Electronic Supporting Information

for

Modelling the Reduced Xanthine Oxidase in Active Sulfo and Inactive Desulfo Forms

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1. Table S1: X-Ray Crystallographic Parameters of 1a and 1b

Complex	**1a**	**1b**
Empirical Formula	$C_{37}H_{50}Mo$ N_5OS_3	$C_{39}H_{51}Mo$ $N_5OS_3.H_2O$
Formula Wt.	773.98	1602.00
Crystal System	Triclinic	Monoclinic
Space Group	P-1	C2/c
Temperature (K)	293	293
Z	2	4
a (Å)	9.436 (5)	34.781 (5)
b (Å)	11.629 (5)	13.822 (5)
c (Å)	19.400 (5)	17.232 (5)
α (^{0})	79.233 (5)	90
β (^{0})	75.964 (5)	103.548 (5)
γ (^{0})	83.538 (5)	90
V $(Å)^3$	2023.81 (15)	8053.65 (3)
Dcalc(gcc^{-1})	1.270	1.321
F000	812.0	3360
Absorption (mm^{-1})	0.512	0.518
Theta Range (^{0})	2.23-27.00	2.09-28.00
GOF (F^2)	0.96	1.042
R_1[a] (wR_2[b]), %	6.86 (23.08)	8.67 (26.09)

[a] $R_1=\Sigma||F_0| - |F_c||/ \Sigma||F_0|$ [b] $wR_2=\{ \Sigma[w(F_0^2 - F_c^2)^2]/ \Sigma w(F_0^2)^2]\}^{1/2}$

2. Table S2: X-Ray Crystallographic Parameters of 2a and 2b

Compound	**2a**	**2b**
Empirical Formula	$C_{30}H_{45}MoN_5OS_3$	$C_{32}H_{45}MoN_5OS_3$
Formula Weight	683.86	707.88
Crystal System	Tetragonal	Monoclinic
Space Group	Pca21	P21/c
Temperature (K)	293(2)	293(2)
Z	4	4
a(Å)	21.844(5)	16.381(5)
b(Å)	9.699(5)	8.671(5)
c(Å)	16.066(5)	25.304(5)
$\alpha(^0)$	90.00	90.00
$\beta(^0)$	90.00	106.757(5)
$\gamma(^0)$	90.00	90.00
V($Å^3$)	3403.82(2)	3441.55(2)
D calc (g cc^{-1})	1.334	1.366
F (000)	1432	1480
Absorption (mm^{-1})	0.599	0.595
Theta Range (^{0})	2.10 – 28.35	2.40 – 27.75
GOOF (F^2)	1.091	0.998
$R_1{}^a$ (%)	5.56	7.19
$wR_2{}^b$(%)	21.20	26.67

$^aR_1=\Sigma||F_0| - |F_c||/ \Sigma|F_0|$ $^bwR_2=\{ \Sigma[w(F_0^2 - F_c^2)^2]/ \Sigma w(F_0^2)^2]\}^{1/2}$

3. Table S3: Relevant bond distances and angles:

Relevant bond distances and angles of **1a** – **2b** and the native inhibited Moco in XO.

Parameters		**1a**	**1b**	**2a**	**2b**	**Native**[7]
Distances (Å)	Mo-O	1.689(4)	1.692(5)	1.681(5)	1.673(5)	1.673
	Mo-S(H) / Mo-S_{thiol}	2.428(2)	2.421(2)	2.457(2)	2.456(2)	2.393
	Mo-S_{avg}	2.410	2.421	2.405	2.393	2.393
	Mo-N	2.256	2.263	2.254	2.260	2.280
Angles (°)	O-Mo-S(H)	103.06	104.37	103.78(16)	100.71(2)	110.56
	S-Mo-S	84.31	83.79	85.35(6)	84.81(6)	83.71

