N-Amidothiourea based PET chemosensors for anions†

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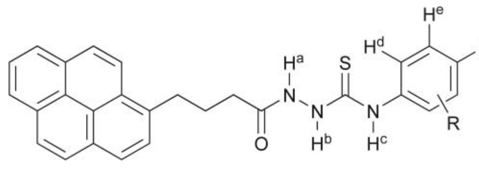
Neutral *N*-amidothiourea based PET anion sensors bearing a pyrene fluorophore, **1–3**, were synthesized and their fluorescent response toward anions was assessed. The anion quenching and binding constants were found to be much higher than those of the corresponding PET sensors bearing a simple thiourea receptor despite a higher oxidation potential of the electron donor and a relatively longer spacer $(CH_2)_3$ between the signal reporter and binding receptor in **1–3**. This was explained in terms of a much more substantial increase in the electron donating ability of amidothiourea upon anion binding.

Introduction

A photo-induced electron transfer (PET) signalling mechanism, developed for reporting the presence of metal cations and protons, was first proposed by Weller[1] and developed further by de Silva[2] and others.[3] The first example of anion sensing under a PET mechanism was described by the Czarnik group who utilized anthrylpolyamines for the detection of phosphate and pyrophosphate in aqueous solutions.[4] Recent PET anion sensors mostly bore charged receptors.[5,6] With neutral PET anion sensors, thiourea is one of the important binding receptors *via* hydrogen bonding.[7] Linking thiourea with pyrene through a CH_2 spacer, Teramae *et al.*[7k] synthesized a neutral PET anion sensor, the fluorescence of which was quenched while a long-wavelength emission developed upon anion binding. This lower energy emission was assigned to exciplex formed from pyrene and an anion–thiourea binding unit. This is the first direct evidence of electron transfer in PET anion sensors. Employing anthracene as a fluorophore and thiourea as the anion binding receptor, Gunnlaugsson *et al.*[7i,e] synthesized a series of PET sensors whose fluorescence was found to be quenched in the presence of anion whereas absorption remained unchanged. This was ascribed to the increased electron-donating ability of the anion–thiourea unit compared to the original thiourea moiety that leads to enhanced PET quenching of fluorescence. In the reported thiourea-based neutral PET sensors, however, the fluorescence quenching constants (K_{sv})[8] were at 10^3 mol^{-1} L orders of magnitude or lower. This could be due to low anion affinity of the sensor and/or less favorable PET thermodynamics (ΔG) in the anion binding complex. We previously reported a new kind of thiourea-based receptor for anions, *N*-benzamidothioureas,[9] that showed a substantially enhanced anion binding affinity despite the lower acidity of the thioureido –NHs. This was attributed to the occurrence of ground-state charge transfer in the anion-*N*-benzamidothiourea binding complexes in which the thiourea moiety is the electron donor. This pointed to a much more substantial increase in the electron-donating ability of amidothiourea upon anion binding compared to that of the traditional thiourea itself. It was therefore envisaged that with *N*-amidothiourea, instead of simply thiourea being introduced into PET anion sensors, K_{sv} would be much higher thus likely allowing a more sensitive anion sensing.

Herein we report the synthesis and evaluation of three neutral PET chemosensors for anions, *N*-(1-pyrenebutanamide)-*N*′-(substituted-phenyl)thioureas (**1–3**, Fig. 1), in which *N*-amidothiourea is the binding receptor that is linked to the pyrene fluorophore *via* a relatively longer $(CH_2)_3$ spacer. Indeed, the K_{sv}'s in acetonitrile (MeCN) were found at 10^5 mol^{-1} L orders of magnitude, 1–2 orders higher than those of the corresponding thiourea-based PET sensors with a shorter CH_2 spacer.



1 R = *p*-CH_3
2 R = H
3 R = *m*-CF_3

Fig. 1 Chemical structure of sensors **1–3**.

