Fluoride-Selective Optical Sensor Based on Dipyrrolyl-tetrathiafulvalene Chromophore

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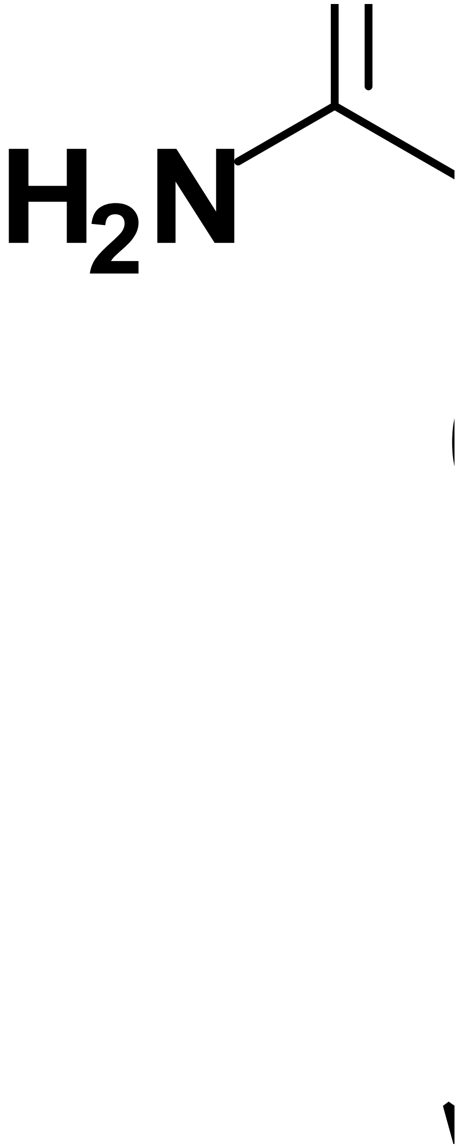
Synthesis of Target molecule 1.



Scheme S1. *Synthesis of 2,3-dipyrrol-2'-yl-TTF-quinoxaline* **1**.

***2,3-dipyrrol-2’-yl-TTF-quinoxaline* 1:**. A mixture of diamino-TTF **2** (86 mg, 1.98 x 10^{-4} M) and 2,3-dipyrrol-2’-yl-ethanedione **3** (37 mg, 1.98 x 10^{-4} M) was dissolved in dichloromethane/pyridine (*v/v*, 4:1, 5 mL) and mixture was heated to reflux under argon atmosphere in the dark for 2 h. Completion of reaction was monitored by TLC. The mixture was evaporated to dryness and the residue purified by chromatography over silica (chloroform). The first major band gave 2,3-Dipyrrol-2’-yl-TTF-quinoxaline **1** (95 mg, 81 %) as a yellow powder. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.63 (s, 2H), 7.75 (s, 2H), 7.05-8.98 (m, 2H), 6.89 (m, 2H), 6.38 (s, 2H), 2.98 (t, 4H, *J* = 7.8 Hz), 1.71 (m, 4H), 0.98 (t, 6H, *J* = 7.03). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 143.2, 139.6, 138.5, 128.8, 127.7, 126.5, 121.2, 119.1, 113.0, 111.5, 110.1, 38.3, 23.1, and 14.1. HRMS *m/z*: calcd for $C_{26}H_{24}N_4S_6$ 584.0325; found 584.0325.

***2,3-dipyrrol-2’-yl ethanedione* 3:** Was synthesized following literature procedure with slight modification.[1] Oxalyl chloride (3.2 g, 0.025mol) and DCM (15 mL) were placed together under and argon atmosphere at -78 °C in a methanol/liquid nitrogen bath, dry pyridine (5 g, 0.06mol) was added, resulting formation of a yellow precipitate observed, stir mixture for additional 40 minutes. To this cooled suspension distilled pyrrole (3.35 g, 0.05 mol) in DCM (13 mL) was added by addition funnel. Immediately, the reaction mixture was seen to turn dark brown from yellow. Upon stirring at -60 °C for 15 minutes, hydrochloric acid (3 M, 50 mL) was added to quench the reaction. The organic phase was collected, followed by extraction of aqueous phase with DCM (2 x 50 mL), and the combined organic phase were washed with brine (100 mL) followed by water (50 mL), dried over anhydrous sodium sulphate, filtered and evaporated to dryness, afforded green solid which further purified by flash column chromatograph eluting with DCM to afford **3** (1.35 g, 54%) as a yellow crystalline powder. ^{1}H NMR (DMSO d_6, 300 MHz) δ: 6.26 (m, 2H), 6.89 (m, 2H), 7.31 (m, 2H), 12.28 (s, 2H, NH); ^{13}C NMR (DMSO d_6, 75 MHz) δ: 111.1, 120.8, 128.4, 128.8, 181.3. Ms (ESI): Molecular formula $C_{10}H_8N_2O_2$, calcd. 188.05, obtained 188.05 $(M)^+$, 189.05 $(M+H)^+$.

4,5-Bis(1-propylthio)-1,3-dithiole-2-thione (**2**): This compound were prepared in two steps, first step involved preparation of zincate[2] followed by reacting zincate with 1-bromopropane in CH_3CN.[3] Both reactions were carried out with known protocols with slight modification.

Bis(tetraethylammonium)bis(1,3-dithiole-2-thione-4,5-dithi-ol)zincate:[2] To degassed DMF (480 mL), CS_2 (240 mL) was added and the mixture was cooled to 0 °C under nitrogen. Sodium [14.5 g, weighed and fragmented as finely as possible (initially cut into small pieces using scissors, then these pieces were sliced further by using a sharp spatula) under hexane; the hexane was then removed by decantation] then above sodium was added in one portion to the reaction mixture and the mixture was vigorously stirred for ca. 8 h with cooling, until all the sodium metal was consumed, giving a blood-red coloured solution. (If any unreacted sodium remains at this stage, an adequate volume of MeOH is slowly added). To this solution, separate solutions of (i) $ZnCl_2$ (21.3 g) dissolved in a mixture of 35% NH_3 (360 mL) and water (100 mL), and (ii) Et_4NBr (66 g) in water (500 mL) were added consecutively in approximately equivalent volume portions over 0.5 h with stirring at room temperature. A red precipitate formed gradually during the addition. The mixture was stirred overnight, then the product was isolated by filtration in vacuo and washed sequentially with large volumes of i-PrOH and Et2O, to afford analytically pure red crystals of salt 1 (90 g, 79% yield, based on the mechanism proposed in Scheme 1); mp 205–207 ˚C (Lit.1 mp 206 – 208 ˚C). CAUTION: The filtrate is extremely malodorous and should be disposed of with care. Large (several mm_3) red prisms of salt zincate are obtained by dissolving crystals of above salt in acetone, filtering, and precipitation with addition of i-PrOH.

***Preparation of* 4**:[3] a mixture of the above zincate (11.5 g, 16.0 mmol) and 1-bromopropane (12 mL, 16.2 g, 132 mmol) in MeCN (250 mL) was heated under reflux for 4 h. After being cooled down to room temperature, the reaction mixture was filtered, whereupon the filtrate was concentrated in vacuo and the residue was subjected to column chromatography [SiO_2, eluent: dichloromethane-cyclohexane (1:1,*v/v*)]. The yellow band (r_f 0.6) was collected and the solvent evaporated to give **4** (7.92 g, 88%) as a yellow brownish oil. All spectroscopic characterization i.e. NMR, Mass and ^{13}C NMR matched with literature values **4** [3].