4. Best-fit Superposition of Oxypurinol Inhibited Moco of XO with 2a and 2b:

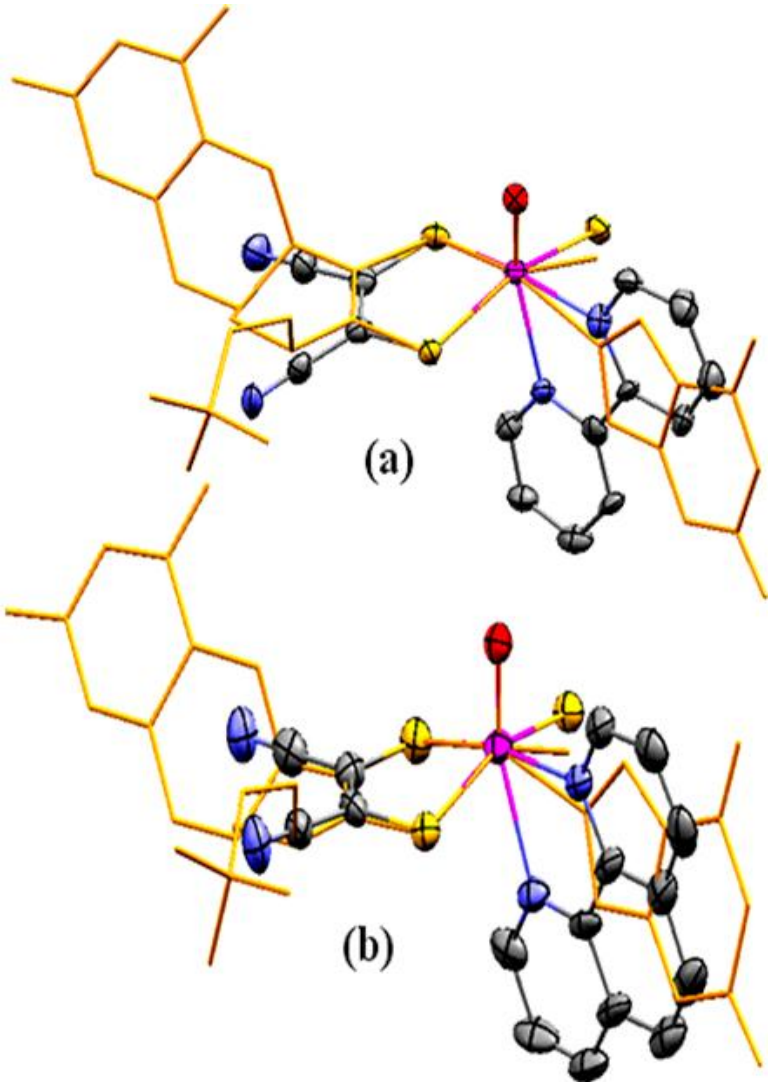

Figure S1. Best fit superposition of oxypurinol inhibited reduced XO [30] with (a) **2a** (RMS deviation 0.0543) and (b) **2b** (RMS deviation 0.0437). X-ray structural data for the enzyme in PDB format was obtained from the Brookhaven Protein Data Bank (PDB code 3BDJ). Native structure is shown in orange whereas ORTEP images of **2a** and **2b** are used.

