

A novel hybrid organic-inorganic silsesquioxane and cobalt(II) tetrasulphophthalocyanine material as an efficient electrochemical sensor for the simultaneous determination of the anti-hypertensive nifedipine and its metabolite

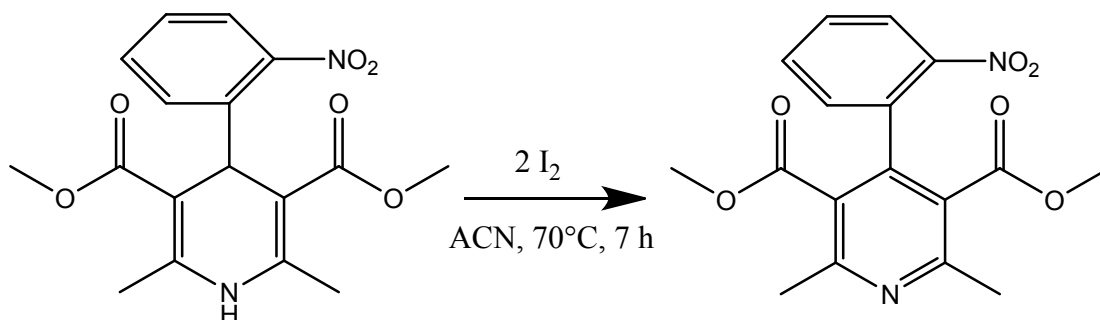
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SUPPLEMENTARY INFORMATION

Synthesis of dHNIF*

An amount of 48.3 mg (0.14 mmol) of NIF was added to a 25 mL round bottom flask with 10 mL of acetonitrile. Then 74.8 mg of molecular iodine (0.29 mmol) was added and the reaction mixture was refluxed in an oil bath for 7 hours. After reflux, the acetonitrile was rotaevapored forming a reddish oil. This oil was solubilized in approx. 50 mL of ethyl acetate and transferred to a separator funnel. 50 mL of sodium thiosulfate solution (0.1 mol L^{-1}) was added to remove excess iodine. The aqueous phase was extracted with ethyl acetate (8 x 50 mL). The recovered organic phase was dried with anhydrous sodium sulfate and rotaevaporated to give pale yellow crystals. Yield: 89.5%.

*Adapted from: R. F. Affeldt, R. S. Iglesias, F. S. Rodembusch and D. Russowsky. J. Phys. Org. Chem., 2012, 25, 769-777.



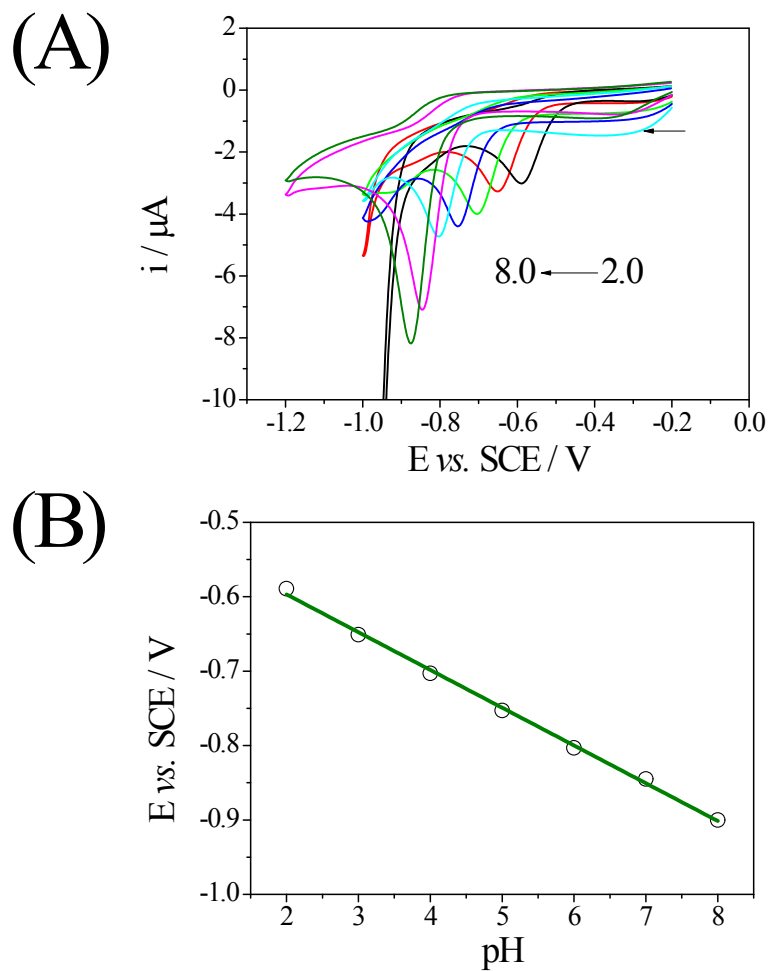


Fig. S1: (A) Cyclic voltammograms recorded in different 0.2 mol L⁻¹ B-R buffer solutions from pH 2.0 to 8.0 with fixed concentration of NIF 32 μ mol L⁻¹. (B) Variation of NIF reduction peak potential in function of pH value.