***Preparation of* 5**: A mixture of above compound **4** (4.6 gm 0.015 mol) in $CHCl_3$/AcOH (3:1, 120 mL) and mercury(II)acetate ($Hg(OAc)_2$, 12 g, 0.04 mol) were stirred under argon atmosphere at room temperature for overnight under argon atmosphere. The resulting white precipitate was filtered using Celite and followed by washing with $CHCl_3$. Combined organic layer washed with sat. sodium bicarbonate (2 x 50 mL) followed by water (100 mL), dried over sodium sulphate and concentrated in vacuo affording **5** as pale yellow needles in quantitative yields (4.32 g), m.p. 64-65 ^oC. All spectroscopic characterization i.e. NMR, Mass and ^{13}C NMR matched with literature values for compound **5** [4].

***Preparation of 1,2-Diamino-benzene-4,5-bis(thiocyanate)* 6**: Preparation of compound **6** was carried out followed by literature method.[5] A solution of bromine (29.8 g, 0.190 mol) in 100 mL of cold MeOH was added slowly over 2-3 h to a solution of potassium thiocyanate (36.1 g, 0.370 mol) and *o*-phenylenediamine (10.0 g, 0.0930 mol) in 500 mL of MeOH at -78 °C. The mixture was allowed to warm slowly to room temperature and was poured into water (500 mL). The resulting dark-red slurry was filtered and the filtrate made basic by the addition of aqueous ammonia. The bright-yellow precipitate so formed was filtered off, washed with water, and air-dried. The crude product 6 (9.80 g, 48%) was purified by passing a solution of it in ethyl acetate through a bed of silica. Removal of the solvent from the eluate and recrystallization from chlorobenzene afforded pale-yellow feathers, decompose >135 °C. All other spectroscopic characterization (^1H-NMR, ^{13}C NMR, mass and IR) data matched with literature values.[5]

***5,6-Diaminobenzene-1,3-dithiole-2-thione* 7**: [6] 1,2-diaminobenzene-4,5-bis(thiocyanate) **6** (4.88 g, 22 mmol) was added to a degassed solution of $Na_2S{\cdot}9H_2O$ (17.42g, 72 mmol) in water (270 mL), and the mixture was heated to 75 ^oC for 1 h to produce a clear brownish solution. The mixture was cooled to 50 ^oC, and CS_2 (2.8 mL, 46.4 mmol) was slowly added dropwise. The mixture was stirred for 2 h at 50 ^oC and for another 3 h at room temperature. The precipitate was filtered off, washed with water, and air-dried. The crude product was purified by flash column chromatography (silica gel, eluate using $CHCl_3$/ EtOAc (1:3, *v/v*)) to give **7** as a yellow powder (2.43 g, 52 %). Product were fully characterized and found to be identical with literature values, [6] M.p. 210– 211 °C.

***5,6-Diamino-2-(4,5-bis(propylthio)-1,3-dithio-2-ylidene)benzo [d]-1,3-di- thiole* 2**:[6] Condensastion of **5** and **7** were carried out utilizing triethylphosphite followed by known literature procedure.[6] Triethylphosphite (60 mL) was added slowly to a solution of 4,5-bis(propylthio)-1,3-dithiole-2-one (2.48 g, 9.76 mmol) and compound 2 (1.0 g, 4.68 mmol) in toluene (40 mL) under argon. The mixture was heated to 120 °C and stirred for 3 h. After the reaction, the excess solvent was removed under vacuum to afford an oily red residue, which was subjected to chromatography (silica gel, CH_2Cl_2/EtOAc (1/3, *v/v*)). The crude product was further purified by recrystallization from CH_2Cl_2/ hexane to give compound 2 as a yellow solid (0.74 g, 38%). All data were identical to known literature compound.[6]

UV/vis absorption spectroscopy

UV/vis titrations: all stock solutions of **1** ($1.0x10^{-5}$ M) were prepared in dichloromethane. Spectra were collected on a Cary Bio 100 UV/vis spectrophotometer. Anion binding titrations were carried out by monitoring changes in the UV band at 484 nm as a function of added anion concentration.

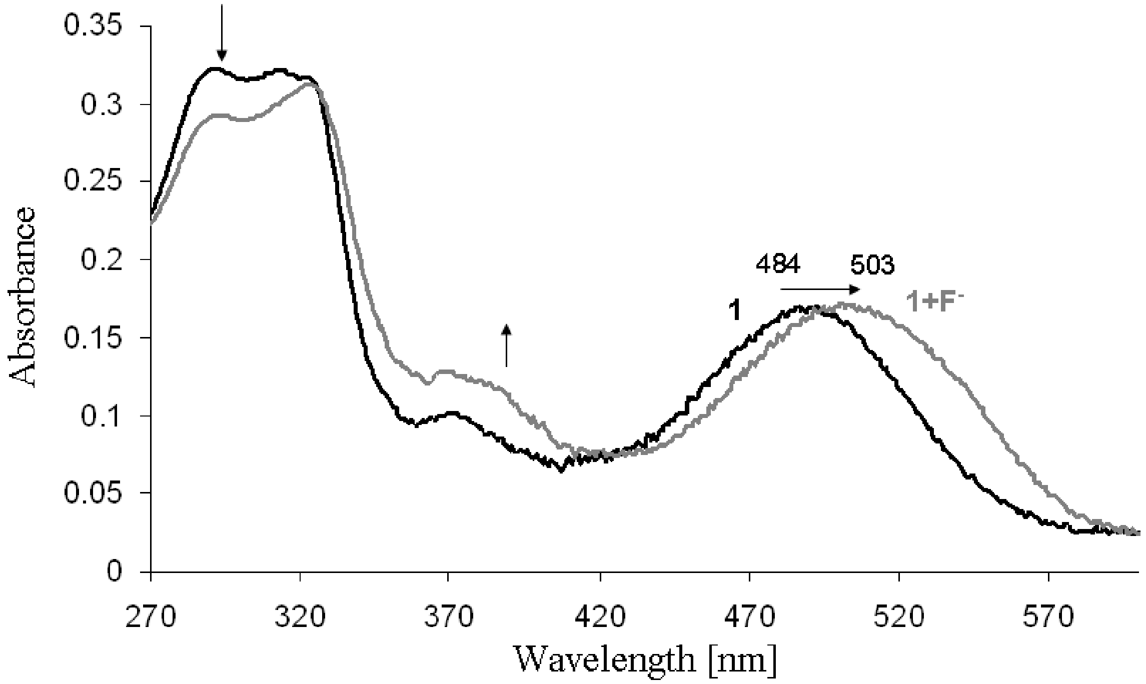


Figure S1. Normalized absorption spectra of **1** ($1.2x10^{-5}$ M, black line) and after addition of 2 equiv F^- (gray line, with its tetrabutylammonium salts)) in DCM.

