Synthesis and Biological Evaluation of Copper(II) Pyrenethiosemicarbazone

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Supporting Information

Figure Captions:

Fig. S1 Changes in the electronic absorption spectra of (**A**) PyTSC and (**B**) CuPyTSC (20 μM) with increasing concentrations (0-300 μM) of CT-DNA (phosphate buffer, pH 7.2); the inset shows a fitting of the absorbance data at 360 nm for PyTSC and CuPyTSC used to obtain the binding constants.

Fig. S2 Photograph of 1% Agarose gel showing cleavage of plasmid pBR 322 DNA by PyTSC (A) and its copper complex (B) incubated at 37 ^{o}C for 30 min. [DNA] = 200 ng, (A) Lane 1 DNA control, Lanes 2-6, DNA + 10, 20, 30, 40, 50 μM PyTSC; (B) Lane 1: DNA control, Lanes 2 to 7, DNA + 5, 10, 20, 30, 40, 50 μM CuPyTSC

Fig. S3 Photograph of 1% Agarose gel showing cleavage of plasmid pBR 322 DNA by PyTSC incubated at 37^{o} C for 30 min followed by irradiation for 60 min. [DNA] = 200 ng, Lane 1 and 8, DNA control; Lanes 2-7, DNA + 5, 10, 15, 20, 25, 30 μM PyTSC.

Fig. S4 ESI-mass spectrum of PyTSC.

Fig. S5 ESI-mass spectrum of CuPyTSC.

Fig. S6 Frontier orbitals in (a) TSC, (b) Py and (c) PyTSC (isovalue of $\pm$0.54 eV). See text for details.

Fig. S7 Double-log plot to calculate the binding constant and number of binding site(s) for BSA - PyTSC (A) and BSA- CuPyTSC (B) interactions. the formation constant, K_a, was determined by the slope and number of binding sites from the intercept.

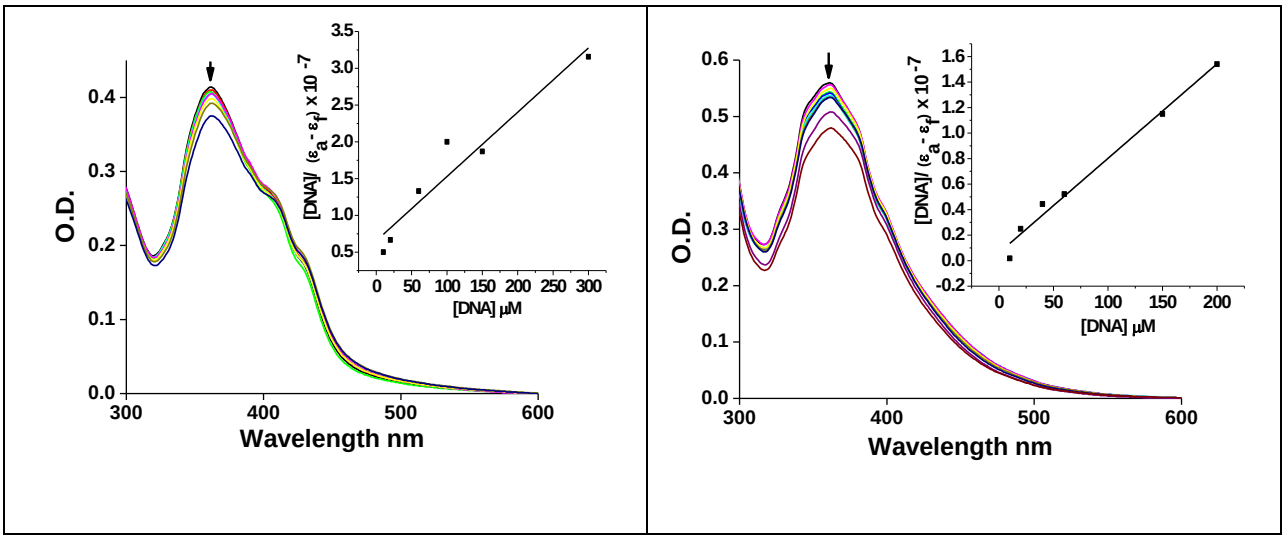

O.D.
Wavelength nm
[DNA]/ (εa - εf) x 10 -7
[DNA] μM
O.D.
Wavelength nm
[DNA]/ (εa - εf) x 10 -7
[DNA] μM