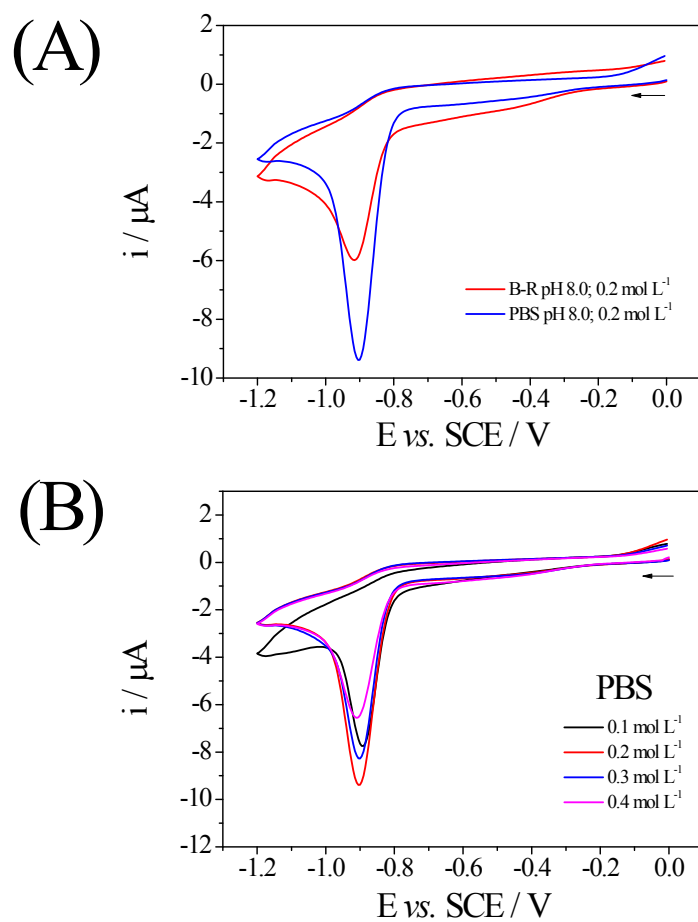


Fig. S2: (A) Cyclic voltammograms of NIF recorded in 0.2 mol L^{-1} B-R buffer solution and 0.2 mol L^{-1} PBS; (B) Cyclic voltammograms recorded in different PBS buffer concentrations varying from 0.1 to 0.4 mol L^{-1} . Experimental conditions: GCE/CoTsPc-Si4DMAP⁺Cl⁻, $\nu = 50 \text{ mVs}^{-1}$, NIF $30 \text{ } \mu\text{mol L}^{-1}$. pH 8.0.

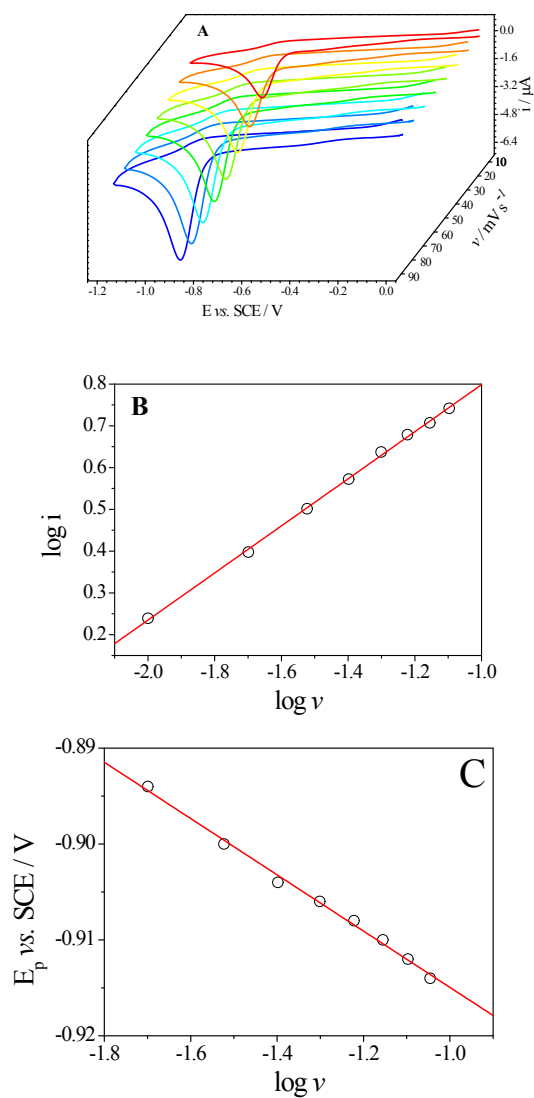
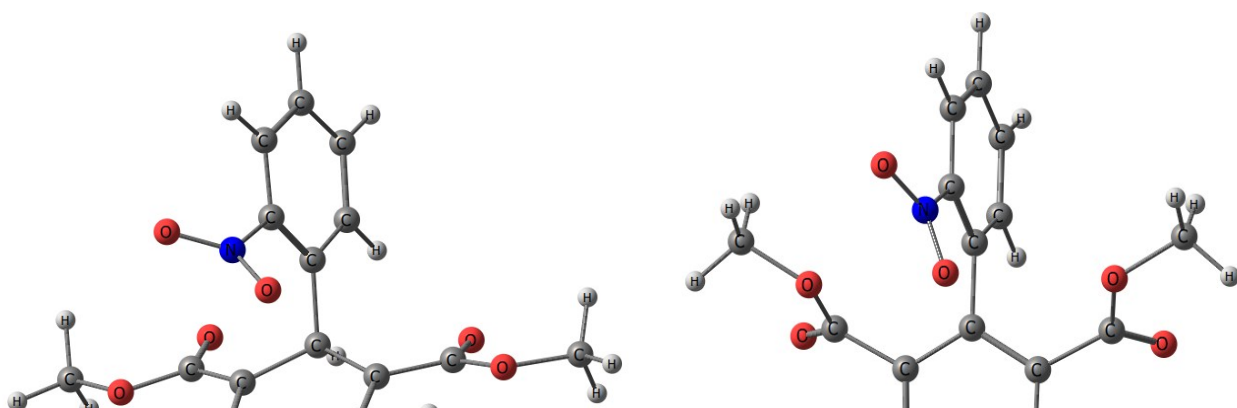


