Electronic supplementary Information (ESI)

Figure S1. Powder XRD pattern (experimental, fitted theoretical and their difference) for Fe(1-MeIm)$_2$[Fe(CN)$_5$NO] refined by the Rietveld method. Inset: Coordination environment of the involved metal centers.

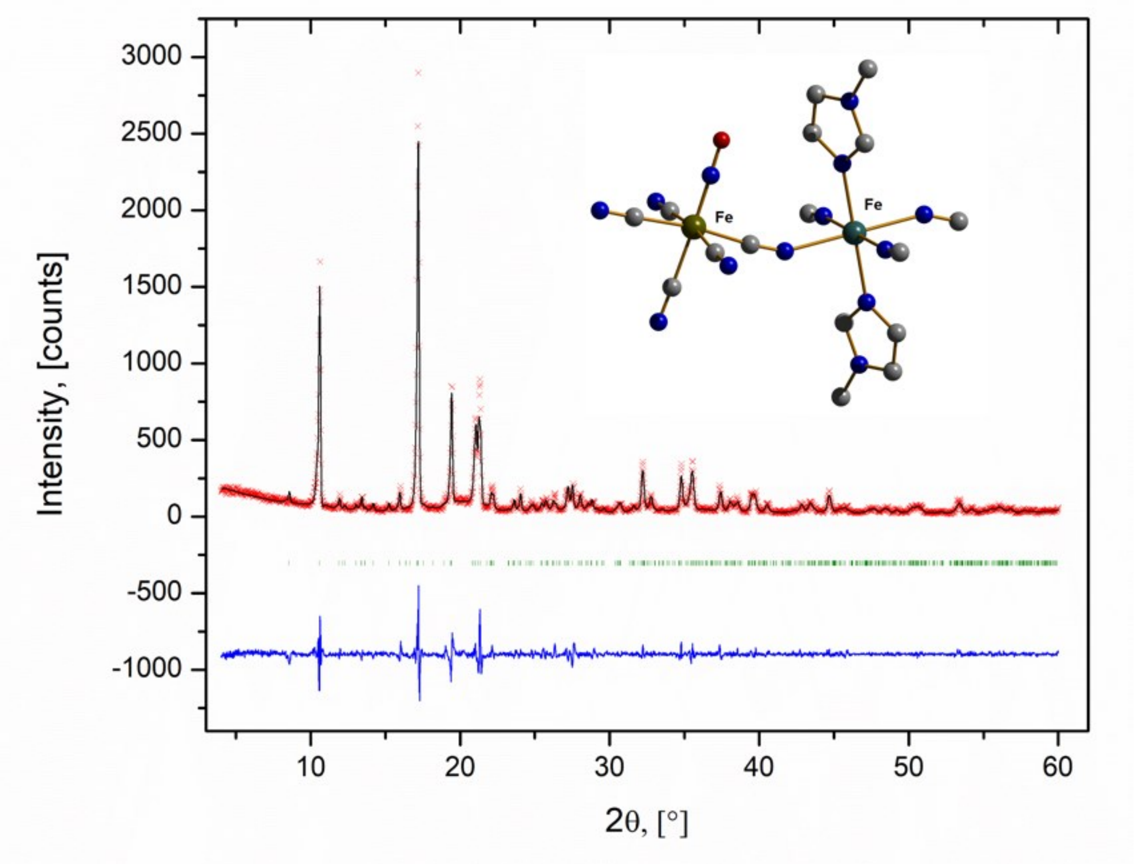


Figure S2. (a) Coordination environment of the Fe(II) ions in complex **2** with the atom numbering scheme. H-atoms are omitted for clarity (b). View of the crystal packing showing C-H···N hydrogen bonds, chalcogen O···N5, π···π and lone-pair(O)···π interactions.

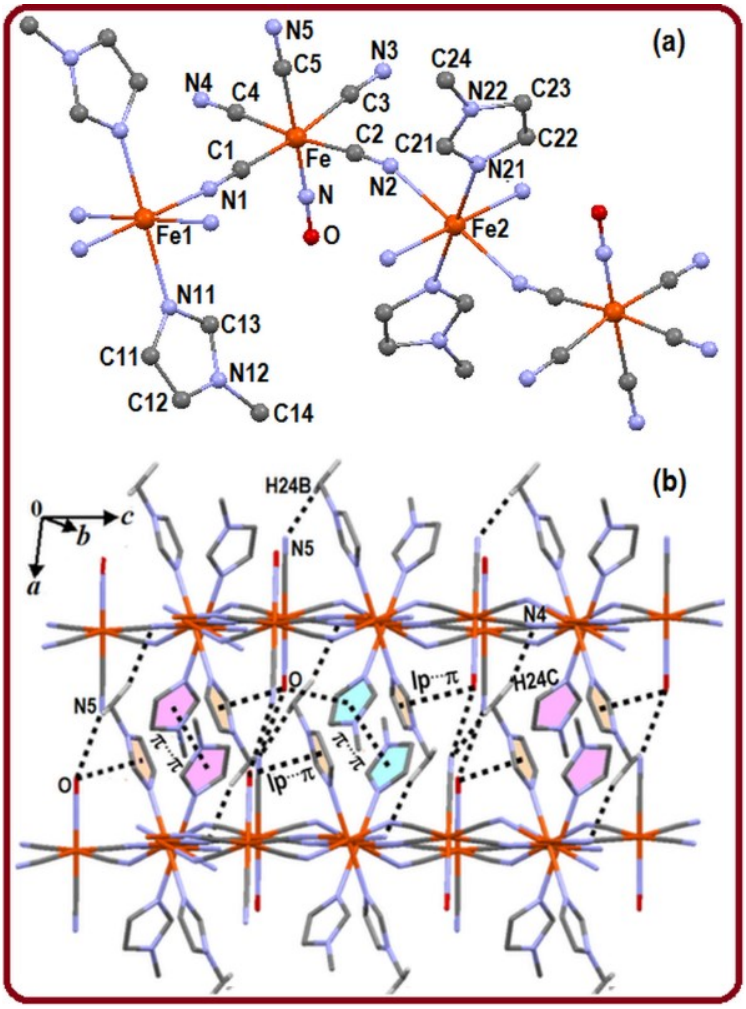


Figure S3. (a) Coordination environment of the Cd(II) and Fe(II) ions in complex **5** with the atom numbering scheme. H-atoms are omitted for clarity (b). View of the crystal packing showing C-H···N hydrogen bonds, chalcogen O···N5, π···π and lone-pair(O)···π interactions.

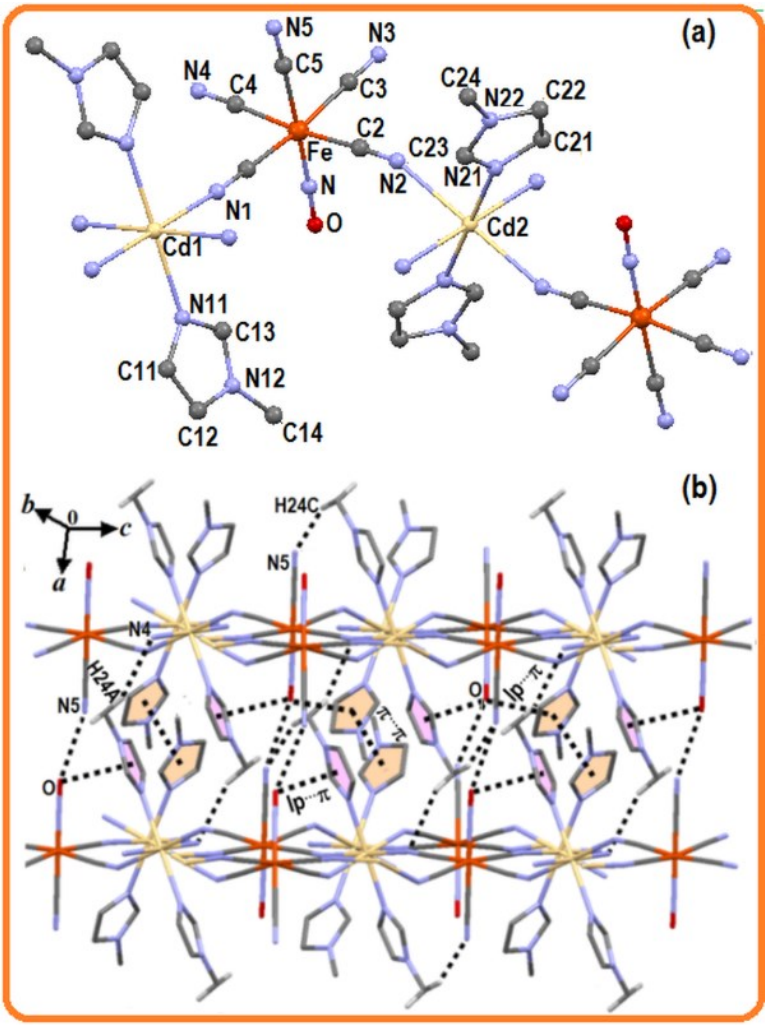
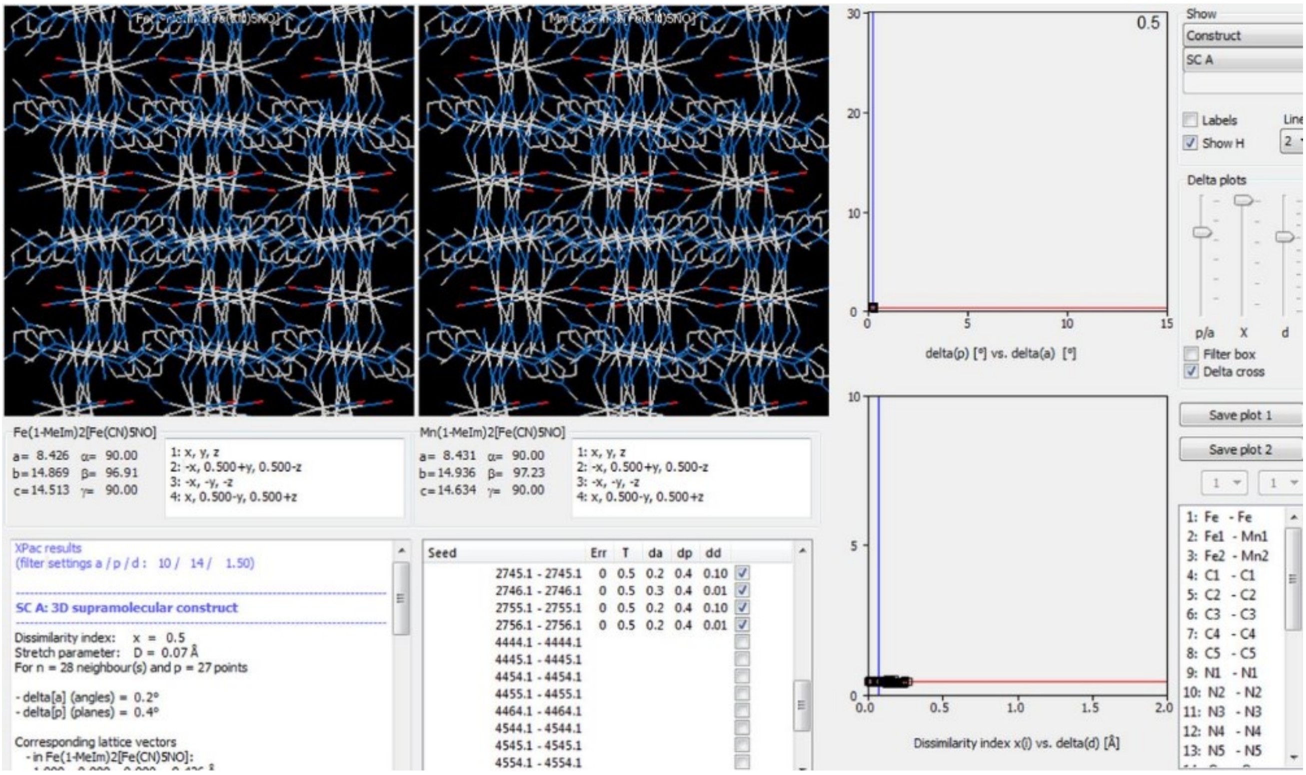


Figure S4. XPac results window showing the comparison of complexes **1** and **2.**



Fe(1-MeIm)2[Fe(CN)5NO]

a= 8.426 α= 90.00
b=14.869 β= 96.91
c=14.513 γ= 90.00

1: x, y, z
2: -x, 0.500+y, 0.500-z
3: -x, -y, -z
4: x, 0.500-y, 0.500+z

Mn(1-MeIm)2[Fe(CN)5NO]

a= 8.431 α= 90.00
b=14.936 β= 97.23
c=14.634 γ= 90.00

1: x, y, z
2: -x, 0.500+y, 0.500-z
3: -x, -y, -z
4: x, 0.500-y, 0.500+z

XPac results
(filter settings a / p / d : 10 / 14 / 1.50)

SC A: 3D supramolecular construct

Dissimilarity index: x = 0.5
Stretch parameter: D = 0.07 Å
For n = 28 neighbour(s) and p = 27 points

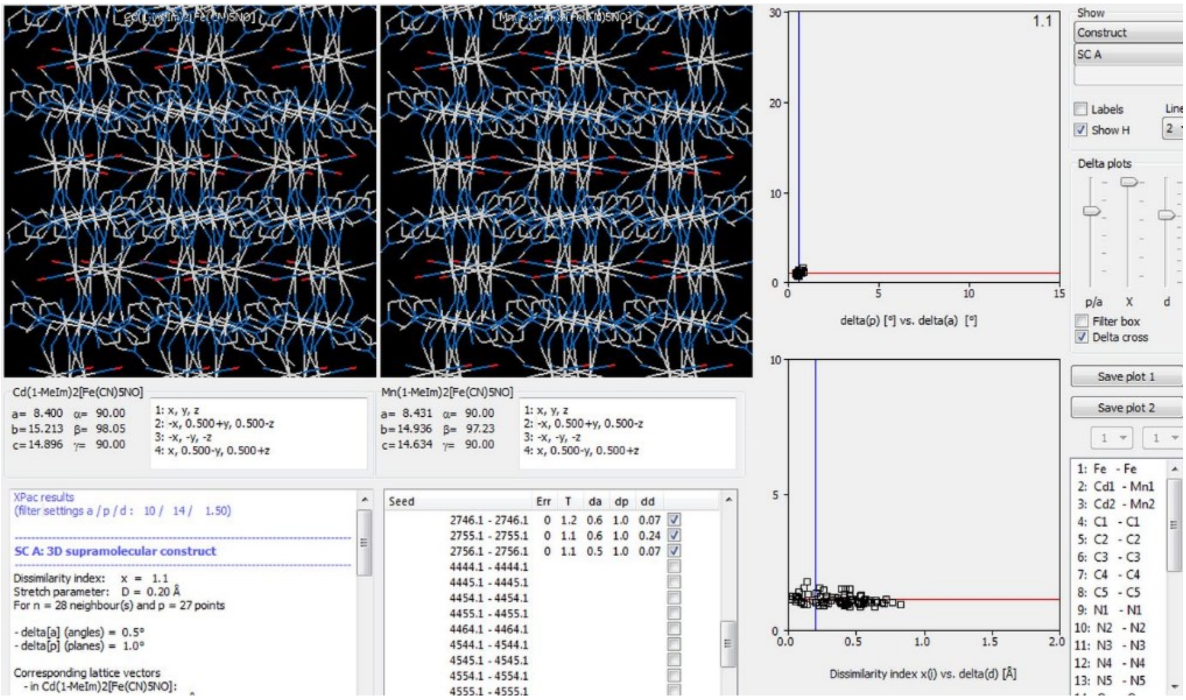
- delta[a] (angles) = 0.2°
- delta[p] (planes) = 0.4°

Corresponding lattice vectors
- in Fe(1-MeIm)2[Fe(CN)5NO]:

Seed	Err	T	da	dp	dd	
2745.1 - 2745.1	0	0.5	0.2	0.4	0.10	☑
2746.1 - 2746.1	0	0.5	0.3	0.4	0.01	☑
2755.1 - 2755.1	0	0.5	0.2	0.4	0.10	☑
2756.1 - 2756.1	0	0.5	0.2	0.4	0.01	☑
4444.1 - 4444.1						☐
4445.1 - 4445.1						☐
4454.1 - 4454.1						☐
4455.1 - 4455.1						☐
4464.1 - 4464.1						☐
4544.1 - 4544.1						☐
4545.1 - 4545.1						☐
4554.1 - 4554.1						☐

1: Fe - Fe
2: Fe1 - Mn1
3: Fe2 - Mn2
4: C1 - C1
5: C2 - C2
6: C3 - C3
7: C4 - C4
8: C5 - C5
9: N1 - N1
10: N2 - N2
11: N3 - N3
12: N4 - N4
13: N5 - N5

Figure S5. XPac results window showing the comparison of complexes **1** and **5.**



Cd(1-MeIm)2[Fe(CN)5NO]

a= 8.400 α= 90.00
b=15.213 β= 98.05
c=14.896 γ= 90.00

1: x, y, z
2: -x, 0.500+y, 0.500-z
3: -x, -y, -z
4: x, 0.500-y, 0.500+z

Mn(1-MeIm)2[Fe(CN)5NO]

a= 8.431 α= 90.00
b=14.936 β= 97.23
c=14.634 γ= 90.00

1: x, y, z
2: -x, 0.500+y, 0.500-z
3: -x, -y, -z
4: x, 0.500-y, 0.500+z

XPac results
(filter settings a / p / d : 10 / 14 / 1.50)

SC A: 3D supramolecular construct

Dissimilarity index: x = 1.1
Stretch parameter: D = 0.20 Å
For n = 28 neighbour(s) and p = 27 points

- delta[a] (angles) = 0.5°
- delta[p] (planes) = 1.0°

Corresponding lattice vectors
- in Cd(1-MeIm)2[Fe(CN)5NO]:

