Available online at www.sciencedirect.com
SCIENCE DIRECT
Tetrahedron
Tetrahedron 60 (2004) 11109–11115

Ratiometric dual fluorescent receptors for anions under intramolecular charge transfer mechanism

Zhen-Chang Wen and Yun-Bao Jiang*

Department of Chemistry and the MOE Key Laboratory of Analytical Sciences, Xiamen University, Xiamen 361005, China

Received 29 January 2004; revised 5 July 2004; accepted 19 August 2004

Available online 15 September 2004

Abstract—A series of the intramolecular charge transfer (ICT) dual fluorescent receptors with anion binding site in the electron acceptor were designed and synthesized. These receptors exhibited dual fluorescence in acetonitrile and the charge transfer (CT) emission energy was found to correlate linearly with the Hammett constant of the substituent existing in the electron acceptor, which is the basis for anion sensing. Dual fluorescence of these receptors was found to be sensitive to the presence of anions such as fluoride and acetate and the receptors can be employed as ratiometric fluorescent sensors for anions.

1. Introduction

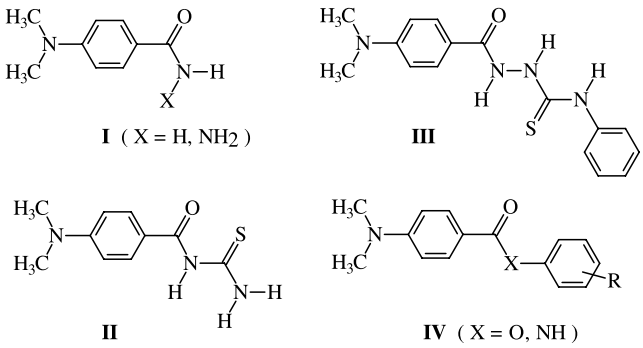
Anion recognition and sensing have received increasing recent attention in supramolacular, organic and inorganic chemistry.[1] Because of the high sensitivity of fluorescence detection, many fluorescent receptors for anions have been developed. Similar to a cation fluorescent receptor,[2] an anion receptor includes two important moieties, i.e. a recognition binding site and a signal reporter that are either integrated directly or connected by a flexible spacer. A major fluorescent signaling mechanism hitherto employed is photo-induced electron transfer,[3] while other mechanisms such as competitive binding,[4] metal-to-ligand charge transfer,[5] excimer or exciplex formation,[6] excited-state proton transfer (ESPT)[7] and proton coupled electron transfer (PCET)[8] have also been reported.

It is known that the ICT photophysics and emission are highly dependent of the electron donor/acceptor strength and in many cases dual fluorescence can been observed with the ICT fluorophores.[9] This suggests that a sensitive ratiometric dual fluorescent anion receptor could be constructed if the dual fluorescent ICT fluorophore is appropriately linked to an anion-binding site. This is significant for a fluorescent sensor since normal fluorescent sensing based on intensity change suffers from the excitation source fluctuation as the emission intensity is proportional to the excitation intensity. It should be pointed out that receptors operating under the ICT signaling mechanism for cation sensing, either single[2,10] or dual fluorescent,[11] have been exploited, whereas received much less attention in anion sensing.[8]

We understand that a ratiometric ICT dual fluorescent anion receptor replies heavily on the choice of a spacer that links the ICT fluorophore and the anion binding site to allow for a highly efficient communication of the anion binding messages to the fluorophore. As with the ICT fluorophore the photophysics and emission of the CT state are subject to the electron donor/acceptor strength, the anion binding site is assumed to be better incorporated in either electron donor or acceptor moiety. We have been investigating to employ the ICT photophysics of *p*-dimethylaminobenzonitrile (DMABN) and its family molecules in constructing anion receptors. We showed that, with *p*-dimethylaminobenzamide (**I**, Scheme 1),[8a] *N*-(*p*-dimethylaminobenzoyl) thiourea (**II**, Scheme 1),[8b] and *N*-(*p*-dimethylaminobenzamido)thiourea (**III**, Scheme 1)[8c] in which the anion binding sites incorporated in the electron acceptors are amide and thiourea, respectively, their ICT dual fluorescence was sensitive to the presence of anions such as AcO^-, F^-, and $H_2PO_4^-$ etc. In those cases, however, the CT emission band position showed essentially no shift upon anion binding. This might suggest that the sensing is not due to the variation in the electron accepting strength of the acceptor. We therefore continue to search for ICT dual fluorescent receptors that respond to anions due to variations of the electron donor/acceptor strength as would be indicated by shifted CT emission upon anion binding. Previously we

Keywords: Receptor; Anion sensing; Thiourea; Intramolecular charge transfer; Dual fluorescence; Ratiometric.
* Corresponding author. Tel./fax: +86-592-2185662;
e-mail: ybjiang@xmu.edu.cn

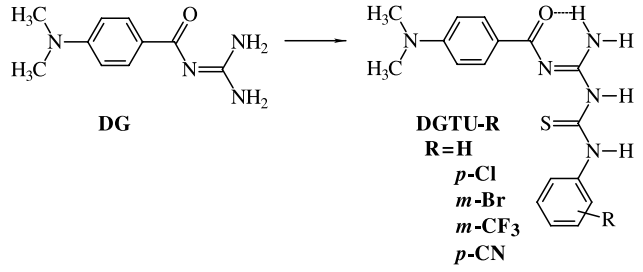
0040–4020/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2004.08.045



