Fluoride recognition by a chiral urea receptor linked to a phthalimide chromophore†

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The anion chemosensor **1** based on a urea-activated phthalimide with a stereogenic centre was synthesized using an efficient procedure involving a Curtius rearrangement. Its photophysical properties were estimated in several solvents. Sensor **1** detected fluoride with absorption as well as fluorescence changes and was only observable for this case and not for other halides. The appearance of a new CT complex emission at a longer wavelength and no changes in the singlet lifetime of **1** in the presence of fluoride supported a fluorescence static quenching mechanism. ^{1}H-NMR studies, together with theoretical calculations based on DFT methods at the B3lYP/6–31G* level of theory confirmed the formation of a [**1**–F]$^-$ complex through H-bonding interactions rather than receptor deprotonation in the recognition process. Reversibility of this process was observed upon addition of a protic solvent.

Introduction

Anion recognition and sensing has attracted considerable interest due to its importance from industrial, biological/medicinal and environmental points of view.[1] In biological systems, anion recognition is often achieved by H-bonding of well-defined complex sites in the interior of proteins.[2] Chemically, the design and development of new anion receptors has emerged substantially during the last decade.[3] In general, anion-receptor interactions take place by H-bonding and/or electrostatic interactions. Fluorescent sensors appear to be the most suitable and attractive tools for anion recognition because of high sensitivity at low analyte concentration.[4] A variety of signaling mechanisms has been described such as ground-state charge transfer,[3c,h] photoinduced electron transfer (PET),[5] excimer/exciplex formation,[6] intramolecular charge transfer,[5e,7] and excited-state proton transfer.[8]

Since the seminal papers by Wilcox and coworkers[9] and Hamilton and coworkers[10] based on urea moieties as appropriate receptors for anions, examples of chemosensors such as acyclic, cyclic and polycyclic compounds containing urea/thiourea fragments have been reported.[5b,11] It is well-known that simple *N*-alkylated-phthalimides possess extremely low fluorescence quantum yields ($\Phi_F < 0.02$). Ring substitution with amino as well as alkoxy groups has been described to enhance the fluorescence and 4-amino-*N*-methylphthalimide was shown as a convenient solvatochromic fluorescent dye[12] and fluorescent 4,5-dimethoxyphthalimide derivatives were applied as sensors for intra- and intermolecular PET processes.[13]

The urea moiety is a suitable anion receptor and phthalimide derivatives have high fluorescence quantum yields and are well-studied classical chromophores. Recently, Fabbrizzi and coworkers[14] have used urea/thiourea-phthalimide derivatives as chemosensors, where binding tendencies of the sensor towards anions were investigated by UV-Vis and ^{1}H-NMR titration. More recently, Samanta and coworkers[15] have studied the behavior of an amido-phthalimide derivative in the absence/presence of halide ions, suggesting F$^-$-induced deprotonation of the amido moiety of the sensor system as a signaling mechanism. However, one could also expect that a urea as an anion receptor may establish a H-bond interaction and form a stable complex instead of deprotonation (due to weak acidity of its N–H protons).[16]

With this premise, we were particularly interested in developing a new receptor–fluorophore system based on urea-phthalimide conjugates in order to observe the sensing of halide ions and to verify the occurrence of the formation of stable species in the ground state. Therefore, we report here on detection of a [**1**–F]$^-$ complex by fluorescence studies and confirmation of the H-bonding interaction between **1** and fluoride ions by ^{1}H-NMR titration experiments as well as computational calculations based on DFT methods at the B3lYP/6–31G* level of theory. Furthermore, we want to establish the use of a chiral urea-phthalimide combination as a potential detector for chiral PET-quenchers by diastereoselective interactions.