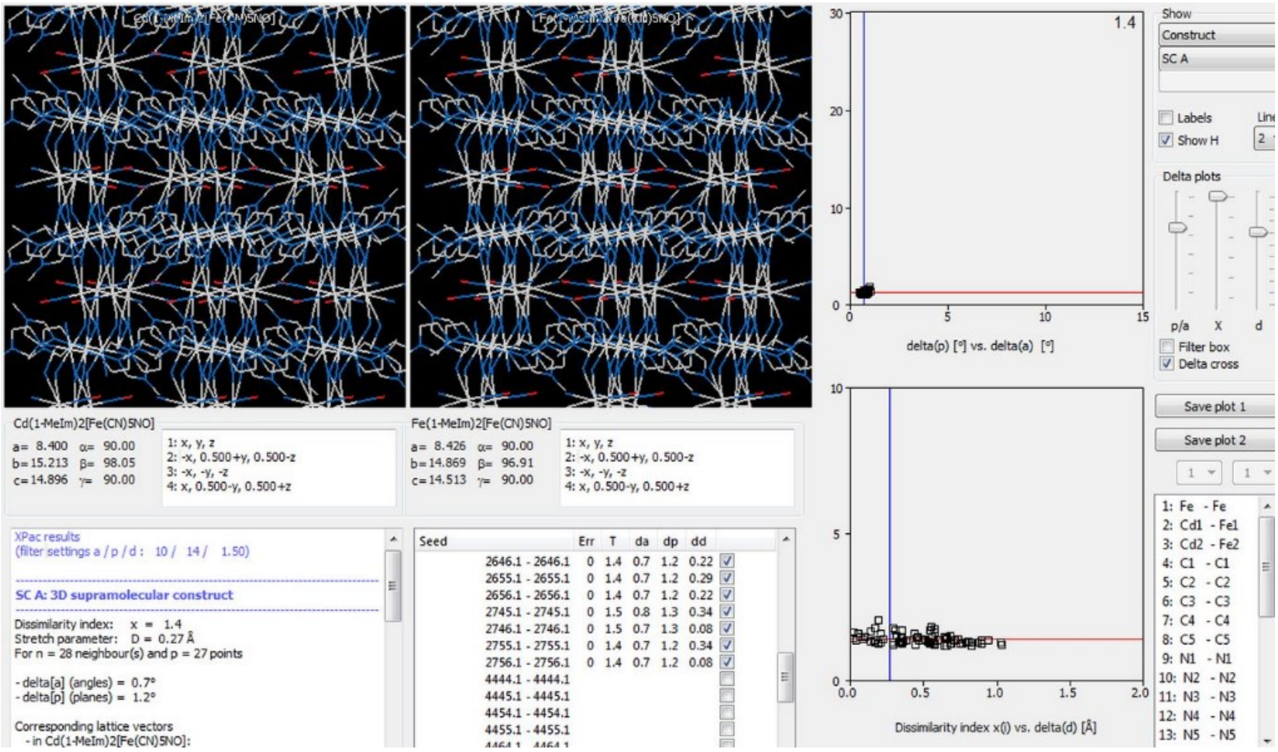
Seed	Err	T	da	dp	dd	
2746.1 - 2746.1	0	1.2	0.6	1.0	0.07	☑
2755.1 - 2755.1	0	1.1	0.6	1.0	0.24	☑
2756.1 - 2756.1	0	1.1	0.5	1.0	0.07	☑
4444.1 - 4444.1						☐
4445.1 - 4445.1						☐
4454.1 - 4454.1						☐
4455.1 - 4455.1						☐
4464.1 - 4464.1						☐
4544.1 - 4544.1						☐
4545.1 - 4545.1						☐
4554.1 - 4554.1						☐
4555.1 - 4555.1						☐

Show
Construct
SC A

☐ Labels
☑ Show H

1: Fe - Fe
2: Cd1 - Mn1
3: Cd2 - Mn2
4: C1 - C1
5: C2 - C2
6: C3 - C3
7: C4 - C4
8: C5 - C5
9: N1 - N1
10: N2 - N2
11: N3 - N3
12: N4 - N4
13: N5 - N5

Figure S6. XPac results window showing the comparison of complexes **2** and **5.**



Cd(1-MeIm)2[Fe(CN)5NO]

a= 8.400 α= 90.00
b= 15.213 β= 98.05
c= 14.896 γ= 90.00

1: x, y, z
2: -x, 0.500+y, 0.500-z
3: -x, -y, -z
4: x, 0.500-y, 0.500+z

Fe(1-MeIm)2[Fe(CN)5NO]

a= 8.426 α= 90.00
b= 14.869 β= 96.91
c= 14.513 γ= 90.00

1: x, y, z
2: -x, 0.500+y, 0.500-z
3: -x, -y, -z
4: x, 0.500-y, 0.500+z

XPac results
(filter settings a / p / d : 10 / 14 / 1.50)

SC A: 3D supramolecular construct

Dissimilarity index: x = 1.4
Stretch parameter: D = 0.27 Å
For n = 28 neighbour(s) and p = 27 points

- delta[a] (angles) = 0.7°
- delta[p] (planes) = 1.2°

Corresponding lattice vectors
- in Cd(1-MeIm)2[Fe(CN)5NO]:

Seed	Err	T	da	dp	dd	
2646.1 - 2646.1	0	1.4	0.7	1.2	0.22	☑
2655.1 - 2655.1	0	1.4	0.7	1.2	0.29	☑
2656.1 - 2656.1	0	1.4	0.7	1.2	0.22	☑
2745.1 - 2745.1	0	1.5	0.8	1.3	0.34	☑
2746.1 - 2746.1	0	1.5	0.7	1.3	0.08	☑
2755.1 - 2755.1	0	1.4	0.7	1.2	0.34	☑
2756.1 - 2756.1	0	1.4	0.7	1.2	0.08	☑
4444.1 - 4444.1						☐
4445.1 - 4445.1						☐
4454.1 - 4454.1						☐
4455.1 - 4455.1						☐

Construct
SC A

☐ Labels
☑ Show H

☐ Filter box
☑ Delta cross

1: Fe - Fe
2: Cd1 - Fe1
3: Cd2 - Fe2
4: C1 - C1
5: C2 - C2
6: C3 - C3
7: C4 - C4
8: C5 - C5
9: N1 - N1
10: N2 - N2
11: N3 - N3
12: N4 - N4
13: N5 - N5

Figure S7. PXRD patterns for complexes **1**, **2** and **5**.

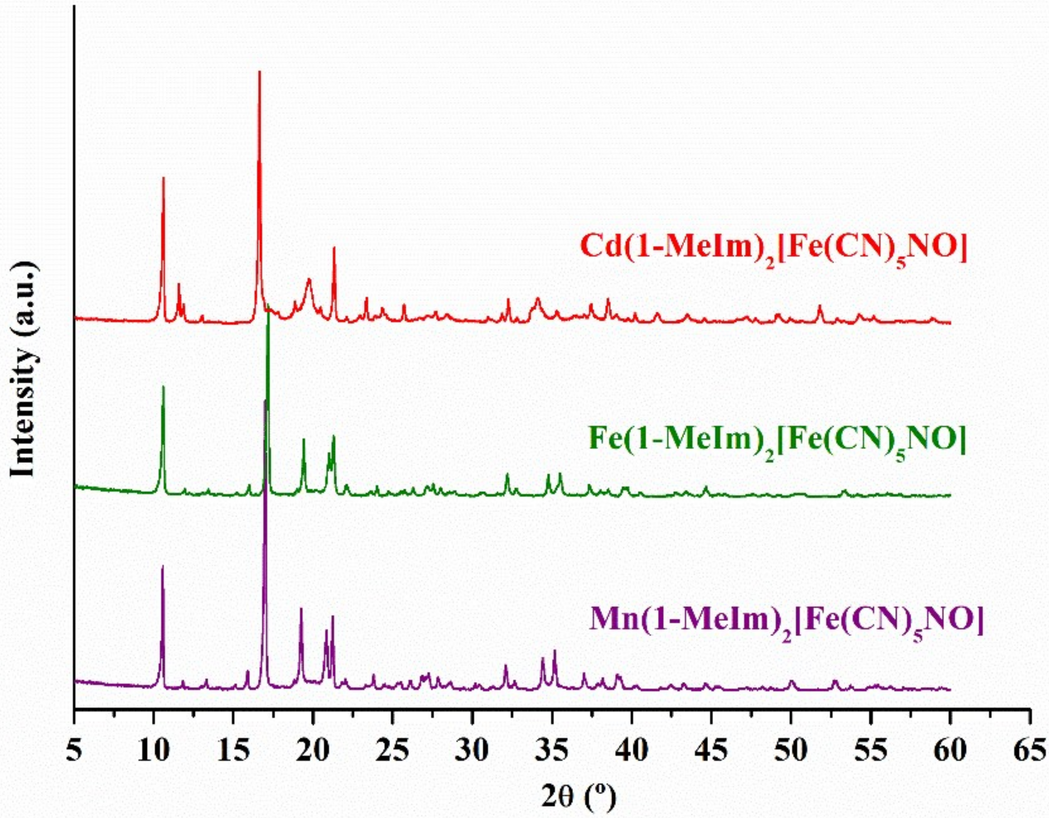
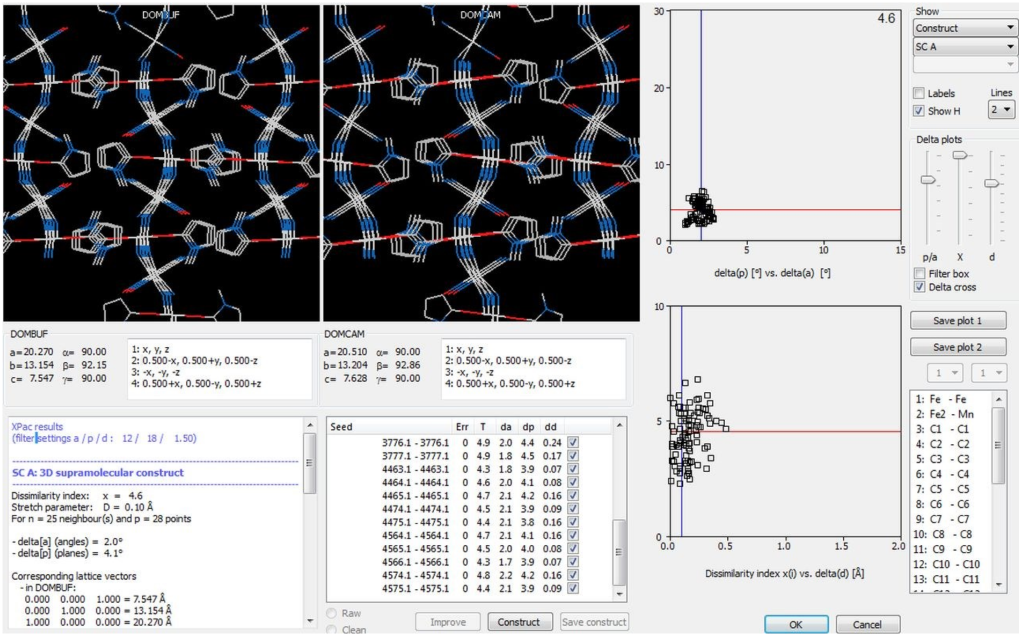


Figure S8. XPac results window showing the comparison of complexes of the series M(1-Me_2P)$_2$[Fe$(CN)_5$NO] (M = Mn, Fe, Co, Ni, Zn, Cd).

DOMBUF - DOMCAM



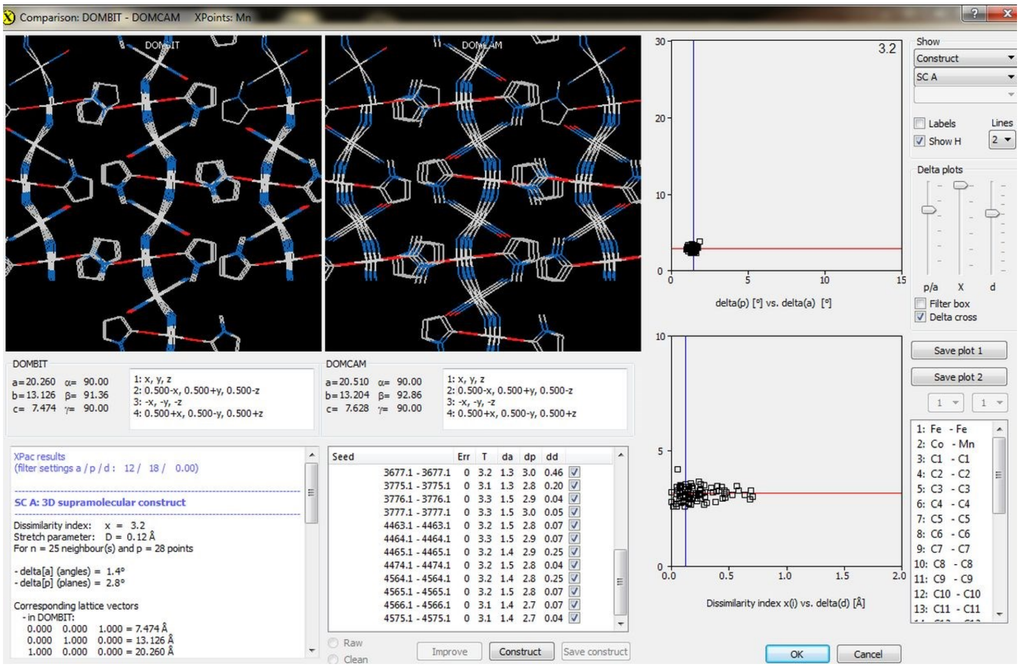
```
DOMBUF
a=20.270  α=  90.00
b=13.154  β=  92.15
c=  7.547  γ=  90.00

1: x, y, z
2: 0.500-x, 0.500+y, 0.500-z
3: -x, -y, -z
4: 0.500+x, 0.500-y, 0.500+z

DOMCAM
a=20.510  α=  90.00
b=13.204  β=  92.86
c=  7.628  γ=  90.00

1: x, y, z
2: 0.500-x, 0.500+y, 0.500-z
3: -x, -y, -z
4: 0.500+x, 0.500-y, 0.500+z
```

```
XPac results
(filter settings a / p / d :   12 /   18 /   1.50)

-----------------------------------------------
SC A: 3D supramolecular construct
-----------------------------------------------
Dissimilarity index:     x  =   4.6
Stretch parameter:    D =  0.10 Å
For n = 25 neighbour(s) and p = 28 points

- delta[a] (angles) =  2.0°
- delta[p] (planes) =  4.1°

Corresponding lattice vectors
  - in DOMBUF:
    0.000    0.000    1.000 = 7.547 Å
    0.000    1.000    0.000 = 13.154 Å
    1.000    0.000    0.000 = 20.270 Å
```

```
Seed                     Err   T    da   dp   dd
      3776.1 - 3776.1    0   4.9  2.0  4.4  0.24  ☑
      3777.1 - 3777.1    0   4.9  1.8  4.5  0.17  ☑
      4463.1 - 4463.1    0   4.3  1.8  3.9  0.07  ☑
      4464.1 - 4464.1    0   4.6  2.0  4.1  0.08  ☑
      4465.1 - 4465.1    0   4.7  2.1  4.2  0.16  ☑
      4474.1 - 4474.1    0   4.5  2.1  3.9  0.09  ☑
      4475.1 - 4475.1    0   4.4  2.1  3.8  0.16  ☑
      4564.1 - 4564.1    0   4.7  2.1  4.1  0.16  ☑
      4565.1 - 4565.1    0   4.5  2.0  4.0  0.08  ☑
      4566.1 - 4566.1    0   4.3  1.7  3.9  0.07  ☑
      4574.1 - 4574.1    0   4.8  2.2  4.2  0.16  ☑
      4575.1 - 4575.1    0   4.4  2.1  3.9  0.09  ☑
```

```
1:  Fe   - Fe
2:  Fe2  - Mn
3:  C1   - C1
4:  C2   - C2
5:  C3   - C3
6:  C4   - C4
7:  C5   - C5
8:  C6   - C6
9:  C7   - C7
10:  C8   - C8
11:  C9   - C9
12:  C10  - C10
13:  C11  - C11
```

DOMBIT-DOMCAM



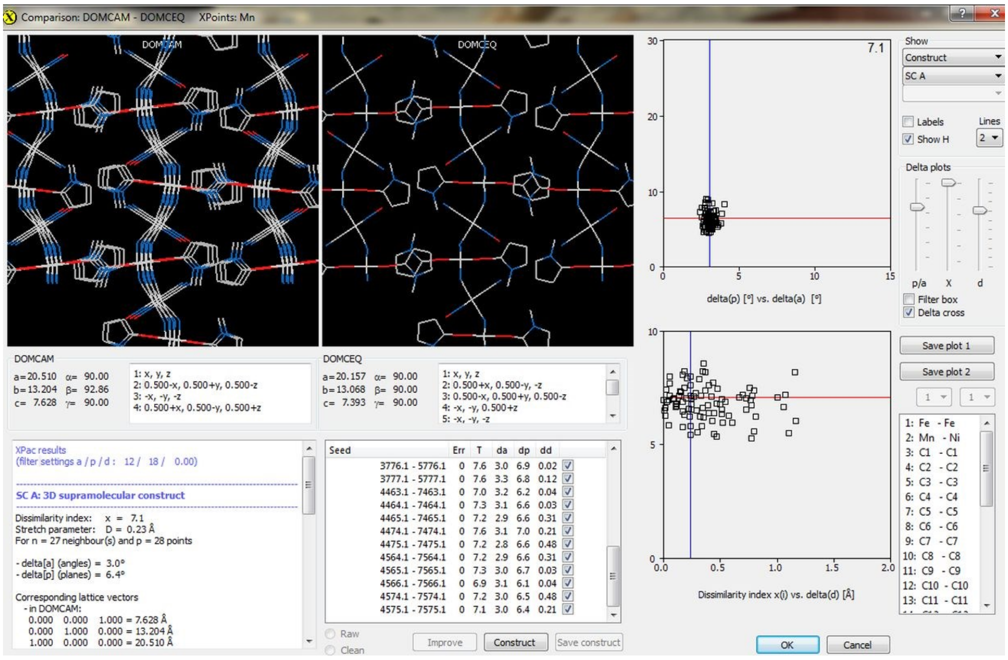
```
DOMBIT
a=20.260  α=  90.00
b=13.126  β=  91.36
c=  7.474  γ=  90.00

1: x, y, z
2: 0.500-x, 0.500+y, 0.500-z
3: -x, -y, -z
4: 0.500+x, 0.500-y, 0.500+z

DOMCAM
a=20.510  α=  90.00
b=13.204  β=  92.86
c=  7.628  γ=  90.00

1: x, y, z
2: 0.500-x, 0.500+y, 0.500-z
3: -x, -y, -z
4: 0.500+x, 0.500-y, 0.500+z
```

```
XPac results
(filter settings a / p / d :   12 /   18 /   0.00)

-----------------------------------------------
SC A: 3D supramolecular construct
-----------------------------------------------
Dissimilarity index:     x  =   3.2
Stretch parameter:    D =  0.12 Å
For n = 25 neighbour(s) and p = 28 points

- delta[a] (angles) =  1.4°
- delta[p] (planes) =  2.8°

Corresponding lattice vectors
  - in DOMBIT:
    0.000    0.000    1.000 = 7.474 Å
    0.000    1.000    0.000 = 13.126 Å
    1.000    0.000    0.000 = 20.260 Å
```

```
Seed                     Err   T    da   dp   dd
      3677.1 - 3677.1    0   3.2  1.3  3.0  0.46  ☑
      3775.1 - 3775.1    0   3.1  1.3  2.8  0.20  ☑
      3776.1 - 3776.1    0   3.3  1.5  2.9  0.04  ☑
      3777.1 - 3777.1    0   3.3  1.5  3.0  0.05  ☑
      4463.1 - 4463.1    0   3.2  1.5  2.8  0.07  ☑
      4464.1 - 4464.1    0   3.3  1.5  2.9  0.07  ☑
      4465.1 - 4465.1    0   3.2  1.4  2.9  0.25  ☑
      4474.1 - 4474.1    0   3.2  1.5  2.8  0.04  ☑
      4564.1 - 4564.1    0   3.2  1.4  2.8  0.25  ☑
      4565.1 - 4565.1    0   3.2  1.5  2.8  0.07  ☑
      4566.1 - 4566.1    0   3.1  1.4  2.7  0.07  ☑
      4575.1 - 4575.1    0   3.1  1.4  2.7  0.04  ☑
```

```
1:  Fe   - Fe
2:  Co   - Mn
3:  C1   - C1
4:  C2   - C2
5:  C3   - C3
6:  C4   - C4
7:  C5   - C5
8:  C6   - C6
9:  C7   - C7
10:  C8   - C8
11:  C9   - C9
12:  C10  - C10
13:  C11  - C11
```

