

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 (CH₂)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 Weller¹ and developed further by de Silva² 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 CH₂ 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.*^{7ie} 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 10³ 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 (CH₂)₃ spacer. Indeed, the K_{sv} 's in acetonitrile (MeCN) were found at 10⁵ mol⁻¹ L orders of magnitude, 1–2 orders higher than those of the corresponding thiourea-based PET sensors with a shorter CH₂ spacer.

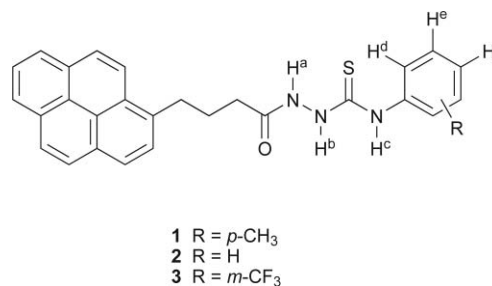


Fig. 1 Chemical structure of sensors **1–3**.

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⁻, H₂PO₄⁻, HSO₄⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, ClO₄⁻) 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 H₂PO₄⁻ produced similar effects. Φ_F 's of anion-**2** complexes were 0.0112, 0.0084 and 0.0109, respectively, for AcO⁻, F⁻, and H₂PO₄⁻. 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⁻, H₂PO₄⁻) systems; 2D COSY spectrum of *N*-acetamidothiourea in CD₃CN; ¹H and ¹³C NMR of **1–3**. See DOI: 10.1039/b703122j

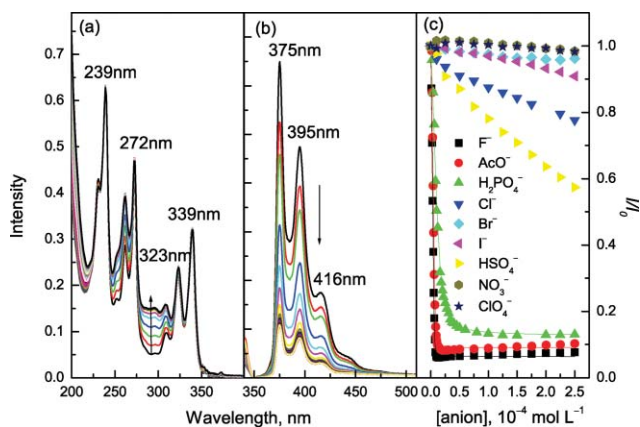


Fig. 2 Absorption (a) and fluorescence (b) spectra of **2** in MeCN in the presence of AcO^- and plots of I/I_0 versus anion concentration (c). $[\mathbf{2}] = 8.55 \times 10^{-6} \text{ mol L}^{-1}$, $[\text{anion}] = 0-2.5 \times 10^{-4} \text{ mol L}^{-1}$. Excitation wavelength was 340 nm.

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 $\text{F}^- > \text{AcO}^- > \text{H}_2\text{PO}_4^- \gg \text{HSO}_4^- > \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{NO}_3^-, \text{ClO}_4^-$.

The nature of the interactions of **1-3** with anions was investigated by ^1H NMR titrations in CD_3CN . As seen in Fig. 3, two of the three $-\text{NH}$ 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 $-\text{NH}$ 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^- . ^1H 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 fitting¹² the fluorescence intensity versus anion concentration (Fig. 2c) and are listed in Table 1. They are at $10^5-10^7 \text{ mol}^{-1} \text{ L}$ orders of magnitude. The observations that the binding constant decreases in the order of $\mathbf{1} < \mathbf{2} < \mathbf{3}$ 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

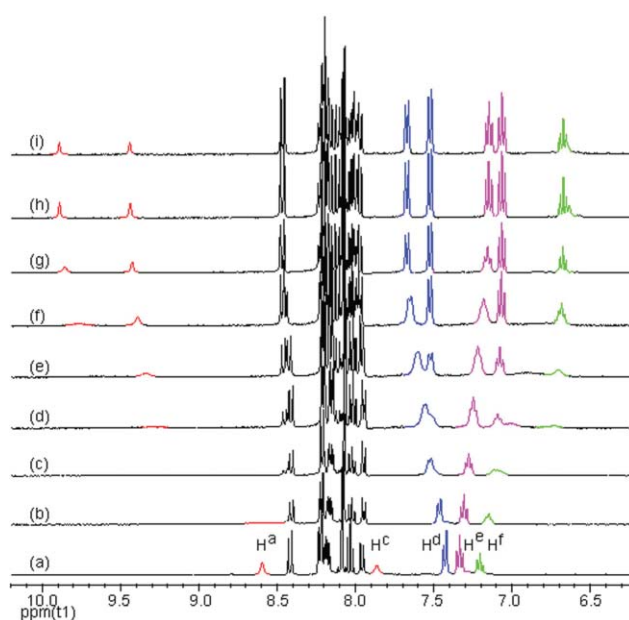


Fig. 3 Trace of NMR titration by F^- of **2** in CD_3CN . $[\mathbf{2}] = 6.0 \times 10^{-3} \text{ mol L}^{-1}$. The spectra were recorded after addition of 0 (a), 0.25 (b), 0.50 (c), 0.75 (d), 1.0 (e), 1.5 (f), 2.0 (g), 4.0 (h) and 8.0 (i) equiv. of F^- , respectively.

