

Supplementary Information

Iron Intercalation in Covalent-Organic Frameworks: A Promising Approach for Semiconductors

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1 Individual spins of the Fe atoms in the intercalated COFs

We used the dispersion-corrected unrestricted B3LYP-D hybrid Density Functional Theory (DFT) method in this work, i.e. UB3LYP-D.[1–9] All the computations were performed using CRYSTAL14 program NOT VASP as stated in the main manuscript. This means that we have used Gaussian basis sets not plane-wave basis sets. Thus, we used the unrestricted wave function to consider the spin polarization of Fe atoms. To specify the spin unrestricted calculations, we used “SPIN” keyword. The spins of Fe atoms were fixed by the “ATOMSPIN” and “SPINLOCK” keywords in the calculations using the aforementioned program/code. In order to converge the Self-Consistent Field (SCF) calculations, we assigned the spins of the individual Fe atoms in the intercalated COFs. Initially, we locked the spins of Fe atoms up to four SCF cycles, and after that, the spins of all atoms were relaxed. We have also performed Mulliken spin population analysis in the present computations. We found that C, H, N, B, O have no unpaired spins and Fe atoms have unpaired spins. Table S1 shows the individual spins of Fe and average spin of Fe. The individual spins of the iron atoms (Fe) and average spin of Fe in the intercalated COFs (COF-Fe-0, COF-Fe-1A, COF-Fe-1B, COF-Fe-2, COF-Fe-3, COF-Fe-4A, COF-Fe-4B and COF-Fe-5) are shown in Table S1.

Table S1: Individual spins of the Fe atoms in COF-Fe-0, COF-Fe-1A, COF-Fe-1B, COF-Fe-2, COF-Fe-3, COF-Fe-4A, COF-Fe-4B and COF-Fe-5.

COFs	No of Fe	Fe1	Fe2	Fe3	Fe4	Fe5	Average Spin of Fe
COF-Fe-0	0	N/A	N/A	N/A	N/A	N/A	N/A
COF-Fe-1A	1	2.373	N/A	N/A	N/A	N/A	2.373
COF-Fe-1B	1	N/A	2.334	N/A	N/A	N/A	2.334
COF-Fe-2	2	2.363	3.283	N/A	N/A	N/A	2.826
COF-Fe-3	3	N/A	N/A	2.635	2.635	2.635	2.635
COF-Fe-4A	4	2.129	N/A	2.624	2.624	2.624	2.500
COF-Fe-4B	4	N/A	2.878	2.606	2.606	2.606	2.674
COF-Fe-5	5	2.326	2.876	2.610	2.610	2.610	2.606

2 Optimized Structures (.cif format)

The optimized structures are provided below in .cif format.

2.1 COF-Fe-0: Pristine COF

Total Energy $E_{COF-Fe-0} = -1271.9764747$ a.u.

```
data_COF-Fe-0
_symmetry_space_group_name_H-M      'P-6M2'
_symmetry_Int_Tables_number          187
_symmetry_cell_setting                hexagonal
loop_
_symmetry_equiv_pos_as_xyz
  x,y,z
  -y,x-y,z
  -x+y,-x,z
  x,y,-z
  -y,x-y,-z
  -x+y,-x,-z
  -y,-x,z
  -x+y,y,z
  x,x-y,z
  -y,-x,-z
```

```

-x+y,y,-z
x,x-y,-z
_cell_length_a      14.7275
_cell_length_b      14.7275
_cell_length_c       3.2408
_cell_angle_alpha    90.0000
_cell_angle_beta     90.0000
_cell_angle_gamma    120.0000
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_adp_type
_atom_site_occupancy
C001  C    -0.38821 -0.44832  0.00000  0.00000  Uiso  1.00
C007  C     0.04784 -0.39468 -0.00000  0.00000  Uiso  1.00
H013  H     0.40727  0.10371 -0.00000  0.00000  Uiso  1.00
H019  H    -0.40041 -0.30980  0.00000  0.00000  Uiso  1.00
C025  C    -0.38476  0.38476 -0.00000  0.00000  Uiso  1.00
C028  C    -0.44247  0.44247  0.00000  0.00000  Uiso  1.00
B031  B     0.38811 -0.38811 -0.00000  0.00000  Uiso  1.00
N034  N    -0.27996  0.27996 -0.00000  0.00000  Uiso  1.00
C037  C     0.44818 -0.44818 -0.00000  0.00000  Uiso  1.00
O040  O     0.27968 -0.27968  0.00000  0.00000  Uiso  1.00

