Supplementary Information

Density Functional Theory-Assisted Electrochemical Sensing of Caffeic Acid Using an Iron(II) Complex of Diethyl Thiophene-2,5-Dicarboxylate-Modified Carbon Paste Electrode

Contents

Section S1. Cartesian coordinates of the optimized structures

Coordinates are reproduced below in XYZ-style format using the charge and multiplicity reported in the uploaded input files. Each block begins with the atom count.

S1.1. Graphene nanoflake (G)

Atoms: 180 | *Charge: 0* | *Multiplicity: 1*

```
Input header: !PBE def2-SVP RI D3BJ DEF2/J VERYSLOWCONV KDIIS TIGHTSCF PAL8 !KEEPDENS XYZFILE

  180
  C      -0.315422000      0.426741000     -9.924580000
  C      -2.795645000      0.626749000     -9.892966000
  C      -5.277857000      0.828182000     -9.866202000
  C      -3.988963000      0.774960000     -7.746946000
  C      -4.000597000      0.741186000     -9.194346000
  C      -5.206347000      0.889293000     -7.020945000
  C      -6.451443000      0.941193000     -9.166439000
  C      -6.470685000      0.976700000     -7.721091000
  C      -7.657801000      1.090585000     -6.992557000
  C      -8.867555000      1.237509000     -4.822900000
  C       4.646615000      0.020620000     -9.990698000
  C       2.164722000      0.225504000     -9.955221000
  C       0.948880000      0.377855000     -7.810206000
  C       0.926542000      0.343806000     -9.254706000
  C      -0.274615000      0.493634000     -7.083363000
  C      -1.518525000      0.575996000     -7.779214000
  C      -1.537554000      0.542507000     -9.223772000
  C      -2.741319000      0.690657000     -7.051452000
  C      -2.722101000      0.722643000     -5.619317000
  C      -3.943426000      0.835522000     -4.890865000
  C      -5.190744000      0.920164000     -5.590361000
  C      -6.412097000      1.034485000     -4.860155000
  C      -7.670239000      1.122327000     -5.565439000
  C      -6.394474000      1.063937000     -3.432757000
  C      -7.615388000      1.178756000     -2.701469000
  C      -8.871824000      1.267677000     -3.409681000
  C     -10.076617000      1.384203000     -2.652833000
  C     -11.290609000      1.533843000     -0.483238000
  C       5.839784000     -0.062046000     -9.320436000
  C       4.656694000      0.092614000     -7.144678000
  C       5.900339000     -0.030026000     -7.876162000
  C       3.419210000      0.177035000     -7.839948000
  C       3.389399000      0.142892000     -9.287106000
  C       2.191976000      0.294830000     -7.113419000
  C       2.213637000      0.327369000     -5.681310000
  C       0.988391000      0.442077000     -4.951705000
  C      -0.254214000      0.525115000     -5.649491000
  C      -1.476595000      0.638738000     -4.920734000
  C      -1.456651000      0.669665000     -3.491824000
  C      -2.680143000      0.782359000     -2.762035000
  C      -3.924228000      0.865991000     -3.460703000
  C      -5.146336000      0.978531000     -2.731324000
  C      -5.126443000      1.008836000     -1.304128000
  C      -6.350610000      1.122786000     -0.572605000
  C      -7.596566000      1.208853000     -1.274300000
  C      -8.819033000      1.324701000     -0.539490000
  C     -10.074230000      1.413757000     -1.255660000
  C      -8.798809000      1.355507000      0.882105000
  C     -10.033245000      1.475929000      1.629288000
```