DOMCAM-DOMCEQ

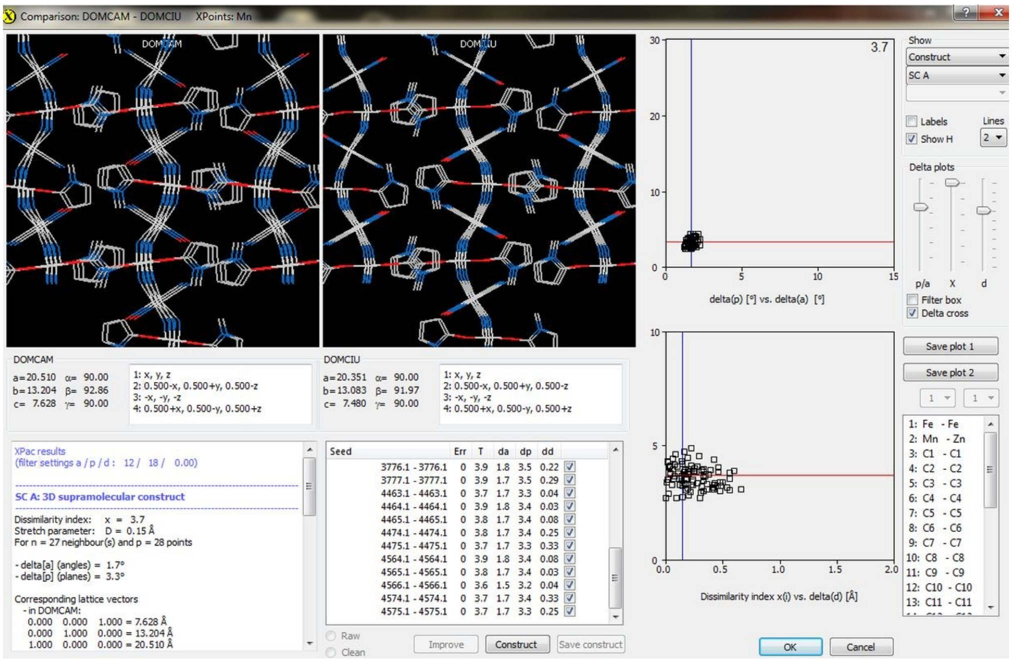


```
DOMCAM
a=20.510  α=  90.00
b=13.204  β=  92.86
c=  7.628  γ=  90.00

1: x, y, z
2: 0.500-x, 0.500+y, 0.500-z
3: -x, -y, -z
4: 0.500+x, 0.500-y, 0.500+z

DOMCEQ
a=20.157  α=  90.00
b=13.068  β=  90.00
c=  7.393  γ=  90.00

1: x, y, z
2: 0.500+x, 0.500-y, -z
3: 0.500-x, 0.500+y, 0.500-z
4: -x, -y, 0.500+z
5: -x, -y, -z
```

```
XPac results
(filter settings a / p / d :   12 /   18 /   0.00)
------------------------------------------------------------
SC A: 3D supramolecular construct
------------------------------------------------------------
Dissimilarity index:    x  =   7.1
Stretch parameter:    D =  0.23 Å
For n = 27 neighbour(s) and p = 28 points

- delta[a] (angles) =  3.0°
- delta[p] (planes) =  6.4°

Corresponding lattice vectors
  - in DOMCAM:
    0.000    0.000    1.000 = 7.628 Å
    0.000    1.000    0.000 = 13.204 Å
    1.000    0.000    0.000 = 20.510 Å
```

```
Seed                  Err   T    da   dp   dd
3776.1 - 5776.1        0   7.6  3.0  6.9  0.02  ☑
3777.1 - 5777.1        0   7.6  3.3  6.8  0.12  ☑
4463.1 - 7463.1        0   7.0  3.2  6.2  0.04  ☑
4464.1 - 7464.1        0   7.3  3.1  6.6  0.03  ☑
4465.1 - 7465.1        0   7.2  2.9  6.6  0.31  ☑
4474.1 - 7474.1        0   7.6  3.1  7.0  0.21  ☑
4475.1 - 7475.1        0   7.2  2.8  6.6  0.48  ☑
4564.1 - 7564.1        0   7.2  2.9  6.6  0.31  ☑
4565.1 - 7565.1        0   7.3  3.0  6.7  0.03  ☑
4566.1 - 7566.1        0   6.9  3.1  6.1  0.04  ☑
4574.1 - 7574.1        0   7.2  3.0  6.5  0.48  ☑
4575.1 - 7575.1        0   7.1  3.0  6.4  0.21  ☑
```

DOMCAM-DOMCIU

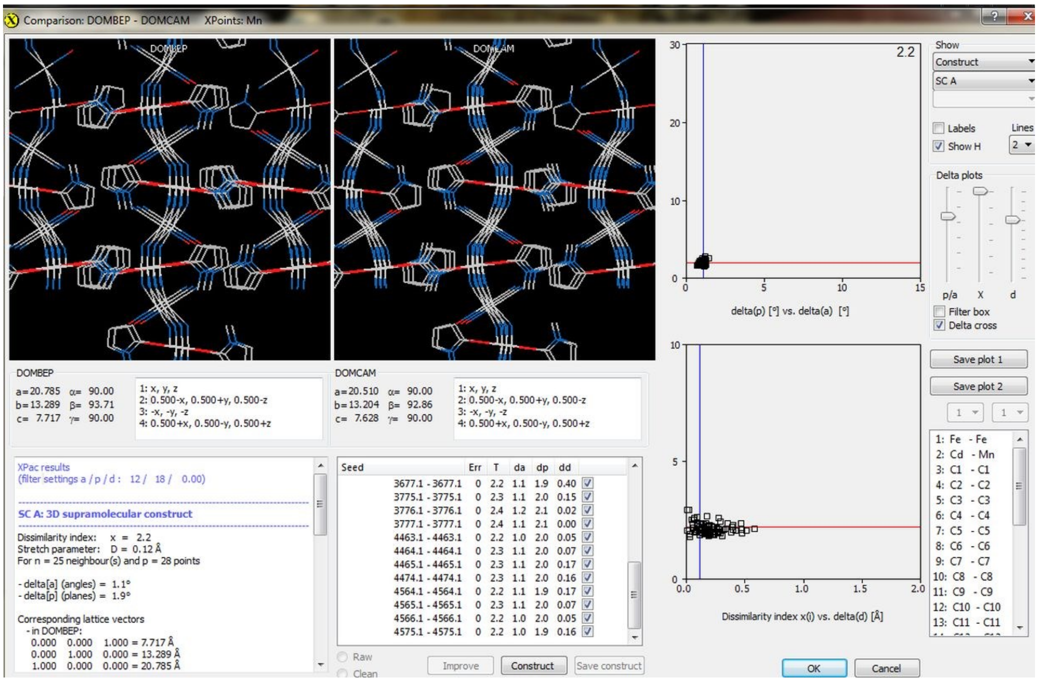


```
DOMCAM
a=20.510  α=  90.00
b=13.204  β=  92.86
c=  7.628  γ=  90.00

1: x, y, z
2: 0.500-x, 0.500+y, 0.500-z
3: -x, -y, -z
4: 0.500+x, 0.500-y, 0.500+z

DOMCIU
a=20.351  α=  90.00
b=13.083  β=  91.97
c=  7.480  γ=  90.00

1: x, y, z
2: 0.500-x, 0.500+y, 0.500-z
3: -x, -y, -z
4: 0.500+x, 0.500-y, 0.500+z
```

```
XPac results
(filter settings a / p / d :   12 /   18 /   0.00)
------------------------------------------------------------
SC A: 3D supramolecular construct
------------------------------------------------------------
Dissimilarity index:    x  =   3.7
Stretch parameter:    D =  0.15 Å
For n = 27 neighbour(s) and p = 28 points

- delta[a] (angles) =  1.7°
- delta[p] (planes) =  3.3°

Corresponding lattice vectors
  - in DOMCAM:
    0.000    0.000    1.000 = 7.628 Å
    0.000    1.000    0.000 = 13.204 Å
    1.000    0.000    0.000 = 20.510 Å
```

```
Seed                  Err   T    da   dp   dd
3776.1 - 3776.1        0   3.9  1.8  3.5  0.22  ☑
3777.1 - 3777.1        0   3.9  1.7  3.5  0.29  ☑
4463.1 - 4463.1        0   3.7  1.7  3.3  0.04  ☑
4464.1 - 4464.1        0   3.9  1.8  3.4  0.03  ☑
4465.1 - 4465.1        0   3.8  1.7  3.4  0.08  ☑
4474.1 - 4474.1        0   3.8  1.7  3.4  0.25  ☑
4475.1 - 4475.1        0   3.7  1.7  3.3  0.33  ☑
4564.1 - 4564.1        0   3.9  1.8  3.4  0.08  ☑
4565.1 - 4565.1        0   3.8  1.7  3.4  0.03  ☑
4566.1 - 4566.1        0   3.6  1.5  3.2  0.04  ☑
4574.1 - 4574.1        0   3.7  1.7  3.4  0.33  ☑
4575.1 - 4575.1        0   3.7  1.7  3.3  0.25  ☑
```

DOMBEP-DOMCAM



DOMBEP

a=20.785 α= 90.00
b=13.289 β= 93.71
c= 7.717 γ= 90.00

1: x, y, z
2: 0.500-x, 0.500+y, 0.500-z
3: -x, -y, -z
4: 0.500+x, 0.500-y, 0.500+z

DOMCAM

a=20.510 α= 90.00
b=13.204 β= 92.86
c= 7.628 γ= 90.00

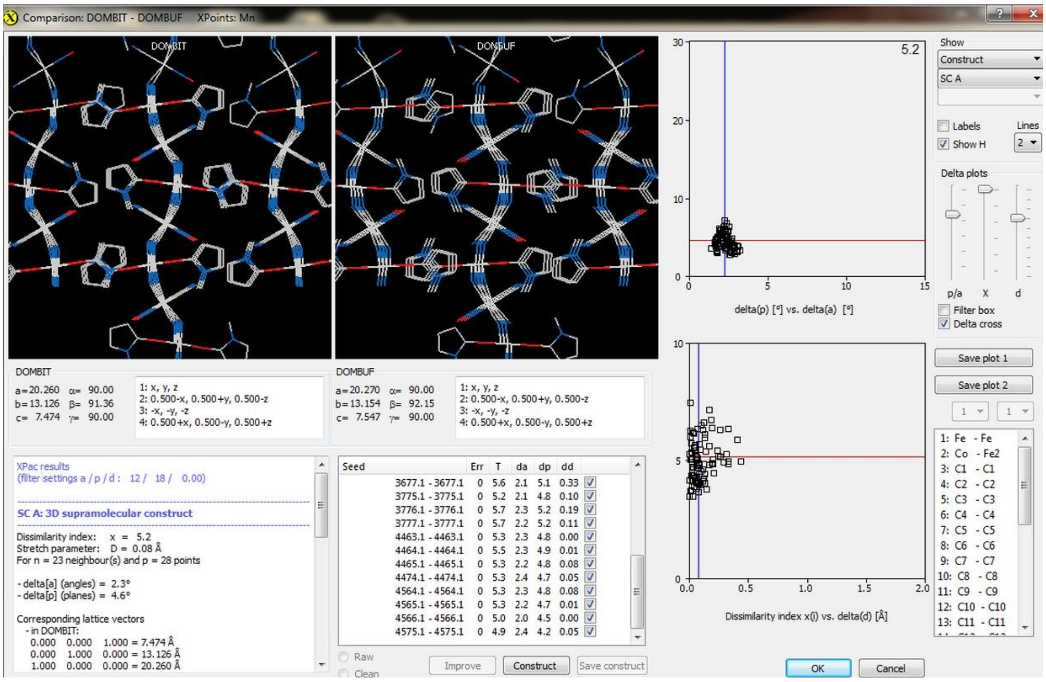
1: x, y, z
2: 0.500-x, 0.500+y, 0.500-z
3: -x, -y, -z
4: 0.500+x, 0.500-y, 0.500+z

```
XPac results
(filter settings a / p / d :   12 /   18 /   0.00)

--------------------------------------------------------
SC A: 3D supramolecular construct
--------------------------------------------------------
Dissimilarity index:     x  =   2.2
Stretch parameter:    D =  0.12 Å
For n = 25 neighbour(s) and p = 28 points

- delta[a] (angles) =  1.1°
- delta[p] (planes) =  1.9°

Corresponding lattice vectors
  - in DOMBEP:
    0.000    0.000    1.000 = 7.717 Å
    0.000    1.000    0.000 = 13.289 Å
    1.000    0.000    0.000 = 20.785 Å
```

Seed	Err	T	da	dp	dd	
3677.1 - 3677.1	0	2.2	1.1	1.9	0.40	☑
3775.1 - 3775.1	0	2.3	1.1	2.0	0.15	☑
3776.1 - 3776.1	0	2.4	1.2	2.1	0.02	☑
3777.1 - 3777.1	0	2.4	1.1	2.1	0.00	☑
4463.1 - 4463.1	0	2.2	1.0	2.0	0.05	☑
4464.1 - 4464.1	0	2.3	1.1	2.0	0.07	☑
4465.1 - 4465.1	0	2.3	1.1	2.0	0.17	☑
4474.1 - 4474.1	0	2.3	1.1	2.0	0.16	☑
4564.1 - 4564.1	0	2.2	1.1	1.9	0.17	☑
4565.1 - 4565.1	0	2.3	1.1	2.0	0.07	☑
4566.1 - 4566.1	0	2.2	1.0	2.0	0.05	☑
4575.1 - 4575.1	0	2.2	1.0	1.9	0.16	☑

1: Fe - Fe
2: Cd - Mn
3: C1 - C1
4: C2 - C2
5: C3 - C3
6: C4 - C4
7: C5 - C5
8: C6 - C6
9: C7 - C7
10: C8 - C8
11: C9 - C9
12: C10 - C10
13: C11 - C11

DOMBIT-DOMBUF



DOMBIT

a=20.260 α= 90.00
b=13.126 β= 91.36
c= 7.474 γ= 90.00

1: x, y, z
2: 0.500-x, 0.500+y, 0.500-z
3: -x, -y, -z
4: 0.500+x, 0.500-y, 0.500+z

DOMBUF

a=20.270 α= 90.00
b=13.154 β= 92.15
c= 7.547 γ= 90.00

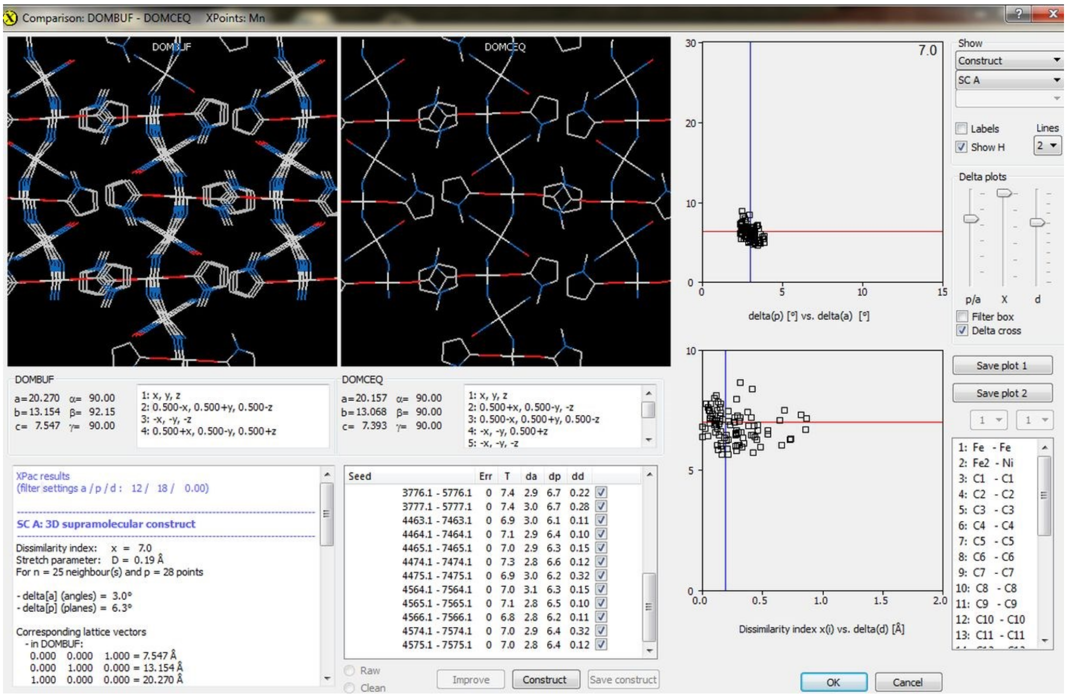
1: x, y, z
2: 0.500-x, 0.500+y, 0.500-z
3: -x, -y, -z
4: 0.500+x, 0.500-y, 0.500+z

```
XPac results
(filter settings a / p / d :   12 /   18 /   0.00)

--------------------------------------------------------
SC A: 3D supramolecular construct
--------------------------------------------------------
Dissimilarity index:     x  =   5.2
Stretch parameter:    D =  0.08 Å
For n = 23 neighbour(s) and p = 28 points

- delta[a] (angles) =  2.3°
- delta[p] (planes) =  4.6°

Corresponding lattice vectors
  - in DOMBIT:
    0.000    0.000    1.000 = 7.474 Å
    0.000    1.000    0.000 = 13.126 Å
    1.000    0.000    0.000 = 20.260 Å
```