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}

The corresponding quenching constants (K_{SV})⁸ in MeCN are at $10^5 \text{ mol}^{-1} \text{ L}$ 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 $10^2-10^3 \text{ mol}^{-1} \text{ L}$ orders of magnitude, the K_{SV} 's of **1-3** with the *N*-amidothiourea receptor are much higher despite a relatively longer $(\text{CH}_2)_3$ 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}	$K_{\text{SV}}/10^5 \text{ mol}^{-1} \text{ L}$	$K/10^6 \text{ mol}^{-1} \text{ L}$	Φ_{F}	$K_{\text{SV}}/10^5 \text{ mol}^{-1} \text{ L}$	$K/10^6 \text{ mol}^{-1} \text{ L}$	Φ_{F}	$K_{\text{SV}}/10^5 \text{ mol}^{-1} \text{ L}$	$K/10^6 \text{ mol}^{-1}$
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 H₂O–MeCN binary solvents

%H ₂ O (v/v)	1			2			3					
	Φ_F^a	Φ_F^b	$K_{SV}/10^5 \text{ mol}^{-1} \text{ L}$	$K/10^6 \text{ mol}^{-1} \text{ L}$	Φ_F^a	Φ_F^b	$K_{SV}/10^5 \text{ mol}^{-1} \text{ L}$	$K/10^6 \text{ mol}^{-1} \text{ L}$	Φ_F^a	Φ_F^b	$K_{SV}/10^5 \text{ mol}^{-1} \text{ L}$	$K/10^6 \text{ mol}^{-1} \text{ L}$
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

^aQuantum yields of **1–3** in water–MeCN binary solvents, ^bQuantum yields of AcO⁻–sensor complex in H₂O–MeCN binary solvents, ^cSpectral change was too minor to allow for an accurate evaluation.

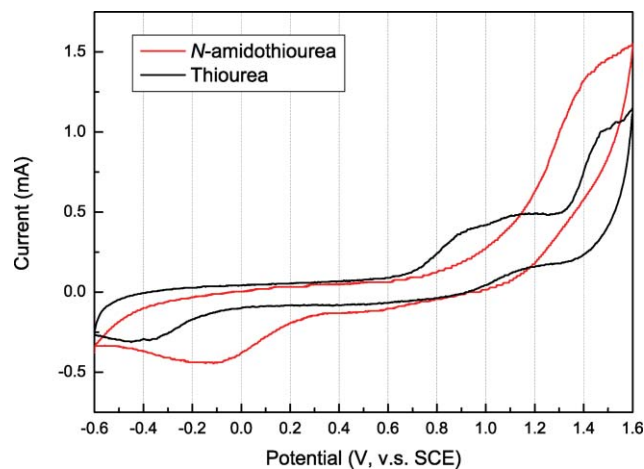


Fig. 4 Cyclic voltammograms of receptors vs. SCE in MeCN containing 0.1 mol L⁻¹ (n-C₄H₉)₄NClO₄. The working electrode was a glassy carbon electrode. The scan rate was 50 mV s⁻¹.

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, CHCl₃ 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% H₂O–MeCN binary solvent with a binding constant as high as 10⁵ mol⁻¹ L orders of magnitude. Detailed *K*, *K*_{SV} and Φ_F values of **1–3** with AcO⁻ in H₂O–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 (CH₂)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 10⁵ 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. ¹H NMR (400 MHz) and ¹³C

NMR (100 MHz) spectra in DMSO-*d*₆ or CD₃CN 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 SOCl₂ 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 NaHCO₃ 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-pyrenebutyrylhydrazide, 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).** ¹H 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). ¹³C 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 [C₂₈H₂₅N₃OS + H]⁺ 452.1797, found 452.1805.

***N*-(1-Pyrenebutanamido)-*N'*-phenylthiourea (2).** ¹H 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). ¹³C 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 [C₂₇H₂₃N₃OS + H]⁺ 438.1640, found 438.1642; for [C₂₇H₂₃N₃OS + Na]⁺ 460.1460, found 460.1457.

***N*-(1-Pyrenebutanamido)-*N'*-(*m*-trifluoromethylphenyl)thiourea (3).** ¹H 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). ¹³C 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 [C₂₈H₂₂F₃N₃OS + H]⁺ 506.1514, found 506.1516.

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