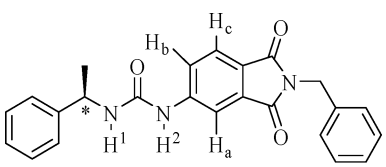

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Chart 1

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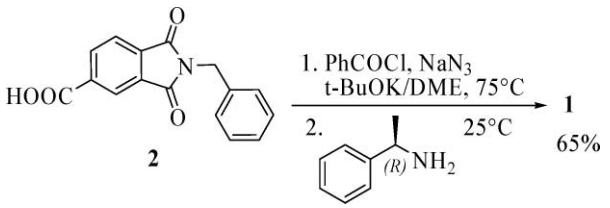
† Electronic supplementary information (ESI) available: Additional experimental details; ^{1}H, ^{13}C and ^{1}H-^{1}H correlation spectra of compound **1** in acetonitrile and DMSO. Color changes observed in the emission on addition of F$^-$ in the absence/presence of methanol (10%) to an acetonitrile solution of **1** Normalized emission and excitation spectra of **1** in the presence of F$^-$. Emission spectra of **1** in the presence of the corresponding amines as well as alcohols. Normalized fluorescence decays traces of **1** in different solvents and in the presence of F$^-$. Optimized geometry coordinates of model systems. See DOI: 10.1039/b908433a

Results and discussion

The synthesis of the urea-phthalimide sensor **1** was achieved following a recently reported procedure.[17] *N*-Benzyl-1,3-dioxoisoindoline-5-carboxylic acid **2** (1 eq.) was reacted with phenylchloroformate (1.5 eq.) and sodium azide (1.7 eq.) to give the corresponding acyl azide that undergoes a Curtius rearrangement to the isocyanate derivative. After reaction with (*R*)-methylbenzylamine (1.5 eq.) compound **1** was obtained in analytically pure form as a colourless solid (Scheme 1).



Scheme 1 Synthesis of sensor **1** from precursor **2**.

Sensor **1** is soluble in polar solvents such as DMSO, MeOH and MeCN. In the ^{1}H-NMR significant differences appeared for the signals corresponding to the urea protons. In DMSO-d_6 these resonances were observed at 6.97 ppm (H^1) and 9.21 ppm (H^2). In CD_3CN they were strongly shifted to 5.89 ppm (H^1) and 7.81 ppm (H^2). (see ESI†). In both cases, these signals appeared as a doublet (due to the coupling with the proton in the stereogenic centre) and a singlet, respectively. The photophysical properties of sensor **1** were determined in different solvents and are summarized in Table 1.

No significant changes were observed with increasing solvent polarity, however, the substantial red-shift in emission in the protic solvent methanol and the strongly increased Stokes shift account for the formation of an internal charge transfer state after excitation to the first excited singlet state. Singlet state deactivation by non-radiative pathways is also increased in the protic solvent methanol; in comparison with acetonitrile, the fluorescence quantum yield drops to one-third and the fluorescence lifetime increases to 17 ns.

The capability of **1** to sense anions such as halides was tested in acetonitrile solution using the anions of the corresponding tetrabutylammonium salts (TBA^+). The absorption spectrum of **1** in the absence of anions showed bands centred at 241, 253 and 340 (log ε = 2.95) nm. Upon titration of F^-, the ground state was affected and the absorption was weakly shifted to the red because of recognition of the anion and three distinctive isosbestic points were observed at 258, 317 and 342 nm, respectively (Fig. 1).

Table 1 Photophysical data of sensor **1**

	λ_{exc} [a]	λ_{em} [a]	Stokes[b]	E_S [c]	τ_F [d]	Φ_F [e]	k_F x10^7 [f]
DMSO	353	443	5755	72	11.8	0.31	2.6
MeCN	339	430	6242	75	13.0	0.37	2.8
MeOH	337	465	8168	72	16.9	0.11	0.6
DCM	337	428	6309	75	14.8	0.22	1.4

[a] In nm [b] In cm^{-1} [c] Singlet energy in kcal/mol [d] In ns [e] From comparison with quinine sulfate reference (see Experimental) [f] Fluorescence rate constant ($k_F = (\Phi_F/\tau_F)$) in s^{-1}.