Scheme 1. Molecular structures of *p*-dimethylaminobenzamide and *p*-dimethylaminobenzoate derivatives.

showed that, with substituted phenyl *p*-dimethylaminobenzoates (**IV**, X=O, Scheme 1)[12a] and *p*-dimethylaminobenzalinides (**IV**, X=NH, Scheme 1),[12c] the CT fluorescence depends on the substituent at the ester and amido phenyl moieties, respectively. In the former case a linear correlation was found between the CT emission energy and the Hammett constant of the substituent but the dependence was weak in particular in highly polar solvent, whereas in the latter case an additional benzanilide-like CT channel complicated the charge transfer photophysics. These results, however, suggested that new ICT dual fluorescent receptors for anions could be constructed within this framework.

We therefore, came to **DGTU-R**s (Scheme 2) in which the *p*-dimethylaminobenzamide moiety is the ICT fluorophore with dual fluorescence emission while the thiourea moiety is a well-known anion binding site. These two parts are conjugated by an iminoyl group, hopefully to enhance the substituent (R) effect than in their ester counterparts (**IV**, X=O, Scheme 1). Substituent was introduced in the phenylthiourea moiety of **DGTU-R** for the purposes of understanding the sensing mechanism and modulating the acidity of the thioureido –NH protons[3c,d] important for anion binding.



Scheme 2. Synthesis of **DGTU-R**s. Reagents and conditions: substituted isothiocyanate, CH_2Cl_2, room temperature.

2. Results and discussion

DGTU-Rs were easily prepared from the reactions of **DG** with isothiocyanates at room temperature (Scheme 2), while **DG** was obtained according the reported method.[13] It was expected that in **DGTU-R**s with an iminoyl linker the thiourea anion-binding site was electronically conjugated to the ICT fluorophore, *p*-dimethylaminobenzamide. Substituent effect on the NMR signals of the four –NH protons in **DGTU-R**s was examined and linear correlations were found with varied slopes, Figure 1. It was found that with three of the –NH protons the NMR signals were correlated with Hammett substituent constant[14] with positive slopes of 0.311, 0.401, and 0.538, respectively. The NMR signal of the fourth –NH proton, however, appeared at far downfield and showed a negative linear dependence of the Hammett substituent constant by a slope of −0.388. These observations suggested a completely different electronic environment of this –NH proton that it is involved in an intramolecular six-membered ring hydrogen bond[15] (Scheme 2). This was also supported by the AM1 calculations. This negative yet sensitive dependence of the chemical shift indicated that the substituent effect could indeed be communicated into the carbonyl oxygen atom, meaning that the thiourea moiety is conjugated with the ICT fluorophore, the dual fluorescence signal reporter in the anion receptors.

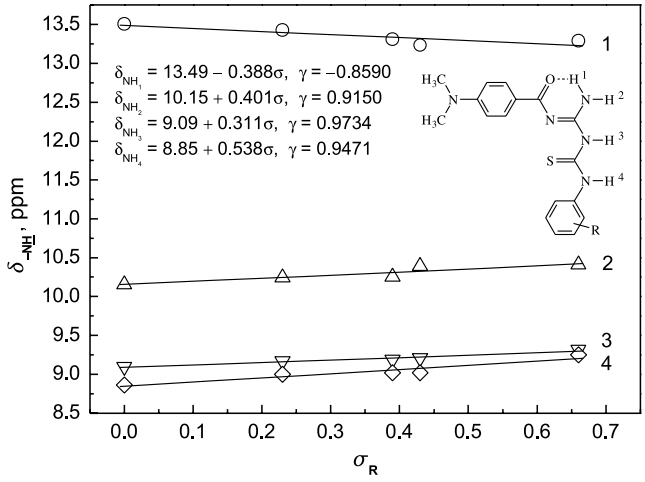


Figure 1. Plots of –NH proton chemical shifts against Hammett constants of the substituent, σ_R.[14]

The absorption and fluorescence spectra of **DGTU-R**s were recorded. It was found that the absorption spectra were independent of the substituent within the series with maximum wavelength of 344 nm and molar absorption coefficients of $10^4\ M^{-1}\ cm^{-1}$ order of magnitude (Table 1). The transitions responsible for the absorption could then be assigned as of the (π,π^*) character. Dual fluorescence typical of the occurrence of the ICT with electron donor/acceptor *para*-substituted benzenes, such as *p*-dimethylaminobenzonitrile[9] and *p*-dimethylamino-benzamide,[8a] was observed with all of the **DGTU-R**s in highly polar solvents such as acetonitrile. As an example, fluorescence spectra of **DGTU**–*m*-$\mathbf{CF_3}$ in ethyl acetate–acetonitrile binary solvents are shown in Figure 2. It was noted that, while the short-wavelength LE (locally excited state) emission showed very weak dependence on the solvent composition, a continuous red-shift occurred in the long-wavelength emission with increasing solvent polarity, which is in line of the CT nature of its emissive state. Similar observations were made with other **DGTU-R**s and detailed spectral parameters are summarized in Table 1.