```

2.2 COF-Fe-1A: Fe-intercalated COF

Total Energy $E_{COF-Fe-0} = -2535.4864722$ a.u.

```

data_COF-Fe-1A
_symmetry_space_group_name_H-M    'P-6M2'
_symmetry_Int_Tables_number       187
_symmetry_cell_setting             hexagonal
loop_
_symmetry_equiv_pos_as_xyz
x,y,z
-y,x-y,z
-x+y,-x,z
x,y,-z
-y,x-y,-z
-x+y,-x,-z
-y,-x,z
-x+y,y,z
x,x-y,z
-y,-x,-z
-x+y,y,-z
x,x-y,-z
_cell_length_a      14.8551
_cell_length_b      14.8551
_cell_length_c       3.3120
_cell_angle_alpha    90.0000

```

```

_cell_angle_beta          90.0000
_cell_angle_gamma        120.0000
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_adp_type
_atom_site_occupancy
C001  C    -0.38781 -0.45017  0.00000  0.00000  Uiso  1.00
C007  C     0.04457 -0.39692  0.00000  0.00000  Uiso  1.00
H013  H     0.40944  0.10555 -0.00000  0.00000  Uiso  1.00
H019  H    -0.39947 -0.31275  0.00000  0.00000  Uiso  1.00
C025  C    -0.38433  0.38433 -0.00000  0.00000  Uiso  1.00
C028  C    -0.44148  0.44148 -0.00000  0.00000  Uiso  1.00
B031  B     0.39123 -0.39123  0.00000  0.00000  Uiso  1.00
N034  N    -0.28036  0.28036 -0.00000  0.00000  Uiso  1.00
C037  C     0.44999 -0.44999  0.00000  0.00000  Uiso  1.00
O040  O     0.27929 -0.27929 -0.00000  0.00000  Uiso  1.00
FE043 Fe     0.33333 -0.33333  0.50000  0.00000  Uiso  1.00

```

2.3 COF-Fe-1B: Fe-intercalated COF

Total Energy $E_{COF-Fe-0} = -2535.5437897$ a.u.

```

data_COF-Fe-1B
_symmetry_space_group_name_H-M  'P-6M2'
_symmetry_Int_Tables_number     187
_symmetry_cell_setting          hexagonal
loop_
_symmetry_equiv_pos_as_xyz
  x,y,z
  -y,x-y,z
  -x+y,-x,z
  x,y,-z
  -y,x-y,-z
  -x+y,-x,-z
  -y,-x,z
  -x+y,y,z
  x,x-y,z
  -y,-x,-z
  -x+y,y,-z
  x,x-y,-z
_cell_length_a                14.8000
_cell_length_b                14.8000
_cell_length_c                 3.2922
_cell_angle_alpha              90.0000
_cell_angle_beta               90.0000
_cell_angle_gamma              120.0000
loop_
_atom_site_label
_atom_site_type_symbol

```

```

_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_adp_type
_atom_site_occupancy
C001  C    -0.38947  -0.44767   0.00000   0.00000  Uiso  1.00
C007  C     0.04916  -0.39445  -0.00000   0.00000  Uiso  1.00
H013  H     0.40661   0.10137  -0.00000   0.00000  Uiso  1.00
H019  H    -0.40166  -0.30998   0.00000   0.00000  Uiso  1.00
C025  C    -0.38663   0.38663   0.00000   0.00000  Uiso  1.00
C028  C    -0.44354   0.44354   0.00000   0.00000  Uiso  1.00
B031  B     0.38785  -0.38785   0.00000   0.00000  Uiso  1.00
N034  N    -0.27862   0.27862   0.00000   0.00000  Uiso  1.00
C037  C     0.44758  -0.44758  -0.00000   0.00000  Uiso  1.00
O040  O     0.27992  -0.27992   0.00000   0.00000  Uiso  1.00
FE043 Fe    -0.33333   0.33333   0.50000   0.00000  Uiso  1.00

```

2.4 COF-Fe-2: Fe-intercalated COF

Total Energy $E_{COF-Fe-0} = -3799.0160587$ a.u.

```

data_COF-Fe-2
_symmetry_space_group_name_H-M    'P-6M2'
_symmetry_Int_Tables_number       187
_symmetry_cell_setting             hexagonal
loop_
_symmetry_equiv_pos_as_xyz
  x,y,z
  -y,x-y,z
  -x+y,-x,z
  x,y,-z
  -y,x-y,-z
  -x+y,-x,-z
  -y,-x,z
  -x+y,y,z
  x,x-y,z
  -y,-x,-z
  -x+y,y,-z
  x,x-y,-z
_cell_length_a                     14.9492
_cell_length_b                     14.9492
_cell_length_c                     3.3717
_cell_angle_alpha                   90.0000
_cell_angle_beta                   90.0000
_cell_angle_gamma                   120.0000
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_adp_type