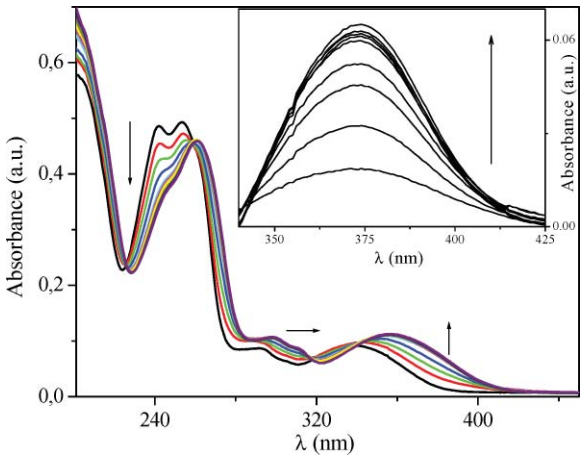


Fig. 1 Absorption spectra of **1** (10^{-4} M) in the presence of increasing amounts of F^- (0, 0.033 → 0.3 mM) in acetonitrile. Inset: Difference UV-spectra of [**1** + F^-]–**1** in the long wavelength region.

To examine the formation of a charge transfer (CT) complex, difference spectra ([**1** + F^-]–**1**) were obtained (Fig. 1, inset). A new band was clearly observed at *ca.* 380 nm which was attributed to the CT complex absorption maximum. The formation constant of a CT complex (K_{CT}) was estimated spectro-photometrically by the Benesi–Hildebrand procedure (eqn 1).[18] A concentration plot is shown in Fig. 2.

$$[\mathbf{1}]/\mathrm{Abs}_{CT} = [1/(K_{CT}\,\varepsilon_{CT}[F^-])] + (1/\varepsilon_{CT}) \quad (1)$$

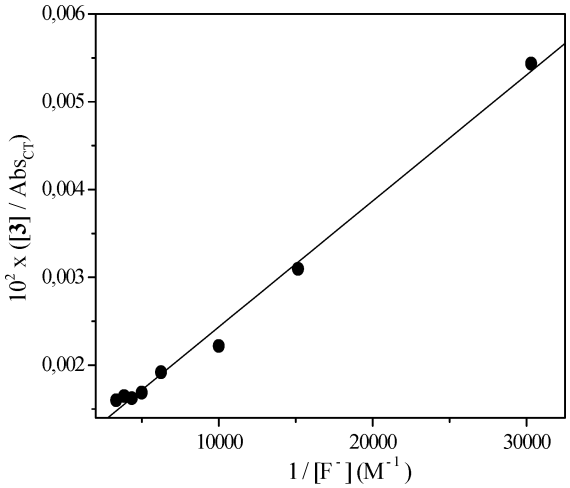


Fig. 2 Benesi–Hildebrand plot to obtain the formation constant from the absorbance of the CT complex (λ_{max} = 380 nm) at different concentrations of F^-.

Abs_{CT} describes the absorbance due to the CT band at 380 nm at different concentrations of F^-, and ε_{CT} represents the molar absorption coefficient. The ε_{CT} value in acetonitrile was calculated from the intercept and found to be 1000 $M^{-1}cm^{-1}$ (log ε_{CT} = 3). The corresponding K_{CT} value, as determined from the slope, was 6966 M^{-1}. The high value of K_{CT} indicates a strong intermolecular interaction between **1** and F^- in the ground state. This behavior was not observed in the presence of Cl^-, Br^- and I^-.

In order to detect changes in the excited state, the fluorescence of **1** was studied in the presence of increasing amounts of anions.

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In contrast to the small variations observed in the ground state, the emission of **1** was dramatically affected in the presence of F^- (Fig. 3) where it was fully quenched. A weak band at *ca.* 520–550 nm was detected with the formation of an isoemissive point at 515 nm. Concerning to Cl^-, Br^- and I^- no changes in the maximum fluorescence intensity of **1** were observed (Fig. 3; inset) clearly supporting that sensor **1** was suitable for F^- recognition in the family of halides. Besides, color changes in the emission of **1** upon addition of F^- were perceptible to the naked eye whereas no variation in the fluorescence was observed in the rest of halides.