Different from the absorption spectra of the **DGTU-R**

Table 1. Absorption and fluorescence spectral parameters of **DGTU-Rs** in acetonitrile in the absence and presence of anions

R	λ_{abs}^{max} (nm)	ε (10^4 M^{-1} cm^{-1})	λ_{LE} (nm)	λ_{CT} (nm)	I_{CT}/I_{LE}	Φ
H	344/326[a]/336[b]	3.47/4.28[a]/3.40[b]	385/385[a]/385[b]	507/501[a]/501[b]	0.43/0.04[a]/0.34[b]	0.0051
p-Cl	344/329/339	4.18/5.00/4.23	388/388/388	516/510/514	1.03/0.05/0.69	0.0045
m-Br	344/327/336	3.39/4.44/3.45	388/388/388	526/516/522	2.62/0.08/1.26	0.0031
m-CF_3	344//327/329	3.47/4.54/4.12	388/388/388	530/520/524	1.31/0.04/0.29	0.0026
p-CN	344/330/332	3.74/4.39/4.12	385/385/385	550/524/535	0.85/0.07/0.20	0.0021

[a] In the presence of fluoride anion.
[b] In the presence of acetate anion.

series, the fluorescence emission in particular the long-wavelength CT emission showed a sensitive dependence on the substituent at thiourea moiety. As can be seen in Figure 3a, the CT emission of **DGTU-R** in acetonitrile shifted to the red when the substituent (R) became increasingly electron-withdrawning from H to *p*-CN, which is in the same trend as that observed with substituted-phenyl *p*-dimethylamisnobezoates.[12a] This observation also confirms that the substituent is located in the electron acceptor moiety.

We previously established[12] that, in case of a series of CT fluorophores of similar structure and practically the same absorption spectra, the CT emission energy correlated linearly with the Hammett constant of the substituent existing in the electron donor/acceptor. Obviously these criteria were fulfilled with the **DGTU-R** series. As seen in Figure 3b, a linear correlation indeed existed between the CT emission energies of **DGTU-Rs** and the Hammett substituent constants. This indicated that the electron acceptor strength was monotonically enhanced with increasing electron-withdrawing ability of the substituent in the phenylthiourea moiety. The slope in acetonitrile of −0.273 eV was much higher in its absolute value than those observed with substituted-phenyl *p*-dimethylaminobenzoates in solvents of much lower polarity, for example, −0.180, −0.169, and −0.138 eV in DEE, THF, and ethyl acetate, respectively.[12a] This means that a higher substituent effect on the CT emission occurs with **DGTU-Rs** than that in their ester counterparts. This can be readily ascribed to the higher conjugating efficiency of the iminoyl linker in comparison with the oxygen bridge (–O–) present in the ester molecules.[12a] Also noted in Table 1 and Figure 3a was that the CT to LE intensity ratio (I_{CT}/I_{LE}) became lower in case of lower electron acceptor strength. It was therefore expected that sensitive receptors for anions could be achieved based on the dual fluorescent **DGTU-Rs**, since it has been shown that anion binding to the thiourea moiety increases its electron donating ability[3c,d] which will consequently decrease the strength of electron acceptors in these dual fluorescent receptors.

The ICT dual fluorescence of all **DGTU-Rs** was found to be sensitive to the presence of anions such as F^- and AcO^-, to extents depending on the substituent R. Figure 4a shows the fluorescence spectra of **DGTU–*m*-CF_3** in ACN in the presence of F^-. It was found that addition of F^- resulted in a substantial quenching of the long-wavelength CT emission and an obvious blue shift in its band position, for instance, from 530 to 520 nm in the presence of 3 equiv of F^-. Meanwhile, only small changes were observed in the LE emission in both its position and intensity. An isoemissive point at 425 nm was noted, which means that

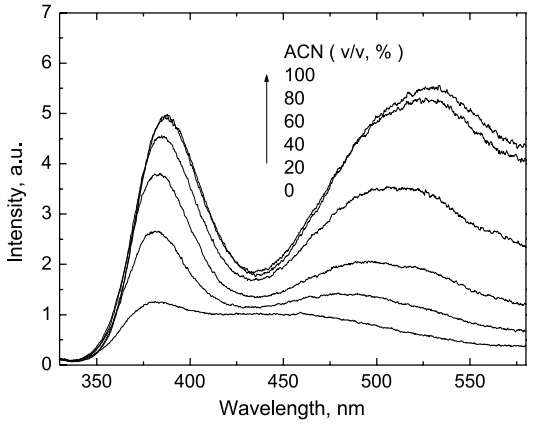


Figure 2. Fluorescence spectra of **DGTU–*m*-CF_3** in ethyl acetate–acetonitrile binary solvents. Excitation wavelength was 298 nm. [**DGTU–*m*-CF_3**] = 2.0×10^{-5} M.