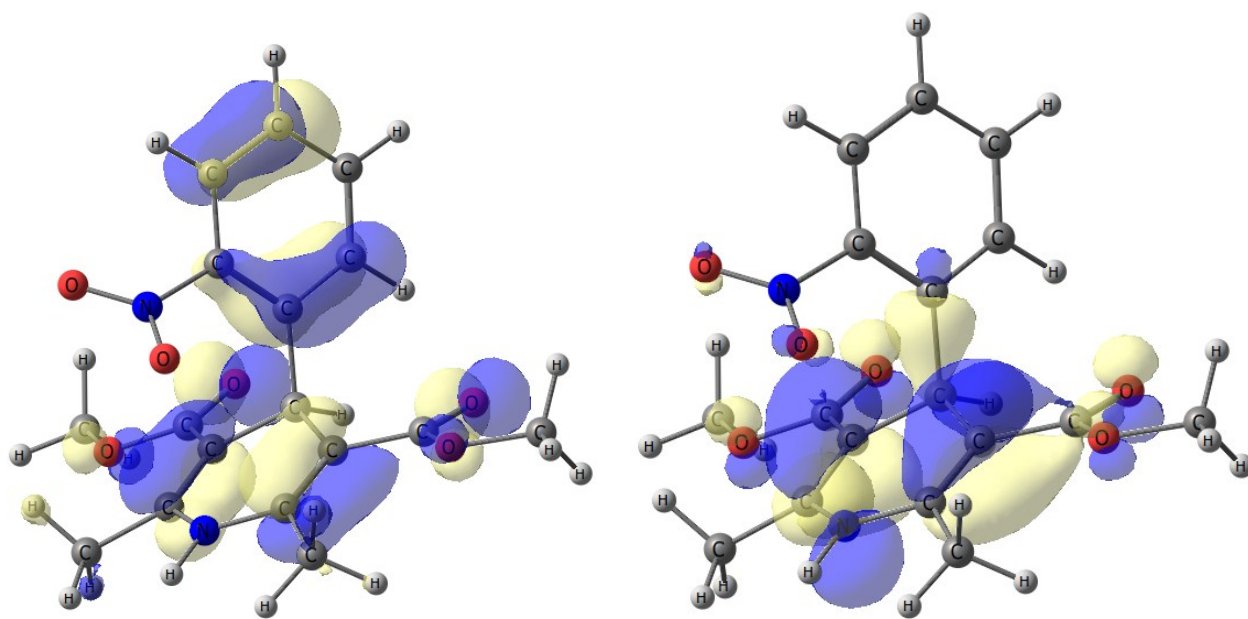
Fig. S3: (A) Cyclic voltammetry plots for NIF applying different scan rates from 10 to 80 mV s⁻¹; (B) Plot of logarithm of peak current vs. logarithm of scan rate; (C) Correlation of E_p vs. log v. Experimental conditions: GCE/CoTsPc-Si4DMAP⁺Cl⁻, v = 50 mVs⁻¹, NIF 30 μmol L⁻¹. PBS buffer, pH 8.0.



(A)

(B)

Fig. S4: Geometrical conformation of (A) NIF, structure 1, and (B) dHNIF, structure 2.



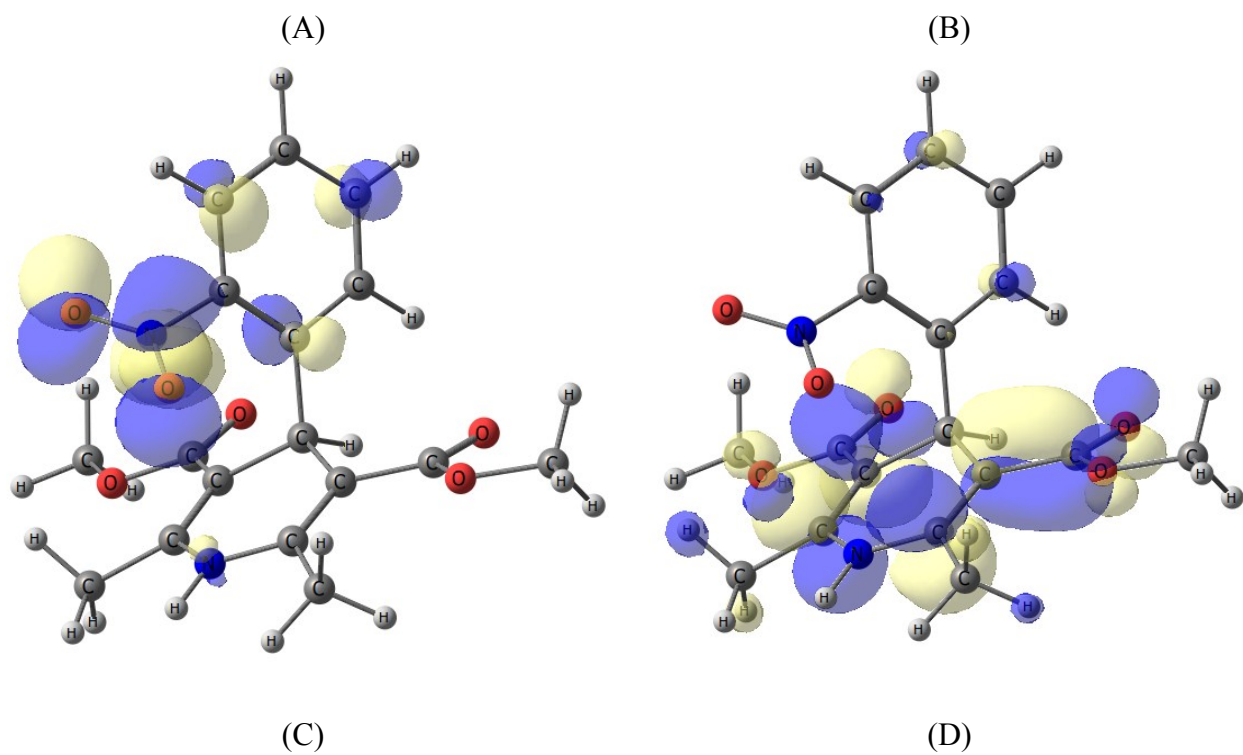
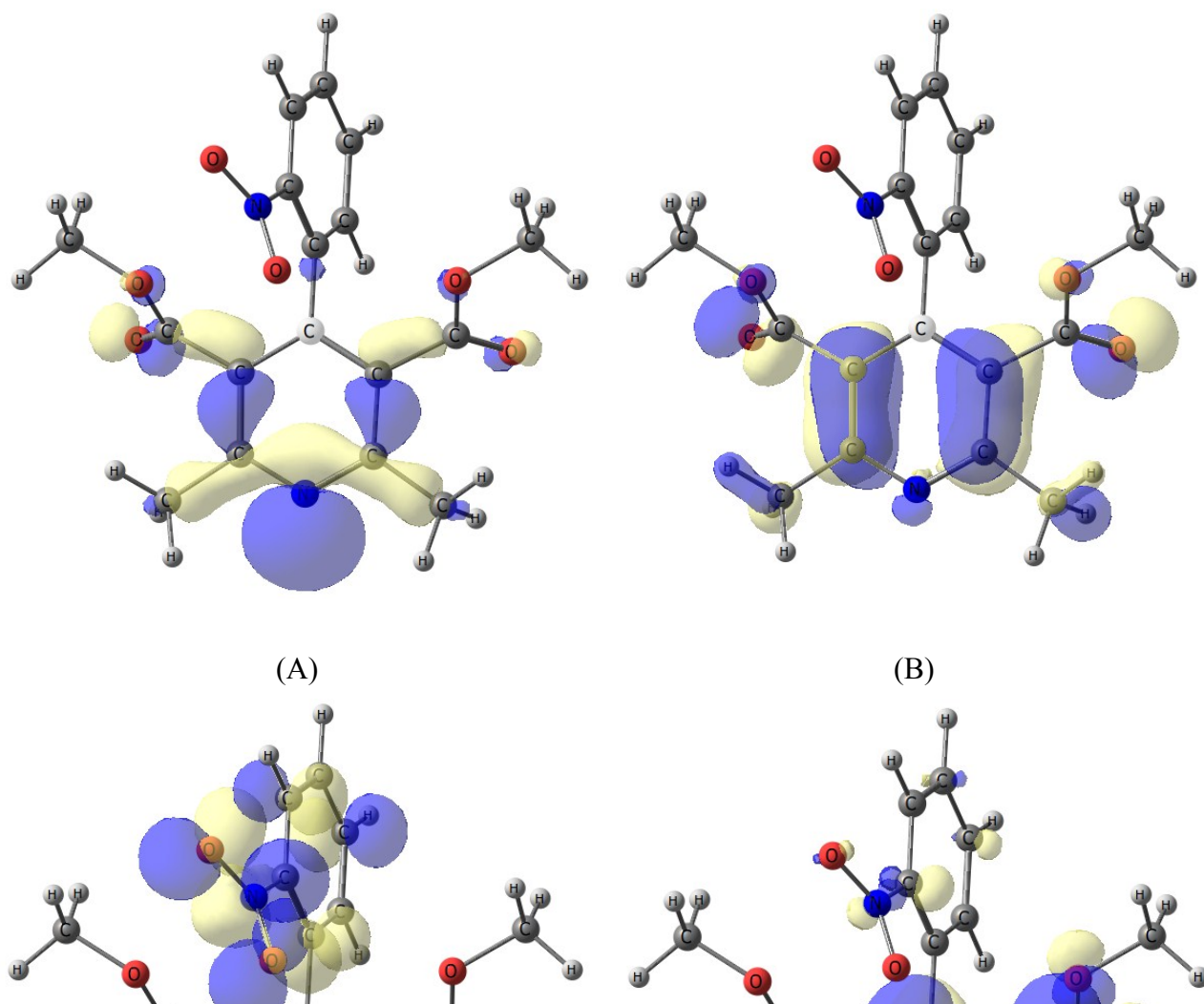