Seed	Err	T	da	dp	dd	
3677.1 - 3677.1	0	5.6	2.1	5.1	0.33	☑
3775.1 - 3775.1	0	5.2	2.1	4.8	0.10	☑
3776.1 - 3776.1	0	5.7	2.3	5.2	0.19	☑
3777.1 - 3777.1	0	5.7	2.2	5.2	0.11	☑
4463.1 - 4463.1	0	5.3	2.3	4.8	0.00	☑
4464.1 - 4464.1	0	5.5	2.3	4.9	0.01	☑
4465.1 - 4465.1	0	5.3	2.2	4.8	0.08	☑
4474.1 - 4474.1	0	5.3	2.4	4.7	0.05	☑
4564.1 - 4564.1	0	5.3	2.3	4.8	0.08	☑
4565.1 - 4565.1	0	5.3	2.2	4.7	0.01	☑
4566.1 - 4566.1	0	5.0	2.0	4.5	0.00	☑
4575.1 - 4575.1	0	4.9	2.4	4.2	0.05	☑

1: Fe - Fe
2: Co - Fe2
3: C1 - C1
4: C2 - C2
5: C3 - C3
6: C4 - C4
7: C5 - C5
8: C6 - C6
9: C7 - C7
10: C8 - C8
11: C9 - C9
12: C10 - C10
13: C11 - C11

DOMBUF-DOMCEQ



DOMBUF

a=20.270 α= 90.00
b=13.154 β= 92.15
c= 7.547 γ= 90.00

1: x, y, z
2: 0.500-x, 0.500+y, 0.500-z
3: -x, -y, -z
4: 0.500+x, 0.500-y, 0.500+z

DOMCEQ

a=20.157 α= 90.00
b=13.068 β= 90.00
c= 7.393 γ= 90.00

1: x, y, z
2: 0.500+x, 0.500-y, -z
3: 0.500-x, 0.500+y, 0.500-z
4: -x, -y, 0.500+z
5: -x, -y, -z

XPac results
(filter settings a / p / d : 12 / 18 / 0.00)

SC A: 3D supramolecular construct

Dissimilarity index: x = 7.0
Stretch parameter: D = 0.19 Å
For n = 25 neighbour(s) and p = 28 points

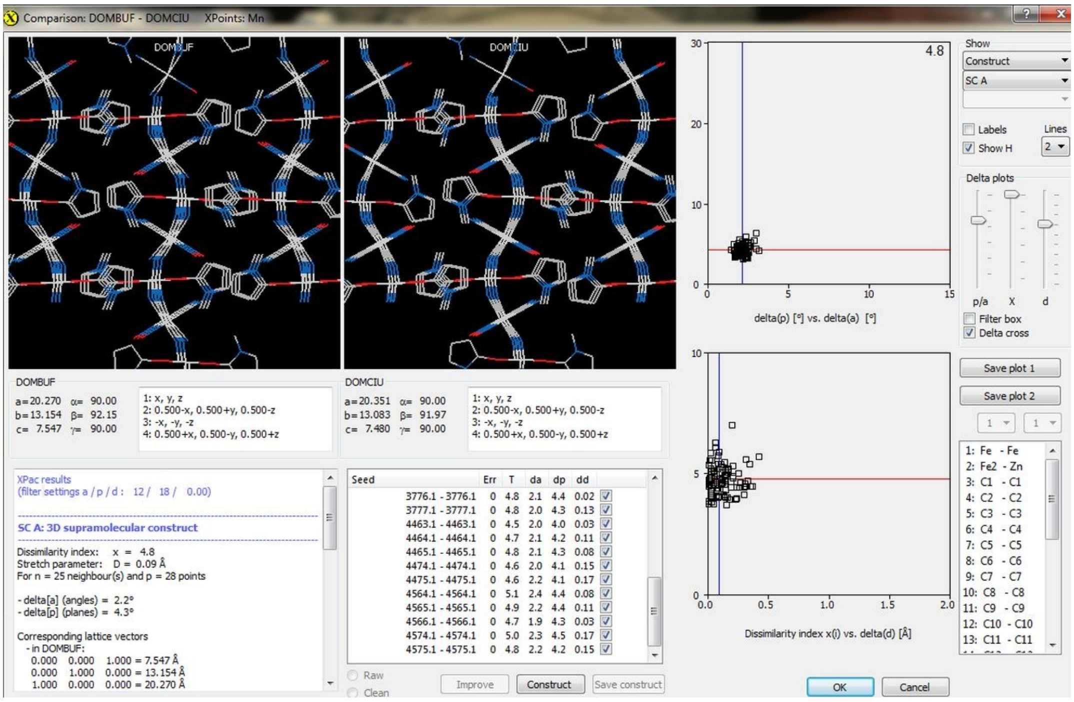
- delta[a] (angles) = 3.0°
- delta[p] (planes) = 6.3°

Corresponding lattice vectors
- in DOMBUF:
0.000 0.000 1.000 = 7.547 Å
0.000 1.000 0.000 = 13.154 Å
1.000 0.000 0.000 = 20.270 Å

Seed	Err	T	da	dp	dd	
3776.1 - 5776.1	0	7.4	2.9	6.7	0.22	☑
3777.1 - 5777.1	0	7.4	3.0	6.7	0.28	☑
4463.1 - 7463.1	0	6.9	3.0	6.1	0.11	☑
4464.1 - 7464.1	0	7.1	2.9	6.4	0.10	☑
4465.1 - 7465.1	0	7.0	2.9	6.3	0.15	☑
4474.1 - 7474.1	0	7.3	2.8	6.6	0.12	☑
4475.1 - 7475.1	0	6.9	3.0	6.2	0.32	☑
4564.1 - 7564.1	0	7.0	3.1	6.3	0.15	☑
4565.1 - 7565.1	0	7.1	2.8	6.5	0.10	☑
4566.1 - 7566.1	0	6.8	2.8	6.2	0.11	☑
4574.1 - 7574.1	0	7.0	2.9	6.4	0.32	☑
4575.1 - 7575.1	0	7.0	2.8	6.4	0.12	☑

1: Fe - Fe
2: Fe2 - Ni
3: C1 - C1
4: C2 - C2
5: C3 - C3
6: C4 - C4
7: C5 - C5
8: C6 - C6
9: C7 - C7
10: C8 - C8
11: C9 - C9
12: C10 - C10
13: C11 - C11

DOMBUF-DOMCIU



DOMBUF

a=20.270 α= 90.00
b=13.154 β= 92.15
c= 7.547 γ= 90.00

1: x, y, z
2: 0.500-x, 0.500+y, 0.500-z
3: -x, -y, -z
4: 0.500+x, 0.500-y, 0.500+z

DOMCIU

a=20.351 α= 90.00
b=13.083 β= 91.97
c= 7.480 γ= 90.00

1: x, y, z
2: 0.500-x, 0.500+y, 0.500-z
3: -x, -y, -z
4: 0.500+x, 0.500-y, 0.500+z

XPac results
(filter settings a / p / d : 12 / 18 / 0.00)

SC A: 3D supramolecular construct

Dissimilarity index: x = 4.8
Stretch parameter: D = 0.09 Å
For n = 25 neighbour(s) and p = 28 points

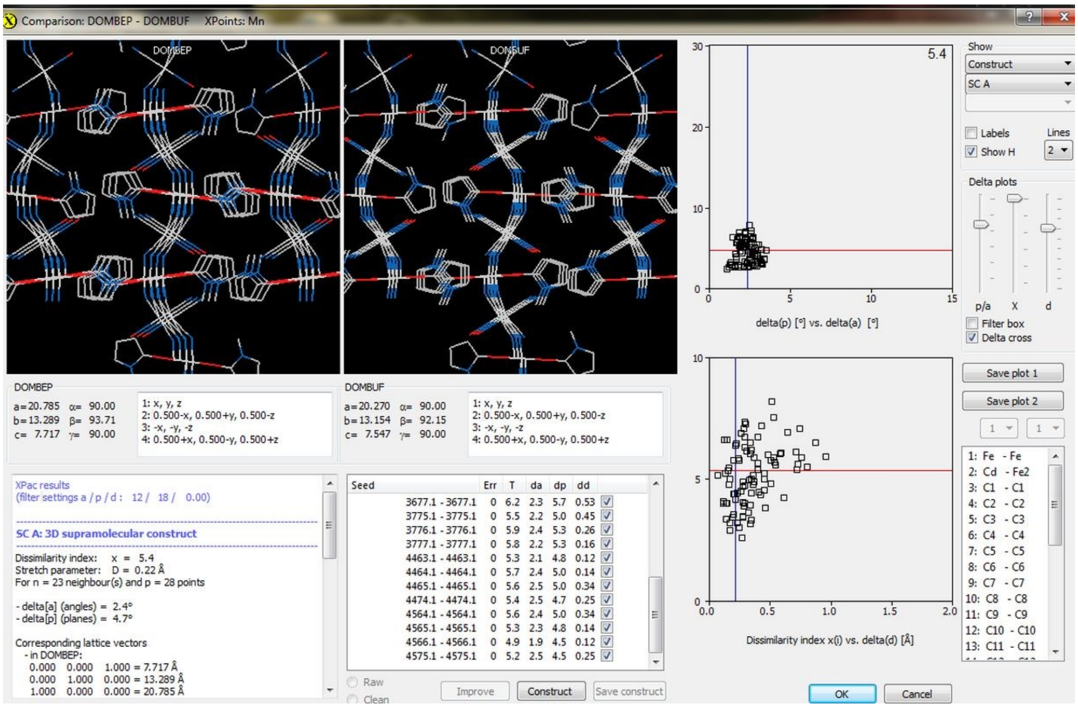
- delta[a] (angles) = 2.2°
- delta[p] (planes) = 4.3°

Corresponding lattice vectors
- in DOMBUF:
0.000 0.000 1.000 = 7.547 Å
0.000 1.000 0.000 = 13.154 Å
1.000 0.000 0.000 = 20.270 Å

Seed	Err	T	da	dp	dd	
3776.1 - 3776.1	0	4.8	2.1	4.4	0.02	☑
3777.1 - 3777.1	0	4.8	2.0	4.3	0.13	☑
4463.1 - 4463.1	0	4.5	2.0	4.0	0.03	☑
4464.1 - 4464.1	0	4.7	2.1	4.2	0.11	☑
4465.1 - 4465.1	0	4.8	2.1	4.3	0.08	☑
4474.1 - 4474.1	0	4.6	2.0	4.1	0.15	☑
4475.1 - 4475.1	0	4.6	2.2	4.1	0.17	☑
4564.1 - 4564.1	0	5.1	2.4	4.4	0.08	☑
4565.1 - 4565.1	0	4.9	2.2	4.4	0.11	☑
4566.1 - 4566.1	0	4.7	1.9	4.3	0.03	☑
4574.1 - 4574.1	0	5.0	2.3	4.5	0.17	☑
4575.1 - 4575.1	0	4.8	2.2	4.2	0.15	☑

1: Fe - Fe
2: Fe2 - Zn
3: C1 - C1
4: C2 - C2
5: C3 - C3
6: C4 - C4
7: C5 - C5
8: C6 - C6
9: C7 - C7
10: C8 - C8
11: C9 - C9
12: C10 - C10
13: C11 - C11

DOMBEP-DOMBUF



Comparison: DOMBEP - DOMBUF XPoints: Mn

DOMBEP
a=20.785 α= 90.00
b=13.289 β= 93.71
c= 7.717 γ= 90.00

1: x, y, z
2: 0.500-x, 0.500+y, 0.500-z
3: -x, -y, -z
4: 0.500+x, 0.500-y, 0.500+z

DOMBUF
a=20.270 α= 90.00
b=13.154 β= 92.15
c= 7.547 γ= 90.00

1: x, y, z
2: 0.500-x, 0.500+y, 0.500-z
3: -x, -y, -z
4: 0.500+x, 0.500-y, 0.500+z

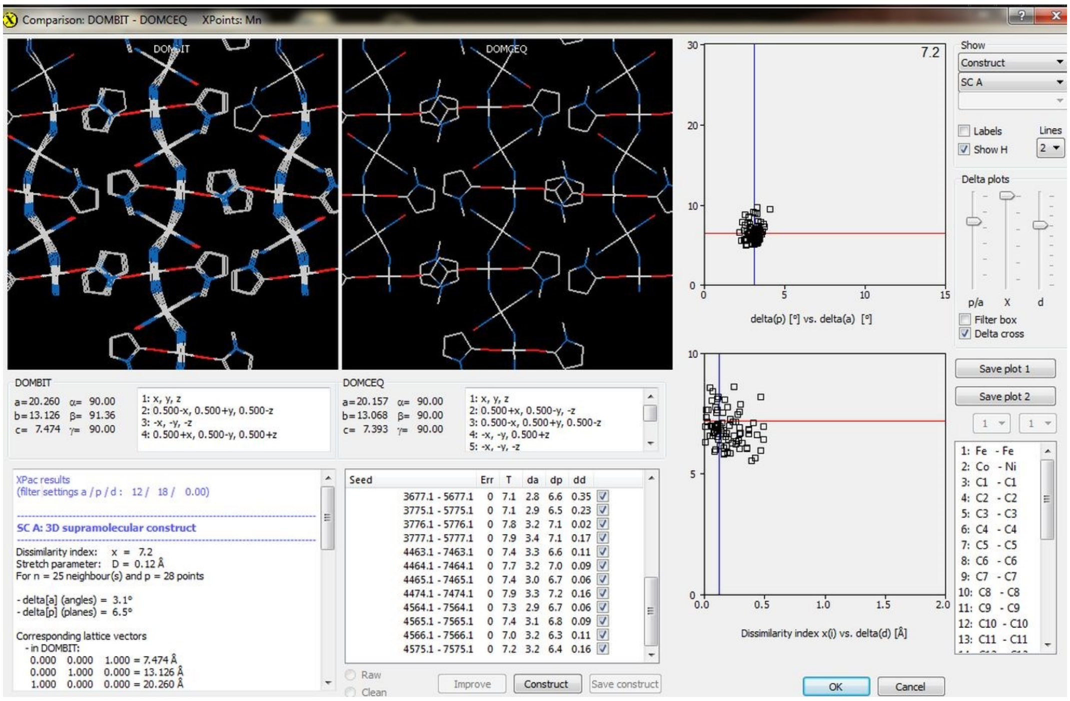
```
XPac results
(filter settings a / p / d :   12 /   18 /   0.00)

-----------------------------------------------------------
SC A: 3D supramolecular construct
-----------------------------------------------------------
Dissimilarity index:    x  =  5.4
Stretch parameter:    D  =  0.22 Å
For n = 23 neighbour(s) and p = 28 points

- delta[a] (angles) =  2.4°
- delta[p] (planes) =  4.7°

Corresponding lattice vectors
  - in DOMBEP:
    0.000    0.000    1.000 = 7.717 Å
    0.000    1.000    0.000 = 13.289 Å
    1.000    0.000    0.000 = 20.785 Å
```

Seed	Err	T	da	dp	dd	
3677.1 - 3677.1	0	6.2	2.3	5.7	0.53	☑
3775.1 - 3775.1	0	5.5	2.2	5.0	0.45	☑
3776.1 - 3776.1	0	5.9	2.4	5.3	0.26	☑
3777.1 - 3777.1	0	5.8	2.2	5.3	0.16	☑
4463.1 - 4463.1	0	5.3	2.1	4.8	0.12	☑
4464.1 - 4464.1	0	5.7	2.4	5.0	0.14	☑
4465.1 - 4465.1	0	5.6	2.5	5.0	0.34	☑
4474.1 - 4474.1	0	5.4	2.5	4.7	0.25	☑
4564.1 - 4564.1	0	5.6	2.4	5.0	0.34	☑
4565.1 - 4565.1	0	5.3	2.3	4.8	0.14	☑
4566.1 - 4566.1	0	4.9	1.9	4.5	0.12	☑
4575.1 - 4575.1	0	5.2	2.5	4.5	0.25	☑

Show: Construct
SC A
☐ Labels
☑ Show H
Lines: 2
☐ Filter box
☑ Delta cross

1: Fe - Fe
2: Cd - Fe2
3: C1 - C1
4: C2 - C2
5: C3 - C3
6: C4 - C4
7: C5 - C5
8: C6 - C6
9: C7 - C7
10: C8 - C8
11: C9 - C9
12: C10 - C10
13: C11 - C11

DOMBIT-DOMCEQ



Comparison: DOMBIT - DOMCEQ XPoints: Mn

DOMBIT
a=20.260 α= 90.00
b=13.126 β= 91.36
c= 7.474 γ= 90.00

1: x, y, z
2: 0.500-x, 0.500+y, 0.500-z
3: -x, -y, -z
4: 0.500+x, 0.500-y, 0.500+z

DOMCEQ
a=20.157 α= 90.00
b=13.068 β= 90.00
c= 7.393 γ= 90.00

1: x, y, z
2: 0.500+x, 0.500-y, -z
3: 0.500-x, 0.500+y, 0.500-z
4: -x, -y, 0.500+z
5: -x, -y, -z

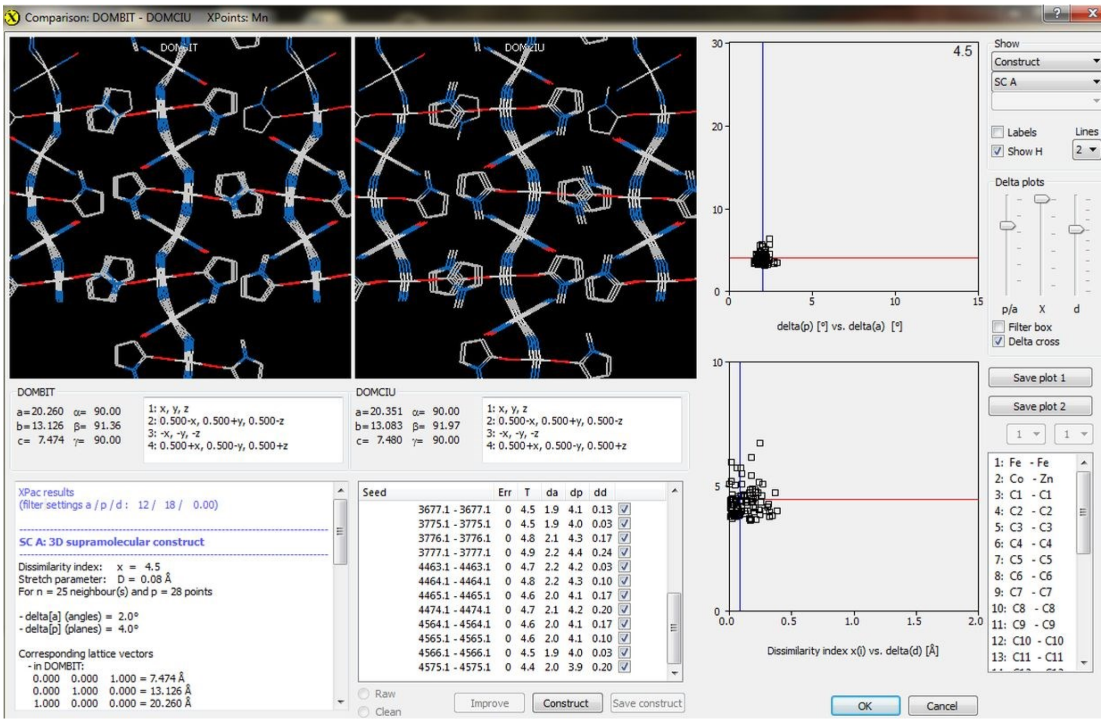
```
XPac results
(filter settings a / p / d :   12 /   18 /   0.00)

-----------------------------------------------------------
SC A: 3D supramolecular construct
-----------------------------------------------------------
Dissimilarity index:    x  =  7.2
Stretch parameter:    D  =  0.12 Å
For n = 25 neighbour(s) and p = 28 points

- delta[a] (angles) =  3.1°
- delta[p] (planes) =  6.5°

Corresponding lattice vectors
  - in DOMBIT:
    0.000    0.000    1.000 = 7.474 Å
    0.000    1.000    0.000 = 13.126 Å
    1.000    0.000    0.000 = 20.260 Å
```