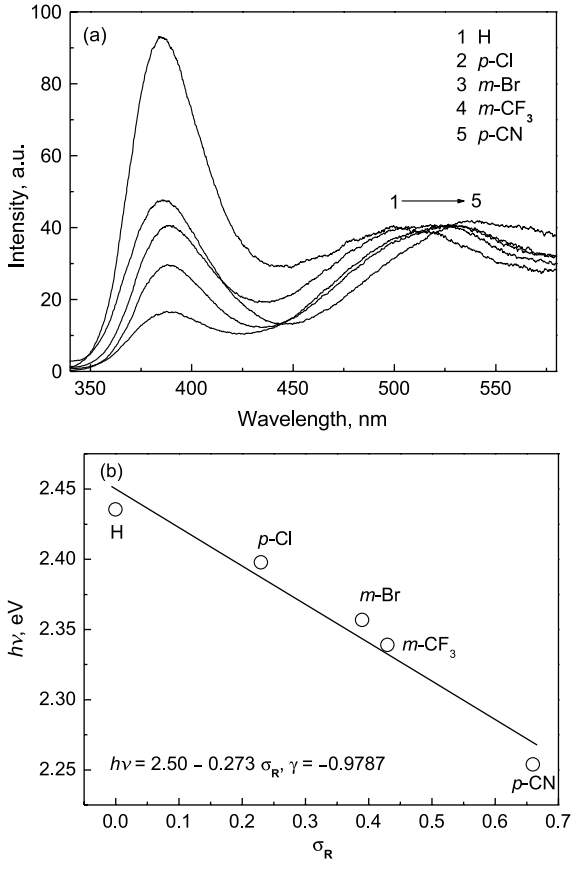


Figure 3. (a) The CT-emission normalized fluorescence spectra of **DGTU-Rs** in acetonitrile with excitation wavelength of 298 nm and (b) plot of the CT emission energy against Hammett substituent constant.

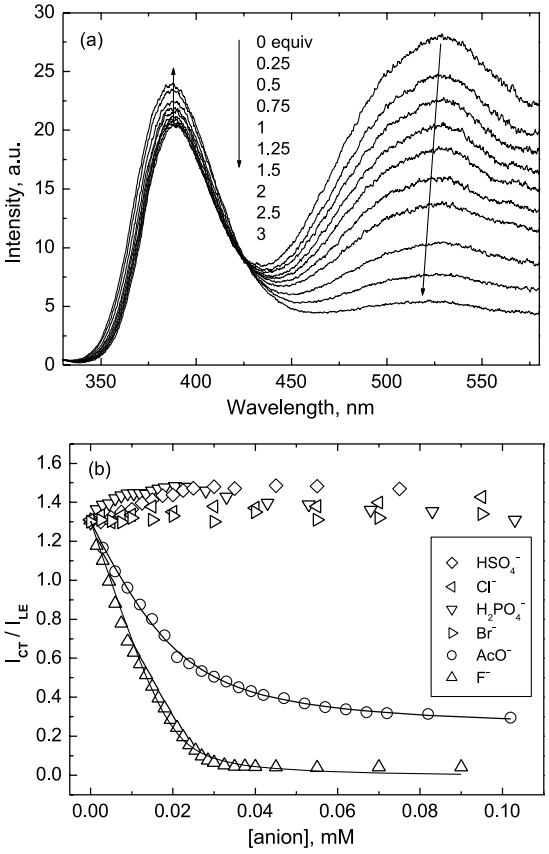
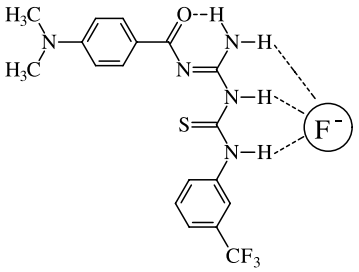


Figure 4. (a) Fluorescence spectra of **DGTU**–*m*-**CF**$_3$ in ACN (2.0×10^{-5} M) in the presence of F^- with excitation wavelength of 298 nm, an isosbestic wavelength, and (b) plot of the I_{CT}/I_{LE} ratio versus anion concentration. Data points in (b) are experimental results and the lines through them are nonlinearly fitted curves.



Scheme 3. Schematic diagram for the binding of **DGTU**–*m*-**CF**$_3$ with F^-.

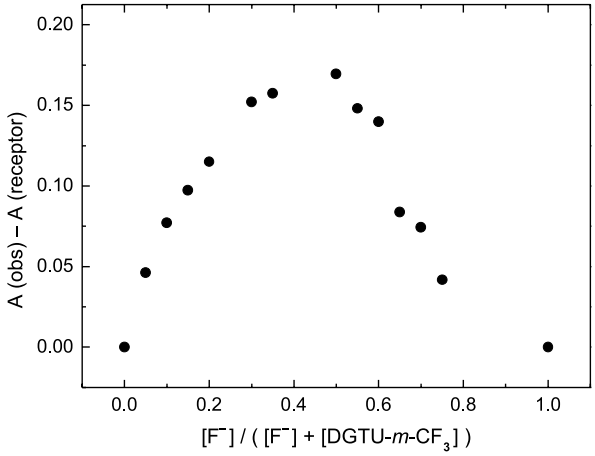


Figure 5. Job plot for binding of F^- to **DGTU**–*m*-**CF**$_3$ in acetonitrile. A(obs) and A(receptor) are absorbances at 327 nm of the anion/receptor mixture and receptor, respectively. The total concentration of F^- and **DGTU**–*m*-**CF**$_3$ is 4.0×10^{-5} M.