Results and discussion

Sensors **1–3** in MeCN show characteristic absorption and fluorescence of pyrene (Fig. 2), with quantum yields (Φ_F)[10] of 0.0532, 0.0537 and 0.0515, respectively. Compared with that of 1-methylpyrene ($\Phi_F = 0.77$ in MeCN)[11] bearing no receptor, it is obvious that PET is active in **1–3** prior to anion binding. With the addition of a series of anions (F^-, AcO^-, $H_2PO_4^-$, HSO_4^-, Cl^-, Br^-, I^-, NO_3^-, ClO_4^-) as their tetrabutylammonium salts, fluorescence of **1–3** in MeCN was quenched whereas the absorption of pyrene, the fluorophore remained unaffected. Fig. 2a and 2b show absorption and fluorescence spectra of **2** in the presence of AcO^-. F^- and $H_2PO_4^-$ produced similar effects. Φ_F's of anion-**2** complexes were 0.0112, 0.0084 and 0.0109, respectively, for AcO^-, F^-, and $H_2PO_4^-$. Obviously PET in **2** becomes more

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† Electronic supplementary information (ESI) available: Job plot of **2** with AcO^-; Stern–Volmer plots for **1–3**–AcO^-(F^-, $H_2PO_4^-$) systems; 2D COSY spectrum of *N*-acetamidothiourea in CD_3CN; ^1H and ^{13}C NMR of **1–3**. See DOI: 10.1039/b703122j

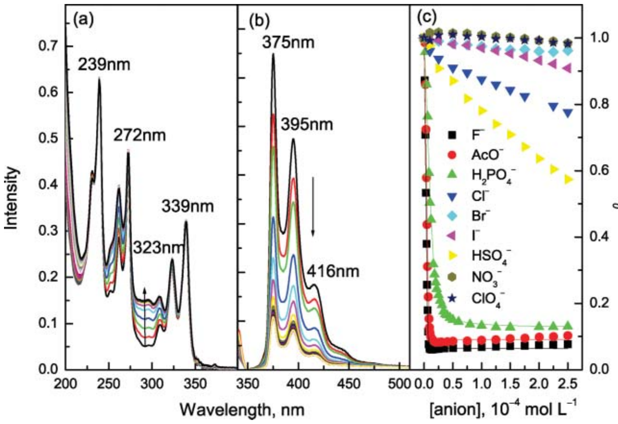

Fig. 2 Absorption (a) and fluorescence (b) spectra of **2** in MeCN in the presence of AcO⁻ and plots of I/I_0 *versus* anion concentration (c). [**2**] = 8.55×10^{-6} mol L^{-1}, [anion] = 0–2.5×10^{-4} mol L^{-1}. Excitation wavelength was 340 nm.

efficient after anion binding. The quenching of other anions is much less. The quantum yields of anion complexes are listed in Table 1. The order of the quenching for **1–3** is F⁻ > AcO⁻ > $H_2PO_4^-$ ≫ HSO_4^- > Cl⁻, Br⁻, I⁻, NO_3^-, ClO_4^-.

The nature of the interactions of **1–3** with anions was investigated by ^{1}H NMR titrations in CD_3CN. As seen in Fig. 3, two of the three –NH resonances of **2** were at 8.60 and 7.87 ppm, respectively. Another one was at *ca.* 8.22 ppm which was wrapped in the pyrene CH resonances (signals of –NH protons were assigned also by referring to the 2D COSY spectrum of *N*-acetamidothiourea, Fig. S1 in the ESI†). The signals of three NH protons were initially broadened in the presence of up to 1.0 equivalent F⁻, after which they were sharpened again. The signals of NH protons moved downfield to 9.89 and 9.44 ppm, respectively. This suggested the hydrogen bonding nature of the interaction between *N*-amidothiourea and F⁻. Meanwhile, the *N′*-phenyl CH^d signal moved downfield because of a deshielding effect, whereas signals of CH^e and CH^f moved upfield, again supporting the hydrogen bonding interaction between **2** and F⁻. ^{1}H NMR titrations by AcO⁻ and $H_2PO_4^-$ showed similar profiles to that of F⁻.