Seed	Err	T	da	dp	dd	
3677.1 - 5677.1	0	7.1	2.8	6.6	0.35	☑
3775.1 - 5775.1	0	7.1	2.9	6.5	0.23	☑
3776.1 - 5776.1	0	7.8	3.2	7.1	0.02	☑
3777.1 - 5777.1	0	7.9	3.4	7.1	0.17	☑
4463.1 - 7463.1	0	7.4	3.3	6.6	0.11	☑
4464.1 - 7464.1	0	7.7	3.2	7.0	0.09	☑
4465.1 - 7465.1	0	7.4	3.0	6.7	0.06	☑
4474.1 - 7474.1	0	7.9	3.3	7.2	0.16	☑
4564.1 - 7564.1	0	7.3	2.9	6.7	0.06	☑
4565.1 - 7565.1	0	7.4	3.1	6.8	0.09	☑
4566.1 - 7566.1	0	7.0	3.2	6.3	0.11	☑
4575.1 - 7575.1	0	7.2	3.2	6.4	0.16	☑

Show: Construct
SC A
☐ Labels
☑ Show H
Lines: 2
☐ Filter box
☑ Delta cross

1: Fe - Fe
2: Co - Ni
3: C1 - C1
4: C2 - C2
5: C3 - C3
6: C4 - C4
7: C5 - C5
8: C6 - C6
9: C7 - C7
10: C8 - C8
11: C9 - C9
12: C10 - C10
13: C11 - C11

DOMBIT-DOMCIU



DOMBIT

a= 20.260 α= 90.00
b= 13.126 β= 91.36
c= 7.474 γ= 90.00

1: x, y, z
2: 0.500-x, 0.500+y, 0.500-z
3: -x, -y, -z
4: 0.500+x, 0.500-y, 0.500+z

DOMCIU

a= 20.351 α= 90.00
b= 13.083 β= 91.97
c= 7.480 γ= 90.00

1: x, y, z
2: 0.500-x, 0.500+y, 0.500-z
3: -x, -y, -z
4: 0.500+x, 0.500-y, 0.500+z

XPac results
(filter settings a / p / d : 12 / 18 / 0.00)

SC A: 3D supramolecular construct

Dissimilarity index: x = 4.5
Stretch parameter: D = 0.08 Å
For n = 25 neighbour(s) and p = 28 points

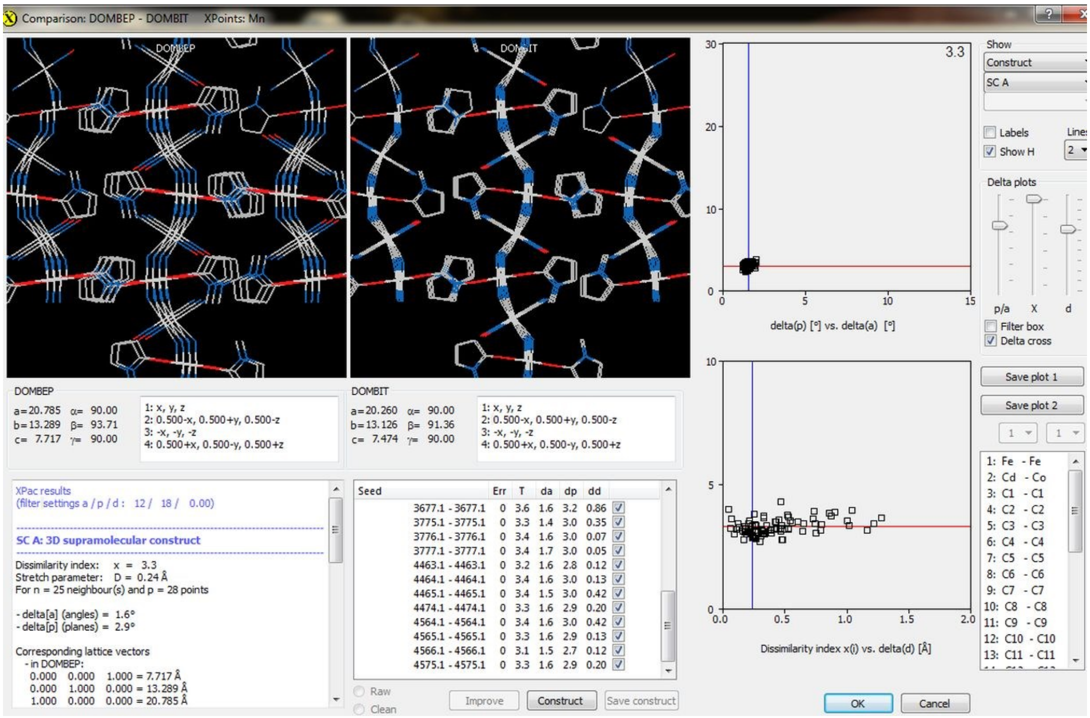
- delta[a] (angles) = 2.0°
- delta[p] (planes) = 4.0°

Corresponding lattice vectors
- in DOMBIT:
0.000 0.000 1.000 = 7.474 Å
0.000 1.000 0.000 = 13.126 Å
1.000 0.000 0.000 = 20.260 Å

Seed	Err	T	da	dp	dd	
3677.1 - 3677.1	0	4.5	1.9	4.1	0.13	☑
3775.1 - 3775.1	0	4.5	1.9	4.0	0.03	☑
3776.1 - 3776.1	0	4.8	2.1	4.3	0.17	☑
3777.1 - 3777.1	0	4.9	2.2	4.4	0.24	☑
4463.1 - 4463.1	0	4.7	2.2	4.2	0.03	☑
4464.1 - 4464.1	0	4.8	2.2	4.3	0.10	☑
4465.1 - 4465.1	0	4.6	2.0	4.1	0.17	☑
4474.1 - 4474.1	0	4.7	2.1	4.2	0.20	☑
4564.1 - 4564.1	0	4.6	2.0	4.1	0.17	☑
4565.1 - 4565.1	0	4.6	2.0	4.1	0.10	☑
4566.1 - 4566.1	0	4.5	1.9	4.0	0.03	☑
4575.1 - 4575.1	0	4.4	2.0	3.9	0.20	☑

1: Fe - Fe
2: Co - Zn
3: C1 - C1
4: C2 - C2
5: C3 - C3
6: C4 - C4
7: C5 - C5
8: C6 - C6
9: C7 - C7
10: C8 - C8
11: C9 - C9
12: C10 - C10
13: C11 - C11

DOMBEP-DOMBIT



DOMBEP

a= 20.785 α= 90.00
b= 13.289 β= 93.71
c= 7.717 γ= 90.00

1: x, y, z
2: 0.500-x, 0.500+y, 0.500-z
3: -x, -y, -z
4: 0.500+x, 0.500-y, 0.500+z

DOMBIT

a= 20.260 α= 90.00
b= 13.126 β= 91.36
c= 7.474 γ= 90.00

1: x, y, z
2: 0.500-x, 0.500+y, 0.500-z
3: -x, -y, -z
4: 0.500+x, 0.500-y, 0.500+z

XPac results
(filter settings a / p / d : 12 / 18 / 0.00)

SC A: 3D supramolecular construct

Dissimilarity index: x = 3.3
Stretch parameter: D = 0.24 Å
For n = 25 neighbour(s) and p = 28 points

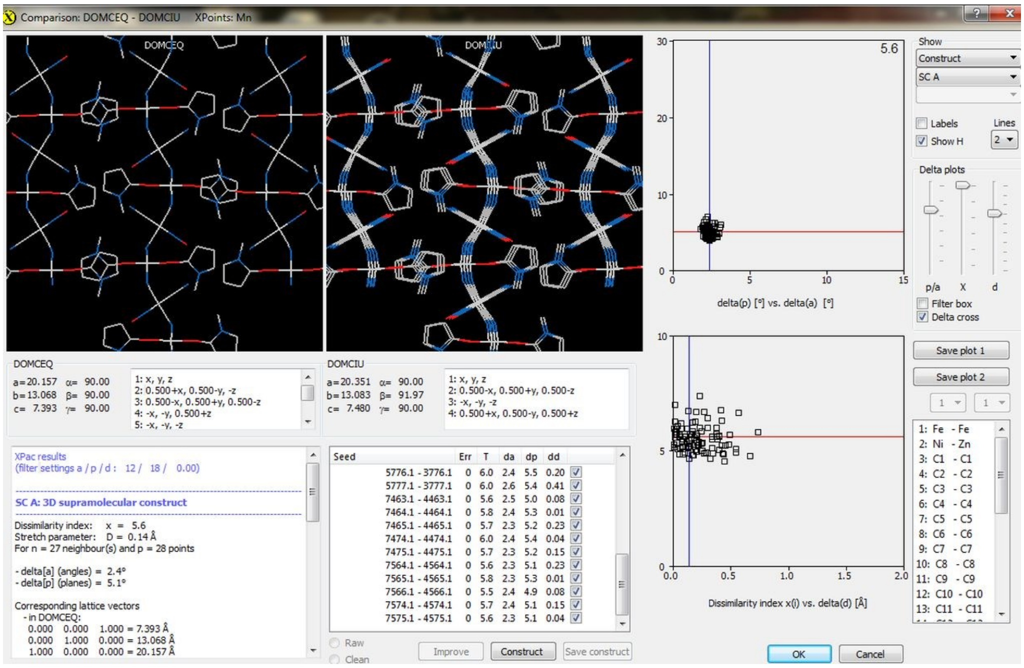
- delta[a] (angles) = 1.6°
- delta[p] (planes) = 2.9°

Corresponding lattice vectors
- in DOMBEP:
0.000 0.000 1.000 = 7.717 Å
0.000 1.000 0.000 = 13.289 Å
1.000 0.000 0.000 = 20.785 Å

Seed	Err	T	da	dp	dd	
3677.1 - 3677.1	0	3.6	1.6	3.2	0.86	☑
3775.1 - 3775.1	0	3.3	1.4	3.0	0.35	☑
3776.1 - 3776.1	0	3.4	1.6	3.0	0.07	☑
3777.1 - 3777.1	0	3.4	1.7	3.0	0.05	☑
4463.1 - 4463.1	0	3.2	1.6	2.8	0.12	☑
4464.1 - 4464.1	0	3.4	1.6	3.0	0.13	☑
4465.1 - 4465.1	0	3.4	1.5	3.0	0.42	☑
4474.1 - 4474.1	0	3.3	1.6	2.9	0.20	☑
4564.1 - 4564.1	0	3.4	1.6	3.0	0.42	☑
4565.1 - 4565.1	0	3.3	1.6	2.9	0.13	☑
4566.1 - 4566.1	0	3.1	1.5	2.7	0.12	☑
4575.1 - 4575.1	0	3.3	1.6	2.9	0.20	☑

1: Fe - Fe
2: Cd - Co
3: C1 - C1
4: C2 - C2
5: C3 - C3
6: C4 - C4
7: C5 - C5
8: C6 - C6
9: C7 - C7
10: C8 - C8
11: C9 - C9
12: C10 - C10
13: C11 - C11

DOMCEQ-DOMCIU



Comparison: DOMCEQ - DOMCIU   XPoints: Mn

DOMCEQ
a=20.157 α= 90.00
b=13.068 β= 90.00
c= 7.393 γ= 90.00

1: x, y, z
2: 0.500+x, 0.500-y, -z
3: 0.500-x, 0.500+y, 0.500-z
4: -x, -y, 0.500+z
5: -x, -y, -z

DOMCIU
a=20.351 α= 90.00
b=13.083 β= 91.97
c= 7.480 γ= 90.00

1: x, y, z
2: 0.500-x, 0.500+y, 0.500-z
3: -x, -y, -z
4: 0.500+x, 0.500-y, 0.500+z

XPac results
(filter settings a / p / d : 12 / 18 / 0.00)

SC A: 3D supramolecular construct

Dissimilarity index: x = 5.6
Stretch parameter: D = 0.14 Å
For n = 27 neighbour(s) and p = 28 points

- delta[a] (angles) = 2.4°
- delta[p] (planes) = 5.1°

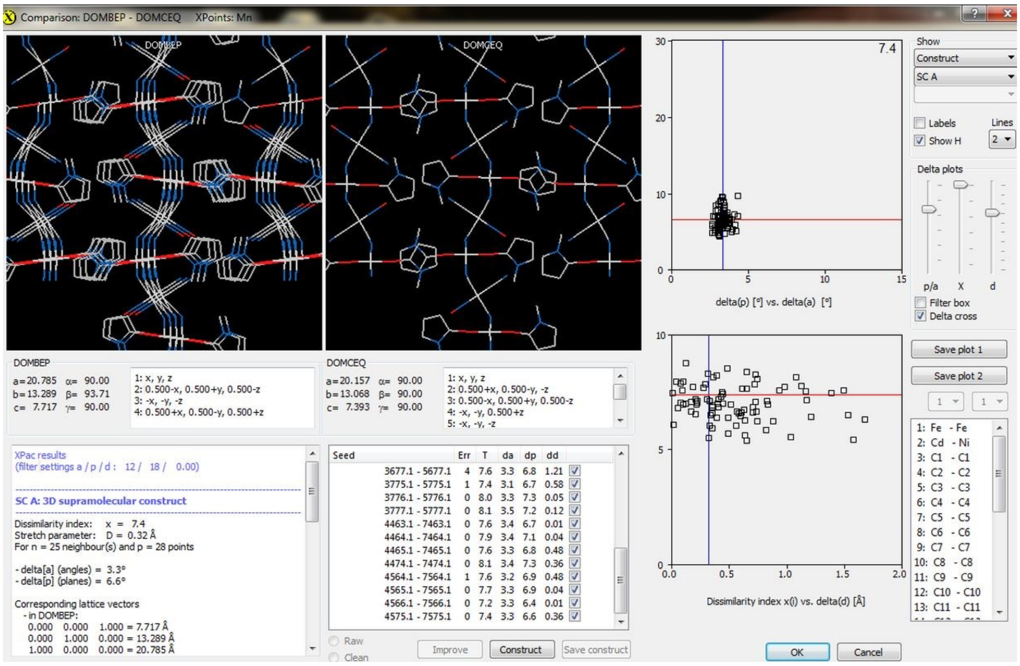
Corresponding lattice vectors
- in DOMCEQ:
0.000 0.000 1.000 = 7.393 Å
0.000 1.000 0.000 = 13.068 Å
1.000 0.000 0.000 = 20.157 Å

Seed	Err	T	da	dp	dd	
5776.1 - 3776.1	0	6.0	2.4	5.5	0.20	☑
5777.1 - 3777.1	0	6.0	2.6	5.4	0.41	☑
7463.1 - 4463.1	0	5.6	2.5	5.0	0.08	☑
7464.1 - 4464.1	0	5.8	2.4	5.3	0.01	☑
7465.1 - 4465.1	0	5.7	2.3	5.2	0.23	☑
7474.1 - 4474.1	0	6.0	2.4	5.4	0.04	☑
7475.1 - 4475.1	0	5.7	2.3	5.2	0.15	☑
7564.1 - 4564.1	0	5.6	2.3	5.1	0.23	☑
7565.1 - 4565.1	0	5.8	2.3	5.3	0.01	☑
7566.1 - 4566.1	0	5.5	2.4	4.9	0.08	☑
7574.1 - 4574.1	0	5.7	2.4	5.1	0.15	☑
7575.1 - 4575.1	0	5.6	2.3	5.1	0.04	☑

Show: Construct
SC A
☐ Labels
☑ Show H
Lines: 2
☐ Filter box
☑ Delta cross

1: Fe - Fe
2: Ni - Zn
3: C1 - C1
4: C2 - C2
5: C3 - C3
6: C4 - C4
7: C5 - C5
8: C6 - C6
9: C7 - C7
10: C8 - C8
11: C9 - C9
12: C10 - C10
13: C11 - C11

DOMBEP-DOMCEQ



Comparison: DOMBEP - DOMCEQ   XPoints: Mn

DOMBEP
a=20.785 α= 90.00
b=13.289 β= 93.71
c= 7.717 γ= 90.00

1: x, y, z
2: 0.500-x, 0.500+y, 0.500-z
3: -x, -y, -z
4: 0.500+x, 0.500-y, 0.500+z

DOMCEQ
a=20.157 α= 90.00
b=13.068 β= 90.00
c= 7.393 γ= 90.00

1: x, y, z
2: 0.500+x, 0.500-y, -z
3: 0.500-x, 0.500+y, 0.500-z
4: -x, -y, 0.500+z
5: -x, -y, -z

XPac results
(filter settings a / p / d : 12 / 18 / 0.00)

SC A: 3D supramolecular construct

Dissimilarity index: x = 7.4
Stretch parameter: D = 0.32 Å
For n = 25 neighbour(s) and p = 28 points