the excited-state LE to CT reaction equilibrium was shifted upon anion binding. Similar variation but to a less extent was observed when AcO^- was introduced, whereas other anions such as $H_2PO_4^-$, HSO_4^-, Cl^- and Br^- led to much less change or no change in the fluorescence spectrum of **DGTU**–*m*-**CF**$_3$. Within **DGTU**-**R** series there are four –NH proton donors, of which the one with its NMR signal appears at far downfield of around 13.2 ppm is involved in an intramolecular hydrogen bond with the carbonyl oxygen[15] (Fig. 1 and Scheme 2). There are hence three –NH protons in **DGTU**-**R**s available for hydrogen bonding with anions. Inspection of the structure of the receptors it can be supposed that **DGTU**-**R**s may bind anions via two thioureido –NH protons and/or two guanidino –NH protons.[3c,d,8,13,16] Control molecule **DG** (Scheme 2) that has only guanidino –NH protons, however, showed not any response to anion in both its absorption and fluorescence spectra. It was therefore assumed that **DGTU**-**R**s bind anions such as F^- via two thioureido –NH protons with additional contribution from the other free guanidino –NH proton (Scheme 3). Job plot (Fig. 5) supported this by confirming a 1:1 stoichiometry between **DGTU**–*m*-**CF**$_3$ and F^-. Further evidence for this binding was obtained from ^{1}H NMR data. In DMSO-d_6, the NMR signals of thioureido –NH protons in **DGTU**–*m*-**CF**$_3$, originally appeared at 9.020 and 9.209 ppm, were shifted and broadened in the presence of 0.25 equiv of AcO^- to appear as a broad band peaked at 9.201 ppm, whereas those of the guanidino –NH protons experienced much less changes. Variation in the absorption spectra confirmed the formation of well-defined binding complexes between receptors and anions. Figure 6a shows the absorption spectra of **DGTU**–*m*-**CF**$_3$ in acetonitrile in the presence of F^-. The absorption spectrum of **DGTU**–*m*-**CF**$_3$, originally peaked at 344 nm, was blue shifted to 327 nm with increasing F^- concentration, which was accompanied by the appearance of three distinct isosbestic points at 336, 298, and 277 nm, respectively.

The fluorescence response observed here can be accounted for under the ICT mechanism that the CT photophysics and emission are highly subject to the electron donor/acceptor strength.[9,11,12] In Figure 3 it is shown that with **DGTU**-**R**s a decrease in the electron acceptor strength results in a blue shift in the CT emission and a lowered CT to LE intensity ratio. Indeed, anion binding to the thiourea moiety in the electron acceptor of **DGTU**-**R**s led to a blue shift in the CT emission and a decrease in the CT to LE intensity ratio (Table 1 and Fig. 4). Accordingly, the CT to LE intensity ratio of the **DGTU**-**R**–F^- complex was found lower than that of the **DGTU**-**R**–AcO^- complex (Table 1), which is obviously due to the higher charge density of F^- because of its smaller size.

Sensing of anions such as AcO^-, F^-, $H_2PO_4^-$, HSO_4^-, Br^-, and Cl^- using **DGTU**-**R** receptors was then examined via both the ICT dual fluorescence intensity ratio and absorption titrations. Figures 4b and 6b show the titration curves of the spectral parameters of **DGTU**–*m*-**CF**$_3$ against anion

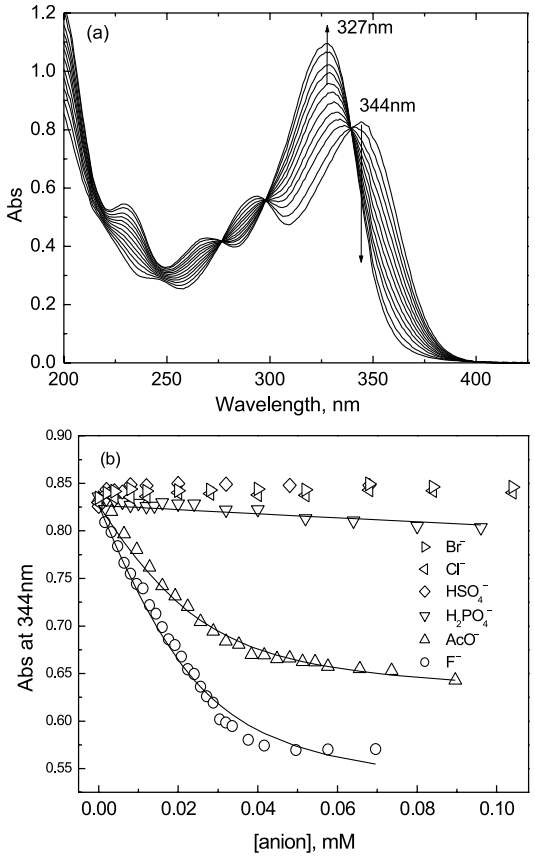


Figure 6. (a) Trace of absorption spectra of **DGTU**–*m*-$\mathbf{CF_3}$ in ACN (2.4×10^{-5} M) upon addition of increasing concentration of F^- and (b) plot of the absorbance at 344 nm versus anion concentration. Data points in (b) are experimental results and the lines though them are nonlinearly fitted curves.

concentrations in acetonitrile. Sensitive and selective sensing of anions can be achieved with this receptor. With other receptors anion sensing was also possible. The anion binding constants of **DGTU-R**s were evaluated by nonlinear fitting of the plots of the CT to LE intensity ratio and the absorbance at 344 nm of the receptor against anion concentration,[7c,8c,17] assuming a 1:1 stoichiometry. The latter was confirmed by the nice fitting shown in Figures 4b and 6b as examples. The obtained binding constants are listed in Table 2. The binding constants ranging from 10^4 to 10^6 M^{-1} varied in general in the order of $F^- > AcO^- > H_2PO_4^- \gg HSO_4^-, Br^-$, Cl^-, in agreement with that observed with other neutral thiourea-based receptors.[3c,d,8b–d] With the same anion, the binding constants varied in the order of **DGTU** < **DGTU**–*p*-**Cl** < **DGTU**–*m*-**Br** < **DGTU**–*p*-$\mathbf{CF_3}$ < **DGTU**–*p*-**CN**, as expected from the increasing acidity of the thioureido –NH protons.