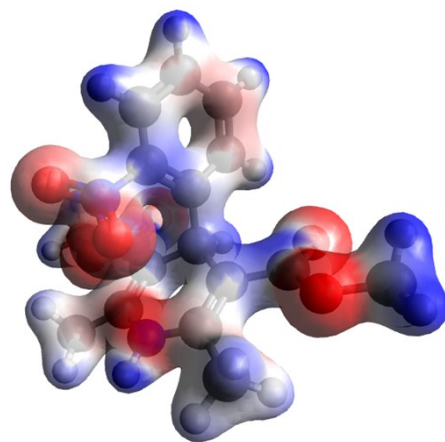
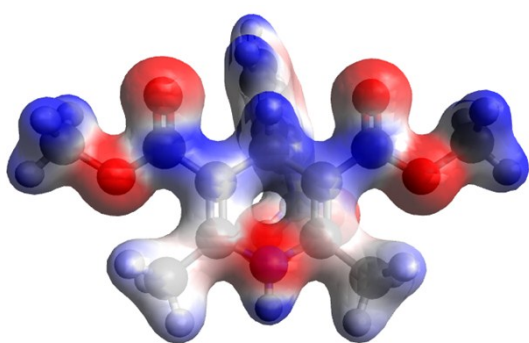
Fig. S5: Frontier orbitals of structure **1**, (A) HOMO-1, (B) HOMO, (C) LUMO, (D) LUMO+1.



(C)

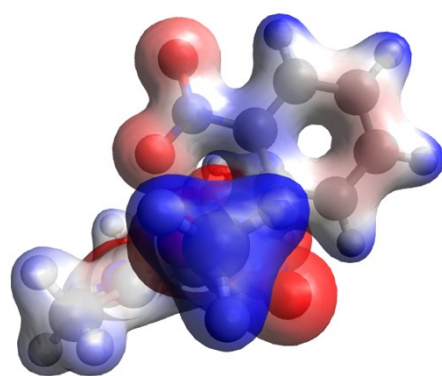
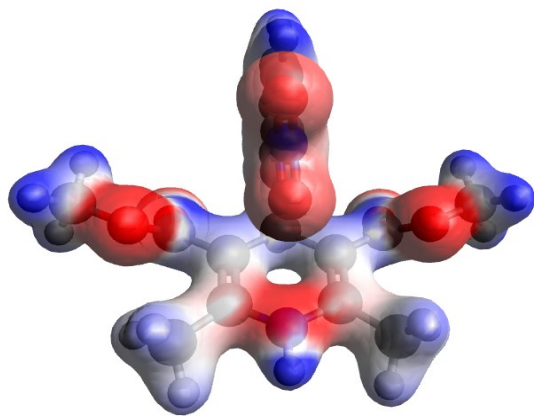
(D)

Fig. S6: Frontiers orbitals of structure **2**, (A) HOMO-1, (B) HOMO, (C) LUMO, (D) LUMO+1.