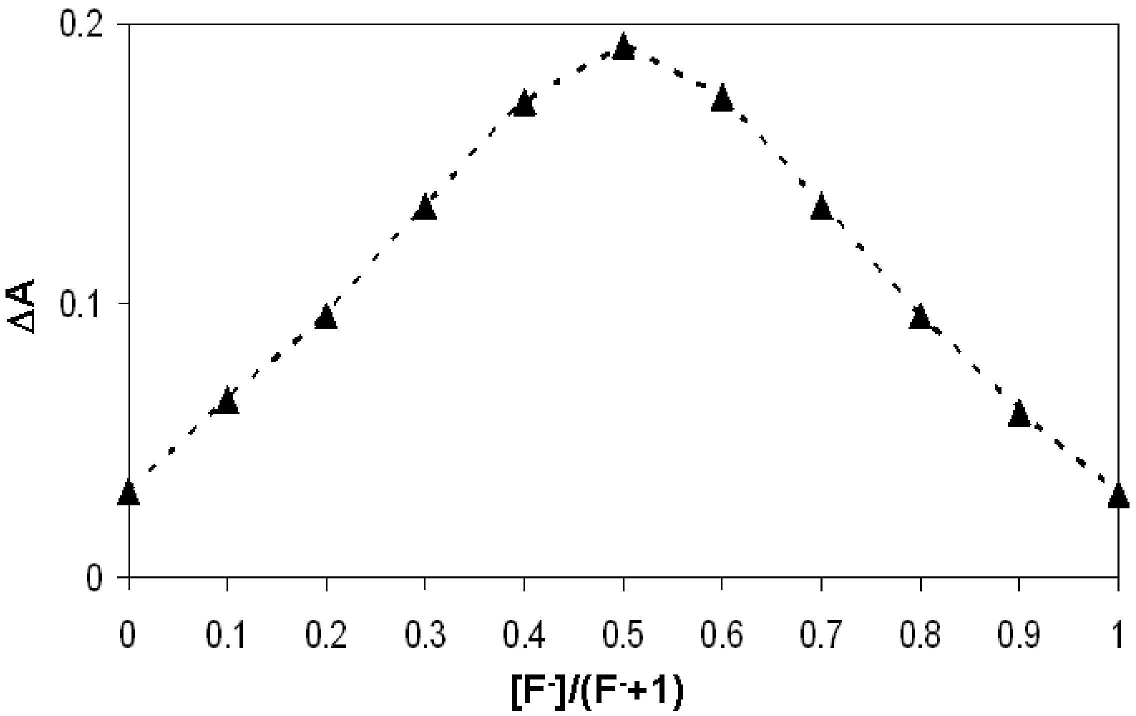


Figure S2. Job plot of receptor **1** with fluoride anion (there Bu_4N salt).

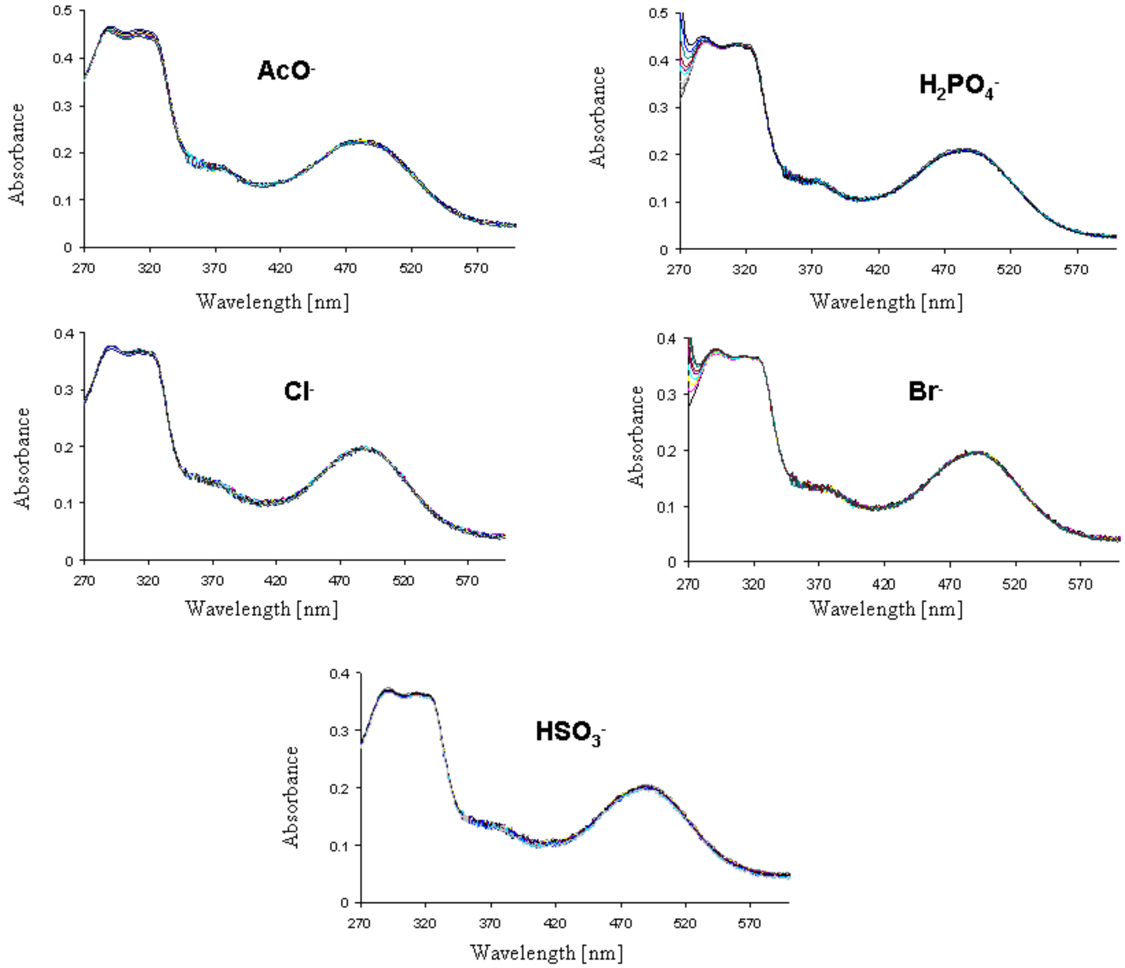


Figure S3. UV-vis spectral changes of complex **1** upon the addition of anions ACO^-, $H_2PO_4^-$, Cl^-, Br^- and HSO_3^- (with their tetrabutylammonium salts); [**1**] = $1.0x10^{-5}$ M, [TBA-anions] = 0-$5x10^{-4}$ M, DCM, 25 °C.

***Crystal Structure of Dipyrrolyl-tetrathiafulvalene Chromophore* 1**

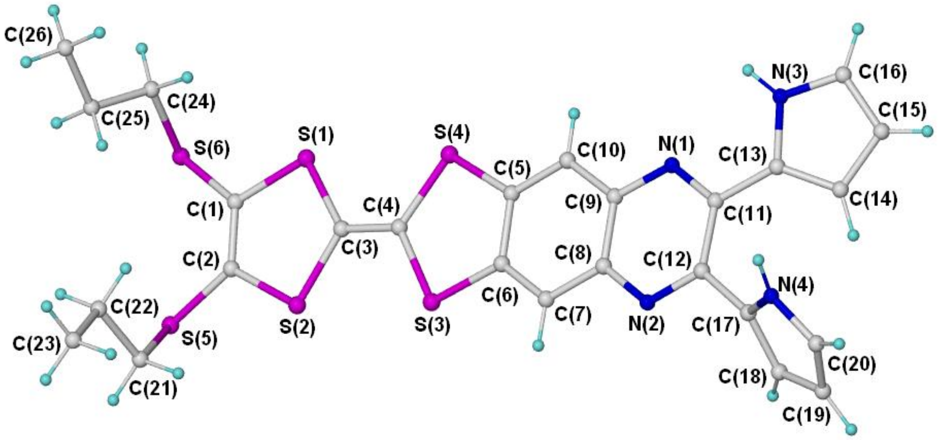


Figure S4. Molecular diagram of **1**, in ball and stick representation.