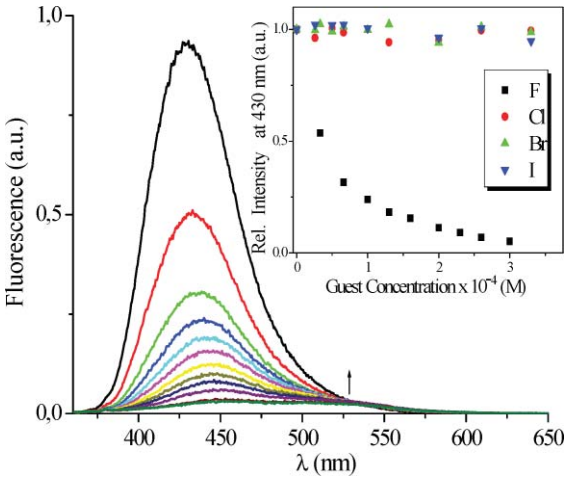

Fig. 3 Emission spectra of **1** ($\lambda_{exc} = 340$ nm) in the presence of increasing amounts of F^- (0, 0.033 → 0.3 mM) in acetonitrile. Inset: Changes in the emission at 430 nm upon titration with F^-, Cl^-, Br^- and I^- with **1**.

To detect a possible fluorescence dynamic quenching, the singlet lifetime, τ_F of **1** (3.3×10^{-6} M) was determined in the absence and in the presence of F^- (3×10^{-3} M) under the same conditions. The τ_F values were found to be 13 ns and 12.5 ns, respectively (Fig. S1, ESI†). The Stern–Volmer plot showed a non-linear behavior at high amounts of F^- enhancing the idea that a static quenching of the fluorescence was occurring (Fig. 4). For comparison, the emission of **1** was recorded in the presence of increasing amounts of a strong non-nucleophilic base such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) which is also depicted in Fig. 4. In this case, fluorescence quenching followed a clearly fitted-linearity in contrast than that found for F^-. In addition, new fluorescence bands at longer wavelengths were not observed (see Fig. S2, ESI†). Therefore, the different effects obtained for the emission of **1** in the presence of DBU and fluoride, appeared to support CT complex formation between sensor **1** and F^-.

Taking into account the formation of a [**1**–F]$^-$ complex, a steady-state fluorescence measurement was carried out with a solution of **1** (10^{-4} M) and F^- (3.4×10^{-3} M) in acetonitrile. Upon selective CT complex excitation (380 nm) its emission was actually observed with a maximum at 520 nm (Fig. 5). The corresponding excitation spectrum is also shown in Fig. 5. The excitation maximum appears at 380 nm, in good agreement with the UV-absorption measurement.

To further confirm the formation of a [**1**–F]$^-$ complex through a H-bonding interaction between F^- and the urea moiety, we also performed ^{1}H-NMR titration experiments in CD_3CN. As stated above, the urea protons appeared at 5.89 ppm (H^1) and

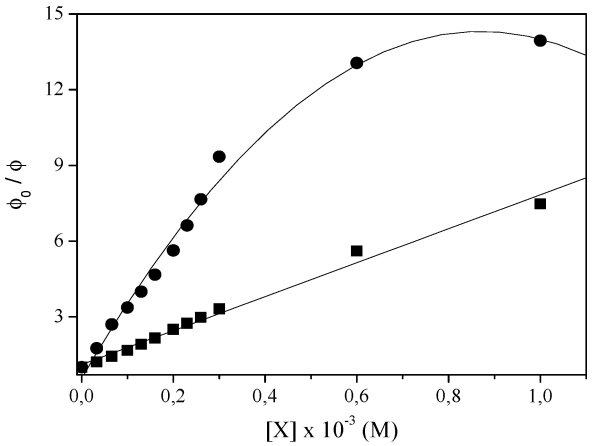

Fig. 4 Stern–Volmer plots for the fluorescence quenching of **1** upon F^- (●) and DBU (■) titration (0, 0.033 → 0.3 mM).