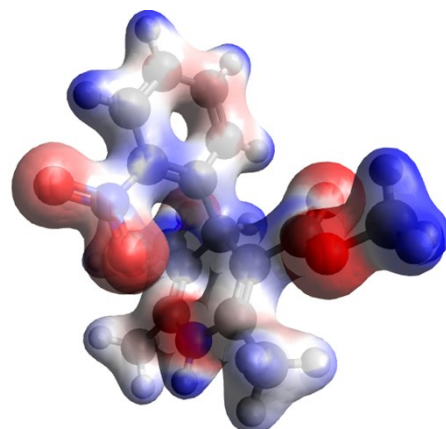
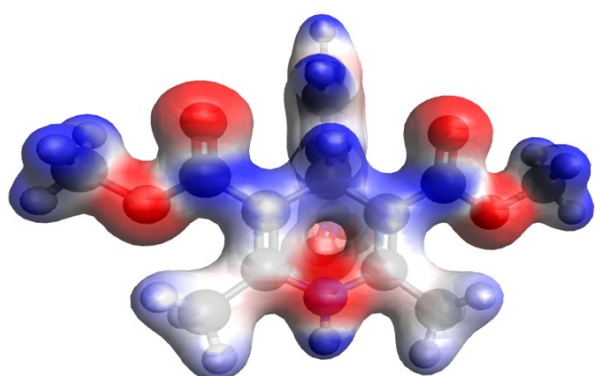
(A)

(B)



(C)

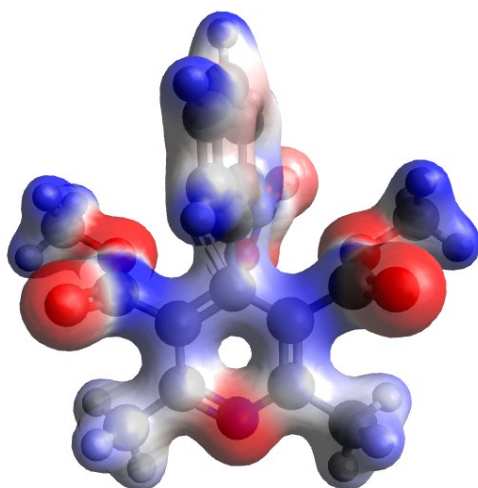
(D)



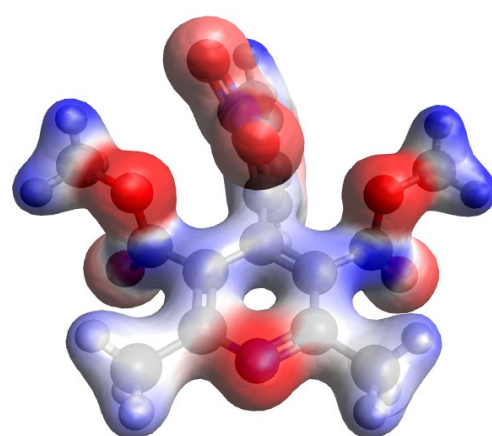
(E)

(F)

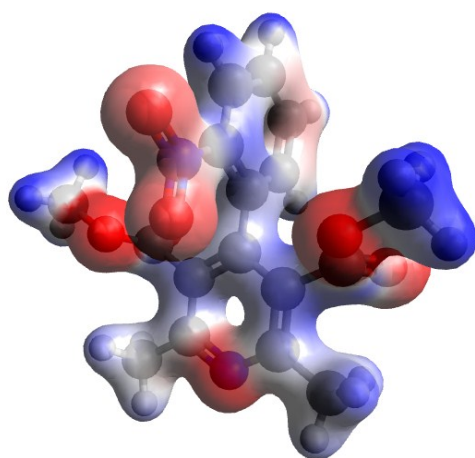
Fig. S7: Electrostatic potential map of 1 (backside view) (A), (lateral view) (B), oxidated state (front view) (C), (lateral view) (D), reduced state (backside view) (E), and (lateral view) (F).



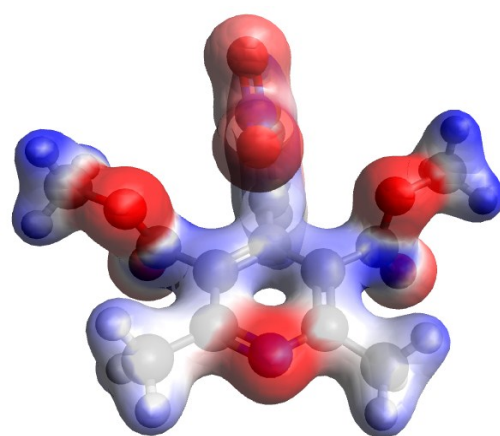
(A)



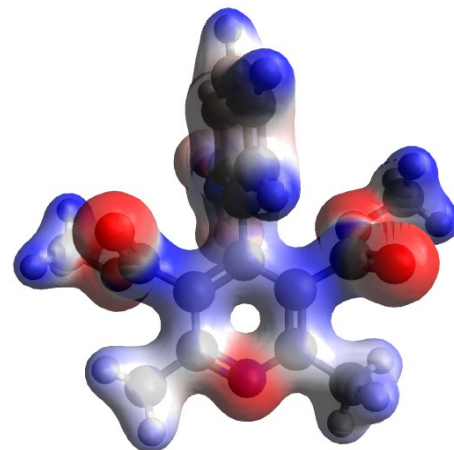
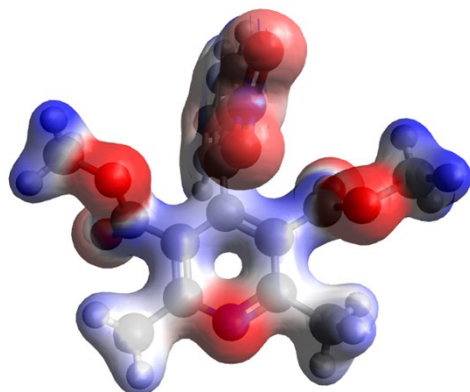
(B)



(C)



(D)



(E) (F)

Fig. S8: Electrostatic Potential map of **2** (backside view) (A), (frontal view) (B), oxidated state (lateral view) (C), (frontal view) (D), reduced state (backside view) (E), and (frontal view) (F).