- delta[a] (angles) = 3.3°
- delta[p] (planes) = 6.6°

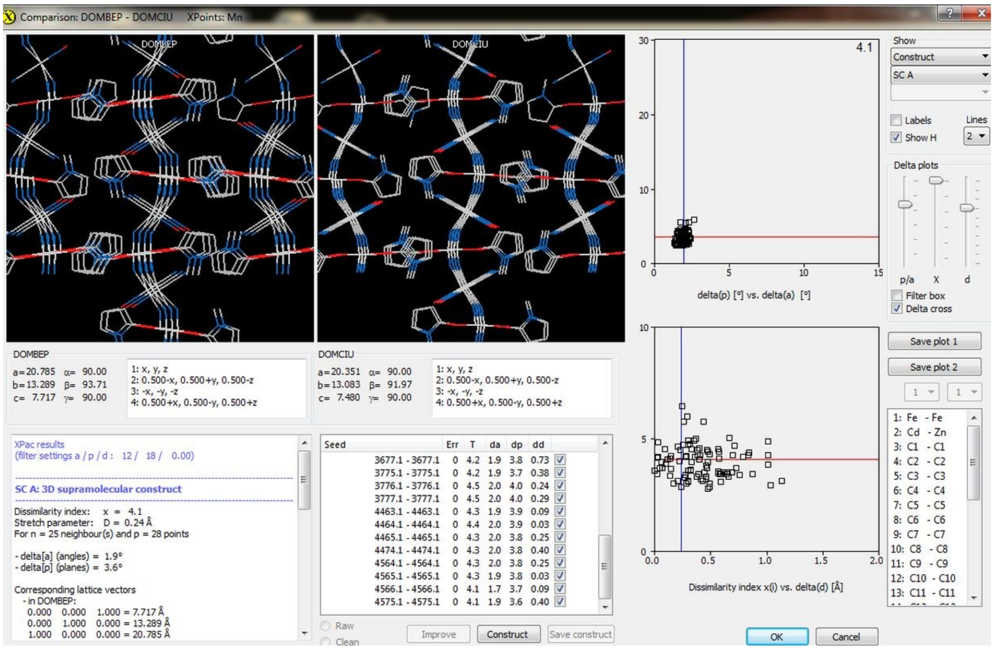
Corresponding lattice vectors
- in DOMBEP:
0.000 0.000 1.000 = 7.717 Å
0.000 1.000 0.000 = 13.289 Å
1.000 0.000 0.000 = 20.785 Å

Seed	Err	T	da	dp	dd	
3677.1 - 5677.1	4	7.6	3.3	6.8	1.21	☑
3775.1 - 5775.1	1	7.4	3.1	6.7	0.58	☑
3776.1 - 5776.1	0	8.0	3.3	7.3	0.05	☑
3777.1 - 5777.1	0	8.1	3.5	7.2	0.12	☑
4463.1 - 7463.1	0	7.6	3.4	6.7	0.01	☑
4464.1 - 7464.1	0	7.9	3.4	7.1	0.04	☑
4465.1 - 7465.1	0	7.6	3.3	6.8	0.48	☑
4474.1 - 7474.1	0	8.1	3.4	7.3	0.36	☑
4564.1 - 7564.1	1	7.6	3.2	6.9	0.48	☑
4565.1 - 7565.1	0	7.7	3.3	6.9	0.04	☑
4566.1 - 7566.1	0	7.2	3.3	6.4	0.01	☑
4575.1 - 7575.1	0	7.4	3.3	6.6	0.36	☑

Show: Construct
SC A
☐ Labels
☑ Show H
Lines: 2
☐ Filter box
☑ Delta cross

1: Fe - Fe
2: Cd - Ni
3: C1 - C1
4: C2 - C2
5: C3 - C3
6: C4 - C4
7: C5 - C5
8: C6 - C6
9: C7 - C7
10: C8 - C8
11: C9 - C9
12: C10 - C10
13: C11 - C11

DOMBEP-DOMCIU



Show: Construct, SC A

☐ Labels

☑ Show H

Lines: 2

☐ Filter box

☑ Delta cross

○ Raw

○ Clean

DOMBEP

a = 20.785 α = 90.00
b = 13.289 β = 93.71
c = 7.717 γ = 90.00

1: x, y, z
2: 0.500-x, 0.500+y, 0.500-z
3: -x, -y, -z
4: 0.500+x, 0.500-y, 0.500+z

DOMCIU

a = 20.351 α = 90.00
b = 13.083 β = 91.97
c = 7.480 γ = 90.00

1: x, y, z
2: 0.500-x, 0.500+y, 0.500-z
3: -x, -y, -z
4: 0.500+x, 0.500-y, 0.500+z

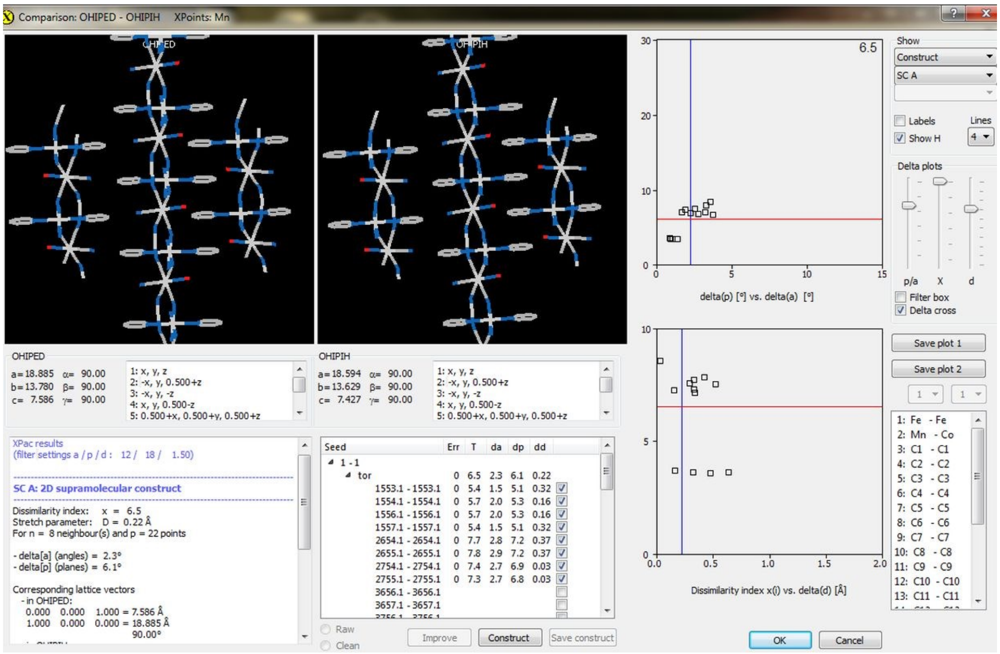
```
XPac results
(filter settings a / p / d :   12 /   18 /   0.00)

------------------------------------------------
SC A: 3D supramolecular construct
------------------------------------------------
Dissimilarity index:    x  =  4.1
Stretch parameter:    D =  0.24 Å
For n = 25 neighbour(s) and p = 28 points

- delta[a] (angles) =  1.9°
- delta[p] (planes) =  3.6°

Corresponding lattice vectors
  - in DOMBEP:
    0.000   0.000   1.000 = 7.717 Å
    0.000   1.000   0.000 = 13.289 Å
    1.000   0.000   0.000 = 20.785 Å
```

Seed	Err	T	da	dp	dd	
3677.1 - 3677.1	0	4.2	1.9	3.8	0.73	☑
3775.1 - 3775.1	0	4.2	1.9	3.7	0.38	☑
3776.1 - 3776.1	0	4.5	2.0	4.0	0.24	☑
3777.1 - 3777.1	0	4.5	2.0	4.0	0.29	☑
4463.1 - 4463.1	0	4.3	1.9	3.9	0.09	☑
4464.1 - 4464.1	0	4.4	2.0	3.9	0.03	☑
4465.1 - 4465.1	0	4.3	2.0	3.8	0.25	☑
4474.1 - 4474.1	0	4.3	2.0	3.8	0.40	☑
4564.1 - 4564.1	0	4.3	2.0	3.8	0.25	☑
4565.1 - 4565.1	0	4.3	1.9	3.8	0.03	☑
4566.1 - 4566.1	0	4.1	1.7	3.7	0.09	☑
4575.1 - 4575.1	0	4.1	1.9	3.6	0.40	☑

1: Fe - Fe
2: Cd - Zn
3: C1 - C1
4: C2 - C2
5: C3 - C3
6: C4 - C4
7: C5 - C5
8: C6 - C6
9: C7 - C7
10: C8 - C8
11: C9 - C9
12: C10 - C10
13: C11 - C11

Figure S9. XPac results window showing the comparison of complexes of the series M(1-Me$_2$P)$_2$[Fe(CN)$_5$NO] (M = Mn, Co, Ni, Zn).

OHIPED-OHIPIH



```
OHIPED
a=18.885  α=  90.00     1: x, y, z
b=13.780  β=  90.00     2: -x, y, 0.500+z
c=  7.586  γ=  90.00     3: -x, y, -z
                          4: x, y, 0.500-z
                          5: 0.500+x, 0.500+y, 0.500+z

OHIPIH
a=18.594  α=  90.00     1: x, y, z
b=13.629  β=  90.00     2: -x, y, 0.500+z
c=  7.427  γ=  90.00     3: -x, y, -z
                          4: x, y, 0.500-z
                          5: 0.500+x, 0.500+y, 0.500+z
```

```
XPac results
(filter settings a / p / d :  12 /  18 /   1.50)

------------------------------------------------
SC A: 2D supramolecular construct
------------------------------------------------
Dissimilarity index:    x  =  6.5
Stretch parameter:    D =  0.22 Å
For n =  8 neighbour(s) and p = 22 points

- delta[a] (angles) =  2.3°
- delta[p] (planes) =  6.1°

Corresponding lattice vectors
   - in OHIPED:
     0.000    0.000    1.000 = 7.586 Å
     1.000    0.000    0.000 = 18.885 Å
                               90.00°
```

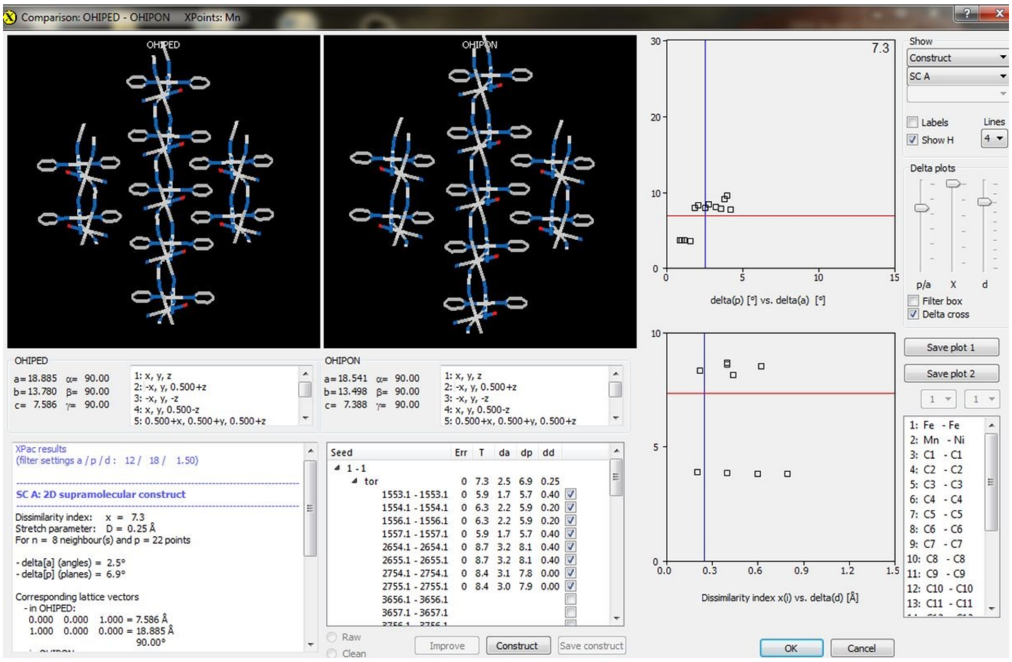
```
Seed                  Err  T    da   dp   dd
◢ 1 - 1
   ◢ tor               0   6.5  2.3  6.1  0.22
      1553.1 - 1553.1  0   5.4  1.5  5.1  0.32  ☑
      1554.1 - 1554.1  0   5.7  2.0  5.3  0.16  ☑
      1556.1 - 1556.1  0   5.7  2.0  5.3  0.16  ☑
      1557.1 - 1557.1  0   5.4  1.5  5.1  0.32  ☑
      2654.1 - 2654.1  0   7.7  2.8  7.2  0.37  ☑
      2655.1 - 2655.1  0   7.8  2.9  7.2  0.37  ☑
      2754.1 - 2754.1  0   7.4  2.7  6.9  0.03  ☑
      2755.1 - 2755.1  0   7.3  2.7  6.8  0.03  ☑
      3656.1 - 3656.1                           ☐
      3657.1 - 3657.1                           ☐
```

○ Raw
○ Clean

☐ Labels
☑ Show H
☐ Filter box
☑ Delta cross

1: Fe - Fe
2: Mn - Co
3: C1 - C1
4: C2 - C2
5: C3 - C3
6: C4 - C4
7: C5 - C5
8: C6 - C6
9: C7 - C7
10: C8 - C8
11: C9 - C9
12: C10 - C10
13: C11 - C11

OHIPED-OHIPON



```
OHIPED
a=18.885  α=  90.00     1: x, y, z
b=13.780  β=  90.00     2: -x, y, 0.500+z
c=  7.586  γ=  90.00     3: -x, y, -z
                          4: x, y, 0.500-z
                          5: 0.500+x, 0.500+y, 0.500+z

OHIPON
a=18.541  α=  90.00     1: x, y, z
b=13.498  β=  90.00     2: -x, y, 0.500+z
c=  7.388  γ=  90.00     3: -x, y, -z
                          4: x, y, 0.500-z
                          5: 0.500+x, 0.500+y, 0.500+z
```

```
XPac results
(filter settings a / p / d :  12 /  18 /   1.50)

------------------------------------------------
SC A: 2D supramolecular construct
------------------------------------------------
Dissimilarity index:    x  =  7.3
Stretch parameter:    D =  0.25 Å
For n =  8 neighbour(s) and p = 22 points

- delta[a] (angles) =  2.5°
- delta[p] (planes) =  6.9°

Corresponding lattice vectors
   - in OHIPED:
     0.000    0.000    1.000 = 7.586 Å
     1.000    0.000    0.000 = 18.885 Å
                               90.00°
```

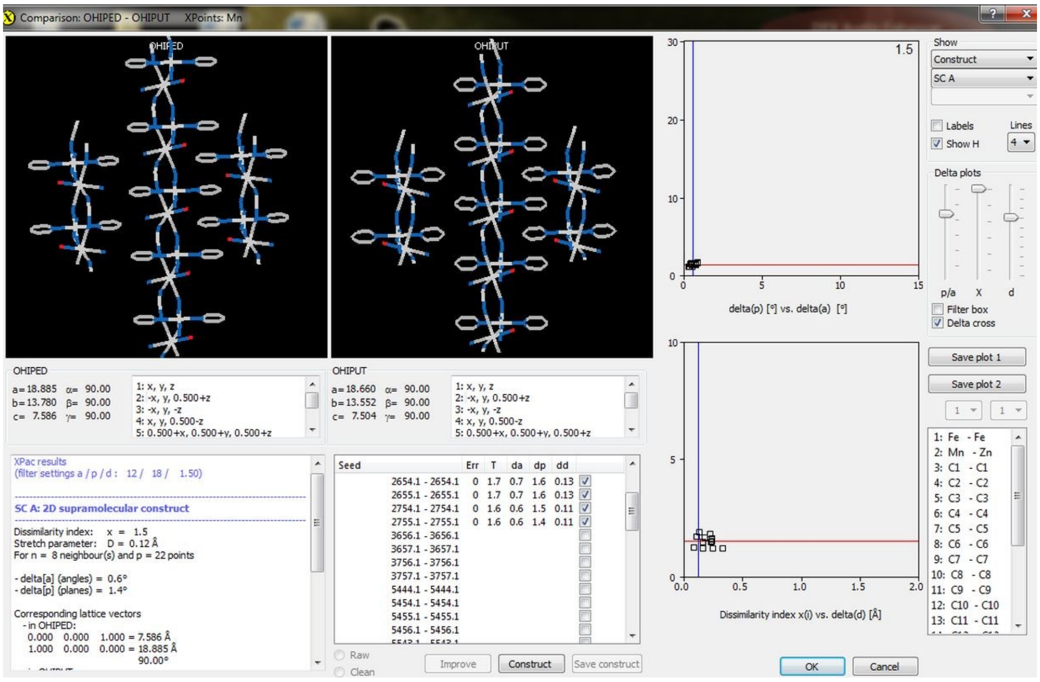
```
Seed                  Err  T    da   dp   dd
◢ 1 - 1
   ◢ tor               0   7.3  2.5  6.9  0.25
      1553.1 - 1553.1  0   5.9  1.7  5.7  0.40  ☑
      1554.1 - 1554.1  0   6.3  2.2  5.9  0.20  ☑
      1556.1 - 1556.1  0   6.3  2.2  5.9  0.20  ☑
      1557.1 - 1557.1  0   5.9  1.7  5.7  0.40  ☑
      2654.1 - 2654.1  0   8.7  3.2  8.1  0.40  ☑
      2655.1 - 2655.1  0   8.7  3.2  8.1  0.40  ☑
      2754.1 - 2754.1  0   8.4  3.1  7.8  0.00  ☑
      2755.1 - 2755.1  0   8.4  3.0  7.9  0.00  ☑
      3656.1 - 3656.1                           ☐
      3657.1 - 3657.1                           ☐
```

○ Raw
○ Clean

☐ Labels
☑ Show H
☐ Filter box
☑ Delta cross

1: Fe - Fe
2: Mn - Ni
3: C1 - C1
4: C2 - C2
5: C3 - C3
6: C4 - C4
7: C5 - C5
8: C6 - C6
9: C7 - C7
10: C8 - C8
11: C9 - C9
12: C10 - C10
13: C11 - C11

OHIPED-OHIPUT



OHIPED

a = 18.885 α = 90.00
b = 13.780 β = 90.00
c = 7.586 γ = 90.00

1: x, y, z
2: -x, y, 0.500+z
3: -x, y, -z
4: x, y, 0.500-z
5: 0.500+x, 0.500+y, 0.500+z

OHIPUT

a = 18.660 α = 90.00
b = 13.552 β = 90.00
c = 7.504 γ = 90.00

1: x, y, z
2: -x, y, 0.500+z
3: -x, y, -z
4: x, y, 0.500-z
5: 0.500+x, 0.500+y, 0.500+z

XPac results
(filter settings a / p / d : 12 / 18 / 1.50)

SC A: 2D supramolecular construct

Dissimilarity index: x = 1.5
Stretch parameter: D = 0.12 Å
For n = 8 neighbour(s) and p = 22 points