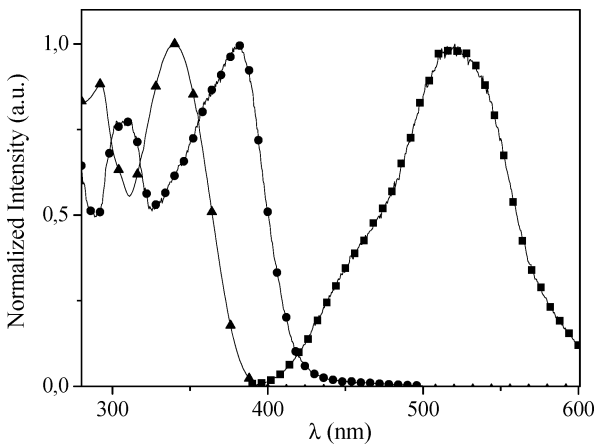

Fig. 5 Normalized absorption band of **1** (▲), excitation (●, $\lambda_{em} = 520$ nm) and emission (■, $\lambda_{exc} = 380$ nm) spectra of **1** (10^{-4} M) and F^- (3.4×10^{-3} M) in acetonitrile. All measurements were made under aerated conditions.

7.81 ppm (H^2) (Fig. 6, top spectrum). In the presence of increasing equivalents of F^-, the urea resonances were gradually shifted to downfield by 2 ppm and 4.5–5 ppm, respectively, reflecting a H-bond between the receptor and anion (Fig. 6).

More information about the nature of the [**1**–F]$^-$ complex could be drawn from aryl-protons H_a and H_b. It is worth considering that H-bonding interaction between urea subunit and anion could induce some effects on aromatic substituents, *i.e.* polarization-induced shift of the C-H bonds *via* a *through-space* effect, producing downfield shifts due to deshielding effect by a partial positive charge formed on the proton.[14] In fact, this electrostatic effect was observed in aromatic protons H_a and H_b as indicated by the weak downfield shift upon addition of F^- equivalents (Fig. 6), being in agreement with previous studies.[14] Besides, proton H_c was too far away from the N–H protons to undergo any electrostatic effect. On the other hand, the H^1 proton did not vanish even at a high concentration of anion concluding that although deprotonation was not taking place, the bond-length of N–H amide may increase sufficiently.

The nature of the H-bonding interaction was supported by the effect of protic solvents on the emission of the [**1**–F]$^-$ complex. Addition of methanol to a mixture of **1** and F^- led to recovery of

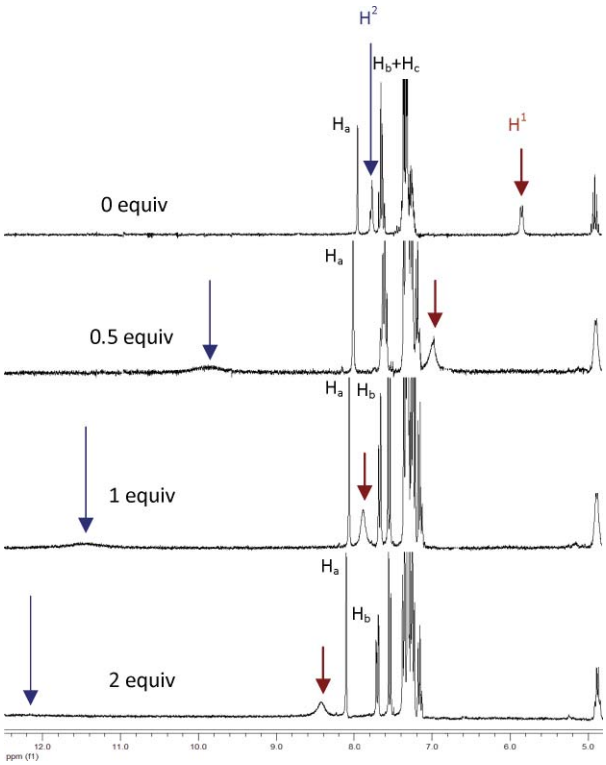

Fig. 6 Changes in the ^{1}H NMR (300 MHz) spectra of **1** in CD_3CN upon addition of F^-.

the blue emission, *i.e.* the [**1**–F]$^-$ interaction was presented (Fig. S3, ESI†). The fluorescence spectrum of **1** in methanol became red-shifted in comparison with acetonitrile as the solvent (see Table 1). Subsequently, addition of F^- to a **1** acetonitrile solution containing 10% of methanol led to no change in the emission, thus, clearly supporting the interaction between the urea moiety and the protic solvent.