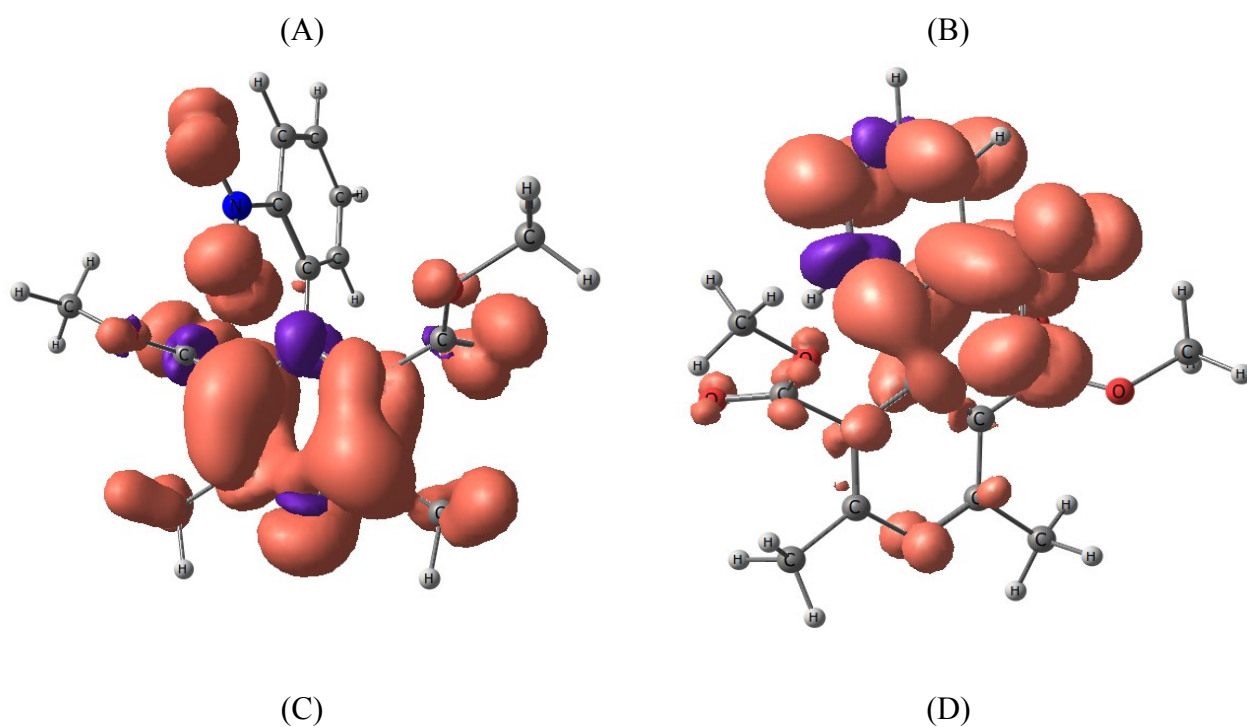
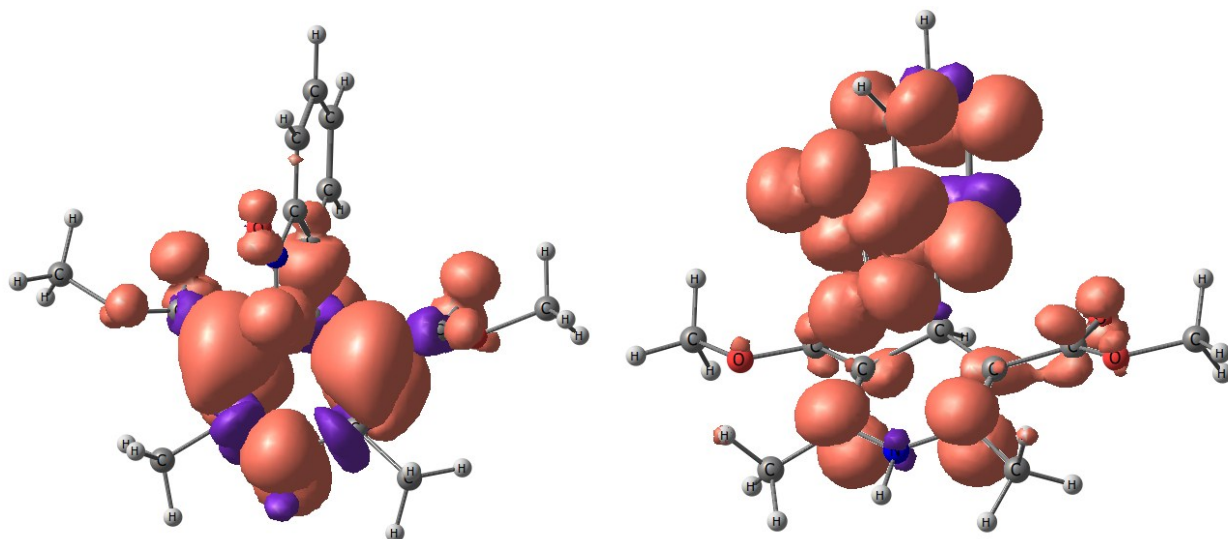


Fig. S9: Spin density of **1** at oxidated state (A), **1** at reduced state (B), **2** at oxidated state (C), and **2** at reduced state (D).

XYZ coordinates of compounds.

1

E = -1219.7892313 h

Negative Frequency = none

C -1.047918000 -0.937637000 -0.557328000
C -0.990805000 -2.092877000 0.191037000
N 0.228724000 -2.489007000 0.706549000
C 1.456770000 -1.916347000 0.415283000
C 1.487532000 -0.761146000 -0.328246000
C 0.192320000 -0.065486000 -0.764885000
C 0.031830000 1.351432000 -0.163829000
H 0.279796000 0.126962000 -1.847474000
C -2.230432000 -0.469155000 -1.284920000
C -2.118700000 -3.037501000 0.508159000
C 2.624735000 -2.704198000 0.945146000
C 2.719292000 -0.170058000 -0.864612000
H 0.242716000 -3.353893000 1.247675000
O 3.857563000 -0.497766000 -0.186208000
O -3.399557000 -1.105178000 -0.982708000
C -4.570769000 -0.648786000 -1.714501000
C 5.095723000 0.026957000 -0.741562000
O 2.747997000 0.582886000 -1.849118000
O -2.192241000 0.451142000 -2.117500000
H 5.086793000 1.126299000 -0.729240000
H 5.242934000 -0.337037000 -1.768422000
H 5.885794000 -0.354885000 -0.083989000
H -4.436118000 -0.804519000 -2.794487000
H -4.763917000 0.413690000 -1.508191000
H -5.396437000 -1.265969000 -1.340486000
H -1.749730000 -3.902424000 1.078796000
H -2.593007000 -3.405805000 -0.412646000
H -2.899119000 -2.536364000 1.098798000
H 2.288698000 -3.683142000 1.318018000
H 3.114463000 -2.168435000 1.772848000
H 3.382536000 -2.866643000 0.167385000
C -0.506363000 1.672676000 1.102253000
C 0.343756000 2.455119000 -0.983062000
C 0.169191000 3.778914000 -0.564415000
C -0.367948000 4.052410000 0.700616000
C -0.727732000 2.991158000 1.531535000
H -0.515037000 5.080681000 1.037791000
H -1.153422000 3.168169000 2.521027000
H 0.434954000 4.597625000 -1.237534000