C	-11.271123000	1.563597000	0.887305000
C	7.107586000	-0.114540000	-7.177392000
C	5.923314000	0.040114000	-5.014869000
C	7.160652000	-0.082741000	-5.751279000
C	4.681907000	0.126059000	-5.714269000
C	3.455017000	0.243235000	-4.983762000
C	3.476540000	0.275911000	-3.553669000
C	2.252704000	0.390226000	-2.824016000
C	1.009097000	0.473861000	-3.522819000
C	-0.213684000	0.586816000	-2.793581000
C	-0.193435000	0.617214000	-1.364485000
C	-1.415946000	0.729695000	-0.635261000
C	-2.660034000	0.812799000	-1.334318000
C	-3.882736000	0.924917000	-0.604827000
C	-3.862419000	0.956175000	0.823753000
C	-5.085922000	1.070065000	1.554021000
C	-6.330264000	1.154686000	0.853449000
C	-7.556016000	1.269971000	1.586091000
C	-7.534156000	1.303179000	3.013149000
C	-8.770015000	1.423573000	3.752467000
C	-9.995860000	1.507832000	3.025838000
C	8.378408000	-0.169059000	-5.038755000
C	7.187234000	-0.013900000	-2.887097000
C	8.422846000	-0.137209000	-3.626344000
C	5.946324000	0.073516000	-3.587626000
C	4.718621000	0.190940000	-2.855201000
C	4.739335000	0.223290000	-1.428060000
C	3.515938000	0.338448000	-0.697822000
C	2.273202000	0.422411000	-1.396340000
C	1.049261000	0.534806000	-0.666257000
C	1.069542000	0.565841000	0.761176000
C	-0.152962000	0.678391000	1.490398000
C	-1.395666000	0.760712000	0.792173000
C	-2.619595000	0.873292000	1.522252000
C	-2.599074000	0.905741000	2.949925000
C	-3.822882000	1.020410000	3.679571000
C	-5.065114000	1.103551000	2.981139000
C	-6.292951000	1.219349000	3.713605000
C	-6.269819000	1.254117000	5.140817000
C	-7.507330000	1.374858000	5.877280000
C	-8.725379000	1.457197000	5.164817000
C	9.648432000	-0.224977000	-2.899670000
C	8.451650000	-0.069050000	-0.756001000
C	9.685763000	-0.193183000	-1.503107000
C	7.209126000	0.019714000	-1.460053000
C	5.983581000	0.137503000	-0.727466000
C	6.003968000	0.169846000	0.698576000
C	4.779947000	0.285595000	1.430059000
C	3.536314000	0.370423000	0.730740000
C	2.313677000	0.483332000	1.460216000
C	2.333893000	0.515034000	2.887901000
C	1.110488000	0.628809000	3.617667000
C	-0.132592000	0.710295000	2.919459000
C	-1.355321000	0.823899000	3.648685000
C	-1.334493000	0.857185000	5.077536000
C	-2.559673000	0.972763000	5.807122000
C	-3.801212000	1.054902000	5.109620000
C	-5.028154000	1.171380000	5.840146000
C	-5.002745000	1.207124000	7.270495000
C	-6.246488000	1.328426000	8.002020000
C	-7.454005000	1.409252000	7.303308000
C	10.923407000	-0.283727000	-0.761071000
C	10.943009000	-0.252469000	0.609443000
C	8.472011000	-0.036625000	0.665558000
C	9.727009000	-0.128059000	1.381776000
C	7.249803000	0.082316000	1.400299000
C	7.268803000	0.114541000	2.827419000
C	6.048129000	0.232294000	3.558641000
C	4.800021000	0.318093000	2.857204000
C	3.578049000	0.432314000	3.586545000
C	3.597423000	0.464903000	5.016655000
C	2.376240000	0.579506000	5.745074000
C	1.130550000	0.661148000	5.046544000
C	-0.091727000	0.776080000	5.775271000
C	-0.071103000	0.810258000	7.209075000
C	-1.294552000	0.926644000	7.935888000
C	-2.537774000	1.008172000	7.239156000
C	-3.765040000	1.125549000	7.965698000
C	-3.735003000	1.162399000	9.412784000
C	-4.992260000	1.284025000	10.116395000
C	-6.185685000	1.363347000	9.446205000
C	9.729608000	-0.095942000	2.778895000
C	8.525175000	0.024828000	3.535644000
C	8.521111000	0.057565000	4.948809000
C	6.065951000	0.264184000	4.985983000
C	7.324050000	0.175807000	5.691272000
C	4.844770000	0.380632000	5.716135000

```
C       4.860587000      0.414055000      7.146659000
C       3.643371000      0.530397000      7.872619000
C       2.395592000      0.613091000      7.177171000
C       1.172903000      0.729078000      7.904898000
C       1.192168000      0.765535000      9.349381000
C      -0.029873000      0.882485000     10.050122000
C      -1.271961000      0.963711000      9.380296000
C      -2.510111000      1.082299000     10.080783000
C       7.311860000      0.210557000      7.118321000
C       6.124970000      0.327178000      7.846780000
C       6.105968000      0.365398000      9.292057000
C       3.655206000      0.566493000      9.319965000
C       4.932549000      0.480391000      9.991766000
C       2.450359000      0.682380000     10.018506000
H      11.862449000     -0.382003000     -1.327087000
H      11.897848000     -0.325753000      1.152394000
H      10.687722000     -0.167642000      3.316546000
H       9.479064000     -0.013277000      5.486587000
H       8.269976000      0.141859000      7.656331000
H       7.066492000      0.299664000      9.825420000
H       4.943643000      0.509518000     11.092608000
H       2.467359000      0.711017000     11.119678000
H      -0.013306000      0.912048000     11.151148000
H      -2.493528000      1.112004000     11.181929000
H      -4.970310000      1.313122000     11.217033000
H      -7.130535000      1.457154000     10.002697000
H      -8.396476000      1.503878000      7.864448000
H      -9.667866000      1.551937000      5.725677000
H     -10.938602000      1.602553000      3.586536000
H     -12.210508000      1.658643000      1.453324000
H     -12.245672000      1.604679000     -1.026115000
H     -11.034847000      1.454573000     -3.190451000
H      -9.825540000      1.307970000     -5.360669000
H      -8.615883000      1.159688000     -7.530574000
H      -7.411890000      1.007900000     -9.699826000
H      -5.288656000      0.800688000    -10.967093000
H      -2.812483000      0.600009000    -10.994188000
H      -0.331966000      0.399550000    -11.025664000
H       2.148407000      0.197374000    -11.056415000
H       4.624639000     -0.006632000    -11.091382000
H       6.784633000     -0.156506000     -9.876811000
H       8.049930000     -0.210599000     -7.738481000
H       9.320702000     -0.265899000     -5.599553000
H      10.590934000     -0.322233000     -3.460315000
```