To ensure whether the recognition process involves a CT complex formation through a H-bonding interaction between **1** and F^-, computational calculations based on B3lYP/6–31G* level of theory using the CPCM method (acetonitrile as solvent) were carried out. Model system geometries were optimized in the absence and presence of the fluoride ion (Fig. 7) and corresponding N–H bond distances were calculated. Hence, N–H^1 and N–H^2 bond lengths in the absence of an anion were found to be 1.022 Å and 1.024 Å, respectively, whereas values of these bond distances after fluoride binding complex optimization were 1.035 Å for the N–H^1 bond and 1.051 Å for the N–H^2 bond. Although bond-elongation was observed in both cases (+0.013 Å for N–H^1 and +0.025 Å for N–H^2), it appeared that it was not sufficient for hydrogen abstraction by F^-, in contrast to previous observations.[15] The H–F distances were also estimated and found to be 1.710 Å (H^1–F) and 1.602 Å (H^2–F) which were close to that experimentally found in the literature for complexation of isophthalimide-like compounds with fluoride ions.[19]

Moreover, both N–H^1 and N–H^2 GIAO-NMR shifts (δ) were also theoretically calculated in the absence/presence of a fluoride ion. These data were in line with that obtained experimentally where δ_{N-H} values for H^1 and H^2 in the absence of F^- were 4.0 ppm and 5.7 ppm, respectively whereas they shifted to downfield to

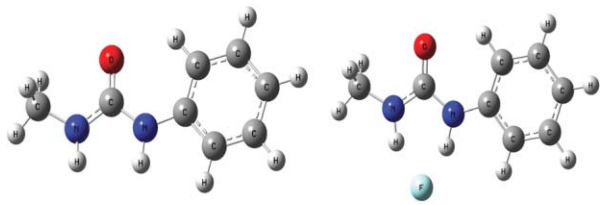

Fig. 7 Geometries of the free (left) and fluoride bonded (right) model system.

7.7 ppm ($\Delta\delta_{N-H}$ = 3.7 ppm) and 10.7 ppm ($\Delta\delta_{N-H}$ = 5 ppm), respectively, after complexation with F^-. Overall, these computational results are in agreement with experimental observations where formation of a complex between sensor **1** and F^- in the ground state prevails over a possible deprotonation of the urea moiety.

Finally, taking into account the stereogenic centre of sensor **1**, we were interested in studying enantiodifferentiation of the fluorescence quenching in the presence of enantiomerically pure amines (*R*- and *S*-methylbenzylamine) as well as alcohols (*R*- and *S*-1-phenylethanol). Fluorescence investigations showed that amines efficiently quenched the emission of **1** whereas no changes were detected in the presence of the alcohols (Fig. S5 and S6, ESI†). No enantiodifferentiation was however observed in the quenching process with chiral amines as quenchers and the chiral model sensor **1** (Fig. 8). Synthesis and investigation of more complex chiral sensors with additional binding sites are in progress.

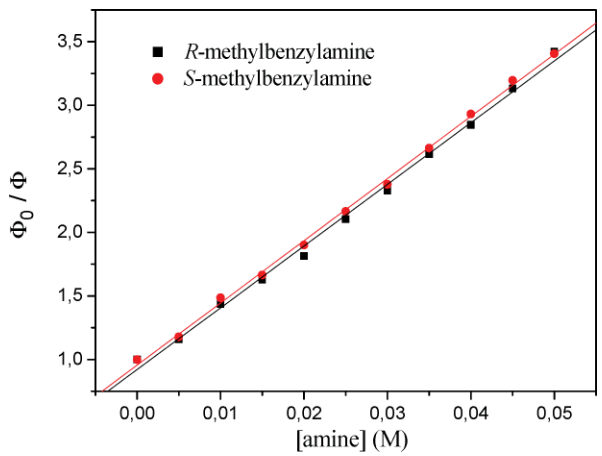

Fig. 8 Stern–Volmer plot for the fluorescence quenching of **1** upon amine titration.