```

_atom_site_occupancy							
C001	C	-0.38942	-0.44890	0.00000	0.00000	Uiso	1.00
C007	C	0.04650	-0.39645	-0.00000	0.00000	Uiso	1.00
H013	H	0.40801	0.10201	-0.00000	0.00000	Uiso	1.00
H019	H	-0.40122	-0.31280	0.00000	0.00000	Uiso	1.00
C025	C	-0.38737	0.38737	0.00000	0.00000	Uiso	1.00
C028	C	-0.44285	0.44285	0.00000	0.00000	Uiso	1.00
B031	B	0.39062	-0.39062	-0.00000	0.00000	Uiso	1.00
N034	N	-0.27840	0.27840	0.00000	0.00000	Uiso	1.00
C037	C	0.44902	-0.44902	-0.00000	0.00000	Uiso	1.00
O040	O	0.27966	-0.27966	-0.00000	0.00000	Uiso	1.00
FE043	Fe	0.33333	-0.33333	-0.50000	0.00000	Uiso	1.00
FE044	Fe	-0.33333	0.33333	-0.50000	0.00000	Uiso	1.00

2.5 COF-Fe-3: Fe-intercalated COF

Total Energy $E_{COF-Fe-0} = -5062.8211239$ a.u.

data_COF-Fe-3							
_symmetry_space_group_name_H-M				'P-6M2'			
_symmetry_Int_Tables_number				187			
_symmetry_cell_setting				hexagonal			
loop_							
_symmetry_equiv_pos_as_xyz							
x,y,z							
-y,x-y,z							
-x+y,-x,z							
x,y,-z							
-y,x-y,-z							
-x+y,-x,-z							
-y,-x,z							
-x+y,y,z							
x,x-y,z							
-y,-x,-z							
-x+y,y,-z							
x,x-y,-z							
_cell_length_a				14.8311			
_cell_length_b				14.8311			
_cell_length_c				3.4436			
_cell_angle_alpha				90.0000			
_cell_angle_beta				90.0000			
_cell_angle_gamma				120.0000			
loop_							
_atom_site_label							
_atom_site_type_symbol							
_atom_site_fract_x							
_atom_site_fract_y							
_atom_site_fract_z							
_atom_site_U_iso_or_equiv							
_atom_site_adp_type							
_atom_site_occupancy							
C001	C	-0.38597	-0.44685	0.00000	0.00000	Uiso	1.00
C007	C	0.04847	-0.39240	0.00000	0.00000	Uiso	1.00
H013	H	0.40659	0.10439	-0.00000	0.00000	Uiso	1.00

H019	H	-0.39936	-0.30842	0.00000	0.00000	Uiso	1.00
C025	C	-0.38441	0.38441	-0.00000	0.00000	Uiso	1.00
C028	C	-0.44073	0.44073	-0.00000	0.00000	Uiso	1.00
B031	B	0.38771	-0.38771	0.00000	0.00000	Uiso	1.00
N034	N	-0.28000	0.28000	-0.00000	0.00000	Uiso	1.00
C037	C	0.44649	-0.44649	0.00000	0.00000	Uiso	1.00
O040	O	0.27983	-0.27983	0.00000	0.00000	Uiso	1.00
FE043	Fe	-0.49763	0.49763	-0.50000	0.00000	Uiso	1.00

2.6 COF-Fe-4A: Fe-intercalated COF

Total Energy $E_{COF-Fe-0} = -6326.3252772$ a.u.

```

data_COF-Fe-4A
_symmetry_space_group_name_H-M      'P-6M2'
_symmetry_Int_Tables_number          187
_symmetry_cell_setting                hexagonal
loop_
_symmetry_equiv_pos_as_xyz
  x,y,z
  -y,x-y,z
  -x+y,-x,z
  x,y,-z
  -y,x-y,-z
  -x+y,-x,-z
  -y,-x,z
  -x+y,y,z
  x,x-y,z
  -y,-x,-z
  -x+y,y,-z
  x,x-y,-z
_cell_length_a                        14.9482
_cell_length_b                        14.9482
_cell_length_c                        3.4482
_cell_angle_alpha                     90.0000
_cell_angle_beta                      90.0000
_cell_angle_gamma                     120.0000
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_adp_type
_atom_site_occupancy
C001  C      -0.38561  -0.44844  0.00000  0.00000  Uiso  1.00
C007  C       0.04584  -0.39468  0.00000  0.00000  Uiso  1.00
H013  H       0.40834   0.10584  0.00000  0.00000  Uiso  1.00
H019  H      -0.39919  -0.31132  0.00000  0.00000  Uiso  1.00
C025  C      -0.38400   0.38400  0.00000  0.00000  Uiso  1.00
C028  C      -0.43988   0.43988  0.00000  0.00000  Uiso  1.00
B031  B       0.39010  -0.39010  0.00000  0.00000  Uiso  1.00
N034  N      -0.28041   0.28041  0.00000  0.00000  Uiso  1.00