A 1 : 1 stoichiometry of anion binding to **1–3** was made evident from Job plots (Fig. S2†). Anion binding constants of **1–3** in MeCN were evaluated by nonlinearly fitting[12] the fluorescence intensity *versus* anion concentration (Fig. 2c) and are listed in Table 1. They are at 10^5–10^7 mol^{-1} L orders of magnitude. The observations that the binding constant decreases in the order of **1** < **2** < **3** for $H_2PO_4^-$ in MeCN (binding constants for F⁻ and AcO⁻ in MeCN are too high thus with high fitting uncertainty) and for AcO⁻ in water containing MeCN (Table 2), and that the binding constant is higher for F⁻ or AcO⁻ than for $H_2PO_4^-$ (Fig. 2c and Table 1) are in line with the hydrogen bonding nature of **1–3** with these anions.[7,9]

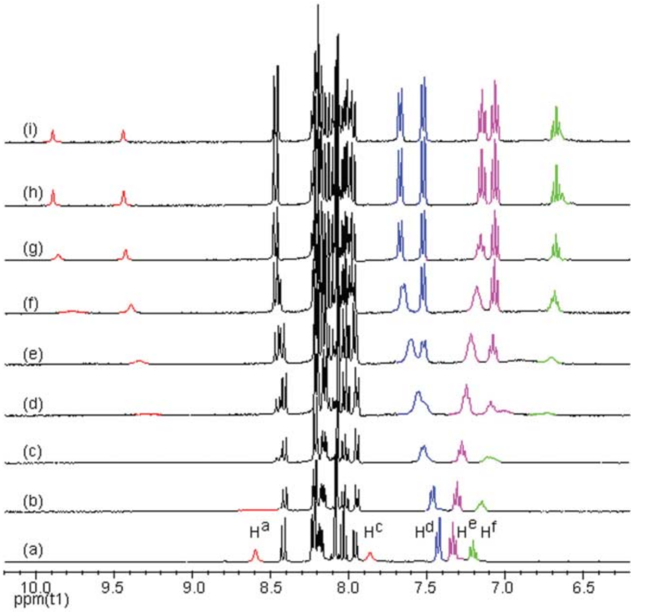

Fig. 3 Trace of NMR titration by F⁻ of **2** in CD_3CN. [**2**] = 6.0×10^{-3} mol L^{-1}. The spectra were recorded after addition of 0 (a), 0.25 (b), 0.50 (c), 0.75 (d), 1.0 (e), 1.5 (f), 2.0 (g), 4.0 (h) and 8.0 (i) equiv. of F⁻, respectively.

The corresponding quenching constants (K_{SV})[8] in MeCN are at 10^5 mol^{-1} L orders of magnitude (Table 1 and Stern–Volmer plots in Fig. S3†). Compared with K_{SV}'s of PET sensors bearing simple thiourea receptors of 10^2–10^3 mol^{-1} L orders of magnitude, the K_{SV}'s of **1–3** with the *N*-amidothiourea receptor are much higher despite a relatively longer $(CH_2)_3$ spacer in **1–3** whereas CH_2 is normally an optimal spacer in classic PET sensors.[2] This is surprising since the oxidation potential of *N*-amidothiourea estimated from CV is higher than that of thiourea (Fig. 4). In terms of PET thermodynamics,[13] the enhanced fluorescence quenching by anions observed with **1–3** means that a much stronger lowering in the oxidation potential of *N*-amidothiourea should occur upon anion binding, so as to promote PET in the binding complexes to a much higher extent than that with the corresponding sensors bearing a simple thiourea receptor. The binding constants of AcO⁻ and F⁻ of **1–3** in MeCN are too high to allow for a credible correlation with the Hammett constant of substituent R, those of $H_2PO_4^-$ in MeCN (Table 1) and of AcO⁻ in water containing MeCN (Table 2) show a stronger substituent dependence than that of the corresponding