Fig. S1

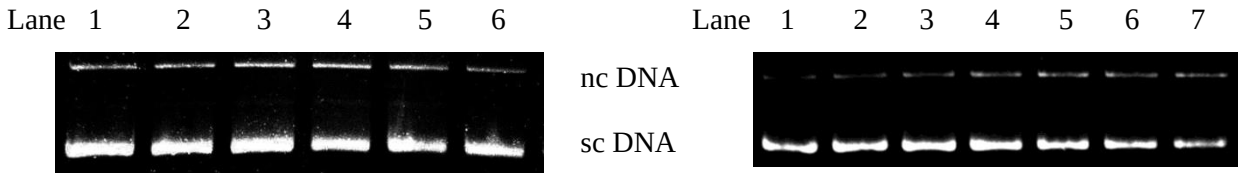

Lane 1 2 3 4 5 6
nc DNA
sc DNA
Lane 1 2 3 4 5 6 7

Fig. S2

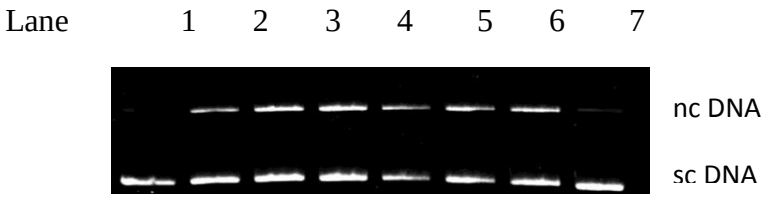
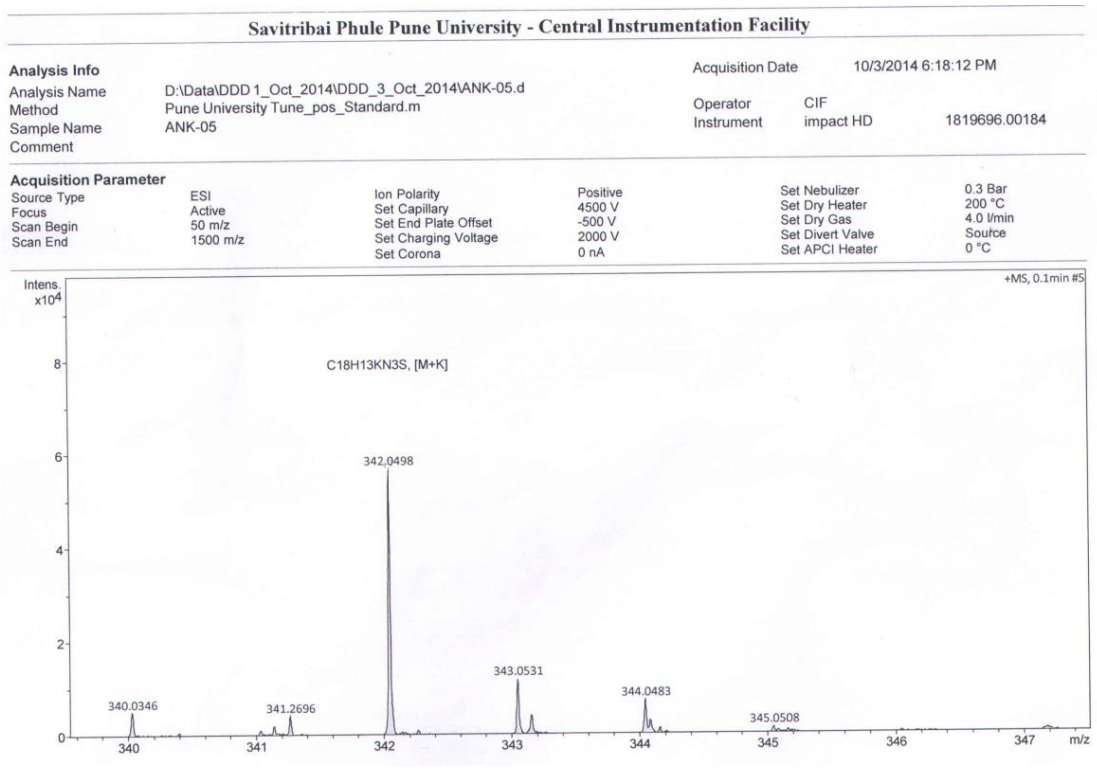

