correlation between solvent polarity and λ_{max} shift. However, methanol deviates from this trend for both **1a** and **1b** (Fig. S2 and S4). For instance, the emission band of **1b** in methanol has a λ_{max} at 475 nm which is 15 nm and 14 nm longer than in acetone and acetonitrile, respectively, and is even close to dimethylformamide (DMF, λ_{max} = 476 nm) (Fig. S4). This deviation could result from the HB ability of the protic methanol. HBing to the amine of the fluoroaniline through an NH···O type HB or to a pyridine nitrogen through an OH···N HB could stabilize the excited state and shift the emission. Additionally, a drop in emission is observed for **1b**, perhaps due to HB enhanced internal conversion and intersystem crossing.[10]

To investigate the XB interaction and how it influences solvatochromism and fluorescence, the receptors were alkylated to increase their electron-deficiency and their binding affinity for anionic guests. Alkylation of the pyridines with octyl chains activated the XB and HB donors of **2a** and **2b**, respectively, while also enabling solubility in organic solvents.

The UV-Vis absorption and fluorescence emission spectra of **2a** and **2b** in various solvents are reported in Fig. 4. A negative solvatochromism was observed in DCM, acetone, MeCN and DMF for the absorption of both **2a** and **2b** which has also been observed in other pyridinium systems.[11] This phenomenon has been explained by the ground state being more polar than the excited state[12] and intramolecular charge transfer being favored by polar solvents.[11] This produces a larger energy difference between the ground and excited states as the polarity of the solvent increases. Chloroform, MeOH and DMSO deviate from this trend, perhaps, due to the binding between the receptors and solvents or environment effect which give rise to conformational changes in the receptor molecule.[13] Additionally, an obvious difference between **2a** and **2b** is the large blue shifting of **2a** in DMF. A linear free energy relationship between the absorbance (ν_{max}) of **2a** and **2b** showed that the absorbance of **2a** is shifted more in DMF compared to **2b** (Fig. S13b). We have solution and crystallographic evidence that derivatives of **2a** can XB to the DMF carbonyl oxygen.[14] This binding interaction may further stabilize the ground state. Ultimately, an 80 nm blue shift of absorbance in DMF is observed compared to DCM (Fig. 4a). The HB in **2b** has a similar but weaker effect, shifting the absorption peak from 472 nm in DCM to 466 nm in DMF (Fig. 4b).

2a was only fluorescent in nonpolar solvents (DCM and chloroform) and was nearly quenched in all other solvents (Fig. 4c). In contrast, **2b** had stronger fluorescence than **2a** due to lack of the heavy atom effect, but was also quenched in polar solvents (Fig. 4d). The fluorescence quenching is consistent with other probes that are weakly fluorescent in hydrophilic environments but strongly fluorescent in hydrophobic environments.[15]