S1.2. Modifier (Fe-TDC)

Atoms: 28 | Charge: 0 | Multiplicity: 1

```
Input header: !PBE def2-SVP RI D3BJ DEF2/J VERYSLOWCONV KDIIS TIGHTSCF PAL8 !KEEPDENS XYZFILE
```

```
28
C       0.014885000      0.023039000      0.024521000
S       0.085095000      0.015613000      1.773779000
C       1.834806000      0.022878000      1.796307000
C       2.345671000      0.035023000      0.490030000
C       1.308469000      0.033698000     -0.517919000
C       2.495650000      0.012470000      3.098490000
O       3.844335000      0.025904000      2.975050000
C       4.611212000     -0.017245000      4.208103000
C       4.781733000     -1.438665000      4.707923000
O       3.584736000      0.030965000      0.013712000
Fe      3.556852000     -0.004523000     -1.796366000
O       1.746385000      0.028934000     -1.770634000
C      -1.252907000      0.014135000     -0.698931000
O      -2.313798000      0.026149000      0.149049000
C      -3.633131000     -0.030988000     -0.452899000
C      -4.041948000     -1.458606000     -0.761083000
O       1.896639000     -0.001354000      4.174862000
O      -1.346020000      0.001350000     -1.925126000
H      -3.633313000      0.596339000     -1.366526000
H      -4.299645000      0.430736000      0.300171000
H      -3.385636000     -1.906260000     -1.533594000
H      -5.081460000     -1.468565000     -1.146214000
H      -4.005460000     -2.089576000      0.149599000
H       4.110069000      0.621463000      4.962560000
H       5.582986000      0.439221000      3.940476000
H       3.809084000     -1.879950000      5.000729000
H       5.441484000     -1.438918000      5.599048000
H       5.247051000     -2.079861000      3.932555000
```

S1.3. Caffeic acid (CA)

Atoms: 21| Charge: 0| Multiplicity: 1

```
Input header: !PBE def2-SVP RI D3BJ DEF2/J VERYSLOWCONV KDIIS TIGHTSCF PAL8 !KEEPDENS XYZFILE
```

```
21
C      -4.348957000      0.157201000     -1.834516000
C      -5.412413000     -0.526344000     -1.214680000
C      -3.226736000      0.554219000     -1.103312000
H      -2.412657000      1.084921000     -1.617377000
C      -5.340832000     -0.816024000      0.176564000
C      -3.139011000      0.276004000      0.283357000
C      -4.215226000     -0.415168000      0.900869000
H      -4.170823000     -0.644784000      1.977548000
H      -4.421212000      0.373691000     -2.912038000
O      -6.400366000     -1.482109000      0.724052000
H      -6.217590000     -1.624338000      1.674757000
O      -6.528174000     -0.934093000     -1.875172000
H      -6.454675000     -0.658721000     -2.811814000
C      -2.003049000      0.666103000      1.104593000
H      -2.070830000      0.383182000      2.168349000
C      -0.884660000      1.335963000      0.701853000
H      -0.736621000      1.656432000     -0.340180000
C       0.217287000      1.698566000      1.596082000
O       1.228162000      2.304821000      1.229532000
O       0.045219000      1.312963000      2.891102000
H       0.842320000      1.616299000      3.379461000
```

S1.4. Graphene–modifier complex (G–Fe-TDC)