Conclusions

In summary, we have synthesized chemosensor **1** based on a chiral urea receptor linked to a phthalimide chromophore using a recent procedure involving a Curtius rearrangement. Sensor **1** was found to selectively detect F^- since absorption as well as fluorescence changes were only observed for this halide anion.[20] In this context, a fluorescence static quenching was proposed for the signaling mechanism: the overall picture is depicted in Scheme 2.

Upon recognition of the anion, absorption studies revealed a typical band of a CT complex at longer wavelengths with a large formation constant. Moreover, not only were there no changes

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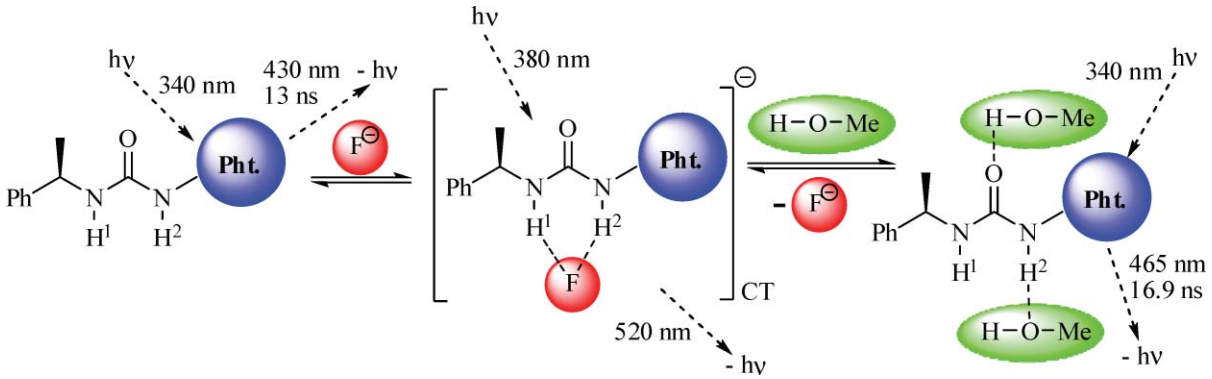

Scheme 2

in the singlet lifetime of **1** found in the presence of F^- but also a non-linear dependence on the Stern–Volmer plot was observed, ruling out the possibility of a dynamic fluorescence quenching. The formation of the [**1**–F]$^-$ complex through H-bonding interactions was proven by ^{1}H-NMR studies and theoretical calculations.

Experimental

Materials

The starting materials phenylchloroformate, sodium azide and potassium *tert*-butoxide as well as (*R*)-phenylethanamine were commercially available. Compound **2** was synthesized following a literature procedure.[21] Spectroscopic grade acetonitrile (MeCN), dimethylsulfoxide (DMSO), methanol (MeOH) and dichloromethane (DCM) were used as solvents.

^{1}H-NMR

The ^{1}H-NMR spectra were recorded on a Bruker AC 300 spectrometer operating at 300 MHz or on a Bruker AV 600 spectrometer instrument operating at 600 MHz. Chemical shifts are reported as δ in ppm and the coupling constant, *J*, in Hz. In all spectra solvent peaks were used as the internal standard. Solvents used were DMSO-d_6 (δ = 2.49 ppm) and CD_3CN (δ = 1.94 ppm). Splitting patterns are designated as follows: s, singlet; d, doublet; dd, double doublet; p, quintet; m, multiplet.

^{13}C-NMR

The ^{13}C-NMR spectra were recorded either on a Bruker AC 300 spectrometer instrument operating at 75 MHz or on a Bruker AV 600 spectrometer instrument operating at 126 MHz.

Absorption spectroscopy

Absorption spectra were recorded using a Beckman Coulter UV-DU800 spectrometer. The samples were placed into quartz cells of 1 cm path length. Compound concentrations were fixed as indicated.