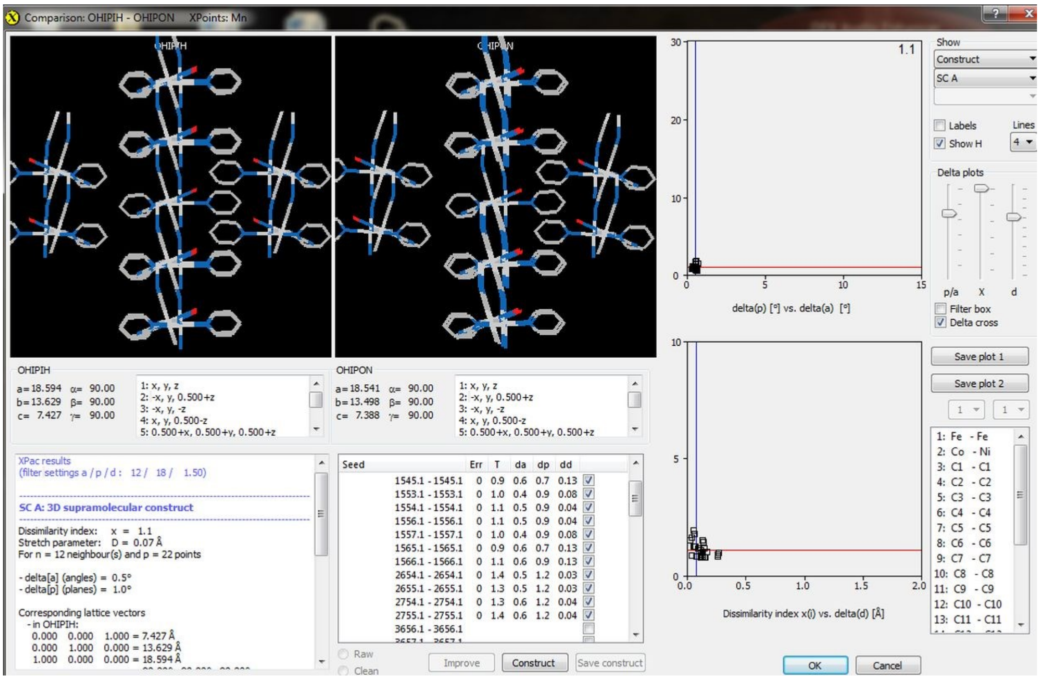
- delta[a] (angles) = 0.6°
- delta[p] (planes) = 1.4°

Corresponding lattice vectors
- in OHIPED:
0.000 0.000 1.000 = 7.586 Å
1.000 0.000 0.000 = 18.885 Å
90.00°

Seed	Err	T	da	dp	dd	
2654.1 - 2654.1	0	1.7	0.7	1.6	0.13	☑
2655.1 - 2655.1	0	1.7	0.7	1.6	0.13	☑
2754.1 - 2754.1	0	1.6	0.6	1.5	0.11	☑
2755.1 - 2755.1	0	1.6	0.6	1.4	0.11	☑
3656.1 - 3656.1						☐
3657.1 - 3657.1						☐
3756.1 - 3756.1						☐
3757.1 - 3757.1						☐
5444.1 - 5444.1						☐
5454.1 - 5454.1						☐
5455.1 - 5455.1						☐
5456.1 - 5456.1						☐

1: Fe - Fe
2: Mn - Zn
3: C1 - C1
4: C2 - C2
5: C3 - C3
6: C4 - C4
7: C5 - C5
8: C6 - C6
9: C7 - C7
10: C8 - C8
11: C9 - C9
12: C10 - C10
13: C11 - C11

OHIPIH-OHIPON



OHIPIH

a = 18.594 α = 90.00
b = 13.629 β = 90.00
c = 7.427 γ = 90.00

1: x, y, z
2: -x, y, 0.500+z
3: -x, y, -z
4: x, y, 0.500-z
5: 0.500+x, 0.500+y, 0.500+z

OHIPON

a = 18.541 α = 90.00
b = 13.498 β = 90.00
c = 7.388 γ = 90.00

1: x, y, z
2: -x, y, 0.500+z
3: -x, y, -z
4: x, y, 0.500-z
5: 0.500+x, 0.500+y, 0.500+z

XPac results
(filter settings a / p / d : 12 / 18 / 1.50)

SC A: 3D supramolecular construct

Dissimilarity index: x = 1.1
Stretch parameter: D = 0.07 Å
For n = 12 neighbour(s) and p = 22 points

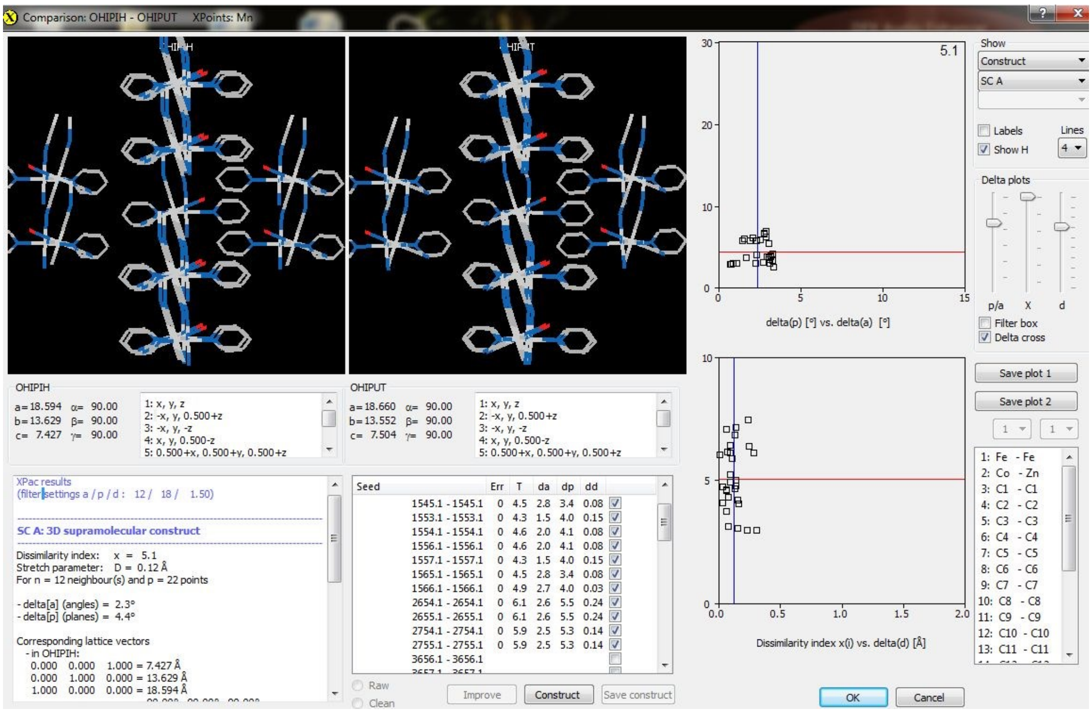
- delta[a] (angles) = 0.5°
- delta[p] (planes) = 1.0°

Corresponding lattice vectors
- in OHIPIH:
0.000 0.000 1.000 = 7.427 Å
0.000 1.000 0.000 = 13.629 Å
1.000 0.000 0.000 = 18.594 Å

Seed	Err	T	da	dp	dd	
1545.1 - 1545.1	0	0.9	0.6	0.7	0.13	☑
1553.1 - 1553.1	0	1.0	0.4	0.9	0.08	☑
1554.1 - 1554.1	0	1.1	0.5	0.9	0.04	☑
1556.1 - 1556.1	0	1.1	0.5	0.9	0.04	☑
1557.1 - 1557.1	0	1.0	0.4	0.9	0.08	☑
1565.1 - 1565.1	0	0.9	0.6	0.7	0.13	☑
1566.1 - 1566.1	0	1.1	0.6	0.9	0.13	☑
2654.1 - 2654.1	0	1.4	0.5	1.2	0.03	☑
2655.1 - 2655.1	0	1.3	0.5	1.2	0.03	☑
2754.1 - 2754.1	0	1.3	0.6	1.2	0.04	☑
2755.1 - 2755.1	0	1.4	0.6	1.2	0.04	☑
3656.1 - 3656.1						☐

1: Fe - Fe
2: Co - Ni
3: C1 - C1
4: C2 - C2
5: C3 - C3
6: C4 - C4
7: C5 - C5
8: C6 - C6
9: C7 - C7
10: C8 - C8
11: C9 - C9
12: C10 - C10
13: C11 - C11

OHIPIH-OHIPUT



OHIPIH

a= 18.594 α= 90.00
b= 13.629 β= 90.00
c= 7.427 γ= 90.00

1: x, y, z
2: -x, y, 0.500+z
3: -x, y, -z
4: x, y, 0.500-z
5: 0.500+x, 0.500+y, 0.500+z

OHIPUT

a= 18.660 α= 90.00
b= 13.552 β= 90.00
c= 7.504 γ= 90.00

1: x, y, z
2: -x, y, 0.500+z
3: -x, y, -z
4: x, y, 0.500-z
5: 0.500+x, 0.500+y, 0.500+z

XPac results
(filter settings a / p / d : 12 / 18 / 1.50)

SC A: 3D supramolecular construct

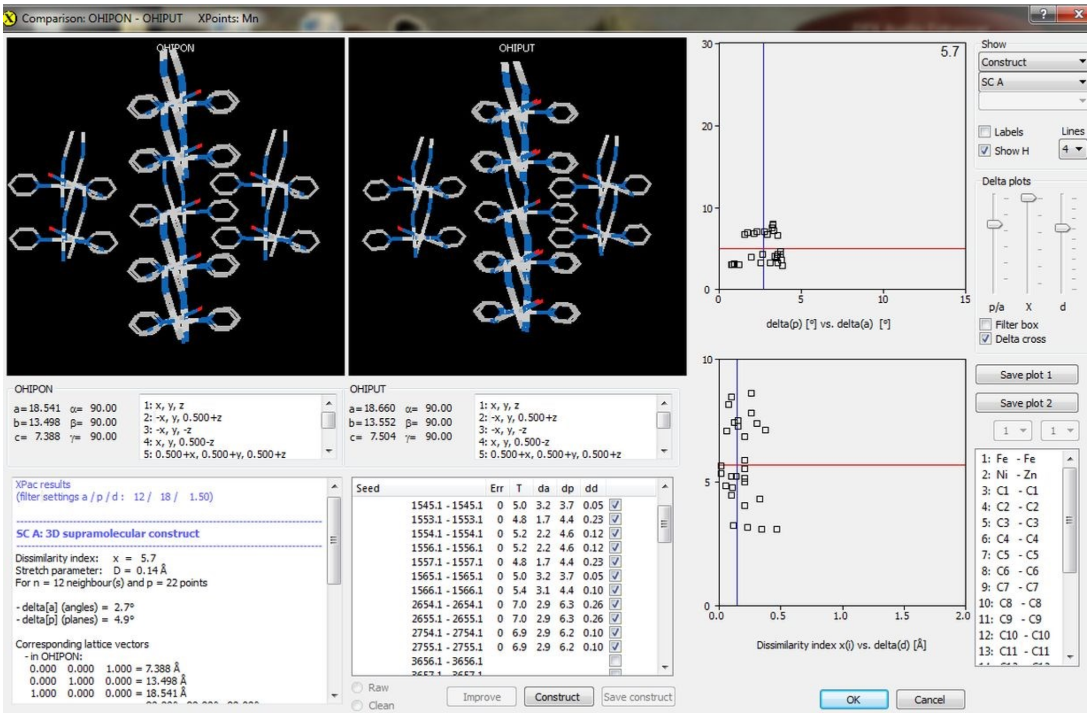
Dissimilarity index: x = 5.1
Stretch parameter: D = 0.12 Å
For n = 12 neighbour(s) and p = 22 points

- delta[a] (angles) = 2.3°
- delta[p] (planes) = 4.4°

Corresponding lattice vectors
- in OHIPIH:
0.000 0.000 1.000 = 7.427 Å
0.000 1.000 0.000 = 13.629 Å
1.000 0.000 0.000 = 18.594 Å

Seed	Err	T	da	dp	dd	
1545.1 - 1545.1	0	4.5	2.8	3.4	0.08	☑
1553.1 - 1553.1	0	4.3	1.5	4.0	0.15	☑
1554.1 - 1554.1	0	4.6	2.0	4.1	0.08	☑
1556.1 - 1556.1	0	4.6	2.0	4.1	0.08	☑
1557.1 - 1557.1	0	4.3	1.5	4.0	0.15	☑
1565.1 - 1565.1	0	4.5	2.8	3.4	0.08	☑
1566.1 - 1566.1	0	4.9	2.7	4.0	0.03	☑
2654.1 - 2654.1	0	6.1	2.6	5.5	0.24	☑
2655.1 - 2655.1	0	6.1	2.6	5.5	0.24	☑
2754.1 - 2754.1	0	5.9	2.5	5.3	0.14	☑
2755.1 - 2755.1	0	5.9	2.5	5.3	0.14	☑
3656.1 - 3656.1						☐

OHIPON-OHIPUT



OHIPON

a= 18.541 α= 90.00
b= 13.498 β= 90.00
c= 7.388 γ= 90.00

1: x, y, z
2: -x, y, 0.500+z
3: -x, y, -z
4: x, y, 0.500-z
5: 0.500+x, 0.500+y, 0.500+z

OHIPUT

a= 18.660 α= 90.00
b= 13.552 β= 90.00
c= 7.504 γ= 90.00

1: x, y, z
2: -x, y, 0.500+z
3: -x, y, -z
4: x, y, 0.500-z
5: 0.500+x, 0.500+y, 0.500+z

XPac results
(filter settings a / p / d : 12 / 18 / 1.50)

SC A: 3D supramolecular construct

Dissimilarity index: x = 5.7
Stretch parameter: D = 0.14 Å
For n = 12 neighbour(s) and p = 22 points

- delta[a] (angles) = 2.7°
- delta[p] (planes) = 4.9°

Corresponding lattice vectors
- in OHIPON:
0.000 0.000 1.000 = 7.388 Å
0.000 1.000 0.000 = 13.498 Å
1.000 0.000 0.000 = 18.541 Å

Seed	Err	T	da	dp	dd	
1545.1 - 1545.1	0	5.0	3.2	3.7	0.05	☑
1553.1 - 1553.1	0	4.8	1.7	4.4	0.23	☑
1554.1 - 1554.1	0	5.2	2.2	4.6	0.12	☑
1556.1 - 1556.1	0	5.2	2.2	4.6	0.12	☑
1557.1 - 1557.1	0	4.8	1.7	4.4	0.23	☑
1565.1 - 1565.1	0	5.0	3.2	3.7	0.05	☑
1566.1 - 1566.1	0	5.4	3.1	4.4	0.10	☑
2654.1 - 2654.1	0	7.0	2.9	6.3	0.26	☑
2655.1 - 2655.1	0	7.0	2.9	6.3	0.26	☑
2754.1 - 2754.1	0	6.9	2.9	6.2	0.10	☑
2755.1 - 2755.1	0	6.9	2.9	6.2	0.10	☑
3656.1 - 3656.1						☐

IR and electronic spectra

The absorption IR spectra of 1-MeIm (solution) and complexes **1-5** (solid state) are shown in **Figures S10-S14, ESI**. The intense bands located at 3107 and 3125 cm^{-1} in the IR spectrum of 1-MeIm are assigned to C-H stretching modes. These modes appear in the IR spectra of the complexes at 3160 and 3110 cm^{-1}. The modes corresponding to the CH_3 stretching vibrations are blue-shifted in 15 cm^{-1} with respect to the free ligand indicating that the methyl group is involved in different intermolecular interactions, as was discussed previously. The antisymmetric and symmetric CH_3 stretching modes appear in the range 2962-2931 cm^{-1} in the complexes, while in the free ligand, these bands are located between 2951 and 2922 cm^{-1}. The bands located between 1423 and 1370 cm^{-1} are attributed to CH_3 bending modes. The band corresponding to the CH_3 rocking mode appears in the 944-938 cm^{-1} range in the complexes, but in the free ligand this band is observed at 927 cm^{-1}. The C-N and C-C stretching modes corresponding to the imidazole ring generally appear coupled and can be observed in the 1600-1400 cm^{-1} range in the spectra of the complexes.

The IR spectra of complexes **1-5** show two absorption bands in the 2185-2170 cm^{-1} range, assignable to the CN stretching modes of bridged cyanide ligands. The bands located between 2168 and 2163 cm^{-1} are assigned to CN stretching vibration corresponding to unbridged cyanide ligands. The intense absorption bands observed in the frequency range 1932-1892 cm^{-1} are attributed to NO stretching mode. The IR bands below 1000 cm^{-1} correspond to ring modes vibrations coupled with the modes attributed to the nitroprusside anion.

The solid-state UV-visible spectra of complexes **1-5** are shown in **Figure S15, ESI**. The bands located in the visible region for complexes **2** and **5** are attributed to *d-d* transitions of the metal center in an octahedral environment. In the case of Mn(II), Zn(II) and Cd(II) complexes, d-d transitions are not possible because it has half-filled 3*d* orbitals. The broad band located at around 550 nm is attributed to intra-ligand charge transfer for Zn(II) and Cd(II) complexes.

Figure S10. IR absorption spectra for 1-MeIm (solution) and complex **1**(solid).

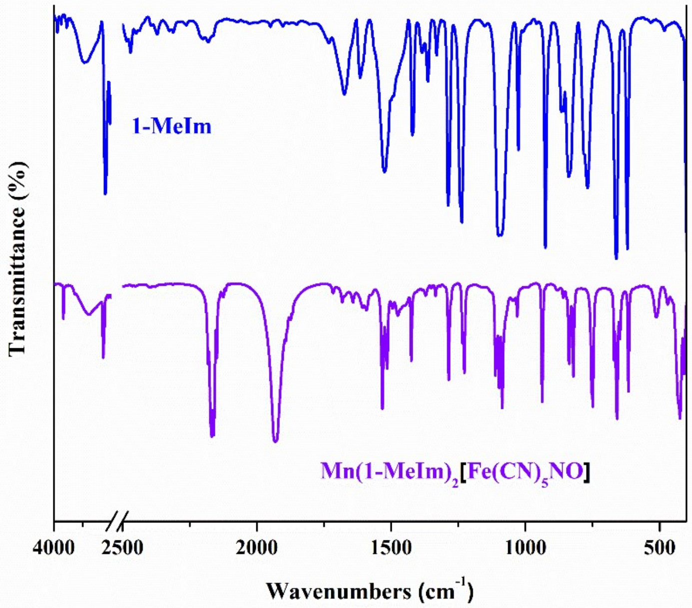


Figure S11. IR absorption spectra for 1-MeIm (solution) and complex **2** (solid).