Atoms: 208 | *Charge: 0* | *Multiplicity: 1*

`Input header: !PBE def2-SVP RI D3BJ DEF2/J VERYSLOWCONV KDIIS TIGHTSCF PAL8 !KEEPDENS XYZFILE`

```
208
C       0.720351000      0.608662000     -9.890733000
C      -1.753424000      0.380557000     -9.903448000
C      -4.226960000      0.122503000     -9.924016000
C      -2.996778000      0.386158000     -7.782361000
C      -2.972461000      0.300180000     -9.227563000
C      -4.228900000      0.293301000     -7.078911000
C      -5.413191000      0.017462000     -9.246446000
C      -5.466321000      0.084676000     -7.803256000
C      -6.658129000     -0.080538000     -7.096902000
C      -7.874573000     -0.351544000     -4.951627000
C       5.676003000      1.040843000     -9.874777000
C       3.196272000      0.825790000     -9.879855000
C       1.931424000      0.822588000     -7.756194000
C       1.943891000      0.752019000     -9.199484000
C       0.692954000      0.753483000     -7.050776000
C      -0.532154000      0.613209000     -7.768207000
C      -0.515751000      0.535837000     -9.210666000
C      -1.771111000      0.544367000     -7.063052000
C      -1.787764000      0.622452000     -5.631668000
C      -3.023915000      0.550416000     -4.927690000
C      -4.248067000      0.374940000     -5.651602000
C      -5.476706000      0.214988000     -4.942896000
C      -6.696407000     -0.052746000     -5.670662000
C      -5.494169000      0.257598000     -3.517284000
C      -6.698414000     -0.022719000     -2.821949000
C      -7.889971000     -0.383150000     -3.540709000
C      -9.042840000     -0.817090000     -2.808715000
C     -10.168531000     -1.430681000     -0.674201000
C       6.853256000      1.175223000     -9.185576000
C       5.621338000      1.164834000     -7.030338000
C       6.880367000      1.242005000     -7.741453000
C       4.399910000      1.030388000     -7.745261000
C       4.404010000      0.963502000     -9.191808000
C       3.157904000      0.958263000     -7.039067000
C       3.146347000      1.019931000     -5.608165000
C       1.905053000      0.949889000     -4.899259000
C       0.678796000      0.820094000     -5.617398000
C      -0.558996000      0.755155000     -4.910172000
C      -0.572560000      0.818323000     -3.483060000
C      -1.813501000      0.754083000     -2.775068000
C      -3.039365000      0.616695000     -3.496660000
C      -4.272695000      0.501338000     -2.788600000
C      -4.276871000      0.550337000     -1.368518000
C      -5.515585000      0.345382000     -0.654392000
C      -6.714643000     -0.006487000     -1.384606000
C      -7.861939000     -0.505893000     -0.680375000
C      -9.038043000     -0.929004000     -1.423325000
C      -7.838846000     -0.607273000      0.758510000
C      -8.995778000     -1.126745000      1.470264000
C     -10.146995000     -1.527995000      0.692316000
C       8.071716000      1.374860000     -7.024047000
C       6.839985000      1.353802000     -4.882278000
C       8.092471000      1.432972000     -5.598127000
C       5.613903000      1.223484000     -5.600961000
C       4.371648000      1.149236000     -4.891138000
C       4.361369000      1.202629000     -3.461609000
C       3.122389000      1.129791000     -2.752808000
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```
C       1.892985000      1.007081000     -3.471282000
C       0.654067000      0.939392000     -2.763691000
C       0.643038000      0.987714000     -1.334129000
C      -0.593416000      0.910617000     -0.625914000
C      -1.824818000      0.797765000     -1.347013000
C      -3.062060000      0.696382000     -0.641114000
C      -3.063926000      0.673830000      0.798351000
C      -4.273646000      0.461689000      1.515169000
C      -5.506908000      0.263306000      0.789077000
C      -6.686376000     -0.176126000      1.498730000
C      -6.653864000     -0.322411000      2.927283000
C      -7.824544000     -0.786318000      3.621671000
C      -8.972756000     -1.178027000      2.859748000
C       9.295166000      1.563411000     -4.867674000
C       8.058438000      1.530310000     -2.736870000
C       9.309291000      1.612961000     -3.455499000
C       6.832059000      1.404492000     -3.456065000
C       5.589026000      1.326711000     -2.744160000
C       5.580056000      1.370710000     -1.317937000
C       4.341589000      1.292406000     -0.608488000
C       3.112461000      1.176168000     -1.326012000
C       1.872862000      1.100920000     -0.616685000
C       1.865531000      1.133927000      0.810196000
C       0.628842000      1.043474000      1.518948000
C      -0.599651000      0.929979000      0.801452000
C      -1.834119000      0.804614000      1.513731000
C      -1.831701000      0.758589000      2.941477000
C      -3.048303000      0.522649000      3.651580000
C      -4.265748000      0.344182000      2.931258000
C      -5.466360000     -0.019531000      3.642099000
C      -5.447531000     -0.139203000      5.063859000
C      -6.644431000     -0.532611000      5.771064000
C      -7.802973000     -0.859634000      5.030927000
C      10.520359000      1.741300000     -2.711109000
C       9.279911000      1.694805000     -0.587827000
C      10.529238000      1.782410000     -1.314633000
C       8.051036000      1.572508000     -1.310372000
C       6.810879000      1.489727000     -0.598306000
C       6.803509000      1.522271000      0.826995000
C       5.565338000      1.434808000      1.538152000
C       4.334370000      1.324932000      0.819798000
C       3.097920000      1.241015000      1.528884000
C       3.093864000      1.249159000      2.956555000
C       1.858689000      1.138570000      3.666878000
C       0.627381000      1.040117000      2.949610000
C      -0.601188000      0.886385000      3.660109000
C      -0.594654000      0.811000000      5.087580000
C      -1.815275000      0.575808000      5.796626000
C      -3.034426000      0.410479000      5.079193000
C      -4.240474000      0.099428000      5.787155000
C      -4.225801000     -0.007968000      7.212676000
C      -5.444469000     -0.347254000      7.918956000
C      -6.609760000     -0.608668000      7.195771000
C      11.752321000      1.910592000     -0.554189000
C      11.744959000      1.943560000      0.816243000
C       9.272401000      1.728121000      0.833482000
C      10.513818000      1.850984000      1.568776000
C       8.036074000      1.638144000      1.547754000
C       8.028714000      1.659561000      2.974743000
C       6.795446000      1.559682000      3.685925000
C       5.559971000      1.450206000      2.964983000
C       4.325837000      1.348284000      3.674336000
C       4.323216000      1.335630000      5.104904000
C       3.093737000      1.202169000      5.813778000
C       1.860155000      1.098541000      5.095530000
C       0.633687000      0.930075000      5.804794000
C       0.639705000      0.856523000      7.237991000
C      -0.580334000      0.636167000      7.944205000
C      -1.803766000      0.477209000      7.226789000
C      -3.016318000      0.198214000      7.931261000
C      -2.998818000      0.101827000      9.375778000
C      -4.238065000     -0.204095000     10.055290000
C      -5.399809000     -0.424017000      9.362257000
C      10.490208000      1.875303000      2.965471000
C       9.271677000      1.777410000      3.702209000
C       9.243052000      1.787944000      5.115039000
C       6.789363000      1.562413000      5.113078000
C       8.033883000      1.677479000      5.837987000
C       5.557699000      1.443001000      5.823865000
C       5.552314000      1.421596000      7.254356000
C       4.327658000      1.274906000      7.961058000
C       3.094355000      1.158750000      7.245455000
C       1.867585000      0.984266000      7.953521000
C       1.870607000      0.918611000      9.397219000
C       0.651173000      0.705503000     10.077751000
C      -0.571207000      0.549074000      9.386382000
C      -1.798936000      0.288594000     10.065596000
```