Table 1 Fluorescence quantum yield Φ_F, fluorescence quenching constant K_{SV} and anion binding constant K of **1–3** in MeCN

	1			**2**			**3**		
	Φ_F	$K_{SV}/10^5$ mol^{-1} L	$K/10^6$ mol^{-1} L	Φ_F	$K_{SV}/10^5$ mol^{-1} L	$K/10^6$ mol^{-1} L	Φ_F	$K_{SV}/10^5$ mol^{-1} L	$K/10^6$ mol^{-1}
Free	0.0532			0.0537			0.0515		
AcO⁻	0.0099	5.87 ± 0.22	25.9 ± 9.6	0.0112	5.81 ± 0.15	7.89 ± 1.93	0.0036	3.81 ± 0.21	32.9 ± 20.6
F⁻	0.0065	5.05 ± 0.12	27.4 ± 7.9	0.0084	5.80 ± 0.09	14.5 ± 1.80	0.0034	9.28 ± 0.52	58.6 ± 22.3
$H_2PO_4^-$	0.0091	1.41 ± 0.06	0.429 ± 0.026	0.0109	2.60 ± 0.04	1.63 ± 0.22	0.0036	1.74 ± 0.08	8.86 ± 4.23

Table 2 Fluorescence quantum yields, fluorescence quenching constants, and binding constants of **1–3**–AcO$^-$ complexes in H_2O–MeCN binary solvents

	1				**2**				**3**			
%H_2O (v/v)	Φ_F [a]	Φ_F [b]	$K_{SV}/10^4$ mol^{-1} L	$K/10^6$ mol^{-1} L	Φ_F [a]	Φ_F [b]	$K_{SV}/10^4$ mol^{-1} L	$K/10^6$ mol^{-1} L	Φ_F [a]	Φ_F [b]	$K_{SV}/10^4$ mol^{-1} L	$K/10^6$ mol^{-1} L
1%	0.0548	0.0249	12.0 ± 0.8	1.05 ± 0.28	0.0532	0.0195	19.2 ± 1.0	1.47 ± 0.22	0.0564	0.0052	23.5 ± 5.6	6.69 ± 1.09
3%	0.0572	0.0472	3.29 ± 0.56	0.27 ± 0.079	0.0578	0.0433	1.61 ± 0.46	0.28 ± 0.113	0.0554	0.0161	15.8 ± 0.5	0.81 ± 0.13
5%	0.0608	0.0563	0.07 ± 0.02	0.01 ± 0.004	0.0594	0.0538	0.54 ± 0.19	0.08 ± 0.02	0.0564	0.0310	3.34 ± 0.13	0.16 ± 0.026
8%	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]	0.0610	0.0512	1.11 ± 0.12	0.066 ± 0.011

[a] Quantum yields of **1–3** in water–MeCN binary solvents. [b] Quantum yields of AcO$^-$–sensor complex in H_2O–MeCN binary solvents. [c] Spectral change was too minor to allow for an accurate evaluation.

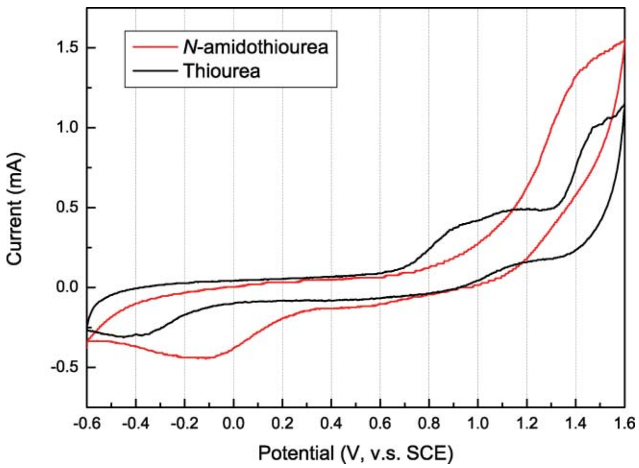

Fig. 4 Cyclic voltammograms of receptors *vs.* SCE in MeCN containing 0.1 mol L^{-1} (n-C_4H_9)$_4$$NClO_4$. The working electrode was a glassy carbon electrode. The scan rate was 50 mV s^{-1}.