5. Electronic Spectra of 1a and 1b.

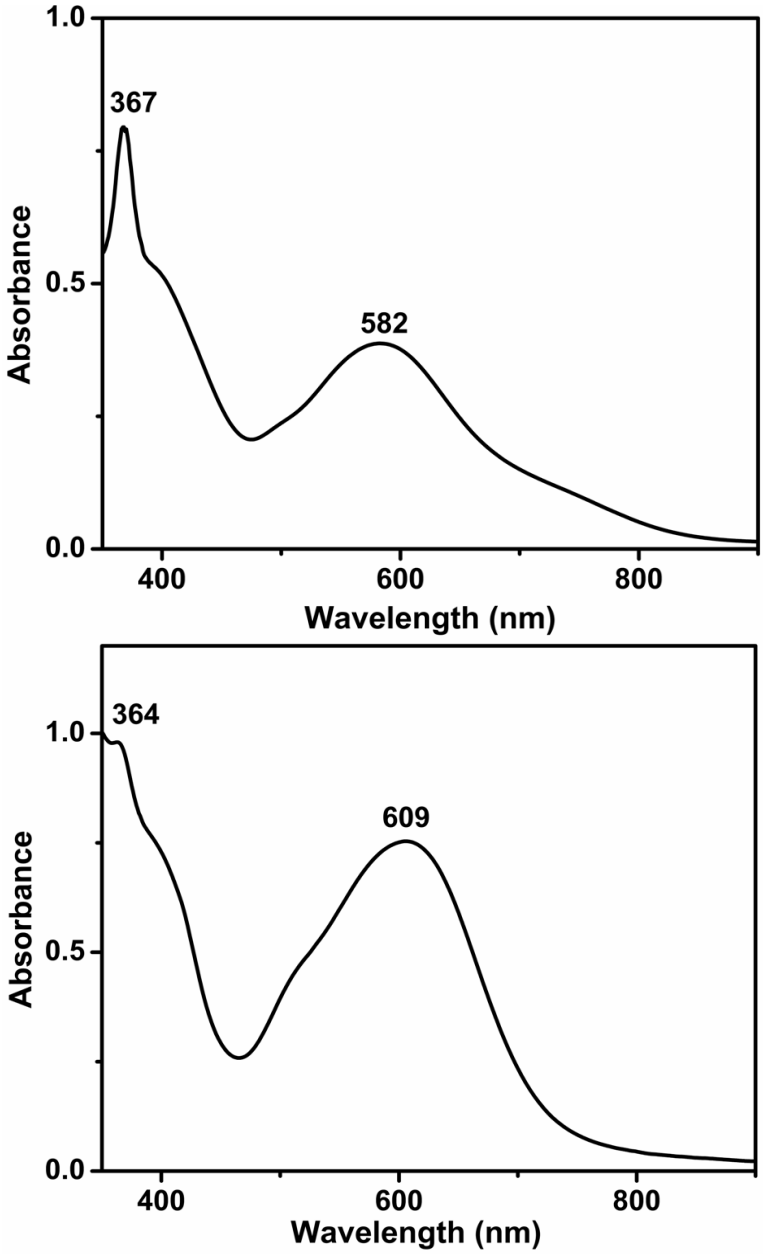

Figure S2: Electronic spectra of 10^{-4}M solution of **1a** and **1b** in DCM

6. Infrared Spectra:

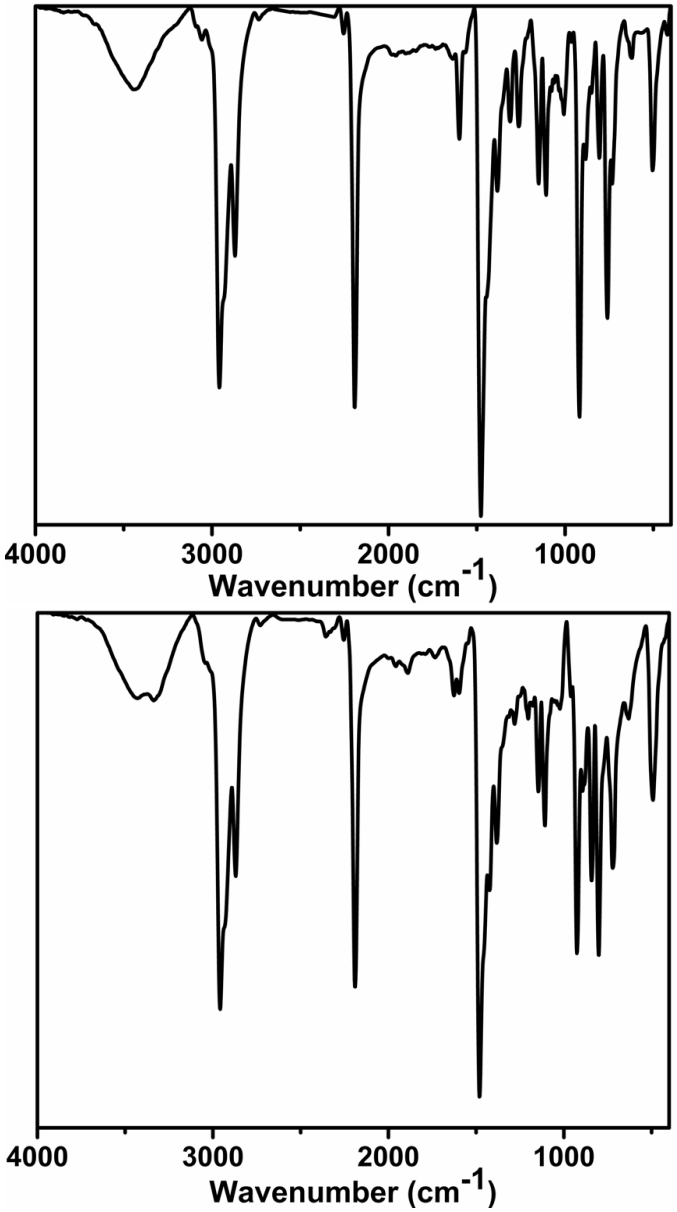