Lane 1 2 3 4 5 6 7
nc DNA
sc DNA

Fig. S3


Savitribai Phule Pune University - Central Instrumentation Facility
Analysis Info
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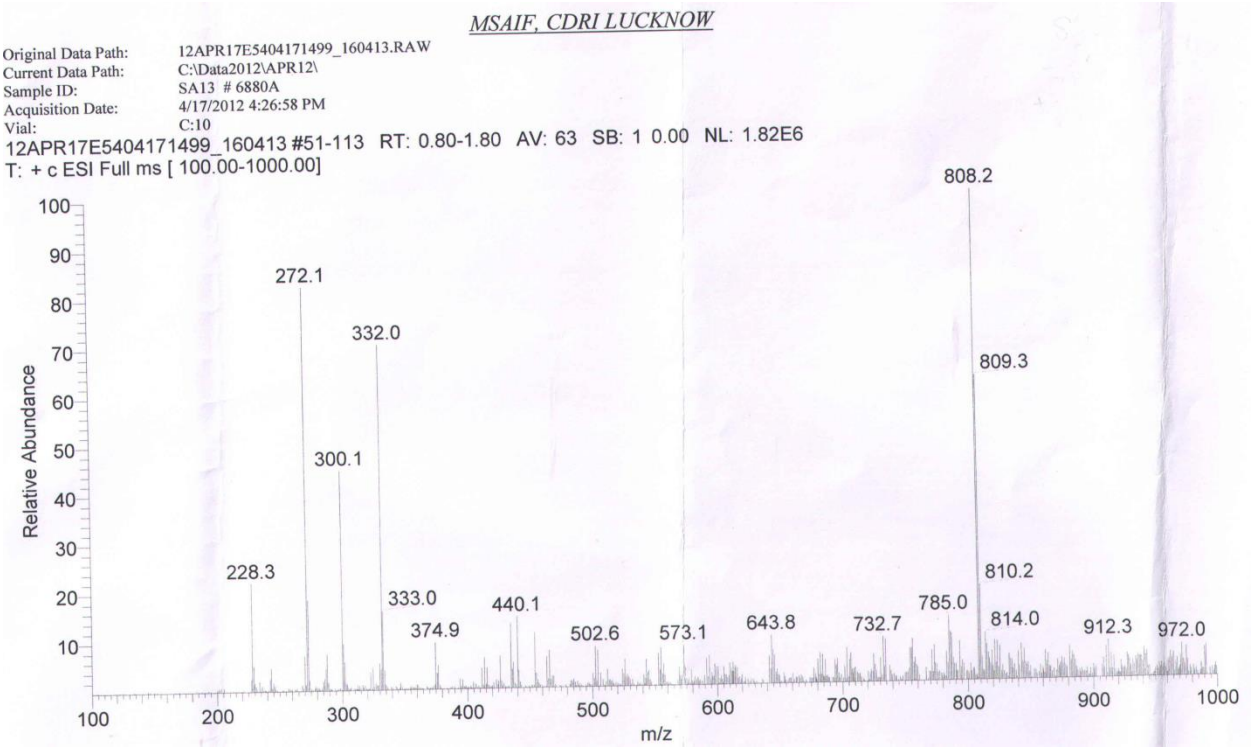
Sample Name ANK-05
Comment
Acquisition Date 10/3/2014 6:18:12 PM
Operator CIF
Instrument impact HD 1819696.00184
Acquisition Parameter
Source Type ESI
Focus Active
Scan Begin 50 m/z
Scan End 1500 m/z
Ion Polarity Positive
Set Capillary 4500 V
Set End Plate Offset -500 V
Set Charging Voltage 2000 V
Set Corona 0 nA
Set Nebulizer 0.3 Bar
Set Dry Heater 200 °C
Set Dry Gas 4.0 l/min
Set Divert Valve Source
Set APCI Heater 0 °C
+MS, 0.1min #5
Intens.
x10^4
C18H13KN3S, [M+K]
342.0498
343.0531
344.0483
340.0346
341.2696
345.0508
m/z