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C       7.999176000      1.668980000      7.264897000
C       6.802936000      1.539784000      7.974742000
C       6.762747000      1.511084000      9.419888000
C       4.320186000      1.231419000      9.408584000
C       5.582671000      1.361810000     10.101218000
C       3.112212000      1.056368000     10.087699000
H      12.701889000      1.983089000     -1.106101000
H      12.688525000      2.042915000      1.374218000
H      11.437450000      1.970250000      3.518128000
H      10.190692000      1.879649000      5.667303000
H       8.947234000      1.760822000      7.816665000
H       7.712724000      1.607281000      9.966958000
H       5.576169000      1.334115000     11.201939000
H       3.113265000      1.013263000     11.188262000
H       0.655396000      0.643966000     11.177263000
H      -1.790744000      0.215691000     11.164471000
H      -4.224804000     -0.270427000     11.154200000
H      -6.328910000     -0.672259000      9.897018000
H      -7.527650000     -0.893695000      7.732038000
H      -8.704211000     -1.198474000      5.563750000
H      -9.862997000     -1.539125000      3.396967000
H     -11.023173000     -1.916588000      1.232906000
H     -11.061379000     -1.741909000     -1.236810000
H      -9.945987000     -1.103706000     -3.368284000
H      -8.790535000     -0.610221000     -5.503716000
H      -7.591922000     -0.272778000     -7.646639000
H      -6.356342000     -0.131974000     -9.793095000
H      -4.206139000      0.062630000    -11.023174000
H      -1.740073000      0.315001000    -11.002788000
H       0.730660000      0.548933000    -10.990321000
H       3.205272000      0.770942000    -10.979860000
H       5.678792000      0.987850000    -10.974576000
H       7.810354000      1.233815000     -9.725526000
H       9.026104000      1.436108000     -7.569123000
H      10.248746000      1.627431000     -5.413607000
H      11.473417000      1.809358000     -3.257715000
C      -2.751074000     -2.753406000     -1.899233000
S      -1.340442000     -2.803284000     -0.853088000
C      -2.319667000     -2.691191000      0.600952000
C      -3.684931000     -2.617148000      0.281281000
C      -3.931999000     -2.639546000     -1.148162000
C      -1.714205000     -2.612288000      1.926369000
O      -0.359006000     -2.550996000      1.852768000
C       0.358370000     -2.513289000      3.108247000
C       1.829915000     -2.362177000      2.797346000
O      -4.744993000     -2.406853000      1.039957000
Fe     -6.038822000     -1.530824000     -0.051280000
O      -5.183639000     -2.414278000     -1.506425000
C      -2.497834000     -2.758561000     -3.337194000
O      -3.629060000     -2.897749000     -4.068437000
C      -3.439680000     -3.014691000     -5.500509000
C      -4.786560000     -3.281250000     -6.130609000
O      -2.338888000     -2.592130000      2.985546000
O      -1.374012000     -2.668450000     -3.835841000
H      -2.719990000     -3.837040000     -5.695140000
H      -2.977329000     -2.081784000     -5.880470000
H      -4.675758000     -3.337974000     -7.231439000
H      -5.508269000     -2.474821000     -5.896662000
H      -5.209507000     -4.241954000     -5.774451000
H       0.146053000     -3.447561000      3.670059000
H      -0.029982000     -1.671795000      3.717581000
H       2.016847000     -1.456537000      2.188087000
H       2.215703000     -3.239760000      2.241149000
H       2.404201000     -2.269843000      3.739477000
```

S1.5. Graphene–caffeic acid complex (G–CA)

Atoms: 201 | *Charge: 0* | *Multiplicity: 1*

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Input header: !PBE def2-SVP RI D3BJ DEF2/J VERYSLOWCONV KDIIS TIGHTSCF PAL8 !KEEPDENS XYZFILE

201
C      -0.117830000     -0.369736000    -10.036162000
C      -2.599066000     -0.209941000    -10.002357000
C      -5.084724000     -0.076023000     -9.972015000
C      -3.783063000      0.058467000     -7.863050000
C      -3.802219000     -0.076661000     -9.304590000
C      -4.999424000      0.178041000     -7.137007000
C      -6.257661000      0.041347000     -9.272167000
C      -6.269708000      0.167878000     -7.831858000
C      -7.456864000      0.270695000     -7.102484000
C      -8.660996000      0.464678000     -4.935709000
C       4.841979000     -0.768287000    -10.103380000
C       2.361596000     -0.556641000    -10.067966000
C       1.158340000     -0.248912000     -7.931617000
C       1.127968000     -0.390842000     -9.369541000
C      -0.061348000     -0.090419000     -7.206678000
```