Figure S3: Infrared Spectra of **1a** and **1b** as pressed KBr discs.

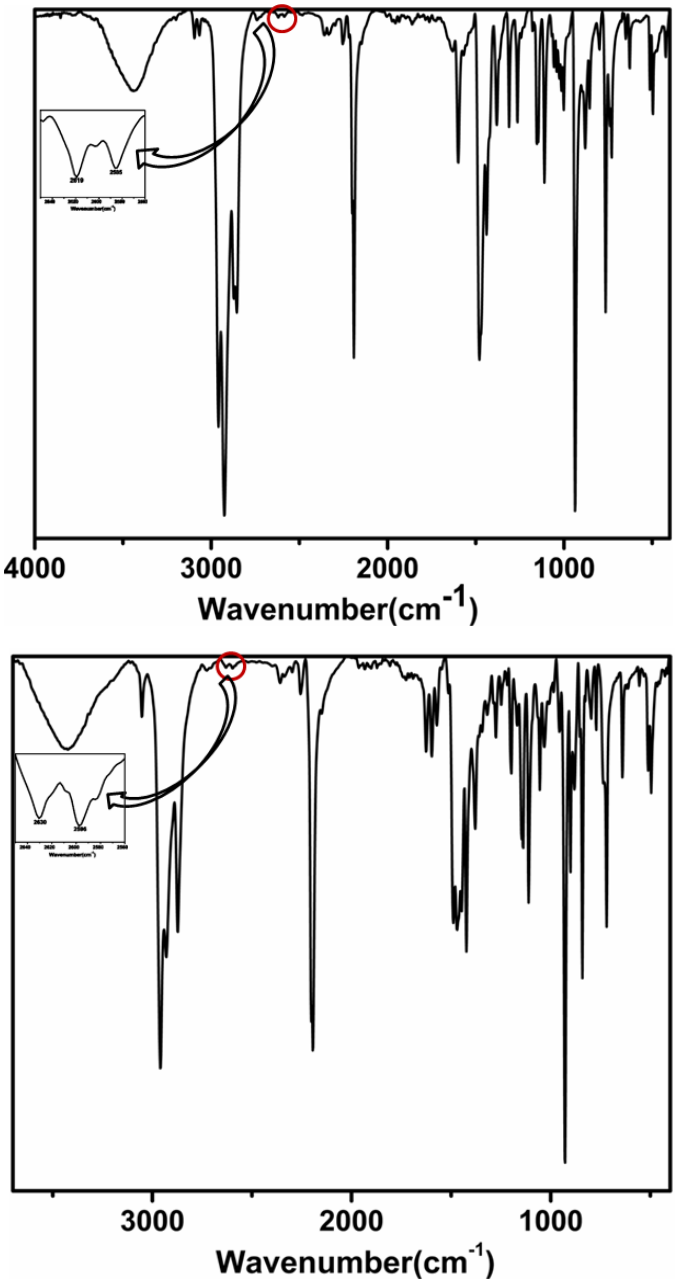

Figure S4: Infrared Spectra of **2a** and **2b** as pressed KBr discs. Stretching frequency due to –SH moiety is shown as inset.