3. Conclusion

In summary, we developed a series of the ICT dual fluorescent anion receptors in which the phenylthiourea anion-binding site was electronically conjugated via an iminoyl linker to the electron acceptor moiety of the CT fluorophore *p*-dimethylaminobenzamide. With the aid of substitution at the phenylthiourea moiety it was established that the substituent electronic effect could be efficiently transmitted to the CT fluorophore and hence influenced its CT dual fluorescence. This formed the basis of anion sensing by these receptors. The anion sensing was signaled by a blue shift in the CT emission and by a decrease in the CT to LE intensity ratio. The CT dual fluorescent receptors (**I–III**, Scheme 1) previously reported from this group responded anions with decreases in the CT to LE intensity ratio, but no shift in both the CT and LE band positions.[8] The present receptors therefore represent, to the best of our knowledge, the first set of ratiometric CT dual fluorescent anion receptors with emissive CT state that sense anions due to variations in the electron acceptor strength. The ICT signaling mechanism outlined here could be applicable for extended investigations of optimal combinations of the CT fluorophore, anion-binding site, and conjugating linker between them.

4. Experimental

4.1. Materials

Solvents employed in organic syntheses were market available AR reagents. Solvents used for spectral study were of spectroscopic grade and were further purified before use so that no fluorescent impurity was detected at the employed excitation wavelength of 298 nm. Tetra(*n*-butyl) ammonium salts of anions were prepared by neutralizing the corresponding acids by tetra(*n*-butyl)ammonium hydroxide. DG was synthesized according to a reported method[13] and it further reacted with substituted phenylisothiocyanate in CH_2Cl_2 at room temperature afforded individual receptor, **DGTU-R** (Scheme 1). The crude products were purified on silica-gel column chromatography using petroleum ether (m.p.60–90 °C) and ethyl acetate mixture (2:1, v/v) as eluent and the purified products were fully characterized. ^1H

Table 2. Binding constants (K_b) of anions with **DGTU-R**s in acetonitrile from absorption (344 nm) and fluorescence (I_{CT}/I_{LE}) titrations[a]

R	K_b (abs), 10^5 M^{-1}[b]		K_b (flu), 10^5 M^{-1}[c]	
	F^-	AcO^-	F^-	AcO^-
H	0.12±0.02	nd[d]	0.22±0.03	nd[d]
p-Cl	0.18±0.03	nd[d]	0.40±0.04	nd[d]
m-Br	0.24±0.03	nd[d]	4.73±0.55	1.33±0.11
m-CF_3	1.47±0.32	1.58±0.14	9.74±1.57	1.95±0.36
p-CN	25.8±7.1	3.60±0.80	16.8±5.2	8.41±1.55

[a] Anions exist in their tetrabutylammonium salts.
[b] Binding constant obtained from absorption titration.
[c] Binding constant obtained from fluorescence titration.
[d] Not determined because of minor spectral change that did not allow for an accurate evaluation of the binding constant. This was also the case with other anions examined such as $H_2PO_4^-$, HSO_4^-, Br^-, and Cl^-.

(500 MHz) and ^{13}C (125 MHz) NMR data were acquired in DMSO-d_6 on a Varian Unity$^+$ 500 MHz NMR spectrometer using TMS as the internal reference. ESI-MS data were obtained on a Bruker ESQUIRE-3000plus LC-MS/MS spectrometer and HRMS data obtained on a Micromass LCT time-of-flight mass spectrometer configured with a standard *Z*-spray electrospray interface.

4.1.1. DGTU. ^1H NMR, δ (ppm): 3.036 (6H, s), 6.818 (2H, d, $J=9$ Hz), 7.045 (1H, s), 7.272 (2H, s), 7.679 (2H, s), 7.925 (2H, d, $J=9$ Hz), 8.863 (1H, s, NH), 9.099 (1H, s, NH), 10.156 (1H, s, NH), 13.507 (1H, s, NH). ^{13}C NMR, δ (ppm): 39.985, 111.087, 117.557, 121.903, 123.295, 123.935, 128.209, 129.893, 139.751, 153.545, 157.029, 167.085. ESI-MS: *m/z* 342.0 ($M+H^+$, MeOH). HRMS found: *m/z* 342.1387; calcd for [$C_{17}H_{20}N_5OS^+$]: 342.1389.

4.1.2. DGTU–*p*-Cl. ^1H NMR, δ (ppm): 3.038 (6H, s), 6.820 (2H, d, $J=8.5$ Hz), 7.295 (2H, d, $J=6.5$ Hz), 7.748 (2H, d, $J=9$ Hz), 7.929 (2H, d, $J=8$ Hz), 8.997 (1H, s, NH), 9.169 (1H, s, NH), 10.245 (1H, s, NH), 13.426 (1H, s, NH). ^{13}C NMR, δ (ppm): 40.009, 111.081, 117.492, 123.366, 125.749, 126.815, 128.019, 129.919, 138.678, 153.564, 157.264, 167.108. ESI-MS: *m/z* 375.9 ($M+H^+$, MeOH). HRMS found: *m/z* 376.0999; calcd for [$C_{17}H_{19}ClN_5OS^+$]: 376.0999.