Fig. S4


MSAIF, CDRI LUCKNOW
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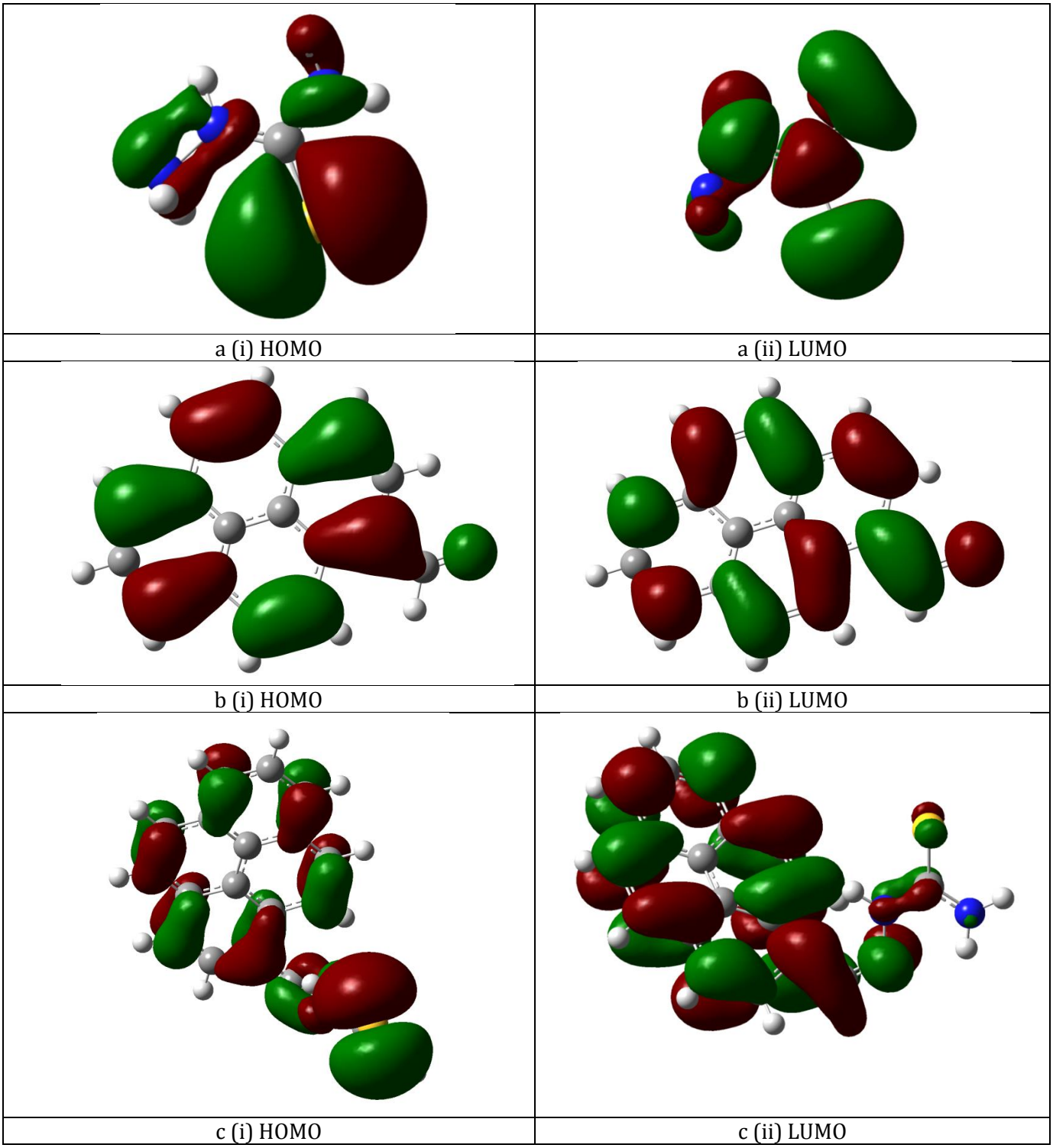
Current Data Path: C:\Data2012\APR12\
Sample ID: SA13 # 6880A
Acquisition Date: 4/17/2012 4:26:58 PM
Vial: C:10
12APR17E5404171499_160413 #51-113 RT: 0.80-1.80 AV: 63 SB: 1 0.00 NL: 1.82E6
T: + c ESI Full ms [100.00-1000.00]
808.2
272.1
332.0
809.3
300.1
228.3
810.2
333.0
440.1
785.0
374.9
814.0
912.3
972.0
502.6
573.1
643.8
732.7
Relative Abundance
m/z