7. Principal orbitals involved in MLCT and ILCT for 2a and 2b

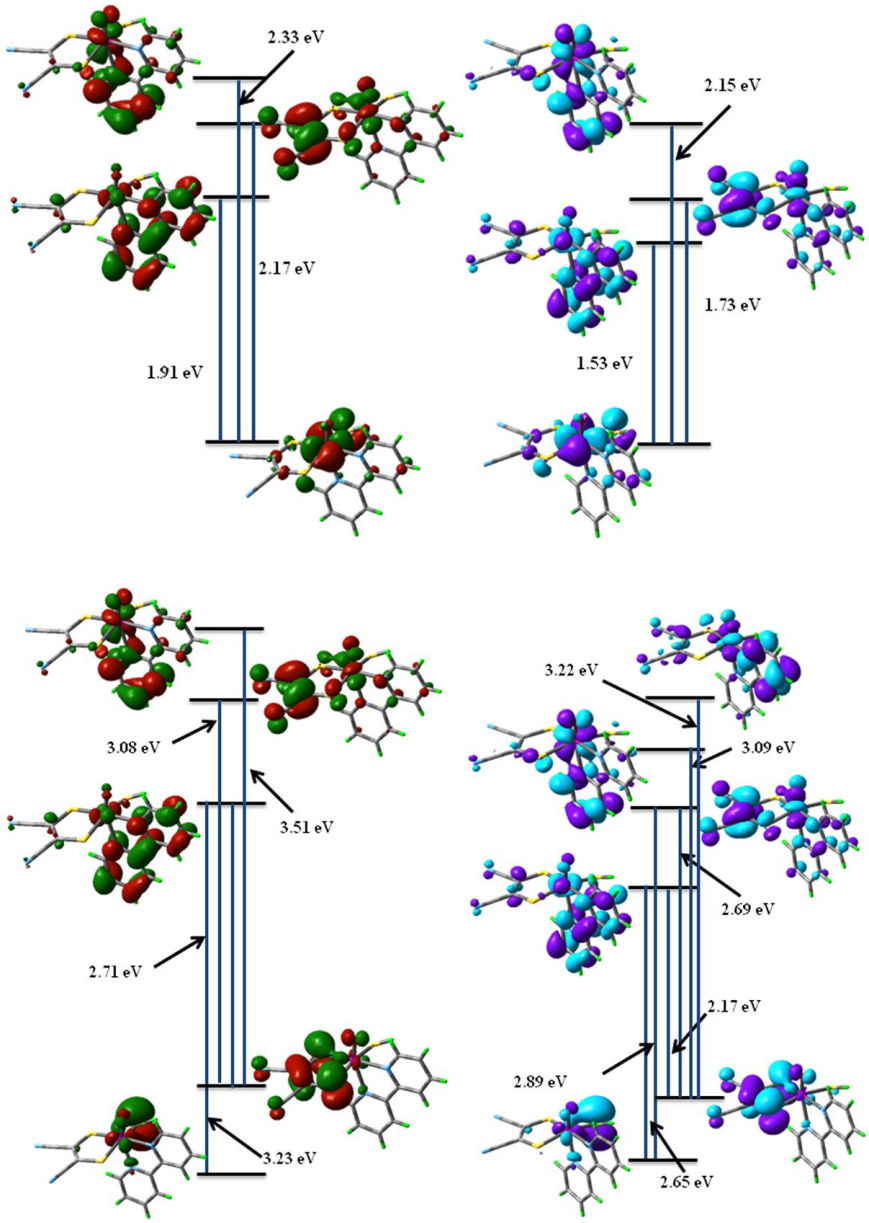

Figure S5: Principal orbitals involved in metal-to-ligand (Top Panel) and ligand-to-ligand (Bottom Panel) electronic transitions in **2a** calculated using B3LYP (red and green lobes) and BP86 (blue and purple lobes) functional. Isosurface cutoff value 0.04.