```

C037	C	0.44820	-0.44820	0.00000	0.00000	Uiso	1.00
O040	O	0.27953	-0.27953	0.00000	0.00000	Uiso	1.00
FE043	Fe	-0.49468	0.49468	-0.50000	0.00000	Uiso	1.00
FE046	Fe	0.33333	-0.33333	-0.50000	0.00000	Uiso	1.00

2.7 COF-Fe-4B: Fe-intercalated COF

Total Energy $E_{COF-Fe-0} = -6326.3861850$ a.u.

data_COF-Fe-4B							
_symmetry_space_group_name_H-M				'P-6M2'			
_symmetry_Int_Tables_number				187			
_symmetry_cell_setting				hexagonal			
loop_							
_symmetry_equiv_pos_as_xyz							
x,y,z							
-y,x-y,z							
-x+y,-x,z							
x,y,-z							
-y,x-y,-z							
-x+y,-x,-z							
-y,-x,z							
-x+y,y,z							
x,x-y,z							
-y,-x,-z							
-x+y,y,-z							
x,x-y,-z							
_cell_length_a				14.9245			
_cell_length_b				14.9245			
_cell_length_c				3.4520			
_cell_angle_alpha				90.0000			
_cell_angle_beta				90.0000			
_cell_angle_gamma				120.0000			
loop_							
_atom_site_label							
_atom_site_type_symbol							
_atom_site_fract_x							
_atom_site_fract_y							
_atom_site_fract_z							
_atom_site_U_iso_or_equiv							
_atom_site_adp_type							
_atom_site_occupancy							
C001	C	-0.38779	-0.44667	0.00000	0.00000	Uiso	1.00
C007	C	0.04995	-0.39220	0.00000	0.00000	Uiso	1.00
H013	H	0.40650	0.10198	-0.00000	0.00000	Uiso	1.00
H019	H	-0.40074	-0.30876	0.00000	0.00000	Uiso	1.00
C025	C	-0.38655	0.38655	0.00000	0.00000	Uiso	1.00
C028	C	-0.44193	0.44193	0.00000	0.00000	Uiso	1.00
B031	B	0.38735	-0.38735	0.00000	0.00000	Uiso	1.00
N034	N	-0.27833	0.27833	0.00000	0.00000	Uiso	1.00
C037	C	0.44580	-0.44579	-0.00000	0.00000	Uiso	1.00
O040	O	0.28013	-0.28013	0.00000	0.00000	Uiso	1.00
FE043	Fe	0.49969	-0.49969	0.50000	0.00000	Uiso	1.00
FE046	Fe	-0.33333	0.33333	0.50000	0.00000	Uiso	1.00

2.8 COF-Fe-5: Fe-intercalated COF

Total Energy $E_{COF-Fe-0} = -7589.8886945$ a.u.

```

data_COF-Fe-5
_symmetry_space_group_name_H-M      'P-6M2'
_symmetry_Int_Tables_number          187
_symmetry_cell_setting                hexagonal
loop_
_symmetry_equiv_pos_as_xyz
  x,y,z
  -y,x-y,z
  -x+y,-x,z
  x,y,-z
  -y,x-y,-z
  -x+y,-x,-z
  -y,-x,z
  -x+y,y,z
  x,x-y,z
  -y,-x,-z
  -x+y,y,-z
  x,x-y,-z
_cell_length_a                        15.0355
_cell_length_b                        15.0355
_cell_length_c                        3.4523
_cell_angle_alpha                     90.0000
_cell_angle_beta                      90.0000
_cell_angle_gamma                     120.0000
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_adp_type
_atom_site_occupancy
C001  C      -0.38729  -0.44814   0.00000   0.00000  Uiso  1.00
C007  C       0.04722  -0.39433   0.00000   0.00000  Uiso  1.00
H013  H       0.40828   0.10364  -0.00000   0.00000  Uiso  1.00
H019  H      -0.40029  -0.31146   0.00000   0.00000  Uiso  1.00
C025  C      -0.38613   0.38613  -0.00000   0.00000  Uiso  1.00
C028  C      -0.44109   0.44109   0.00000   0.00000  Uiso  1.00
B031  B       0.38992  -0.38992  -0.00000   0.00000  Uiso  1.00
N034  N      -0.27876   0.27876   0.00000   0.00000  Uiso  1.00
C037  C       0.44749  -0.44749  -0.00000   0.00000  Uiso  1.00
O040  O       0.27988  -0.27988   0.00000   0.00000  Uiso  1.00
FE043 Fe      -0.49749   0.49749  -0.50000   0.00000  Uiso  1.00
FE046 Fe       0.33333  -0.33333  -0.50000   0.00000  Uiso  1.00
FE047 Fe      -0.33333   0.33333  -0.50000   0.00000  Uiso  1.00

```

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