Fig. S5



a (i) HOMO	a (ii) LUMO
b (i) HOMO	b (ii) LUMO
c (i) HOMO	c (ii) LUMO

Fig. S6

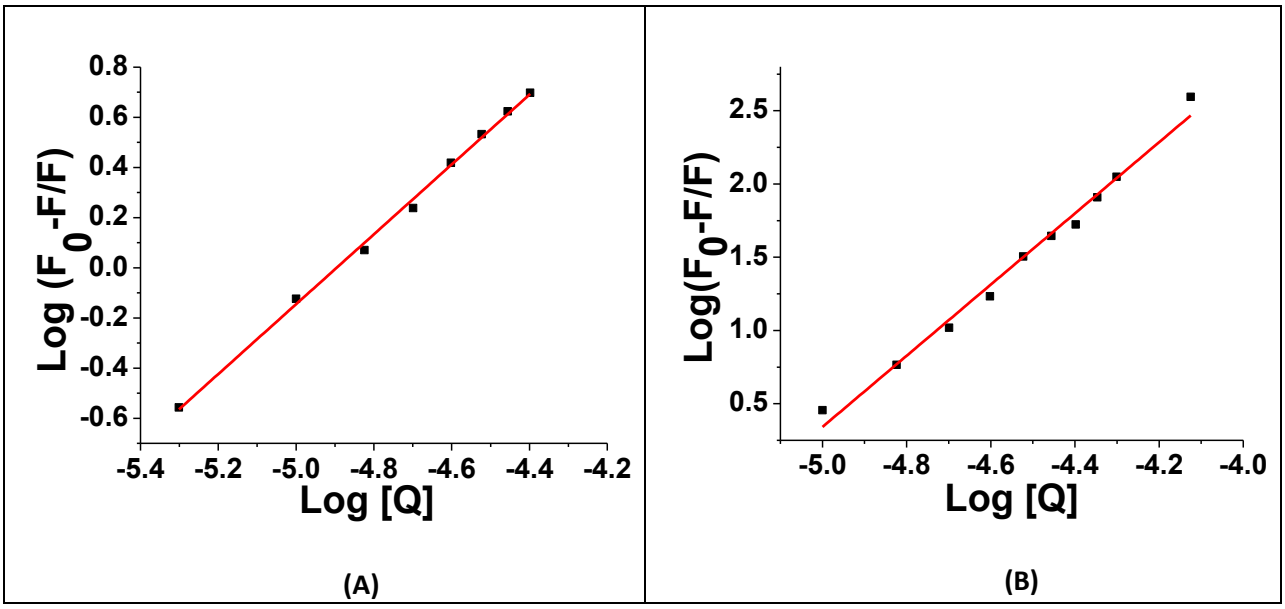

0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
Log (F0-F/F)
-5.4
-5.2
-5.0
-4.8
-4.6
-4.4
-4.2
Log [Q]
(A)
2.5
2.0
1.5
1.0
0.5
Log(F0-F/F)
-5.0
-4.8
-4.6
-4.4
-4.2
-4.0
Log [Q]
(B)

Fig. S7

Table S1: Selected bond- distances (in Å) and -angles (in ^{o}) of (a) 1-pyrenecarboxaldehyde and (b) 1-pyrenecarboxaldehyde thiosemicarbazone optimized at wB97x/6-31G (d, p).