H 0.717542000 2.255209000 -1.989382000
N -0.872782000 0.644189000 2.097657000
O -1.994164000 0.730443000 2.632381000
O -0.022589000 -0.202608000 2.413160000

2

E = -1218.5926444 h

Negative Frequency = none

C 0.438635000 1.622666000 -0.235263000
C -0.203770000 2.863698000 -0.024683000
N -1.535414000 2.943756000 0.177767000
C -2.295205000 1.828817000 0.132578000
C -1.723105000 0.553391000 -0.080280000
C -0.325921000 0.438773000 -0.233547000
C 0.298162000 -0.883496000 -0.569023000
C 1.909678000 1.597077000 -0.538301000
C 0.558193000 4.161467000 -0.018784000
C -3.774588000 2.020971000 0.332115000
C -2.614273000 -0.648353000 -0.182319000
O -2.304750000 -1.595616000 0.726746000
O 2.619184000 0.986200000 0.430529000
C 4.060327000 0.878882000 0.205707000
C -3.108545000 -2.815498000 0.677217000
O -3.531688000 -0.752373000 -0.992840000
O 2.405688000 2.086247000 -1.549421000
H -2.996160000 -3.299084000 -0.302807000
H -4.163724000 -2.576768000 0.868342000
H -2.705365000 -3.451843000 1.472659000
H 4.503345000 1.882263000 0.144113000
H 4.254312000 0.316167000 -0.717512000
H 4.442593000 0.338933000 1.078695000
H -0.008321000 4.923145000 0.534067000
H 0.698914000 4.526505000 -1.050784000
H 1.555733000 4.056246000 0.433577000
H -3.955623000 2.968442000 0.857790000
H -4.227920000 1.198384000 0.904700000
H -4.290475000 2.069602000 -0.642042000
C 1.058746000 -1.679822000 0.315817000
C 0.163054000 -1.349303000 -1.888962000
C 0.744021000 -2.557091000 -2.299302000
C 1.488930000 -3.326853000 -1.396684000
C 1.655094000 -2.883095000 -0.083399000
H 1.938358000 -4.271267000 -1.709957000
H 2.223165000 -3.465802000 0.642570000
H 0.613478000 -2.892045000 -3.330848000
H -0.401058000 -0.745136000 -2.602968000
N 1.242581000 -1.279172000 1.720771000
O 2.225288000 -1.732112000 2.333883000