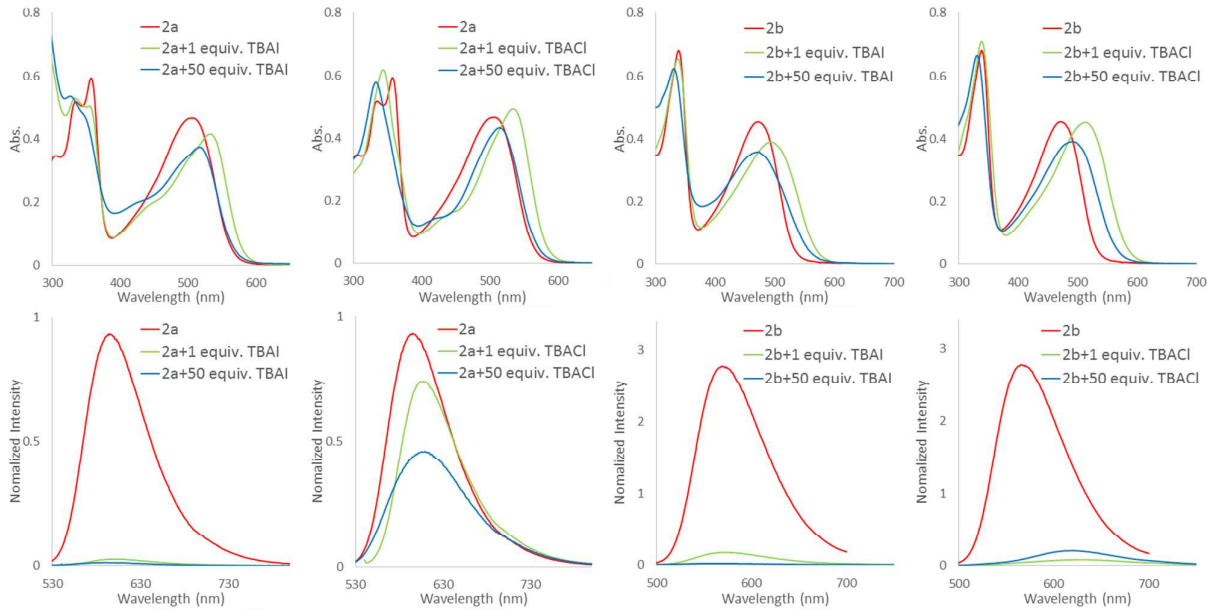

Fig 5. Absorption spectra of **2a** with TBA^+I^- (top left) and with TBA^+Cl^- (top middle-left), **2b** with TBA^+I^- (top middle-right) and with TBA^+Cl^- (top right); followed by fluorescence emission spectra of **2a** with TBA^+I^- (bottom left) and with TBA^+Cl^- (bottom middle-left), **2b** with TBA^+I^- (bottom middle-right) and with TBA^+Cl^- (bottom right). All spectra were recorded at 20 μM of receptor in DCM solution (for excitation wavelengths and details see SI).

Qualitative evaluation of the anion sensing capability of **2a** and **2b** in DCM was performed with a series of anions as their tetrabutylammonium salts (Cl^-, Br^-, I^-, SCN^-, NO_3^-, HSO_4^-, $H_2PO_4^-$ and ReO_4^-). Considering both solubility and polarity which may affect the noncovalent interaction between receptor and anion, we chose DCM as the solvent for these studies. The results are illustrated in Fig. 5 (see SI for full details). In general, the absorption band of XB receptor **2a** at λ_{max} 507 nm is red shifted from 509 to 535 nm when one molar equivalent of anion is added, and hypochromically blue shifted after the addition of excess anion (50 molar equivalents). Additionally, the absorption band of HB receptor **2b** at 472 nm behaves similarly to **2a** which is red shifted from 479 to 513 nm in the presence of one equivalent of anion and hypochromically blue shifted upon addition of excess anion (50 molar equivalents).

In the emission spectra, halides quenched the fluorescence of both **2a** and **2b** from 0 equivalent to 50 equivalents. For instance, fluorescence of **2a** decreased by 20% after adding one equivalent of TBA^+Cl^- and declined to 50% of the initial value after 50 equivalents (Fig. 5, bottom middle-left). However, the receptor is more sensitive to iodide (Fig. 5, bottom left). The intensity significantly dropped to 2% of the original level at just one equivalent of iodide. Inter and intramolecular HBing have been shown to facilitate fluorescence quenching.[16] The efficient fluorescence "turn-off" in **2a** correlates with previous NMR studies[5] that illustrate stronger binding between **2a** and I^- compared to other halide anions.[5] Specifically, the K_{11} values determined by titrations of **2a** with I^-, Br^- and Cl^- were 36,569 M^{-1}, 34,145 M^{-1} and 23,622 M^{-1} respectively in 40% $CDCl_3$/60% CD_3NO_2. In the current system, the formation of strong XBs (C-I···I^-) in the **2a**·I^- complex could allow the necessary spin-orbital coupling for fluorescence quenching to occur.[17] Moreover, the iodine[18] and iodide[19] present can act as heavy-atom quenchers. Considering these effects, intersystem crossing could be favored which leads to fluorescence quenching. Compared to **2a**, fluorescence quenching of **2b** is more efficient with chloride and bromide, and similar with iodide. These results could partially be explained by the weaker binding ability of **2b** (K_{11} for I^-, Br^- and Cl^- are 1,820 M^{-1}, 2,122 M^{-1} and 2,326 M^{-1}, respectively in 40% $CDCl_3$/60% CD_3NO_2).[5] In addition, thiocyanate (SCN^-) quenched the fluorescence of both **2a** and **2b**. SCN^- decreased fluorescence intensity of **2a** to less than 35% of the original level at one equivalent but changed very little at 50 equivalents. However, the fluorescence of **2b** was almost totally quenched after 50 equivalents.