N-(substitued-phenyl)thioureas.[9a] This actually points to a binding signal amplification in *N*-amidothiourea receptors in their binding to anions.

Anion sensing by neutral sensors following hydrogen bonding interactions has, in most cases, been carried out in aprotic organic solvents such as MeCN, $CHCl_3$ and DMSO.[14] In protic solvents, multiple hydrogen bonding would be needed to guarantee a noticeable binding.[15] Neutral sensors **1–3**, however, are able to sense anions in up to 8% H_2O–MeCN binary solvent with a binding constant as high as 10^5 mol^{-1} L orders of magnitude. Detailed K, K_{SV} and Φ_F values of **1–3** with AcO$^-$ in H_2O–MeCN binary solvents are listed in Table 2. With these promising results in hand, we are currently modifying the structure of the sensor molecule in order to enhance its performance in protic and highly competitive solvents such as water.

Conclusions

In summary, we have designed neutral PET anion sensors **1–3** employing *N*-amidothiourea as the receptor that is linked to a pyrene fluorophore by a relatively longer $(CH_2)_3$ spacer. They have a higher E_{ox} than those of the corresponding sensors bearing a simple thiourea receptor, yet show much higher anion quenching constants at 10^5 mol^{-1} L orders of magnitude in MeCN and therefore much higher sensitivity. This suggests a greater drop in the oxidation potential of the electron donors in **1–3** upon anion binding. The present results thus demonstrate that *N*-amidothiourea as an electron donor is much better than thiourea itself in constructing electron transfer type anion sensors and it shows signal amplification in anion binding. Because of the extremely high binding constants in pure MeCN, simple neutral sensor **3** is already able to show a sensitive response toward AcO$^-$ in MeCN containing up to 8% by volume of water.

Experimental

General procedures and materials

UV–Vis spectra were recorded on a Varian Cary-300 spectrophotometer using a 1 cm quartz cell. ^{1}H NMR (400 MHz) and ^{13}C

NMR (100 MHz) spectra in DMSO-d_6 or CD_3CN were obtained on a Bruker AV400 NMR spectrometer using TMS as an internal standard. The HRMS were recorded with Micromass-LCT high resolution mass spectrometer by injection of a methanol solution of the sample. Cyclic voltammograms were obtained on a LabNet VA2000 electrochemical analyzer. Absorption spectral titrations for anion binding were carried out by adding an aliquot of anion solution into bulk sensor solution at a given concentration.

Solvents used for sensor syntheses were commercially available at AR grade. Solvents for spectral titrations were purified by re-distillation until no fluorescent impurity could be detected. Tetrabutylammonium salts of the anions were prepared by neutralization of the corresponding acids with tetrabutylammonium hydroxide.

Syntheses of 1–3

An equal equivalent of $SOCl_2$ was added dropwise to a solution of 1-pyrenebutyric acid in methanol in an ice bath which was kept for 0.5 h. The mixture was refluxed for 8 h before the solvent was removed. After pH adjustment by saturated $NaHCO_3$ solution, methyl 1-pyrenebutyrate was obtained as a white solid. An excess amount of hydrazine monohydrate (80%) was added to the ethanol solution of methyl 1-pyrenebutyrate which was stirred at 80 °C for 8 h. After removing the solvent, the residue was washed with iced ethanol and dried in vacuum to produce 1-pyrenebutyrohydrazide, which, after stirring in ethanol with substituted phenyl isothiocyanate for 3 h at room temperature, afforded products when the solvent was removed. Recrystallization from ethanol yielded white crystals.