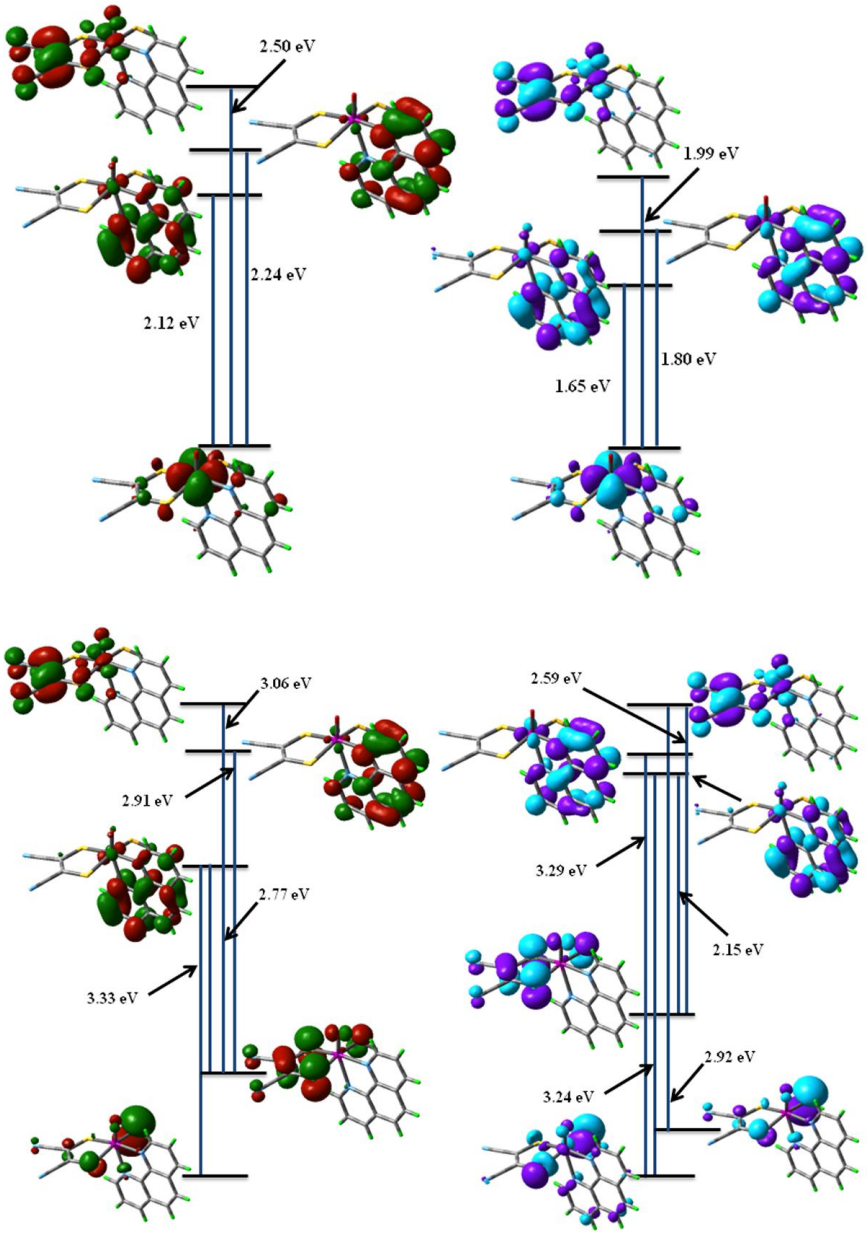

Figure S6: Principal orbitals involved in metal-to-ligand (Top Panel) and ligand-to-ligand (Bottom Panel) electronic transitions in **2b** calculated using B3LYP (red and green lobes) and BP86 (blue and purple lobes) functional. Isosurface cutoff value 0.04.