	1-pyrenecarboxaldehyde	1-pyrenecarboxaldehyde thiosemicarbazone
C_{17}-H_{33}	1.112	1.089
C_{17}-O_{10}		1.212
C_{17}-N_{18}	1.280	
N_{19}-H_{22}	1.013	
C_{20}-S_{21}	1.666	
H_{33}-C_{17}-N_{18}	114	
H_{33}-C_{17}-O_{18}		119

Table S2: Selected vibrational frequencies (ν = Stretching) of 1-pyrenecarboxaldehyde and 1-pyrenecarboxaldehyde thiosemicarbazone.

Assignments	1-pyrenecarboxaldehyde	1-pyrenecarboxaldehyde thiosemicarbazone
ν C-H	2948 (175)	
ν C=O	1849(280)	
ν NH2		3812(112), 3655(83)
ν N-H		3626(51)
ν C-N		1652(395)

Table S3: Electrochemical data for PyTSC and CuPyTSC.

Compound	Oxidation peaks (V)	Assignment	Reduction peaks (V)	Assignment	Ref.
2-Pyrenylacetylene-thiophene(MeCN)	0.02,0.9	Irrversible oxidation of pyrene	-2.11, -1.56, -1.81	One electron reduction of pyrene moiety	1
2-Bromo, 5-pyrenylacetylene-thiophene (MeCN)	0.95,1.07	-- ” --	-1.84, -1.22	-- ” --	1
(5-(1-Pyrenylacetylene)-2-thiophene) carboxaldehyde(MeCN)	1.02	-- ” --	-	-- ” --	1
(5-(1-Pyrenylacetylene)-2-thiophene)ethylene Malonitrile	0.48,1.03	-- ” --	-1.64, -1.36, -1.10	-- ” --	1
2-Pyrenylacetylene-thiopheneDicobaltHexacarbonyl (MeCN)	0.56,0.92	-- ” --	-1.91, -1.71	-- ” --	1
2-Bromo, 5-pyrenylacetylene-thiopheneDicobaltHexacarbonyl(MeCN)	0.67,0.95, 1.02	-- ” --	-1.07,-1.19, -1.88,	-- ” --	1
(5-(1-Pyrenylacetylene)-2-thiophene) carboxaldehydeDicobaltHexacarbonyl(MeCN)	0.56,0.69	-- ” --	-1.48, -1.18, -1.09	-- ” --	1
(5-(1-Pyrenylacetylene)-2-thiophene)ethylene MalonitrileDicobaltHexacarb	0.92,0.71,	-- ” --	-1.37	-- ” --	1

onyl(MeCN)	0.56,0.36				
2MP ([2]metacyclo[2](2,7)pyrenophane) (MeCN)	1.18	-- ” --	-2.41	-- ” --	2
7P ([7](2,7)pyrenophane) (MeCN)	1.24	-- ” --	-2.32	-- ” --	2
4OP (4-oxa[7](2,7)pyrenophane) (MeCN)	1.26	-- ” --	-2.29	-- ” --	2
Pyrene (1:1 MeCN/PhH)	1.28	-- ” --	-2.16	-- ” --	2
1Nitro pyre (DMF)	--	--	-0.61	-- ” --	3
Buckminsterfullerene Ester (BE1) (THF)	--	--	-0.26	Pyrene radical anion	4
Buckminsterfullerene Ester (BE1)(CH_2Cl_2)	0.89	Radical cation of pyrene chromophore	-	-	4
PyTSC (DMF)	0.23	Radical cation of pyrene chromophore	-1.95, -1.65	One electron reduction of pyrene moiety	Present Work
CuPyTSC (DMF)	0.75,0.09	Metal-based oxidation-reduction peaks	-0.73, -1.1, -1.45	-- ” --	Present Work

All potentials are referenced against Ag/AgCl, MeCN = Acetonitrile, DMF = Dimethylformamide,THF = Tetrahydrofuran, PhH = Benzene, CH_2Cl_2 = Dichloromethane

References :

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2. R. Y. Lai, J. F. Fleming, B. L. Merner, R. J. Vermeij, G. J. Bodwell, and A. J. Bard, J. *Phys. Chem. A*, 2004, **108,** 376-383.

3. W. A. Lopes, P. D. de Paula Pereira, H. Viertler and J. B. de Andrade, *J. Braz. Chem. Soc.*, 2005, **16,** 1099-1103.

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