***N*-(1-Pyrenebutanamido)-*N*′-(*p*-tolyl)thiourea (1).** ^{1}H NMR (400 MHz, DMSO-d_6) (ppm): 9.88 (s, 1H), 9.50 (s, 2H), 8.43 (d, $J = 9.2$ Hz, 1H), 8.29–8.21 (m, 4H), 8.16–8.11 (m, 2H), 8.06 (t, $J = 7.6$ Hz, 1H), 7.98 (d, $J = 8.0$ Hz, 1H), 7.28 (d, $J = 6.4$ Hz, 2H), 7.12 (d, $J = 8.4$ Hz, 2H), 3.39 (t, $J = 7.6$ Hz, 2H), 2.36 (t, $J = 7.2$ Hz, 2H), 2.27 (s, 3H), 2.08 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) (ppm): 181.3, 172.0, 136.6, 136.4, 134.2, 130.8, 130.4, 129.3, 128.5, 128.2, 127.4, 127.4, 127.2, 126.4, 126.0, 124.9, 124.7, 124.2, 124.1, 123.5, 33.1, 32.2, 26.9, 20.5. HRMS exact mass calcd for $[C_{28}H_{25}N_3OS + H]^+$ 452.1797, found 452.1805.

***N*-(1-Pyrenebutanamido)-*N*′-phenylthiourea (2).** ^{1}H NMR (400 MHz, DMSO-d_6) (ppm): 9.89 (s, 1H), 9.56 (s, 2H), 8.43 (d, $J = 9.2$ Hz, 1H), 8.29–8.22 (m, 4H), 8.16–8.11 (m, 2H), 8.06 (t, $J = 7.6$ Hz, 1H), 7.98 (d, $J = 8.0$ Hz, 1H), 7.42 (s, 2H), 7.32 (t, $J = 8.0$ Hz, 2H), 7.15 (t, $J = 7.2$ Hz, 1H), 3.39 (t, $J = 8.0$ Hz, 2H), 2.36 (t, $J = 7.2$ Hz, 2H), 2.06 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) (ppm): 181.0, 172.1, 139.2, 136.5, 130.9, 130.4, 129.3, 128.2, 128.1, 127.5, 127.4, 127.2, 126.5, 126.1, 124.9, 124.8, 124.2, 124.1, 123.6, 33.1, 32.2, 26.9. HRMS exact mass calcd for $[C_{27}H_{23}N_3OS + H]^+$ 438.1640, found 438.1642; for $[C_{27}H_{23}N_3OS + Na]^+$ 460.1460, found 460.1457.

***N*-(1-Pyrenebutanamido)-*N*′-(*m*-trifluoromethylphenyl)thiourea (3).** ^{1}H NMR (400 MHz, DMSO-d_6) (ppm): 9.94 (s, 1H), 9.81 (s, 2H), 8.43 (d, $J = 9.2$ Hz, 1H), 8.29–8.21 (m, 4H), 8.17–8.12 (m, 2H), 8.06 (t, $J = 7.6$ Hz, 1H), 7.98 (d, $J = 7.6$ Hz, 1H), 7.81 (d, $J = 7.6$ Hz, 2H), 7.56 (t, $J = 8.0$ Hz, 1H), 7.49 (d, $J = 8.0$ Hz, 1H), 3.39 (t, $J = 7.8$ Hz, 2H), 2.37 (t, $J = 7.2$ Hz, 2H), 2.08 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) (ppm): 180.0, 171.2, 139.0, 135.4, 129.9, 129.4, 128.3, 128.1, 127.2, 126.5, 126.4, 126.2, 125.5, 125.1, 124.4, 123.9, 123.8, 123.2, 123.2, 122.5, 121.7, 120.8, 120.2, 61.8, 32.0, 31.2, 25.9. HRMS exact mass calcd for $[C_{28}H_{22}F_3N_3OS + H]^+$ 506.1514, found 506.1516.

Acknowledgements

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