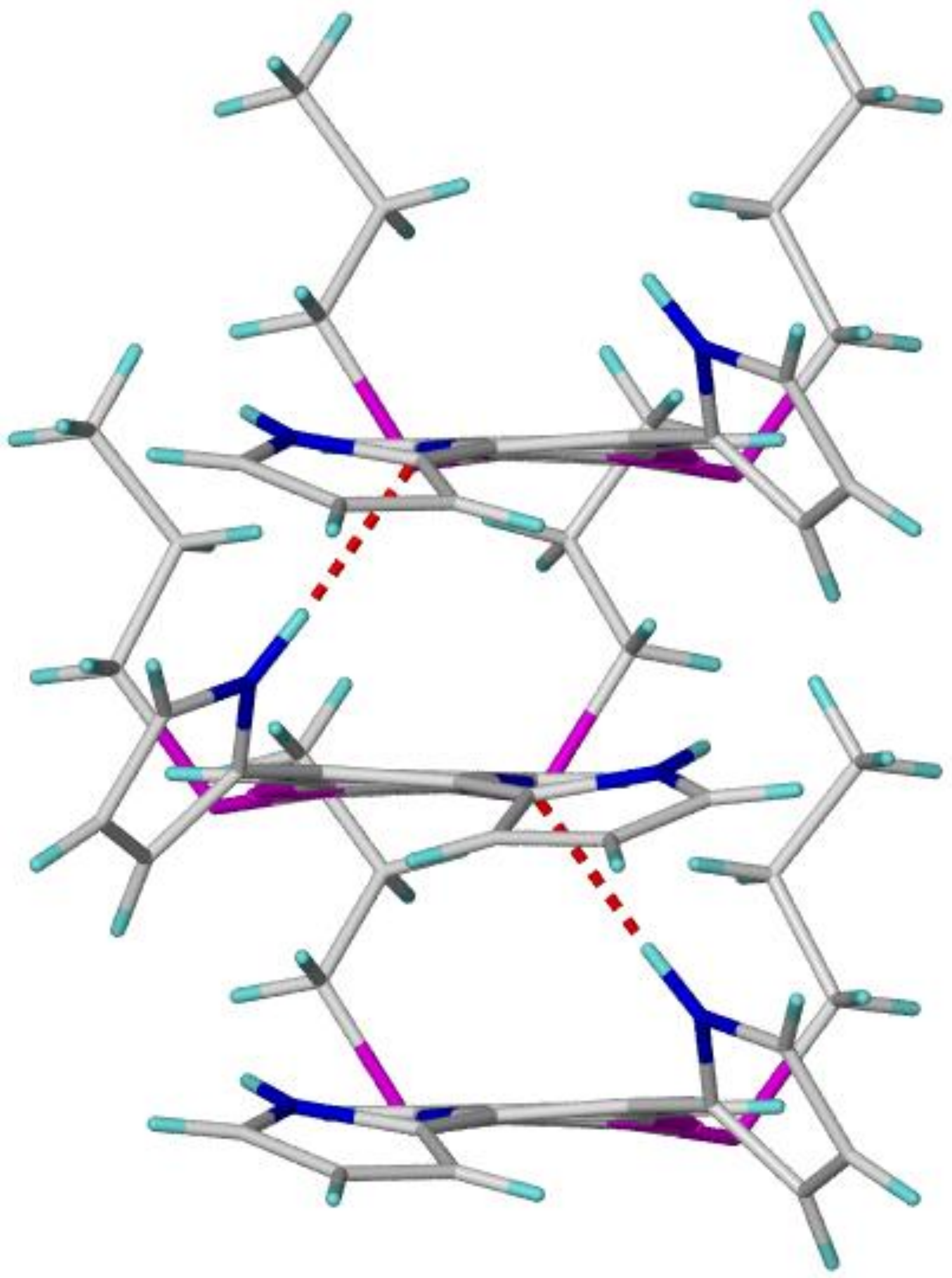


Figure S5. Stacking of neighboring molecules as viewed down the longer molecular axes.

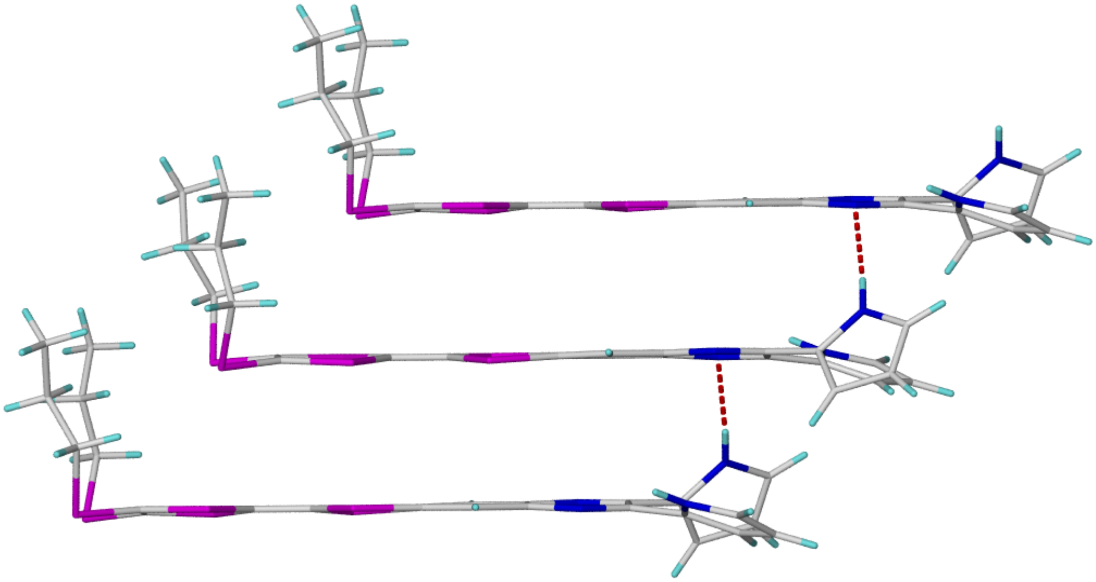


Figure S6. Stacking of neighbouring molecules as viewed down the shorter molecular axes.

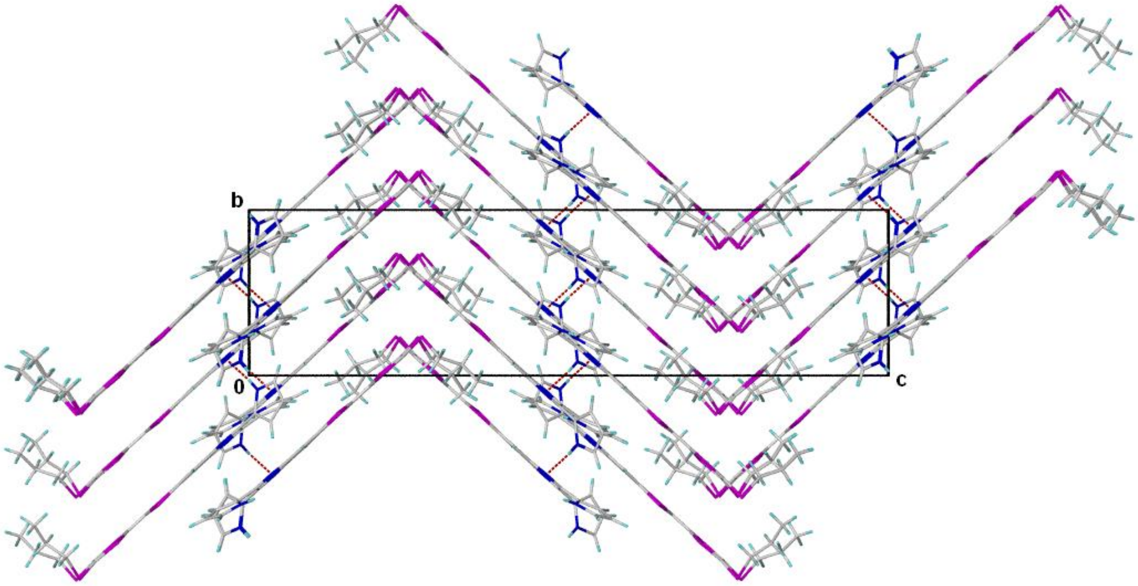


Figure S7. Unit cell content as viewed down the axis direction and showing the herringbone packing motif of the molecules.

Naked eye detection of color changes upon binding of anions:

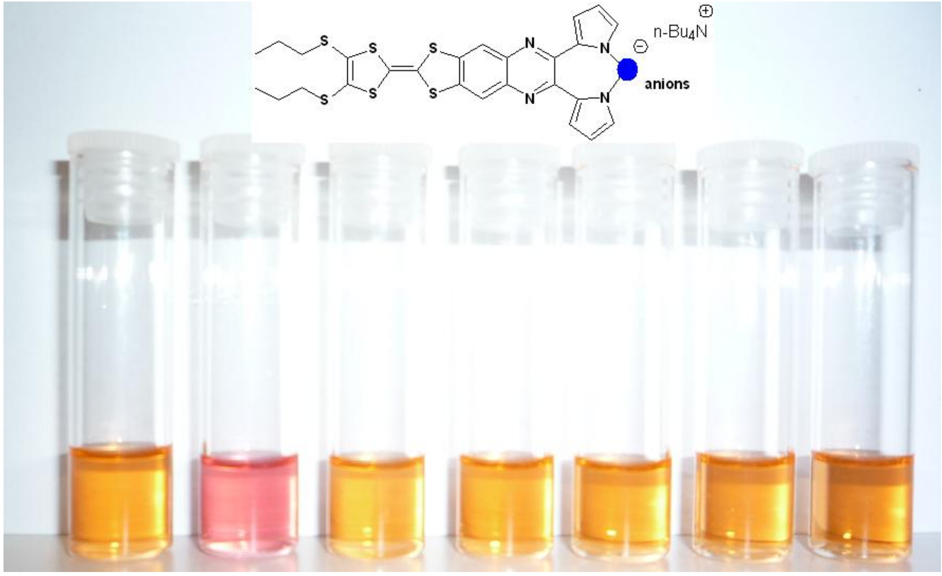
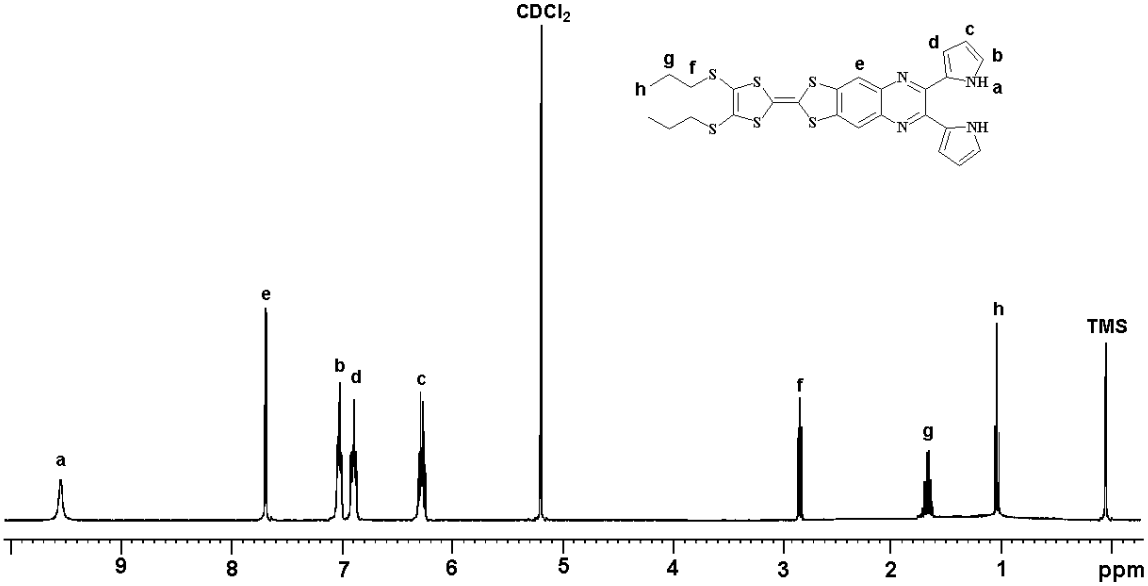
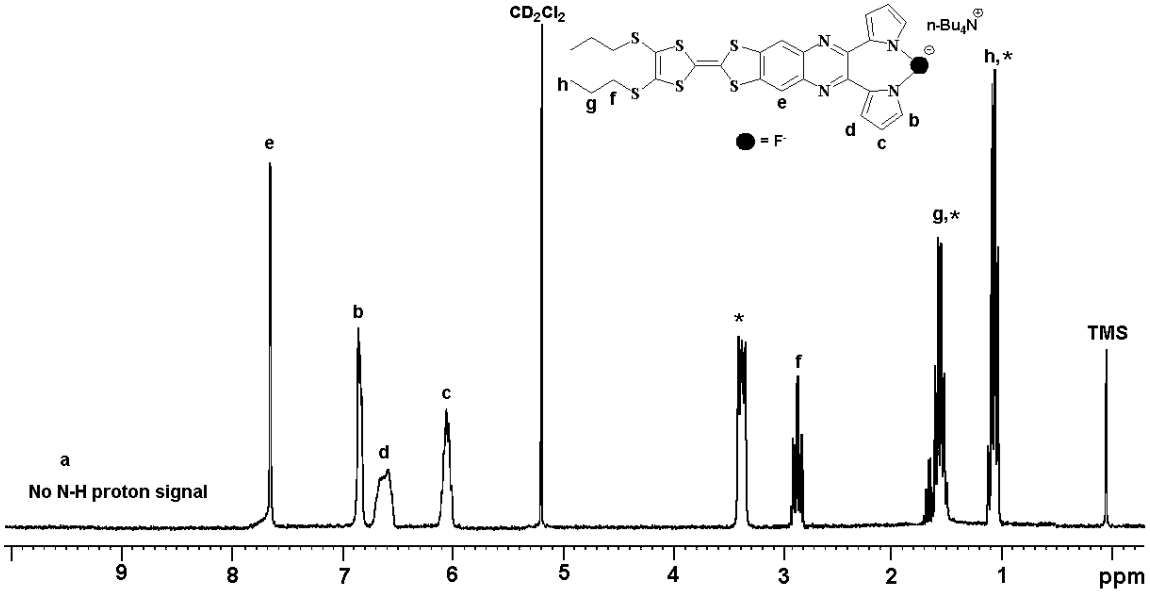


Figure S8. Sensing capability with color changes seen upon addition of 3 equiv of anions to **1** in DCM: no anion, F^-, $H_2PO_4^-$, AcO^-, Cl^-, Br^-, and HSO_4^- (their tetrabutylammonium salts) respectively. [**1**] = $1.0\text{x}10^{-5}$ M.

NMR study of F^- sensing with 1



^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) of compound **1.**



^{1}H NMR (CDCl$_3$, 300 MHz, 298 K) of compound **1**, upon addition 2 equiv of F$^-$ (its tetrabutylammonium salt). * = TBA and solvent peaks.

Electrochemical instrumentation and apparatus

The electrochemical measurements were carried out using a CH instrument model 660B electrochemical workstation. Solution phase experiments were performed in a conventional three-electrode cell comprising a 3-mm in diameter glassy carbon (GC) disk electrode (CH Instruments), a platinum wire auxiliary electrode and a silver wire quasi reference electrode. Potential data were referenced to the formal potential of the ferrocene/ferrocenium couple measured *in situ* and were performed in 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAPF6) (electrochemical grade) in freshly distilled acetonitrile or anhydrous dichloromethane. All scans were conducted at 0.2 V s^{-1} unless otherwise stated and carried out at ambient temperatures (20 ± 2°C). All solutions were deoxygenated using grade 5 nitrogen prior to electrochemical experimentation. The GC working electrode was polished prior to each experiment using BUEHLER Microcloth® Polishing cloth with an aqueous slurry of 0.3 µm alumina.

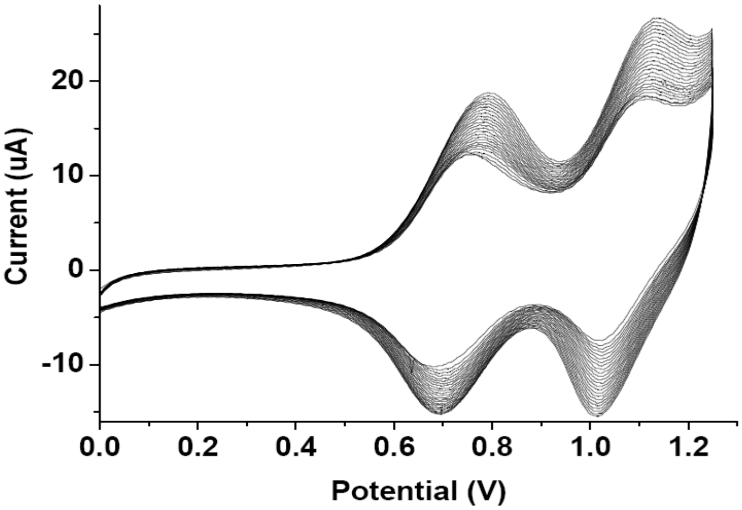
TABLE 1.0: EC data – addition of fluorine to TFF-dipyrrole (solution phase)

			PEAK COUPLE I			
Equiv. F$^-$ added	**$i_{p\ ox}$ (uA)**	**$i_{p\ red}$ (uA)**	**$E_{1/2}$ / mV**	**$E_{p\ ox}$ (mV)**	**$E_{p\ red}$ (mV)**	**ΔE_p (mV)**
0	33.9	-22.3	290	360	221	139
0.2	37.9	-25.1	297	369	226	143
0.4	43.9	-25.6	295	374	216	158
0.6	46.4	-26.2	300	381	219	162
0.8	48.1	-25.3	301	390	213	177
1.0	48.3	-27.3	305	395	216	179

Overall change	incr	incr		Small +ve shift	NC	ΔEp is large due to solvent resistance

PEAK COUPLE II

Equiv. F$^-$ added	**$i_{p\ ox}$ (uA)**	**$i_{p\ red}$ (uA)**	**$E_{1/2}$ / mV**	**$E_{p\ ox}$ (mV)**	**$E_{p\ red}$ (mV)**	**ΔE_p (mV)**
0	47.61	-12.6	645	730	560	170
0.2	53.59	-15.3	648	739	556	183
0.4	58.74	-15.6	645	743	547	196
0.6	62.47	-16.1	648	749	546	203
0.8	65.28	-15.4	649	757	541	216
1.0	64.75	-17.6	647	760	533	227
Overall change	incr	incr		Small +ve shift	Small -ve shift	ΔEp is large due to solvent resistance



Electrochemical deposition of TTF-dipyrrole onto surface of glassy carbon working electrode in 0.1M TBAPF$_6$ (DCM) electrolyte, 0 – 1.3 V, 0.2 V/s scan rate, 50 successive scans. *Insert*: 0 - 0.9 V (0.2 V/s scan rate, 50 successive scans)

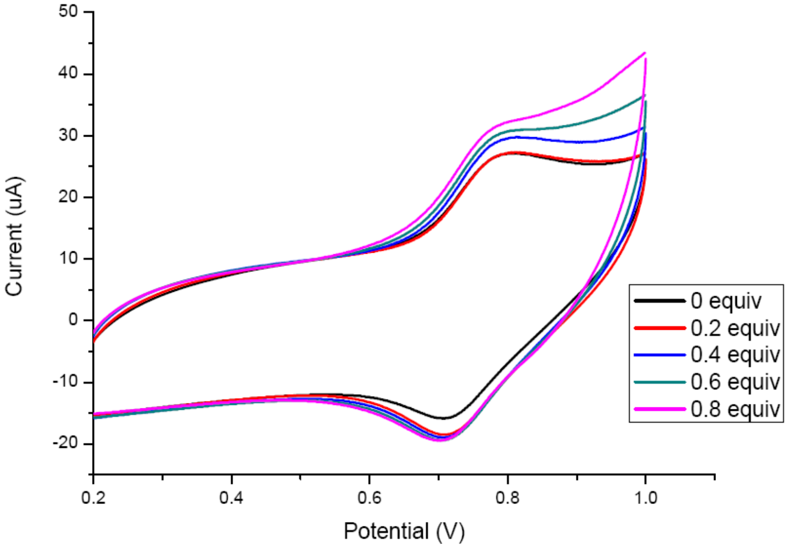


Figure 3 Cyclic voltammogram of 1mM TTF-dipyrrole obtained by adding in increasing quantities of 0.5 M TBAF solution (0 to 1.0 equiv). (Reference electrode: Fc^+/Fc, supporting electrolyte, n-Bu_4NPF_6 (0.1 M) in dichloromethane)

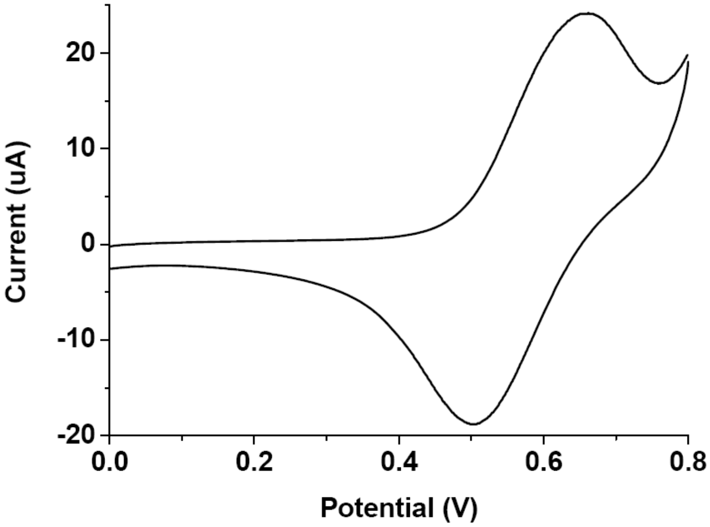


Figure 4 Glassy Carbon WE coated with TTF-Dipyrole, in 0.1M LiClO4, 0 – 0.8 V, 0.2 V/s.

References

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Table 1.  Crystal data and structure refinement for AS1A.

Identification code               as1a

Empirical formula                 C26 H24 N4 S6

Formula weight                    584.85

Temperature                       100(2) K

Wavelength                        0.77051 A

Crystal system, space group       Orthorhombic,  P b c a

Unit cell dimensions
                                   a = 16.337(2) A   alpha = 90 deg.
                                    b = 9.364(2) A    beta = 90 deg.
                                    c = 36.071(3) A   gamma = 90 deg.

Volume                            5518.1(14) A^3

Z, Calculated density             8,    1.408 Mg/m^3
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Absorption coefficient	0.520 mm^-1
F(000)	2432
Crystal size	0.01x0.01x0.01 mm
Theta range for data collection	1.22 to 26.44 deg.
Limiting indices	-18<=h<=18,-10<=k<=10,-40<=l<=40
Reflections collected / unique	58422 / 4416 [R(int) = 0.0446]
Completeness to theta = 26.44	99.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4416 / 0 / 333
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R1 = 0.0351, wR2 = 0.0986
R indices (all data)	R1 = 0.0374, wR2 = 0.1001
Largest diff. peak and hole	0.322 and -0.540 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for AS1A. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	7881(1)	5105(1)	2105(1)	11(1)
S(2)	6071(1)	5084(1)	2050(1)	12(1)
S(3)	6116(1)	2802(1)	1410(1)	9(1)
S(4)	7940(1)	2719(1)	1421(1)	8(1)
S(5)	5827(1)	7286(1)	2639(1)	19(1)
S(6)	7913(1)	7344(1)	2701(1)	19(1)
N(1)	7830(1)	-967(2)	349(1)	8(1)
N(2)	6103(1)	-1018(2)	390(1)	8(1)
N(3)	8676(1)	-2754(2)	-119(1)	11(1)
N(4)	6054(1)	-4162(2)	-137(1)	10(1)
C(1)	7333(1)	6202(2)	2419(1)	12(1)
C(2)	6510(1)	6190(2)	2393(1)	12(1)
C(3)	7006(1)	4370(2)	1892(1)	8(1)
C(4)	7032(1)	3404(2)	1617(1)	8(1)

C(5)	7458(1)	1583(2)	1101(1)	7(1)
C(6)	6584(1)	1598(2)	1104(1)	7(1)
C(7)	6140(1)	728(2)	873(1)	8(1)
C(8)	6557(1)	-160(2)	619(1)	7(1)
C(9)	7426(1)	-156(2)	607(1)	6(1)
C(10)	7874(1)	720(2)	854(1)	8(1)
C(11)	7387(1)	-1785(2)	120(1)	7(1)
C(12)	6501(1)	-1832(2)	149(1)	7(1)
C(13)	7842(1)	-2559(2)	-162(1)	11(1)
C(14)	7634(1)	-3117(2)	-507(1)	19(1)
C(15)	8363(1)	-3645(2)	-669(1)	23(1)
C(16)	8993(1)	-3413(2)	-424(1)	17(1)
C(17)	5987(1)	-2703(2)	-98(1)	8(1)
C(18)	5395(1)	-2241(2)	-342(1)	13(1)
C(19)	5105(1)	-3459(2)	-536(1)	14(1)
C(20)	5516(1)	-4620(2)	-401(1)	12(1)
C(21)	5173(1)	5941(2)	2856(1)	18(1)
C(22)	5590(1)	5137(2)	3170(1)	22(1)
C(23)	5017(1)	4049(2)	3348(1)	25(1)
C(24)	8504(1)	6093(2)	2984(1)	22(1)
C(25)	8094(2)	5650(4)	3334(1)	54(1)
C(26)	8640(3)	4712(5)	3574(1)	76(1)

Table 3. Bond lengths [A] and angles [deg] for AS1A.

S(1)-C(3)	1.7626(18)
S(1)-C(1)	1.7711(19)
S(2)-C(3)	1.7632(18)
S(2)-C(2)	1.7656(19)
S(3)-C(6)	1.7532(18)
S(3)-C(4)	1.7636(18)
S(4)-C(5)	1.7570(18)
S(4)-C(4)	1.7637(18)
S(5)-C(2)	1.757(2)
S(5)-C(21)	1.827(2)
S(6)-C(1)	1.7554(19)
S(6)-C(24)	1.828(2)
N(1)-C(11)	1.339(2)
N(1)-C(9)	1.370(2)
N(2)-C(12)	1.327(2)
N(2)-C(8)	1.370(2)
N(3)-C(16)	1.362(3)
N(3)-C(13)	1.382(3)
N(3)-H(3)	0.86(2)

N(4)-C(20)	1.366(3)
N(4)-C(17)	1.378(2)
N(4)-H(4)	0.88(3)
C(1)-C(2)	1.348(3)
C(3)-C(4)	1.344(3)
C(5)-C(10)	1.380(3)
C(5)-C(6)	1.428(3)
C(6)-C(7)	1.374(3)
C(7)-C(8)	1.412(3)
C(7)-H(7)	0.9500
C(8)-C(9)	1.421(3)
C(9)-C(10)	1.417(3)
C(10)-H(10)	0.9500
C(11)-C(12)	1.451(3)
C(11)-C(13)	1.455(3)
C(12)-C(17)	1.472(3)
C(13)-C(14)	1.391(3)
C(14)-C(15)	1.416(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.377(3)
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
C(17)-C(18)	1.377(3)
C(18)-C(19)	1.420(3)
C(18)-H(18)	0.9500
C(19)-C(20)	1.368(3)
C(19)-H(19)	0.9500
C(20)-H(20)	0.9500
C(21)-C(22)	1.522(3)
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(22)-C(23)	1.525(3)
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-C(25)	1.489(4)
C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900
C(25)-C(26)	1.523(4)
C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900
C(26)-H(26A)	0.9800
C(26)-H(26C)	0.9800
C(26)-H(26B)	0.9800

C(3)-S(1)-C(1)	95.46(9)
C(3)-S(2)-C(2)	95.56(9)
C(6)-S(3)-C(4)	95.81(9)
C(5)-S(4)-C(4)	96.06(9)
C(2)-S(5)-C(21)	100.67(9)
C(1)-S(6)-C(24)	102.59(10)
C(11)-N(1)-C(9)	118.32(15)
C(12)-N(2)-C(8)	117.78(15)
C(16)-N(3)-C(13)	110.12(18)
C(16)-N(3)-H(3)	124.4(15)
C(13)-N(3)-H(3)	125.4(15)
C(20)-N(4)-C(17)	109.35(16)
C(20)-N(4)-H(4)	125.8(16)
C(17)-N(4)-H(4)	124.8(16)
C(2)-C(1)-S(6)	125.69(15)
C(2)-C(1)-S(1)	117.10(14)
S(6)-C(1)-S(1)	116.85(11)
C(1)-C(2)-S(5)	126.46(15)
C(1)-C(2)-S(2)	117.28(14)
S(5)-C(2)-S(2)	116.00(11)
C(4)-C(3)-S(1)	124.04(14)
C(4)-C(3)-S(2)	121.42(14)
S(1)-C(3)-S(2)	114.44(11)
C(3)-C(4)-S(3)	120.04(13)
C(3)-C(4)-S(4)	124.48(14)
S(3)-C(4)-S(4)	115.41(11)
C(10)-C(5)-C(6)	120.20(16)
C(10)-C(5)-S(4)	123.89(14)
C(6)-C(5)-S(4)	115.91(13)
C(7)-C(6)-C(5)	121.14(16)
C(7)-C(6)-S(3)	122.25(14)
C(5)-C(6)-S(3)	116.59(13)
C(6)-C(7)-C(8)	119.25(16)
C(6)-C(7)-H(7)	120.4
C(8)-C(7)-H(7)	120.4
N(2)-C(8)-C(7)	118.37(16)
N(2)-C(8)-C(9)	121.56(16)
C(7)-C(8)-C(9)	120.07(16)
N(1)-C(9)-C(10)	120.01(16)
N(1)-C(9)-C(8)	120.13(16)
C(10)-C(9)-C(8)	119.84(16)
C(5)-C(10)-C(9)	119.45(16)
C(5)-C(10)-H(10)	120.3
C(9)-C(10)-H(10)	120.3
N(1)-C(11)-C(12)	120.83(16)
N(1)-C(11)-C(13)	116.09(16)
C(12)-C(11)-C(13)	123.04(16)