C	-1.309717000	-0.078387000	-7.898756000
C	-1.336621000	-0.219274000	-9.336876000
C	-2.530123000	0.060902000	-7.172038000
C	-2.503219000	0.196338000	-5.745837000
C	-3.723429000	0.317294000	-5.017115000
C	-4.976706000	0.301782000	-5.711561000
C	-6.198048000	0.400496000	-4.980244000
C	-7.462458000	0.381376000	-5.679619000
C	-6.173865000	0.507409000	-3.556682000
C	-7.396676000	0.577586000	-2.823431000
C	-8.659502000	0.556015000	-3.525620000
C	-9.866504000	0.620754000	-2.766837000
C	-11.078915000	0.746765000	-0.596383000
C	6.038254000	-0.811044000	-9.435184000
C	4.867761000	-0.496405000	-7.268774000
C	6.106001000	-0.680945000	-7.996766000
C	3.627399000	-0.451760000	-7.961757000
C	3.589745000	-0.590309000	-9.402651000
C	2.405063000	-0.278337000	-7.237913000
C	2.434342000	-0.142843000	-5.811788000
C	1.213788000	0.026633000	-5.084636000
C	-0.033003000	0.049017000	-5.779082000
C	-1.252438000	0.197169000	-5.051507000
C	-1.224818000	0.337218000	-3.628420000
C	-2.446963000	0.467269000	-2.899168000
C	-3.697308000	0.446323000	-3.592399000
C	-4.919998000	0.535235000	-2.861371000
C	-4.893763000	0.633876000	-1.438011000
C	-6.120136000	0.682691000	-0.703711000
C	-7.372678000	0.658033000	-1.398941000
C	-8.597948000	0.708230000	-0.661329000
C	-9.859693000	0.692205000	-1.371632000
C	-8.574506000	0.767355000	0.758689000
C	-9.812072000	0.811862000	1.509338000
C	-11.056293000	0.803462000	0.773021000
C	7.315610000	-0.734962000	-7.299658000
C	6.143298000	-0.428487000	-5.145984000
C	7.374869000	-0.616404000	-5.878675000
C	4.899999000	-0.368108000	-5.843837000
C	3.678613000	-0.187648000	-5.116542000
C	3.707000000	-0.063959000	-3.691451000
C	2.488680000	0.115159000	-2.964809000
C	1.241977000	0.162220000	-3.661516000
C	0.023634000	0.327438000	-2.934287000
C	0.050943000	0.454807000	-1.510892000
C	-1.169829000	0.588400000	-0.782396000
C	-2.419993000	0.590586000	-1.476310000
C	-3.644230000	0.667893000	-0.745621000
C	-3.619994000	0.735433000	0.681217000
C	-4.846663000	0.761812000	1.415452000
C	-6.096854000	0.744445000	0.720574000
C	-7.325490000	0.778677000	1.456849000
C	-7.302137000	0.820419000	2.883212000
C	-8.541257000	0.858198000	3.626205000
C	-9.772670000	0.857848000	2.904964000
C	8.594113000	-0.684795000	-5.167539000
C	7.414192000	-0.392548000	-3.023551000
C	8.644043000	-0.580369000	-3.759221000
C	6.172471000	-0.314480000	-3.723206000
C	4.950548000	-0.130647000	-2.994149000
C	4.976836000	-0.027065000	-1.570564000
C	3.759076000	0.153884000	-0.843170000
C	2.515541000	0.231334000	-1.541295000
C	1.296323000	0.404744000	-0.814257000
C	1.321748000	0.490944000	0.610397000
C	0.099959000	0.610944000	1.338905000
C	-1.145574000	0.660527000	0.642801000
C	-2.372255000	0.727599000	1.375099000
C	-2.351060000	0.739434000	2.803528000
C	-3.577805000	0.772712000	3.537126000
C	-4.824894000	0.787193000	2.842317000
C	-6.055959000	0.816833000	3.578947000
C	-6.032466000	0.839303000	5.005991000
C	-7.273222000	0.878406000	5.746048000
C	-8.495940000	0.890651000	5.037952000
C	9.870301000	-0.662732000	-3.033619000
C	8.683405000	-0.391102000	-0.896107000
C	9.912264000	-0.574865000	-1.639910000
C	7.441104000	-0.296949000	-1.599772000
C	6.221058000	-0.115747000	-0.870390000
C	6.245211000	-0.036518000	0.553548000
C	5.026542000	0.137171000	1.282415000
C	3.784532000	0.241102000	0.582923000
C	2.566144000	0.406424000	1.309558000
C	2.588483000	0.451999000	2.736899000
C	1.364751000	0.555902000	3.466600000
C	0.121301000	0.630362000	2.768770000