Steady-state fluorescence spectroscopy

Fluorescence and excitation spectra were carried out using a Perkin-Elmer LS-50B luminescence spectrometer. The samples were placed into quartz cells of 1 cm path length. Compound concentrations were fixed as indicated. The excitation and emission slit widths were 2.5 nm. The fluorescence quantum yields in different solvents were measured with reference to quinine sulfate ($\Phi_F = 0.546$ in 0.5 M H_2SO_4) by comparing the area of fluorescence and absorbance at the excitation wavelength of 340 nm, using the formula[22]

$$\Phi_{sample} = (a_{sample}/a_{std})\,(A_{std}/A_{sample})\,(n_{sample}/n_{std})\,\Phi_{std}$$

where Φ_{sample} and Φ_{std}, a_{sample} and a_{std}, n_{sample} and n_{std} and A_{sample} and A_{std} are the quantum yield, area under emission spectra, refractive index and the absorbance of the sample under study (sensor **1**) and the standard (quinine sulfate), respectively.

Time-resolved fluorescence spectroscopy

Fluorescence lifetimes were measured using a gated intensified CCD equipped monochromator. The spectral resolution has been set to 2 nm. The samples were excited with the third harmonic (355 nm) of a Nd–YAG laser. The overall instrument response function is 1.5 ns. The samples were placed into quartz cells of 1 cm path length. Compound concentrations were fixed as indicated.

Computational Calculations

The structures were optimized with GAUSSIAN03,[23] using B3LYP/6–31*[24] and the CPCM-SCRF method, solvent = acetonitrile.[25] NMR shifts were computed of the optimized structures using the GIAO method.[26]

General procedure for the synthesis of chemosensor 1

To a solution of sodium azide (110 mg, 1.70 mmol), potassium *tert*-butoxide (17 mg, 0.150 mmol), and **2** (281 mg, 1.00 mmol) in DME (10.0 mL) at 25 °C, was added the phenylchloroformate (235 μL, 1.5 mmol). The resulting mixture was stirred at 75 °C overnight. Then, the mixture was slowly cooled down to room temperature and *R*-methylbenzylamine (200 μL, 1.50 mmol) was added and the reaction mixture was stirred for 16 h. Afterwards, it was diluted with hexane (40 mL) and the resulting solution was poured into ice-cold water with continuous stirring, 10 mL water was added and the stirring was maintained during 20 min. The white solid was filtered and washed several times with cold chloroform. The urea-activated phthalimide **1** (253 mg, 63% yield) was obtained as a white solid after filtration. R*f* 0.3 (cyclohexane/ethyl acetate 60/40 v/v). ^{1}H-NMR (600 MHz, DMSO-d_6): 1.42 (d, *J* = 7.0 Hz,

3H, CH_3), 4.72 (s, 2H, CH_2), 4.85 (p, J = 7.0 Hz, 1H, CH), 6.98 (d, J = 7.7, 1H, NH^1), 7.25–7.36 (m, 10H, $CH_{aromatic}$), 7.58 (dd, J_1 = 1.7 Hz and J_2 = 8.2 Hz, 1H, $CH_{aromatic}$), 7.73 (d, J = 8.2 Hz, 1H, $CH_{aromatic}$), 8.06 (s, 1H, $CH_{aromatic}$), 9.21 (s, 1H, NH^2); ^{13}C NMR (126 MHz, DMSO-d_6): 22.7 (CH_3), 40.6 (CH_2), 48.7 (CH), 111.14 ($CH_{aromatic}$), 121.48($CH_{aromatic}$), 122.8 ($C_{aromatic}$), 124.37 ($CH_{aromatic}$), 125.82 (2-$CH_{aromatic}$), 126.74 ($CH_{aromatic}$), 127.27 (2-$CH_{aromatic}$), 127.31 ($CH_{aromatic}$), 128.32 (2-$CH_{aromatic}$), 128.53 (2-$CH_{aromatic}$), 133.22 ($C_{aromatic}$), 136.81 ($C_{aromatic}$), 144.65 ($C_{aromatic}$), 146.34 ($C_{aromatic}$), 153.77 ($(NH)_2C$=O), 167.41 (C=O), 167.62 (C=O). MS (m/z (%)): 399 (12), 278 (25), 260 (11), 252 (100), 234 (19), 120 (23), 105 (79), 91 (32), 77 (39). Exact mass (EI): required for $C_{24}H_{21}N_3O_3$: 399.1583 (M^+): found 399.159 Melting point: 212–213°.

Acknowledgements

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Notes and references

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