8. Proton Coupled Electron Transfer in 2a and 2b.

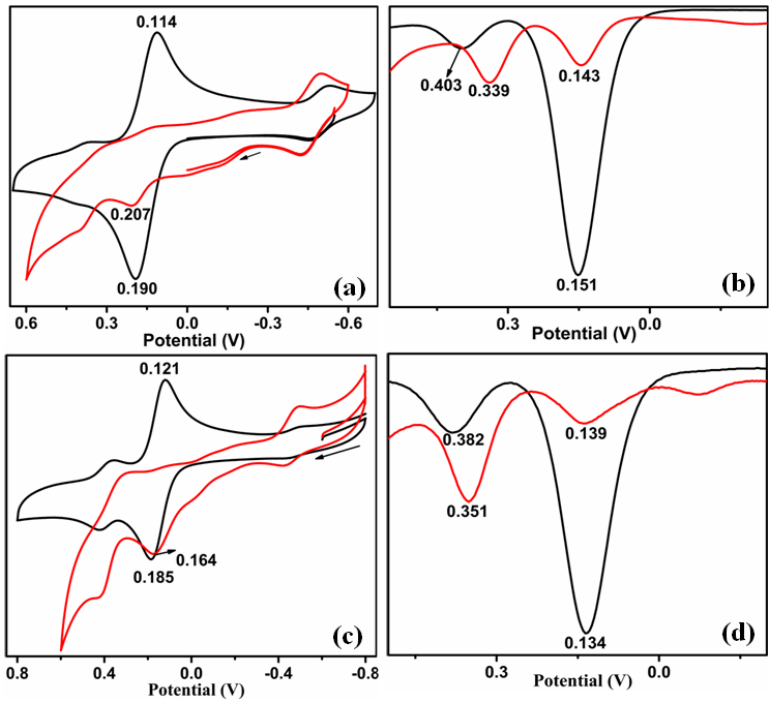

Figure S7. Changes occurring in the electrochemical responses of (a) **2a** and (c) **2b** on adding base in the solution. (b) and (d) depict the corresponding differential pulse polarograms of 2a and 2b respectively. Black and red traces indicate the electrochemical responses corresponding to original 2a and 2b and electrochemistry in basic medium respectively.

9. Complete reference of Ref. 44

M. J. Frisch; G. W. Trucks; H. B. Schlegel; G. E. Scuseria; M. A. Robb; J. R. Cheeseman; J. A. Montgomery, Jr.; T. Vreven; K. N. Kudin; J. C. Burant; J. M. Millam; S. S. Iyengar; J. Tomasi; V. Barone; B. Mennucci; M. Cossi; G. Scalmani; N. Rega; G. A. Petersson; H. Nakatsuji; M. Hada; M. Ehara; K. Toyota; R. Fukuda; J. Hasegawa; M. Ishida; T. Nakajima; Y. Honda; O. Kitao; H. Nakai; M. Klene; X. Li; J. E. Knox; H. P. Hratchian; J. B. Cross; V. Bakken; C. Adamo; J. Jaramillo; R. Gomperts; R. E. Stratmann; O. Yazyev; A. J. Austin; R. Cammi; C. Pomelli; J. W. Ochterski; P. Y. Ayala; K. Morokuma; G. A. Voth; P. Salvador; J. J. Dannenberg; V. G. Zakrzewski; S. Dapprich; A. D. Daniels; M. C. Strain; O. Farkas; D. K. Malick; A. D. Rabuck; K. Raghavachari; J. B. Foresman; J. V. Ortiz; Q. Cui; A. G. Baboul; S. Clifford; J. Cioslowski; B. B. Stefanov; G. Liu; A. Liashenko; P. Piskorz; I. Komaromi; R. L.

Martin; D. J. Fox; T. Keith; M. A. Al-Laham; C. Y. Peng; A. Nanayakkara; M. Challacombe; P. M. W. Gill; B. Johnson; W. Chen; M. W. Wong; C. Gonzalez; J. A. Pople *Gaussian 03* (Revision B.04); Gaussian, Inc.: Pittsburgh, PA, 2003.