C	-1.104362000	0.692202000	3.500484000
C	-1.084891000	0.688019000	4.930032000
C	-2.312681000	0.738256000	5.662919000
C	-3.556926000	0.778395000	4.967769000
C	-4.786934000	0.817118000	5.701877000
C	-4.762332000	0.827840000	7.132573000
C	-6.009187000	0.873586000	7.867572000
C	-7.220350000	0.899470000	7.171900000
C	11.149772000	-0.669491000	-0.898167000
C	11.172975000	-0.596769000	0.470597000
C	8.707493000	-0.315256000	0.523316000
C	9.961236000	-0.421728000	1.239810000
C	7.489864000	-0.142331000	1.255174000
C	7.511124000	-0.086816000	2.681024000
C	6.293714000	0.070924000	3.409840000
C	5.048892000	0.190796000	2.708014000
C	3.830509000	0.340581000	3.435325000
C	3.848635000	0.345734000	4.865590000
C	2.627120000	0.452087000	5.594627000
C	1.382862000	0.550328000	4.895849000
C	0.159208000	0.622013000	5.626661000
C	0.178077000	0.615602000	7.061245000
C	-1.047224000	0.681018000	7.790738000
C	-2.292063000	0.738281000	7.095581000
C	-3.521824000	0.789134000	7.825413000
C	-3.492802000	0.794794000	9.273037000
C	-4.752721000	0.849355000	9.980132000
C	-5.949165000	0.886956000	9.312082000
C	9.966475000	-0.362340000	2.635698000
C	8.765385000	-0.201457000	3.389700000
C	8.763364000	-0.159532000	4.802149000
C	6.312867000	0.099660000	4.836905000
C	7.568451000	-0.016901000	5.542891000
C	5.093312000	0.229886000	5.566272000
C	5.108814000	0.240463000	6.997192000
C	3.891871000	0.350220000	7.723524000
C	2.645418000	0.448147000	7.027457000
C	1.421943000	0.536379000	7.756755000
C	1.439924000	0.535880000	9.201877000
C	0.216716000	0.613017000	9.904905000
C	-1.025932000	0.680858000	9.235708000
C	-2.265908000	0.743815000	9.939374000
C	7.557261000	0.008806000	6.969748000
C	6.371327000	0.131742000	7.697905000
C	6.352478000	0.150098000	9.143520000
C	3.902884000	0.356428000	9.171446000
C	5.178991000	0.257953000	9.843851000
C	2.697404000	0.450827000	9.871193000
H	12.084344000	-0.809294000	-1.462551000
H	12.126356000	-0.677579000	1.014811000
H	10.922359000	-0.449957000	3.174663000
H	9.719174000	-0.250449000	5.340408000
H	8.513968000	-0.078760000	7.507199000
H	7.312447000	0.071378000	9.675870000
H	5.188305000	0.268499000	10.944937000
H	2.712482000	0.453744000	10.972623000
H	0.232188000	0.613394000	11.006208000
H	-2.249153000	0.746709000	11.040781000
H	-4.730136000	0.857998000	11.081013000
H	-6.896880000	0.926199000	9.869979000
H	-8.165732000	0.933487000	7.734806000
H	-9.440870000	0.921392000	5.601556000
H	-10.717346000	0.890705000	3.469147000
H	-11.997363000	0.842300000	1.342699000
H	-12.038228000	0.739097000	-1.136125000
H	-10.829145000	0.607100000	-3.300688000
H	-9.623866000	0.449839000	-5.468833000
H	-8.420072000	0.259720000	-7.635354000
H	-7.223007000	0.036316000	-9.800603000
H	-5.099892000	-0.178648000	-11.068171000
H	-2.621130000	-0.318438000	-11.098154000
H	-0.140813000	-0.481192000	-11.131500000
H	2.337964000	-0.667520000	-11.163485000
H	4.812695000	-0.874655000	-11.198834000
H	6.979430000	-0.952140000	-9.987602000
H	8.253738000	-0.880346000	-7.856827000
H	9.531603000	-0.831995000	-5.725050000
H	10.807735000	-0.808244000	-3.591937000
C	-1.335505000	-2.724270000	-1.616957000
C	-2.687410000	-2.579411000	-1.255048000
C	-0.334329000	-2.763095000	-0.644022000
H	0.714075000	-2.860030000	-0.958678000
C	-3.038868000	-2.493706000	0.120586000
C	-0.662033000	-2.667402000	0.730555000
C	-2.030515000	-2.538012000	1.087448000
H	-2.310636000	-2.456410000	2.149806000
H	-1.079385000	-2.785452000	-2.686352000

```
O      -4.364913000     -2.347138000      0.407243000
H      -4.470535000     -2.251063000      1.374638000
O      -3.699844000     -2.497039000     -2.156522000
H      -3.322913000     -2.526485000     -3.058779000
C       0.340950000     -2.666178000      1.785392000
H      -0.044778000     -2.571880000      2.814185000
C       1.692290000     -2.755680000      1.623142000
H       2.151937000     -2.847201000      0.628350000
C       2.663000000     -2.731269000      2.717541000
O       3.882745000     -2.819727000      2.555447000
O       2.117177000     -2.597829000      3.959281000
H       2.869668000     -2.573007000      4.590439000
```