Some of the oxoanions studied elicited different fluorescence responses compared to halides and SCN^-. NO_3^- and ReO_4^- induced a similar fluorescence response in **2a** and **2b** as SCN^- did. However, $H_2PO_4^-$ produced a 51% and 60% decrease in **2a** and **2b**, respectively, at one equivalent and totally quenched fluorescence when in excess. HSO_4^- affected the fluorescence of **2b** in a similar way to SCN^-, NO_3^- and

ReO_4^-. However, in **2a**, the solution turned cloudy and floccule formed, precipitating out the receptor in a couple minutes upon the addition of 50 equivalents of HSO_4^-. In general, **2b** is quenched more than **2a** with all anions, except for iodide. One hypothesis is that XB between **2a** and the anions rigidifies the structure of the **2a**·anion complex. The more planar/rigid structure which has less vibrational modes to absorb the excess energy leads to less efficient internal conversion. Thus, the more efficient internal conversion of **2b** causes the lower quantum yield, and correspondingly lower fluorescence intensity.[20]

Geometry optimizations and Frontier molecular orbital calculations were performed to further analyse the spectrophotometric properties of the receptors. Density Functional Theory (DFT) calculations were done using the B3LYP/6-31+G(d,p) functional. To simplify calculations, methyl derivatives of the charged receptors were evaluated. The electron density distributions of the HOMO and LUMO for all four receptors is depicted in Fig. S68. The neutral receptors **1a** and **1b** have nearly equivalent HOMO and LUMO distributions. Additionally, **2a** and **2b** also have analogous HOMO and LUMO maps which is consistent with the similarly shaped absorption and emission spectra. The electron density in the HOMO is mainly populated on the central fluoroaniline ring. In the LUMO the electron density is increased on the two flanking pyridine rings. Such electronic configurations lead to the charge-transfer nature of the electronic transitions. The energy differences of the HOMO and LUMO are listed in SI Table 1. Narrower energy band gaps are predicted for the HOMO and LUMO for the halogen containing receptors (**1a** and **2a**) compared to the HB receptors (**1b** and **2b**) which correlate with the larger λ_{max} (for both the absorption and emission) observed for the halogen containing receptors **1a** and **2a**.

In summary, we have demonstrated that XB receptor **1a** and HB receptor **1b** exhibited similar solvatochromism in their UV-Vis and fluorescence spectra. As compared to **1a** and **1b**, octyl derivatives **2a** and **2b** exhibited opposite solvatochromism corresponding to their charged states and differences in binding ability. Theoretical estimations of the electron density distributions of the HOMOs and LUMOs highlighted the charge transfer nature of the receptors and supported the differences observed in the soret band λ_{max} in the UV-Vis spectra. The anion induced fluorescence quenching of XB derivative **2a** is less efficient than **2b** with most anions, possibly due to the loose bolt effect for the weaker binding **2b**. Additionally, **2a** can selectively sense I^- over other anions by a significant fluorescence quenching after the addition of one equivalent. Such effects have been explored to better understand the nature of XB and may provide the opportunity to exploit XB in fluorescent/colorimetric anion sensors.

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Conflicts of interest

There are no conflicts to declare.

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Table of Contents

Sentence:

A pair of 2,6-bis(4-ethynylpyridinyl)-4-fluoroaniline XB and HB receptors display solvatochromic absorption and emission.

Figure: