Supplementary Material (ESI) for Chemical Communications

Supporting Information

Highly Effective Phosphate Electrochemical Sensor Based On Tetrathiafulvalene

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1. Synthetic Experimental
2. CV Study
3. ^{1}H NMR spectra study:
4. X-ray crystallography

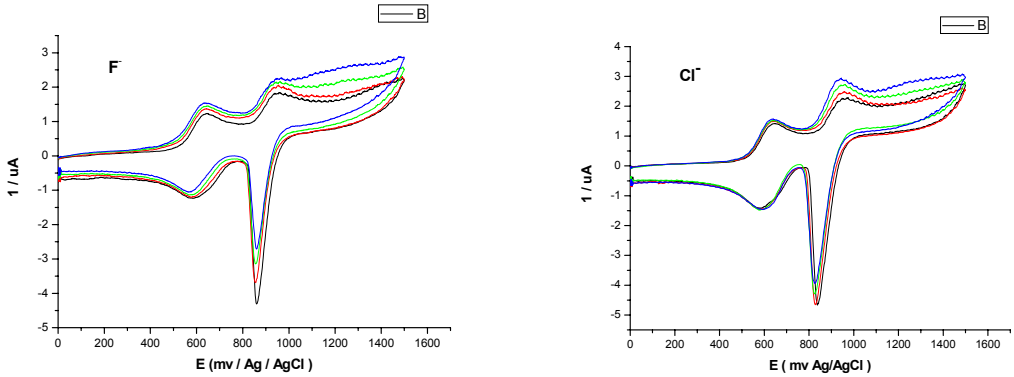
Supplementary Material (ESI) for Chemical Communications

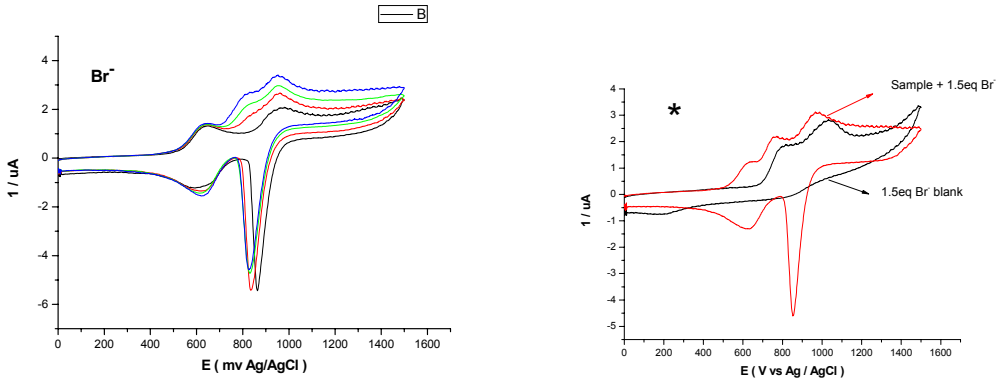
1. Synthetic Experimental

A solution of the acid chloride (100mg, 0.28mmol) in dry THF (10ml) was added dropwise to 2-aminopyridine (120mg, 1.25mmol) in dry THF (20ml), under magnetic stirring. The solution became clear and red precipitate was formed. After 4h of stirring at room temperature, the solvent was evaporated, and the red solid was dissolved in CH_2Cl_2 and washed with water, dried over $MgSO_4$, and filtered. Finally, the extracts were concentrated in vacuo, and the residue was subjected to column chromatography (silica gel, $CHCl_3$) affording **1** (68mg, 59%). ^{1}H NMR (DMSO-d_6) δ 11.00 (s, NH, 1H), 8.38 (d, J=3.27Hz, 1H), 8.13 (s, C=C-H, 1H), 7.97 (d, J=10.05Hz, 1H), 7.82 (t, J=7.59, 7.68Hz, 1H), 7.17(t, J=5.73, 5.46Hz, 1H), 2.50 (s, 6H) ppm; ^{13}C NMR: δ 158.2, 151.8, 148.5, 138.8, 133.7, 128.5, 127.3, 126.7, 120.6, 114.95, 113.2, 107.1,18.99ppm. MS m/z: 416[M^+].

2. CV Study

A. Titration experiments:





(* In the absence of the receptor, the Br^- ion undergoes oxidation in solution at a potential which is shown in CV [a])

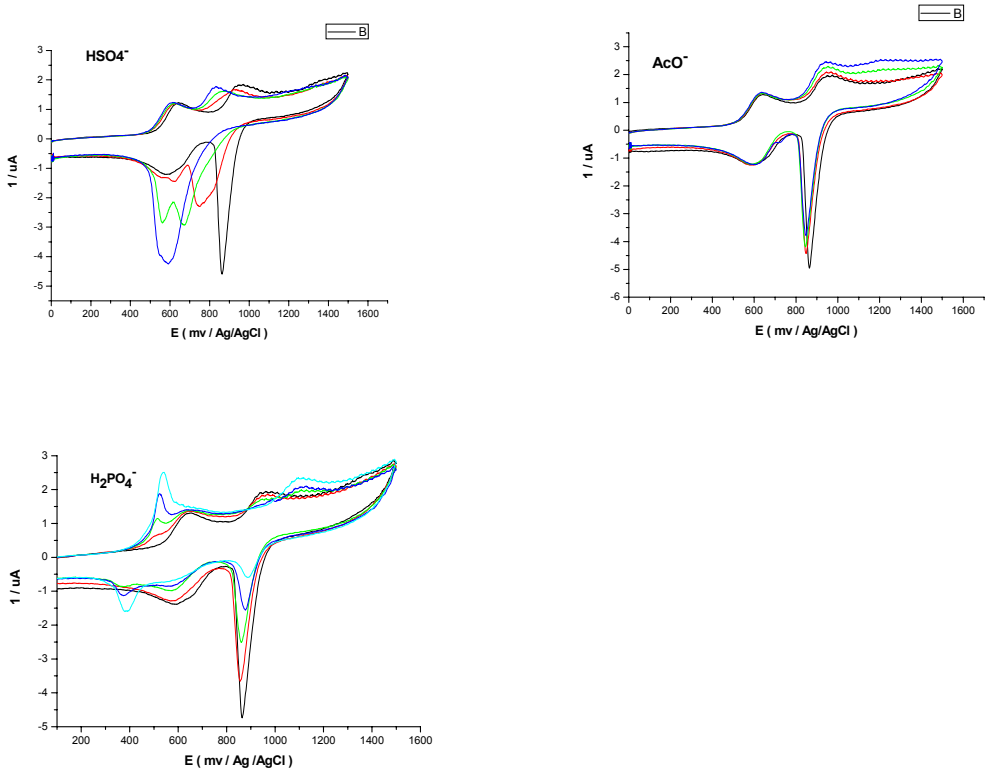
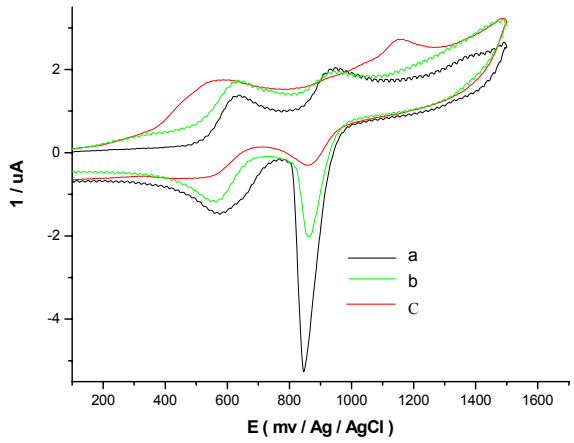


Figure 1. Cyclic Voltammograms of receptor **1** recorded in CH_2Cl_2 ($1.67x10^{-4}M$) and Bu_4NClO_4 (0.1M) as the supporting electrolyte in the increasing amounts of anions (0.5eq; 1eq; 1.5eq).

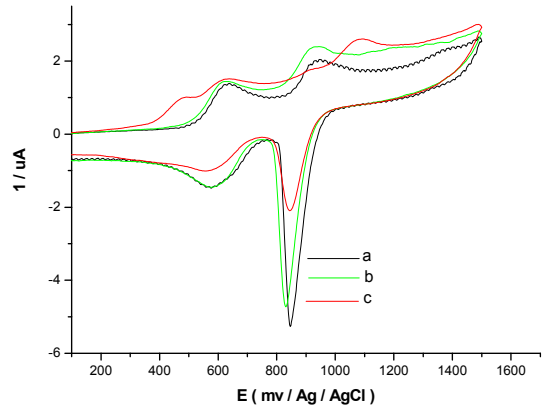
Reference:

a K. A. Nielsen, J. O. Jeppesen, E. Levillain, J. Becher, *Angew. Chem. Int. Ed.* **2003**, 42, 187.

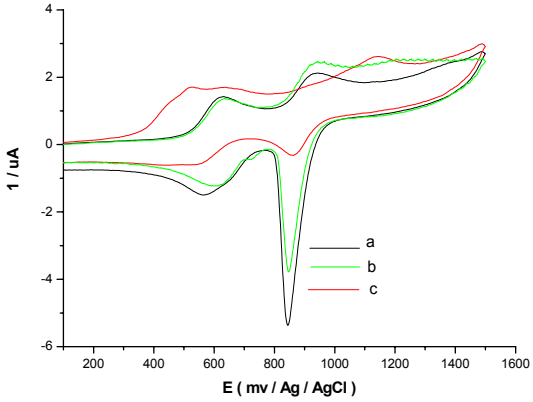
B. Competition experiments:



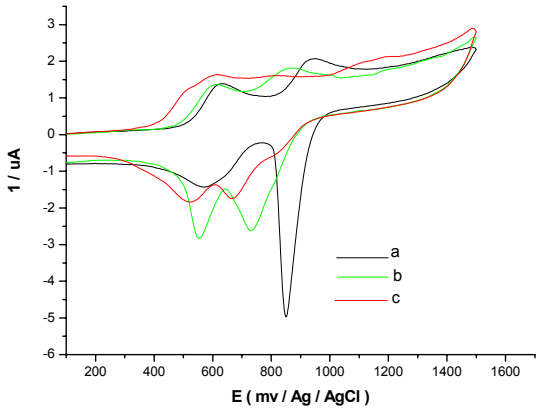
a. receptor **1**; **b**. receptor **1** upon addition of 1.5 equiv F^-; **c**. receptor **1** upon addition of 1.5 equiv $H_2PO_4^-$ in the presence of 1.5 equiv F^-.



a. receptor **1**; **b**. receptor **1** upon addition of 1.5 equiv Cl^-; **c**. receptor **1** upon addition of 1.5 equiv $H_2PO_4^-$ in the presence of 1.5 equiv Cl^-.



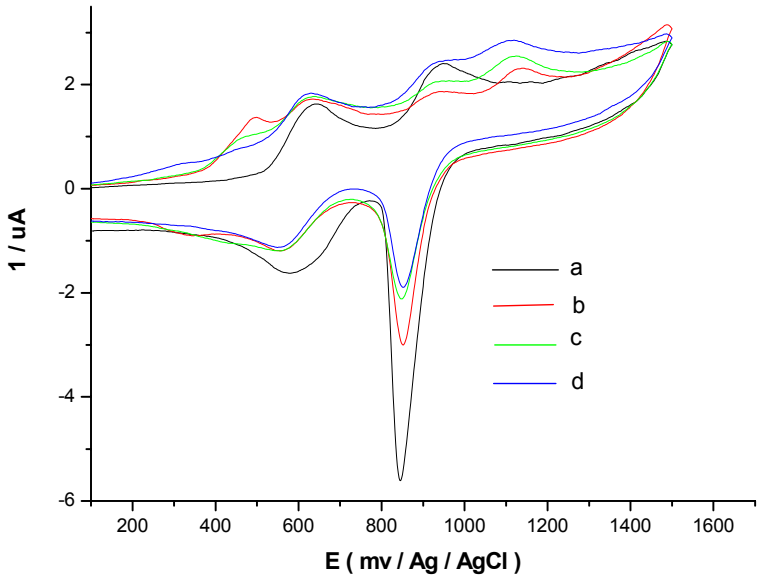
a. receptor **1**; **b**. receptor **1** upon addition of 1.5 equiv AcO^-; **c**. receptor **1** upon addition of 1.5 equiv $H_2PO_4^-$ in the presence of 1.5 equiv AcO^-.



a. receptor **1**; **b**. receptor **1** upon addition of 1.5 equiv HSO_4^-; **c**. receptor **1** upon addition of 1.5 equiv $H_2PO_4^-$ in the presence of 1.5 equiv HSO_4^-.

Figure 2. Cyclic Voltammograms of receptor **1** upon addition of 1.5 equiv $H_2PO_4^-$ recorded in CH_2Cl_2 ($1.67x10^{-4}M$) in the presence of anions (1.5eq) and Bu_4NClO_4 (0.1M) as the supporting electrolyte.

C. The effects of protonation on the CV behavoiur of **1**



a. receptor **1**; **b**. receptor **1** upon addition of 2 equiv $H_2PO_4^-$; **c**. receptor **1** upon addition of 1 equiv Bu_4NOH in the presence of 2 equiv $H_2PO_4^-$; **d.** receptor **1** upon addition of 2 equiv Bu_4NOH in the presence of 2 equiv $H_2PO_4^-$

Figure 3. Cyclic Voltammograms of receptor **1** upon addition of 2 equiv $H_2PO_4^-$ recorded in CH_2Cl_2 ($1.67x10^{-4}M$) in the presence of Bu_4NOH (1eq, 2eq) and Bu_4NClO_4 (0.1M) as the supporting electrolyte.

5. ^1H NMRspectra study:

a. The stoichiometry of receptor 1 – $H_2PO_4^-$ Complex (Job Plots)

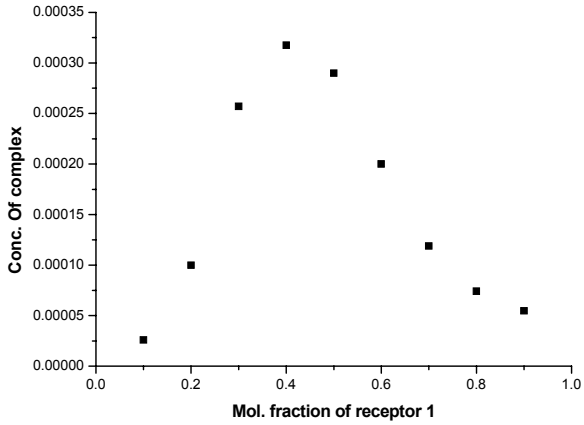


Figure 4. Job plot for the mixtures of 1 and $H_2PO_4^-$ ([1] + [G] = $5x10^{-3}M$) in $CDCl_3$. the solution of **1** ($5x10^{-3}$) and $H_2PO_4^-$ ($5x10^{-3}$) in DMSO-d_6 were prepared in separate volumetric flasks. The chemical shift of C=C-**H** of TTF unit was monitored as a function of mole fractions of receptor **1**.

b. Partial ^1H NMR Spectra (300MHz) recorded in DMSO-d_6.

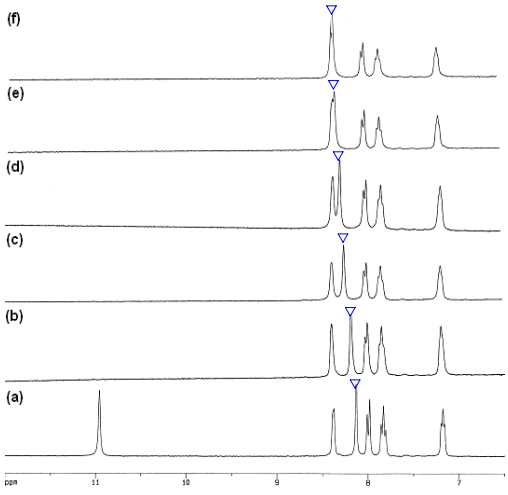


Figure 5. ^1H NMR titrations curves of the peturbation of receptor **1** ($8x10^{-3}$mol L^{-1}) in DMSO-d_6 upon addition of increasing amounts of $H_2PO_4^-$ (0.5eq, 1eq, 1.5eq, 2eq).

4. X-ray crystallography

The crystallographic detail about data collection and structure refinement are summarized in Table 1. The diffraction data were collected at 293K for the compound **1** on a Rigaku R-AXIS RAPID IP area detector. Structures were solved by direct methods using SHELX-97 and refined by the full-matrix least-squares method on F^2 using SHELXL-97 program. All non-hydrogen atoms were treated anisotropically. And the hydrogen atoms were introduced at calculated positions. The atomic coordinations, calculated hydrogen coordinates, full bond lengths and angle, and the displacement parameters are listed in the following tables.

Table 1. Crystal data and structure refinement for compound **1** .

Identification code	1
Empirical formula	$C_{14}\ H_{12}\ N_2\ O\ S_6$
Formula weight	416.62
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 10.683(2) A alpha = 90 deg.
	b = 16.387(3) A beta = 90.98(3) deg.
	c = 10.065(2) A gamma = 90 deg.
Volume	1761.7(6) $Å^3$
Z, Calculated density	4, 1.571 g/cm^3
Absorption coefficient	0.779 mm^{-1}
F(000)	856
Crystal size	0. 68x 0.49 x 0.40 mm
Theta range for data collection	1.91 to 27.40 deg.
Limiting indices	-13<=h<=13, 0<=k<=21, -13<=l<=0
Reflections collected / unique	3989 / 3989 [R(int) = 0.0000]
Completeness to theta = 27.40	99.4 %
Absorption correction	Empirical
Max. and min. transmission	1.1753 and 0.7991
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3989 / 0 / 208
Goodness-of-fit on F^2	1.010
Final R indices [I>2sigma(I)]	R1 = 0.0399, wR2 = 0.1051
R indices (all data)	R1 = 0.0537, wR2 = 0.1106
Largest diff. peak and hole	0.516 and -0.456 $d/e{\cdot}Å^{-3}$

Table 2. Bond lengths [Å] and angles [deg] for compound **1**.

S(1)-C(9)	1.753(2)	N(1)-C(5)	1.325(3)
S(1)-C(7)	1.757(2)	N(1)-C(1)	1.344(3)
S(2)-C(8)	1.713(2)	N(2)-C(6)	1.354(3)
S(2)-C(9)	1.760(2)	N(2)-C(5)	1.406(2)
S(3)-C(11)	1.743(2)	C(1)-C(2)	1.376(3)
S(3)-C(10)	1.751(2)	C(2)-C(3)	1.363(3)
S(4)-C(10)	1.751(2)	C(3)-C(4)	1.381(3)
S(4)-C(12)	1.759(2)	C(4)-C(5)	1.389(3)
S(5)-C(12)	1.743(2)	C(6)-C(7)	1.472(3)
S(5)-C(14)	1.767(3)	C(7)-C(8)	1.340(3)
S(6)-C(11)	1.742(2)	C(9)-C(10)	1.342(3)
S(6)-C(13)	1.778(3)	C(11)-C(12)	1.346(3)
O(1)-C(6)	1.227(2)		

C(9)-S(1)-C(7)	94.43(9)	N(2)-C(6)-C(7)	116.45(18)
C(8)-S(2)-C(9)	94.69(10)	C(8)-C(7)-C(6)	128.39(19)
C(11)-S(3)-C(10)	95.84(10)	C(8)-C(7)-S(1)	116.53(16)
C(10)-S(4)-C(12)	95.17(10)	C(6)-C(7)-S(1)	115.02(14)
C(12)-S(5)-C(14)	103.14(14)	C(7)-C(8)-S(2)	118.97(16)
C(11)-S(6)-C(13)	103.43(12)	C(10)-C(9)-S(1)	124.31(16)
C(5)-N(1)-C(1)	116.7(2)	C(10)-C(9)-S(2)	121.14(15)
C(6)-N(2)-C(5)	127.33(18)	S(1)-C(9)-S(2)	114.55(11)
N(1)-C(1)-C(2)	123.7(2)	C(9)-C(10)-S(4)	124.57(16)
C(3)-C(2)-C(1)	118.1(2)	C(9)-C(10)-S(3)	120.86(16)
C(2)-C(3)-C(4)	120.4(2)	S(4)-C(10)-S(3)	114.56(11)
C(3)-C(4)-C(5)	117.0(2)	C(12)-C(11)-S(6)	123.35(17)
N(1)-C(5)-C(4)	124.15(19)	C(12)-C(11)-S(3)	117.07(18)
N(1)-C(5)-N(2)	112.36(18)	S(6)-C(11)-S(3)	119.57(14)
C(4)-C(5)-N(2)	123.5(2)	C(11)-C(12)-S(5)	123.71(19)
O(1)-C(6)-N(2)	123.81(19)	C(11)-C(12)-S(4)	117.29(17)
O(1)-C(6)-C(7)	119.74(19)	S(5)-C(12)-S(4)	118.98(14)

Table 3. Hydrogen coordinates (Å x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for compound **1**.

	x	y	z	U(eq)
H(2B)	10287	2615	4399	53
H(1A)	13820	3829	4459	68
H(2A)	15013	3250	2838	64
H(3A)	14125	2272	1475	56
H(4A)	12046	1890	1761	50
H(8A)	8509	2522	5155	47
H(13A)	824	565	6607	120
H(13B)	1587	1225	5837	120
H(13C)	2291	553	6670	120
H(14A)	1012	-530	258	152
H(14B)	2047	147	227	152
H(14C)	1004	179	1303	152

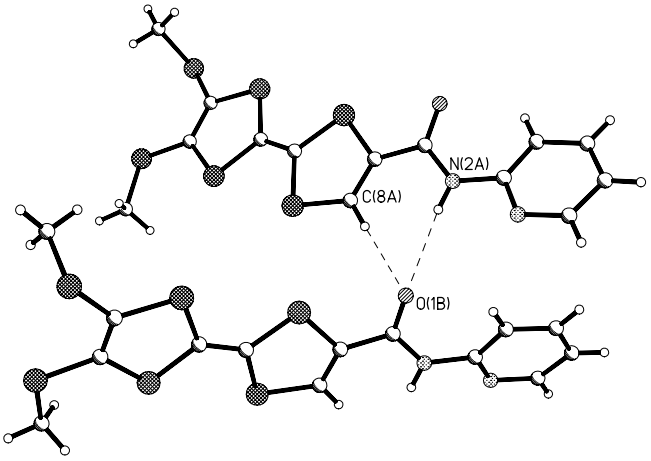


Figure 6. Intermolecular hydrogen bonds in the crystal of compound **1** (N(2)–H(2)···O(1)^i, C(8)–H(8)···O(1)^i, *i*: *x*, 0.5-*y*, 0.5+*z*).

Table 4. Intermolecular hydorgen bonds in the crystal of compound 1.

D	H	A	D-H(Å)	H...A(Å)	D...A(Å)	D-H...A(º)	Symop_for_A
N2	H2B	O1	0.86	2.48	3.339(2)	173	x,1/2-y,1/2+z
C8	H8A	O1	0.93	2.30	3.220(3)	173	x,1/2-y,1/2+z