N(2)-C(12)-C(11)	121.27(16)
N(2)-C(12)-C(17)	115.75(16)
C(11)-C(12)-C(17)	122.87(16)
N(3)-C(13)-C(14)	107.02(17)
N(3)-C(13)-C(11)	119.36(17)
C(14)-C(13)-C(11)	133.44(18)
C(13)-C(14)-C(15)	107.14(18)
C(13)-C(14)-H(14)	126.4
C(15)-C(14)-H(14)	126.4
C(16)-C(15)-C(14)	107.94(18)
C(16)-C(15)-H(15)	126.0
C(14)-C(15)-H(15)	126.0
N(3)-C(16)-C(15)	107.78(18)
N(3)-C(16)-H(16)	126.1
C(15)-C(16)-H(16)	126.1
C(18)-C(17)-N(4)	107.58(16)
C(18)-C(17)-C(12)	127.91(17)
N(4)-C(17)-C(12)	124.44(17)
C(17)-C(18)-C(19)	107.36(17)
C(17)-C(18)-H(18)	126.3
C(19)-C(18)-H(18)	126.3
C(20)-C(19)-C(18)	107.36(16)
C(20)-C(19)-H(19)	126.3
C(18)-C(19)-H(19)	126.3
N(4)-C(20)-C(19)	108.34(17)
N(4)-C(20)-H(20)	125.8
C(19)-C(20)-H(20)	125.8
C(22)-C(21)-S(5)	113.47(15)
C(22)-C(21)-H(21A)	108.9
S(5)-C(21)-H(21A)	108.9
C(22)-C(21)-H(21B)	108.9
S(5)-C(21)-H(21B)	108.9
H(21A)-C(21)-H(21B)	107.7
C(21)-C(22)-C(23)	111.66(18)
C(21)-C(22)-H(22A)	109.3
C(23)-C(22)-H(22A)	109.3
C(21)-C(22)-H(22B)	109.3
C(23)-C(22)-H(22B)	109.3
H(22A)-C(22)-H(22B)	107.9
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(25)-C(24)-S(6)	114.41(18)
C(25)-C(24)-H(24A)	108.7

S(6)-C(24)-H(24A)	108.7
C(25)-C(24)-H(24B)	108.7
S(6)-C(24)-H(24B)	108.7
H(24A)-C(24)-H(24B)	107.6
C(24)-C(25)-C(26)	112.3(3)
C(24)-C(25)-H(25A)	109.1
C(26)-C(25)-H(25A)	109.1
C(24)-C(25)-H(25B)	109.1
C(26)-C(25)-H(25B)	109.1
H(25A)-C(25)-H(25B)	107.9
C(25)-C(26)-H(26A)	109.5
C(25)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
C(25)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
H(26C)-C(26)-H(26B)	109.5

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for AS1A. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
S(1)	9(1)	12(1)	13(1)	-2(1)	-1(1)	-2(1)
S(2)	8(1)	12(1)	15(1)	-4(1)	2(1)	-1(1)
S(3)	4(1)	13(1)	11(1)	-3(1)	0(1)	1(1)
S(4)	4(1)	11(1)	10(1)	-1(1)	-1(1)	-1(1)
S(5)	25(1)	11(1)	20(1)	-4(1)	8(1)	3(1)
S(6)	30(1)	11(1)	17(1)	-2(1)	-10(1)	-5(1)
N(1)	5(1)	8(1)	10(1)	2(1)	1(1)	0(1)
N(2)	6(1)	8(1)	10(1)	2(1)	-1(1)	0(1)
N(3)	6(1)	9(1)	17(1)	-1(1)	1(1)	0(1)
N(4)	8(1)	8(1)	15(1)	0(1)	-4(1)	2(1)
C(1)	19(1)	7(1)	10(1)	0(1)	-1(1)	-2(1)
C(2)	18(1)	7(1)	11(1)	0(1)	2(1)	-2(1)
C(3)	6(1)	8(1)	10(1)	3(1)	0(1)	-1(1)
C(4)	5(1)	9(1)	10(1)	2(1)	-1(1)	-1(1)
C(5)	5(1)	7(1)	8(1)	4(1)	-3(1)	-1(1)
C(6)	6(1)	7(1)	7(1)	3(1)	2(1)	1(1)
C(7)	3(1)	11(1)	11(1)	1(1)	-2(1)	0(1)
C(8)	5(1)	8(1)	7(1)	4(1)	-1(1)	0(1)
C(9)	5(1)	7(1)	7(1)	4(1)	1(1)	1(1)
C(10)	2(1)	11(1)	10(1)	3(1)	1(1)	0(1)
C(11)	6(1)	8(1)	8(1)	3(1)	0(1)	0(1)
C(12)	6(1)	8(1)	8(1)	2(1)	-1(1)	1(1)
C(13)	5(1)	12(1)	16(1)	1(1)	1(1)	-1(1)
C(14)	12(1)	27(1)	18(1)	-10(1)	1(1)	-3(1)
C(15)	20(1)	27(1)	22(1)	-15(1)	9(1)	-3(1)
C(16)	12(1)	11(1)	28(1)	-5(1)	10(1)	1(1)
C(17)	5(1)	8(1)	12(1)	-1(1)	0(1)	1(1)
C(18)	10(1)	10(1)	17(1)	1(1)	-5(1)	2(1)
C(19)	12(1)	16(1)	13(1)	-1(1)	-9(1)	1(1)
C(20)	13(1)	10(1)	15(1)	-4(1)	-4(1)	-1(1)
C(21)	14(1)	20(1)	21(1)	-6(1)	7(1)	0(1)
C(22)	16(1)	24(1)	26(1)	0(1)	6(1)	-2(1)
C(23)	25(1)	25(1)	26(1)	-2(1)	8(1)	-3(1)
C(24)	27(1)	19(1)	20(1)	-1(1)	-11(1)	-1(1)
C(25)	46(2)	82(2)	34(2)	33(2)	-6(1)	-3(2)
C(26)	96(3)	84(3)	47(2)	36(2)	-24(2)	2(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for AS1A.

	x	y	z	U(eq)
H(7)	5559	724	883	9
H(10)	8455	714	851	9
H(14)	7102	-3140	-613	23
H(15)	8408	-4083	-906	27
H(16)	9551	-3666	-460	21
H(18)	5215	-1285	-374	15
H(19)	4699	-3466	-725	16
H(20)	5442	-5581	-479	15
H(21A)	4676	6414	2954	22
H(21B)	4998	5247	2665	22
H(22A)	5774	5827	3361	26
H(22B)	6080	4640	3073	26
H(23A)	5305	3552	3549	38
H(23B)	4842	3354	3161	38
H(23C)	4537	4540	3449	38
H(24A)	8618	5229	2834	26
H(24B)	9036	6538	3046	26
H(25A)	7586	5121	3273	64
H(25B)	7937	6513	3476	64
H(26A)	8344	4442	3800	113
H(26C)	9136	5241	3641	113
H(26B)	8791	3850	3436	113
H(3)	8959(14)	-2480(20)	69(6)	12(6)
H(4)	6390(15)	-4710(30)	-8(7)	22(6)

Table 6. Hydrogen bonds for AS1A [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(4)-H(4)...N(1)#1	0.88(3)	2.16(3)	3.042(2)	175(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+3/2,y-1/2,z