S1.6. Graphene–modifier–caffeic acid complex (G–Fe-TDC–CA)

Atoms: 229 | *Charge: 0* | *Multiplicity: 1*

```
Input header: !PBE def2-SVP RI D3BJ DEF2/J VERYSLOWCONV KDIIS TIGHTSCF PAL8 !KEEPDENS XYZFILE

229
C       0.331839115      2.304427217     -9.417554771
C      -2.143490127      2.215038067     -9.510827553
C      -4.617352491      2.020111393     -9.628033964
C      -3.432212416      1.856403003     -7.450212404
C      -3.378015140      2.041319230     -8.885044764
C      -4.677646417      1.628486891     -6.806699531
C      -5.818706557      1.804129287     -9.006471892
C      -5.900367602      1.586799895     -7.580062446
C      -7.113016427      1.330146283     -6.939042527
C      -8.407682434      0.803980053     -4.889560209
C       5.288101587      2.089428321     -9.302126925
C       2.809600456      2.257415110     -9.347148797
C       1.496362974      2.074497056     -7.260734669
C       1.540819155      2.224783395     -8.695521520
C       0.240633829      2.006931176     -6.589357439
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C	3.687044070	-3.533222298	-2.789207024
H	3.580140211	-2.986734074	-3.734196409
C	4.646903336	-2.962002975	-1.867655957
O	4.970511628	-1.741242392	-1.876420191
O	5.199250611	-3.787660245	-0.975277903
H	5.727843648	-3.243231049	-0.345503001

Section S2. Conformer energy tables

Table S1. Relative energies of the tested conformations for the graphene–Fe-TDC adsorption system.

System	Conformer label	Electronic energy (Eh)	Relative energy (kcal mol^{-1})	Selected for discussion?
Graphene–Fe-TDC-1	Conf. 1	-8223.1418	1.76	
Graphene–Fe-TDC-2	Conf. 2	-8223.1392	3.39	
Graphene–Fe-TDC-3	Conf. 3	-8223.1446	0.00	Yes
Graphene–Fe-TDC-4	Conf. 4	-8223.1373	4.58	

Table S2. Relative energies of the tested conformations for the graphene–caffeic acid adsorption system.

System	Conformer label	Electronic energy (Eh)	Relative energy (kcal mol^{-1})	Selected for discussion?
Graphene–CA-1	Conf. 1	-6372.4377	0.00	Yes
Graphene–CA-2	Conf. 2	-6372.4365	0.75	
Graphene–CA-3	Conf. 3	-6372.4289	5.52	
Graphene–CA-4	Conf. 4	-6372.4312	4.08	

Table S3. Relative energies of the tested conformations for the graphene–Fe-TDC–caffeic acid adsorption system.

System	Conformer label	Electronic energy (Eh)	Relative energy (kcal mol^{-1})	Selected for discussion?
Graphene–Fe-TDC–CA-1	Conf. 1	-8870.6986	1.00	
Graphene–Fe-TDC–CA-2	Conf. 2	-8870.7002	0.00	Yes
Graphene–Fe-TDC–CA-3	Conf. 3	-8870.6852	9.41	
Graphene–Fe-TDC–CA-4	Conf. 4	-8870.6711	18.26	

Section S3. Benchmark single-point energy tables

Table S4. Absolute electronic energies used for the benchmark single-point analysis.

System	Original level (Eh)	Larger basis (Eh)	Alternative functional (Eh)	Solvation test (Eh)
Graphene nanoflake (G)	-5724.8908	-5730.655	-5725.253	-5724.85729
Modifier (Fe-TDC)	-2498.0993	-2499.369	-2498.131	-2498.07611
Caffeic acid (CA)	-647.5084	-648.2369	-647.5244	-647.484023
Graphene–modifier complex (G–Fe-TDC)	-8223.1446	-8230.153	-8223.507	-8223.08917
Graphene–caffeic acid complex (G–CA)	-6372.437	-6378.923	-6372.823	-6372.38571
Graphene–modifier–caffeic acid complex (G–Fe-TDC–CA)	-8870.7002	-8878.419	-8871.088	-8870.61992

Note: Original level: PBE-D3BJ/def2-SVP/SMD(water), using the optimized geometries reported in the main manuscript. Larger basis: PBE-D3BJ/def2-TZVP/SMD(water). Alternative functional: PBE0-D3BJ/def2-SVP/SMD(water). Solvation test: PBE-D3BJ/def2-SVP in gas phase.

Table S5. Adsorption energies (without BSSE correction) derived from the benchmark single-point calculations.

Adsorption process	Original value (kcal mol^{-1})	Larger basis	Alternative functional	Solvation test
Fe-TDC on graphene	96.97	81.26	77.43	97.74
Caffeic acid on graphene	23.52	19.65	28.58	27.86
Caffeic acid on modified graphene	29.55	18.55	35.18	29.32

Note: The benchmark adsorption energies are fixed-geometry, non-BSSE-corrected values and are provided only to evaluate methodological sensitivity. The BSSE-corrected values discussed in the main text remain the primary adsorption-energy dataset.

End of Supplementary Information