4.1.3. DGTU–*m*-Br. ^1H NMR, δ (ppm): 3.041 (6H, s), 6.844 (2H, d, $J=9$ Hz), 7.221 (2H, s), 7.828 (2H, s), 7.928 (2H, d, $J=8$ Hz), 9.020 (1H, s, NH), 9.188 (1H, s, NH), 10.254 (1H, s, NH), 13.311 (1H, s, NH). ^{13}C NMR, δ (ppm): 39.997, 111.090, 117.475, 121.012, 123.873, 125.886, 129.949, 130.214, 141.277, 153.572, 157.337, 167.125. ESI-MS: *m/z* 421.8 ($M+H^+$, MeOH). HRMS found: *m/z* 420.0490; calcd for [$C_{17}H_{19}BrN_5OS^+$]: 420.0494.

4.1.4. DGTU–*m*-CF_3. ^1H NMR, δ (ppm): 3.040 (6H, s), 6.820 (2H, d, $J=8.5$ Hz), 7.369 (1H, s), 7.495 (H, d, $J=7.5$ Hz), 7.918 (1H, s), 7.934 (2H, d, $J=9$ Hz), 8.164 (1H, s), 9.020 (1H, s, NH), 9.209 (1H, s, NH), 10.392 (1H, s, NH), 13.233 (1H, s, NH). ^{13}C NMR, δ (ppm): 40.002, 111.053, 111.095, 117.445, 123.042, 125.205, 128.837, 129.433, 129.918, 140.322, 153.568, 157.364, 167.109. ESI-MS: *m/z* 409.9 ($M+H^+$, MeOH). HRMS found: *m/z* 410.1265; calcd for [$C_{18}H_{19}F_3N_5OS^+$]: 410.1262.

4.1.5. DGTU–*p*-CN. ^1H NMR, δ (ppm): 3.043 (6H, s), 6.826 (2H, d, $J=9.5$ Hz), 7.684 (2H, d, $J=8.5$ Hz), 7.926 (2H, d, $J=9$ Hz), 8.005 (2H, d, $J=8.5$ Hz), 9.250 (1H, s, NH), 9.315 (1H, s, NH), 10.441 (1H, s, NH), 13.290 (1H, s, NH). ^{13}C NMR, δ (ppm): 40.002, 111.058, 117.352, 118.788, 119.236, 121.420, 123.788, 129.949, 132.587, 143.655, 153.591, 157.932, 167.156. ESI-MS: *m/z* 366.9 ($M+H^+$, MeOH). HRMS found: *m/z* 367.1338; calcd for [$C_{18}H_{19}N_6OS^+$]: 367.1341.

4.2. Absorption and fluorescence spectral studies

The absorption and fluorescence spectra were recorded on Varian Cary 300 absorption spectrophotometer and Hitachi F-4500 fluorescence spectrophotometer, respectively. Solutions were measured in 1-cm quartz cell. The solvent employed for spectral titrations was acetonitrile (ACN). Fluorescence quantum yields were measured using quinine sulfate as a standard (0.546 in 0.5 M H_2SO_4).[18]

Spectral titrations were carried out by introducing aliquot of anion solution into the receptor solution of fixed concentration.

4.3. Determination of anion-receptor binding constants

The binding constants of anions with receptors were evaluated by nonlinearly fitting both the variations of the absorbance at 344 nm and the CT to LE fluorescence intensity ratio of the receptors against anion concentration, assuming a 1:1 binding stoichiometry.

Acknowledgements

This work was supported by the Natural Science Foundation of China (20175020), the Ministry of Education (MOE) of China, the Natural Science Foundation of Fujian Province (D0220001), and VolkswagenStiftung (I/77 072). We thank Professor E. V. Anslyn for his kind invitation of this contribution.