O 0.410275000 -0.512747000 2.232768000

1-oxi

E = -1219.5934477 h

Negative Frequency = none

C -1.238252000 -0.998566000 -0.516828000

C -1.201258000 -2.302975000 -0.052218000

N 0.033750000 -2.876840000 0.139170000

C 1.262219000 -2.282825000 -0.029673000

C 1.286614000 -0.976799000 -0.491112000

C 0.021379000 -0.253852000 -0.876902000

C 0.003993000 1.230920000 -0.448377000

H 0.032858000 -0.207397000 -1.991106000

C -2.522745000 -0.315008000 -0.857183000

C -2.376442000 -3.177211000 0.254982000

C 2.446122000 -3.138177000 0.296474000

C 2.567910000 -0.275424000 -0.807072000

H 0.038741000 -3.854964000 0.452146000

O 3.471094000 -0.372036000 0.182806000

O -3.451125000 -0.441128000 0.105861000

C -4.744902000 0.185910000 -0.167377000

C 4.761927000 0.271503000 -0.065328000

O 2.744568000 0.333276000 -1.859146000

O -2.680979000 0.307100000 -1.904544000

H 4.615809000 1.348194000 -0.226410000

H 5.244046000 -0.187173000 -0.939229000

H 5.345401000 0.088686000 0.843317000

H -5.197550000 -0.268561000 -1.059052000

H -4.611600000 1.266735000 -0.311008000

H -5.348455000 -0.017485000 0.723630000

H -2.120474000 -4.235753000 0.097204000

H -3.240907000 -2.921223000 -0.368514000

H -2.667464000 -3.051183000 1.311478000

H 2.211908000 -4.200019000 0.127923000

H 2.714209000 -3.013352000 1.359162000

H 3.318162000 -2.864600000 -0.308787000

C -0.049881000 1.726229000 0.880850000

C 0.037173000 2.190426000 -1.474080000

C 0.024781000 3.564478000 -1.208666000

C -0.024912000 4.025201000 0.113018000

C -0.064485000 3.104142000 1.157465000

H -0.033441000 5.094584000 0.332385000

H -0.103906000 3.433997000 2.195343000

H 0.053761000 4.272671000 -2.039899000

H 0.073124000 1.842676000 -2.508862000

N -0.091496000 0.840476000 2.055070000
O -0.202413000 1.345354000 3.185774000
O -0.013077000 -0.389956000 1.877092000

1-red

E = -1219.9156197 h

Negative Frequency = none

C -1.085114000 -1.044748000 -0.497332000
C -0.957830000 -2.238714000 0.173535000
N 0.298764000 -2.647308000 0.582669000
C 1.489103000 -2.001020000 0.297884000
C 1.452188000 -0.799767000 -0.368029000
C 0.124584000 -0.139564000 -0.765643000
C -0.060860000 1.314697000 -0.250127000
H 0.169069000 0.002236000 -1.860889000
C -2.331781000 -0.599137000 -1.122284000
C -2.044079000 -3.230134000 0.500476000
C 2.704031000 -2.772386000 0.742864000
C 2.653215000 -0.133355000 -0.876537000
H 0.365530000 -3.557959000 1.036392000
O 3.797198000 -0.387004000 -0.167669000
O -3.475710000 -1.110777000 -0.569464000
C -4.717685000 -0.720014000 -1.215574000
C 5.012794000 0.208023000 -0.698550000
O 2.663275000 0.627989000 -1.856642000
O -2.382949000 0.203360000 -2.069034000
H 4.940432000 1.305187000 -0.690696000
H 5.204446000 -0.148090000 -1.721109000
H 5.810887000 -0.124474000 -0.023751000
H -4.725076000 -1.038689000 -2.267964000
H -4.860092000 0.368514000 -1.151981000
H -5.505288000 -1.238616000 -0.655567000
H -1.608116000 -4.195493000 0.799383000
H -2.708275000 -3.397419000 -0.357024000
H -2.667359000 -2.864796000 1.331995000
H 2.431142000 -3.813602000 0.971993000
H 3.137727000 -2.325414000 1.651720000
H 3.486353000 -2.776062000 -0.026412000
C -0.394898000 1.768437000 1.076577000
C 0.019980000 2.307667000 -1.246258000
C -0.198802000 3.673575000 -1.017432000
C -0.547373000 4.091630000 0.277997000
C -0.651668000 3.154837000 1.299838000
H -0.736344000 5.147212000 0.493035000
H -0.914955000 3.464415000 2.311091000
H -0.115887000 4.389563000 -1.838737000
H 0.251303000 1.979039000 -2.263444000

N -0.491940000 0.935172000 2.209000000
O -1.026422000 1.405275000 3.319429000
O -0.000152000 -0.267687000 2.199861000

2-oxi

E = -1218.3494409 h

Negative Frequency = none

C 1.126967000 1.205385000 -0.272782000
C 1.133184000 2.633287000 -0.017067000
N -0.019113000 3.287221000 0.141609000
C -1.199603000 2.651648000 0.042776000
C -1.264846000 1.214655000 -0.076468000
C -0.085687000 0.486330000 -0.281394000
C -0.121362000 -0.975184000 -0.613173000
C 2.431616000 0.506529000 -0.514666000
C 2.410870000 3.370974000 0.142940000
C -2.427323000 3.488171000 0.003214000
C -2.602422000 0.536297000 -0.150168000
O -2.854272000 -0.229172000 0.908923000
O 3.099019000 0.138036000 0.560193000
C 4.398342000 -0.520907000 0.332205000
C -4.143815000 -0.934283000 0.906683000
O -3.348953000 0.707057000 -1.109301000
O 2.773453000 0.350672000 -1.686710000
H -4.186905000 -1.614713000 0.046323000
H -4.961074000 -0.202144000 0.868585000
H -4.157003000 -1.490178000 1.849508000
H 5.063313000 0.167262000 -0.205061000
H 4.239533000 -1.445531000 -0.237009000
H 4.776150000 -0.733856000 1.336857000
H 2.225831000 4.428373000 0.363345000
H 3.011414000 3.283949000 -0.781809000
H 3.020705000 2.920840000 0.945960000
H -2.191120000 4.529547000 0.249672000
H -3.187097000 3.092967000 0.700496000
H -2.883183000 3.447929000 -1.002290000
C 0.109357000 -2.028504000 0.301070000
C -0.393040000 -1.320828000 -1.947582000
C -0.427583000 -2.662156000 -2.352997000
C -0.192136000 -3.687228000 -1.428499000
C 0.075500000 -3.371304000 -0.095132000
H -0.220471000 -4.732951000 -1.740405000
H 0.250175000 -4.151108000 0.646452000
H -0.639546000 -2.900402000 -3.397551000
H -0.569969000 -0.524382000 -2.673214000
N 0.372451000 -1.748244000 1.724127000
O 0.606802000 -2.702592000 2.483164000

O 0.344923000 -0.564719000 2.105760000

2-red

E = -1218.7289202 h

Negative Frequency = none

C 1.375004000 1.185395000 -0.093434000
C 1.338230000 2.591798000 0.054366000
N 0.175632000 3.273565000 0.013243000
C -0.989738000 2.609911000 -0.168730000
C -1.029912000 1.206184000 -0.298225000
C 0.174220000 0.463555000 -0.258199000
C 0.203986000 -1.003336000 -0.544828000
C 2.696319000 0.479613000 -0.066615000
C 2.585048000 3.408499000 0.270519000
C -2.227729000 3.465039000 -0.250079000
C -2.329384000 0.510297000 -0.573927000
O -3.217122000 0.672397000 0.431240000
O 2.778913000 -0.413146000 0.945711000
C 4.029138000 -1.162744000 1.034424000
C -4.537048000 0.082184000 0.220281000
O -2.573871000 -0.120091000 -1.600700000
O 3.617727000 0.705491000 -0.849091000
H -4.446474000 -1.003846000 0.082713000
H -5.016718000 0.540454000 -0.655793000
H -5.098294000 0.311219000 1.132993000
H 4.869018000 -0.475310000 1.205881000
H 4.188748000 -1.738633000 0.112327000
H 3.897456000 -1.832900000 1.891181000
H 2.320800000 4.375293000 0.720661000
H 3.087889000 3.607997000 -0.691193000
H 3.310144000 2.896031000 0.920440000
H -1.958717000 4.472036000 -0.598808000
H -2.692270000 3.567354000 0.745706000
H -2.984211000 3.043212000 -0.927753000
C -0.325756000 -2.025734000 0.308143000
C 0.735648000 -1.385444000 -1.789840000
C 0.718533000 -2.715571000 -2.233693000
C 0.146043000 -3.702950000 -1.410323000
C -0.366099000 -3.368462000 -0.160272000
H 0.107035000 -4.743622000 -1.743368000
H -0.788992000 -4.132677000 0.491678000
H 1.127459000 -2.971200000 -3.213718000
H 1.137187000 -0.604808000 -2.442129000