References and notes

1. (a) Schmidtchen, F. P.; Berger, M. *Chem. Rev.* **1997**, *97*, 1609–1646. (b) Snowden, T. S.; Anslyn, E. V. *Curr. Opin. Chem. Biol.* **1999**, *3*, 740–746. (c) Gale, P. A. *Coord. Chem. Rev.* **2000**, *199*, 181–233. (d) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486–516. (e) Gale, P. A. *Coord. Chem. Rev.* **2001**, *213*, 79–128. (f) Sessler, J. L.; Davis, J. M. *Acc. Chem. Res.* **2001**, *34*, 989–997. (g) Martínez-Máñez, R.; Sancenón, F. *Chem. Rev.* **2003**, *103*, 4419–4476.
2. (a) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515–1566. (b) de Silva, A. P.; Fox, D. B.; Huxley, A. J. M.; Moody, T. S. *Coord. Chem. Rev.* **2000**, *205*, 41–57.
3. (a) Vance, D. H.; Czarnik, A. W. *J. Am. Chem. Soc.* **1994**, *116*, 9397–9398. (b) Kubo, Y.; Tsukahara, M.; Ishihara, S.; Tokita, S. *Chem. Commun.* **2000**, 653–654. (c) Gunnlaugsson, T.; Davis, A. P.; Glynn, M. *Chem. Commun.* **2001**, 2556–2557. (d) Gunnlaugsson, T.; Davis, A. P.; O'Brien, J. E.; Glynn, M. *Org. Lett.* **2002**, *4*, 2449–2452.
4. (a) Niikura, K.; Metzger, A.; Anslyn, E. V. *J. Am. Chem. Soc.* **1998**, *120*, 8533–8534. (b) Metzger, A.; Anslyn, E. V. *Angew. Chem., Int. Ed.* **1998**, *37*, 649–652. (c) Wiskur, S. L.; Ait-Haddou, H.; Anslyn, E. V.; Lavigne, J. J. *Acc. Chem. Res.* **2001**, *34*, 963–972.
5. Beer, P. D. *Acc. Chem. Res.* **1998**, *31*, 71–80.
6. (a) Nishizawa, S.; Kaneda, H.; Uchida, T.; Teramae, N. *J. Chem. Soc., Perkin Trans. 2* **1998**, 2325–2327. (b) Nishizawa, S.; Kato, Y.; Teramae, N. *J. Am. Chem. Soc.* **1999**, *121*, 9463–9464. (c) Liao, J. H.; Chen, C. T.; Fang, J. M. *Org. Lett.* **2002**, *4*, 561–564.
7. (a) Yoshida, H.; Saigo, K.; Hiratani, K. *Chem. Lett.* **2000**, 116–117. (b) Choi, K.; Hamilton, A. D. *Angew. Chem., Int. Ed.* **2001**, *40*, 3912–3915. (c) Zhang, X.; Guo, L.; Wu, F. Y.; Jiang,

Y. B. *Org. Lett.* **2003**, *5*, 2667–2670. (d) Tong, H.; Zhou, G.; Wang, L.; Jing, X.; Wang, F.; Zhang, J. *Tetrahedron Lett.* **2003**, *44*, 131–134.

8. (a) Wu, F. Y.; Jiang, Y. B. *Chem. Phys. Lett.* **2002**, *355*, 438–444. (b) Wu, F. Y.; Ma, L. H.; Jiang, Y. B. *Anal. Sci.* **2001**, *17*(Suppl.), i801–i803. (c) Wu, F. Y.; Li, Z.; Wen, Z. C.; Zhou, N.; Zhao, Y. F.; Jiang, Y. B. *Org. Lett.* **2002**, *4*, 3203–3205. (d) Wu, F. Y.; Zhang, X.; Jiang, Y. B. *Chem. J. Chinese Univ.* **2003**, *24*, 1990–1992.
9. (a) Rettig, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 971–988. (b) Rotkiewicz, K.; Grabowski, Z. R.; Rettig, W. *Chem. Rev.* **2003**, *103*, 3899–4031.
10. (a) Rurack, K.; Rettig, W.; Resch-Genger, U. *Chem. Commun.* **2000**, 407–408. (b) Crochet, P.; Malval, J. P.; Lapouyade, R. *Chem. Commun.* **2000**, 289–290.
11. (a) Létard, J. F.; Delmond, S.; Lapouyade, R.; Braun, D.; Rettig, W.; Kreissler, M. *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 517–527. (b) Collins, G. E.; Choi, L. S.; Callahan, J. H. *J. Am. Chem. Soc.* **1998**, *120*, 1474–1478. (c) Malval, J. P.; Lapouyade, R. *Helv. Chim. Acta* **2001**, *84*, 2439–2451. (d) Malval, J. P.; Lapouyade, R.; Létard, J. F.; Jarry, C. *Photochem. Photobiol. Sci.* **2003**, *2*, 259–266. (e) Wen, Z.-C.; Jiang, Y.-B. *Chin. Chem. Lett.* **2004**, *15*, 551–554.
12. (a) Huang, W.; Zhang, X.; Ma, L. H.; Wang, C. J.; Jiang, Y. B. *Chem. Phys. Lett.* **2002**, *352*, 401–407. (b) Zhang, X.; Sun, X. Y.; Wang, C. J.; Jiang, Y. B. *J. Phys. Chem. A* **2002**, *106*, 5577–5581. (c) Zhang, X.; Wang, C. J.; Liu, L. H.; Jiang, Y. B. *J. Phys. Chem. B* **2002**, *106*, 12432–12440.
13. Hennrich, G.; Sonnenschein, H.; Resch-Genger, U. *Tetrahedron Lett.* **2001**, *42*, 2805–2808.
14. Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165–195.
15. (a) Jubian, V.; Dixon, R. P.; Hamilton, A. D. *J. Am. Chem. Soc.* **1992**, *114*, 1120. (b) Cunha, S.; Costa, M. B.; Napolitano, H. B.; Lariucci, C.; Vencato, I. *Tetrahedron* **2001**, *57*, 1671–1675.
16. Schmuck, C. *Chem. Eur. J.* **2000**, *6*, 709–718.
17. Valeur, B.; Pouget, J.; Bourson, J.; Kaschke, M.; Ernsting, N. P. *J. Phys. Chem.* **1992**, *96*, 6545–6549.
18. Demas, J. N.; Crobys, G. A. *J. Phys. Chem.* **1971**, *75*, 991–1024.