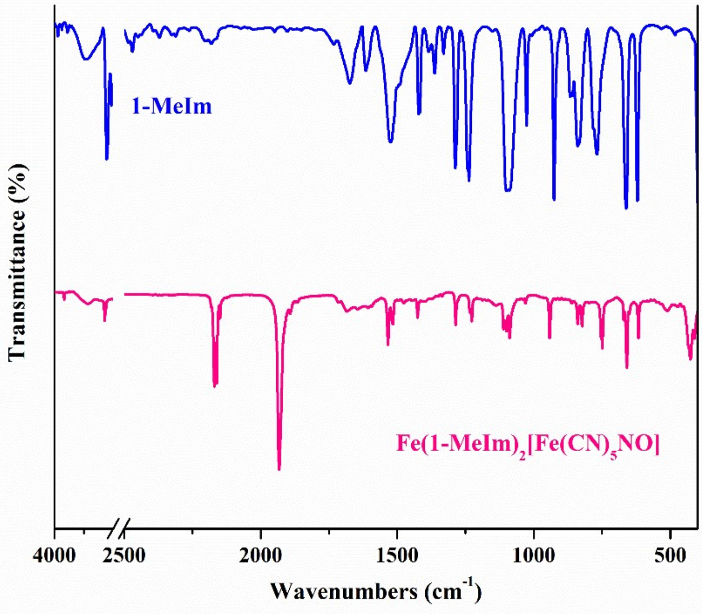


Figure S12. IR absorption spectra for 1-MeIm (solution) and complex **3** (solid).

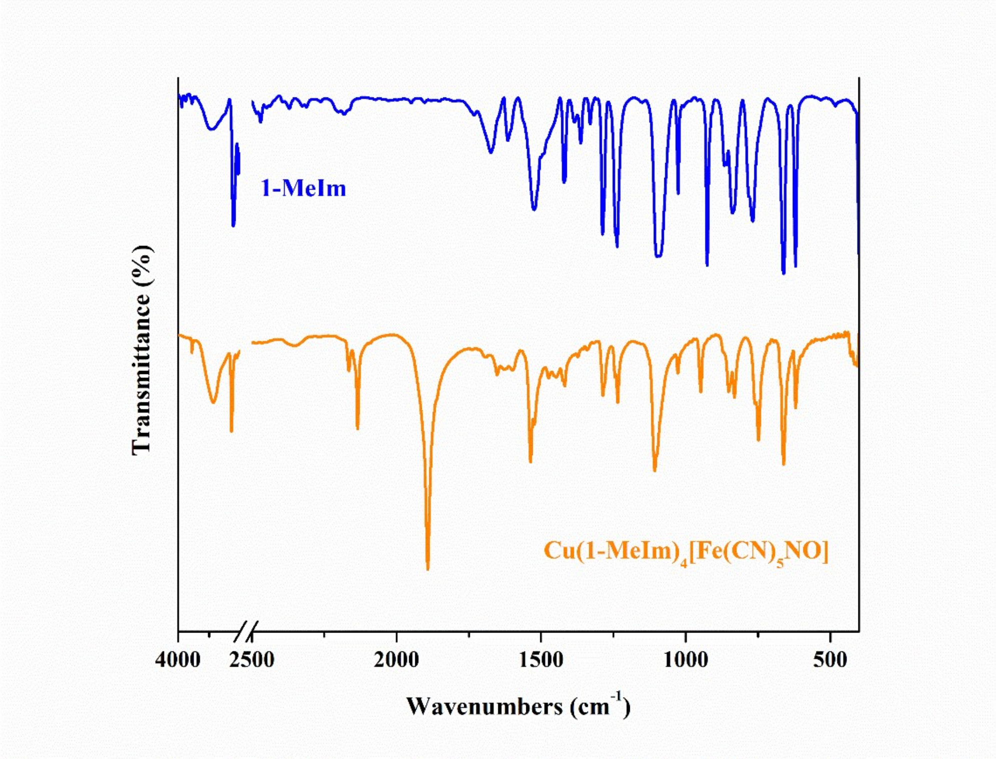


Figure S13. IR absorption spectra for 1-MeIm (solution) and complex **4** (solid).

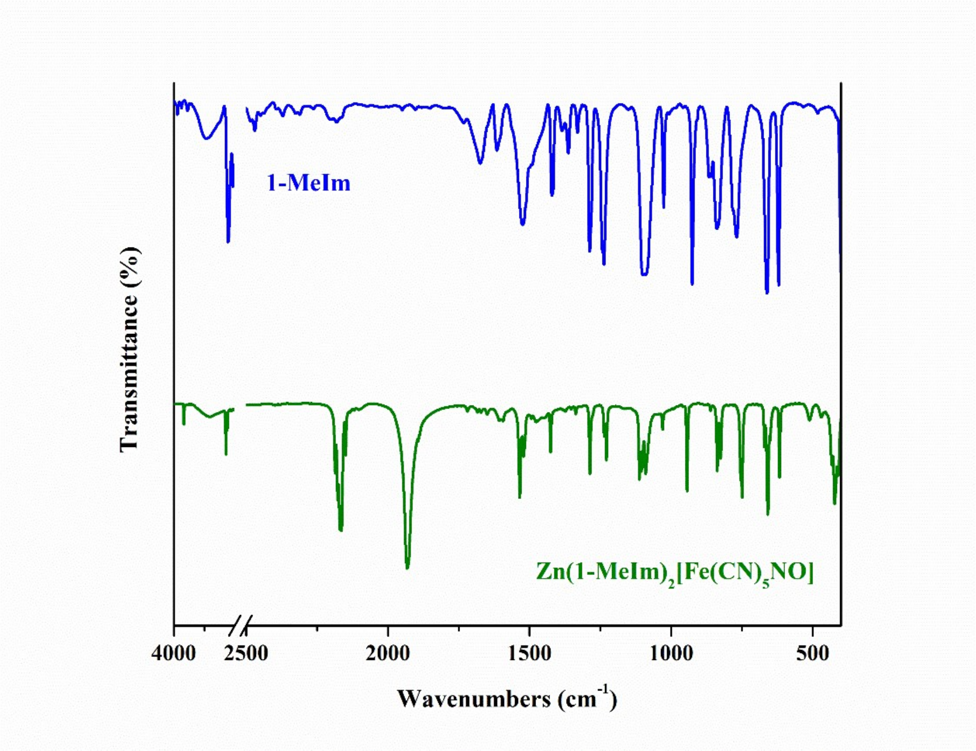


Figure S14. IR absorption spectra for 1-MeIm (solution) and complex **5** (solid).

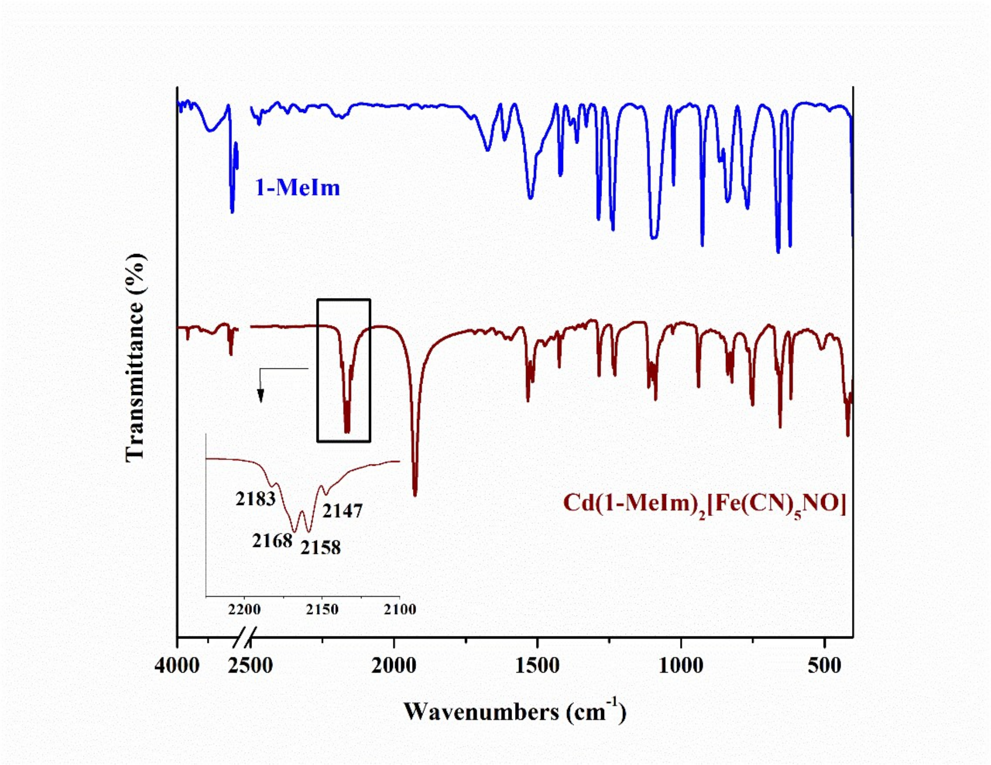
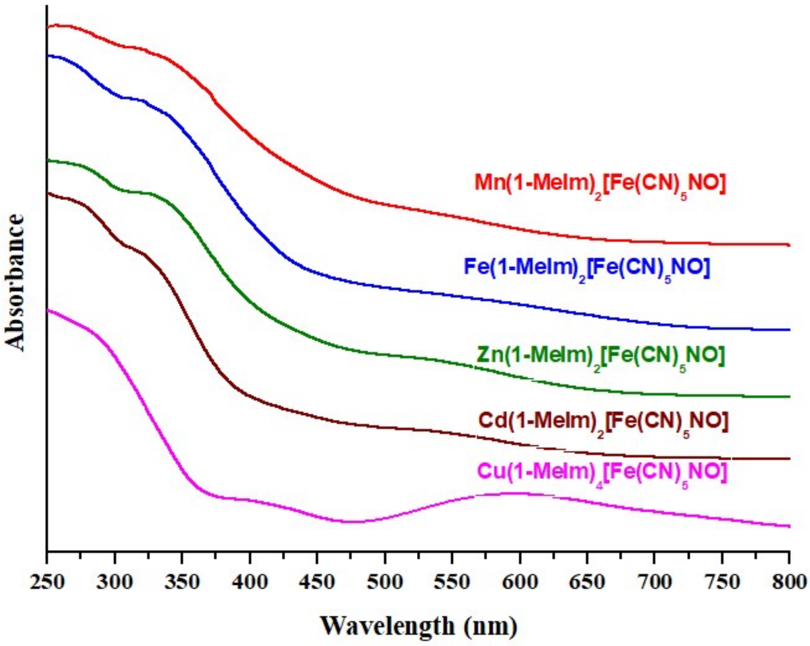


Figure S15. Solid-state UV-Visible spectra of complexes **1-5**.



Thermal analysis

The thermal behavior of complexes **1-5** has been studied by thermogravimetric (TG) and differential thermal analysis (DTA). The TG-DTA curves for the thermal decomposition of complexes **1-5** are shown in **Figures S16-S20, ESI**. The thermal decomposition process for complexes **1** and **2** is similar. The first mass loss is observed above 200 ºC and corresponds to the removal of 1-MeIm ligands and cyanide and NO groups. This decomposition process, not resolved in TGA, is accompanied by two exothermic peaks at 264 and 277 ºC for **1** and at 236 and 271 ºC for **2**.

The second step in the thermal decomposition finishes at 600 and 450 ºC for **1** and **2**, respectively, and corresponds to the elimination of cyanide ligands to form a mixture of MFe_2O_4 and MO (M = Mn, Fe) as final products. These products were identified by powder XRD data. The experimental mass loss (62.0 % for both compounds) is in agreement with the theoretical mass loss (63.6 % for **1** and 65.0% for **2**), which indicates a complete removal of ligands.

Complexes **3** and **4** decompose in three consecutive steps. The first one corresponds to the removal of two molecules of 1-MeIm ligands, the unbridged (axial) CN and NO ligands. The second and third steps correspond to the removal of equatorial CN ligands. DTA curves for the thermal decomposition of both complexes show exothermic peaks at 254, 343, 394 and 519 ºC for **3** and at 284, 323 and 390 ºC for **4**.

The first step for the thermal degradation of complex **5** is observed in the range 120-260 ºC, and corresponds to the evolution of four 1-MeIm ligands (observed mass loss: 43.0%, theoretical: 46.0%), in agreement with the endothermic peak at 190 ºC and an exothermic peak at 220 ºC in DTA. The second step finishes at 430 ºC, and it is attributed to the removal of bridged and unbridged CN ligands and the NO group. The DTA curve shows an exothermic peak at 410 ºC associated to the elimination and oxidation of cyanide and nitrosyl groups.

Figure S16. TG and DTA curves for the thermal decomposition of complex **1** in air.

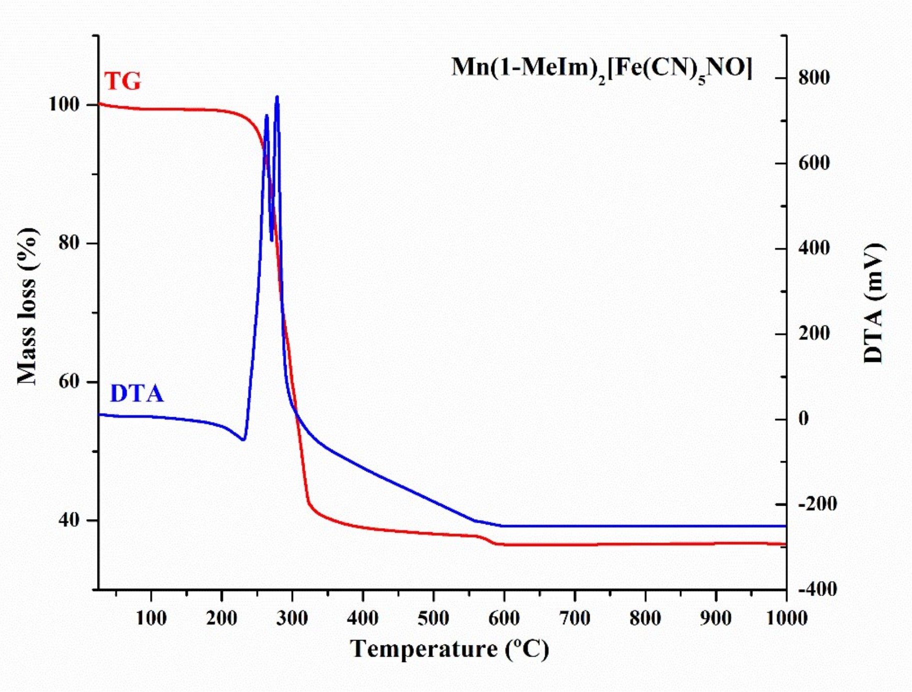


Figure S17. TG and DTA curves for the thermal decomposition of complex **2** in air.

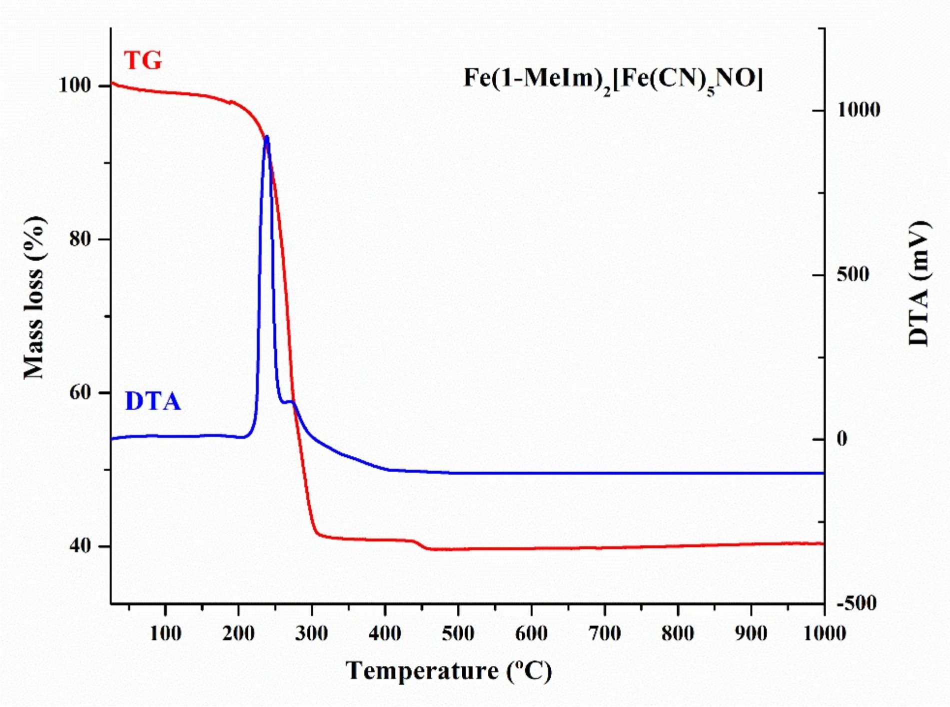


Figure S18. TG and DTA curves for the thermal decomposition of complex **3** in air.

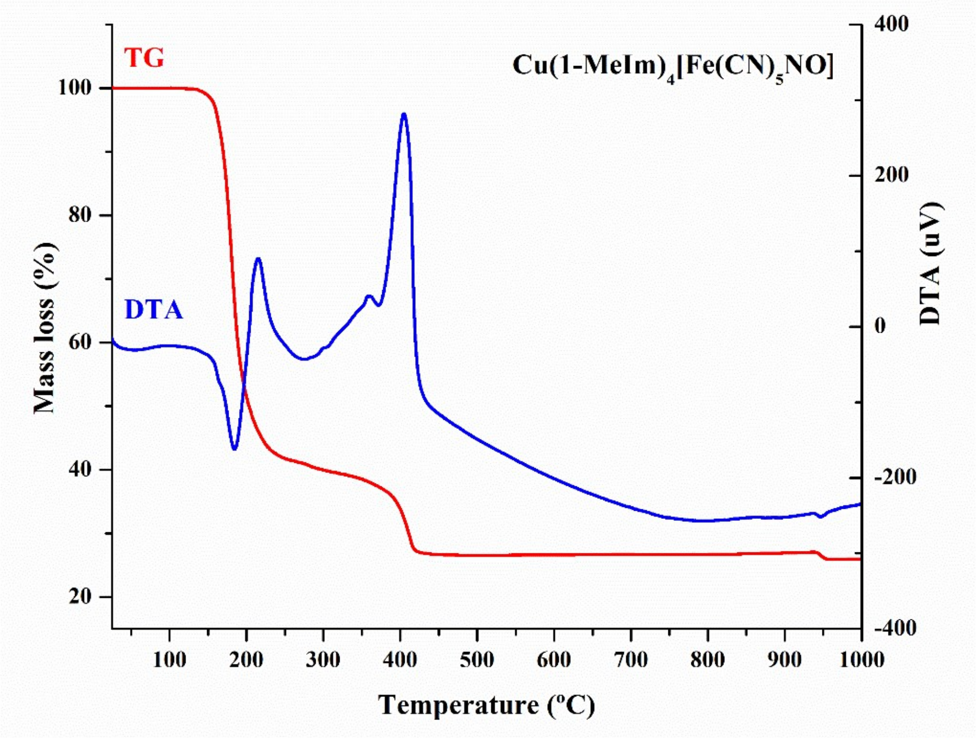


Figure S19. TG and DTA curves for the thermal decomposition of complex **4** in air.

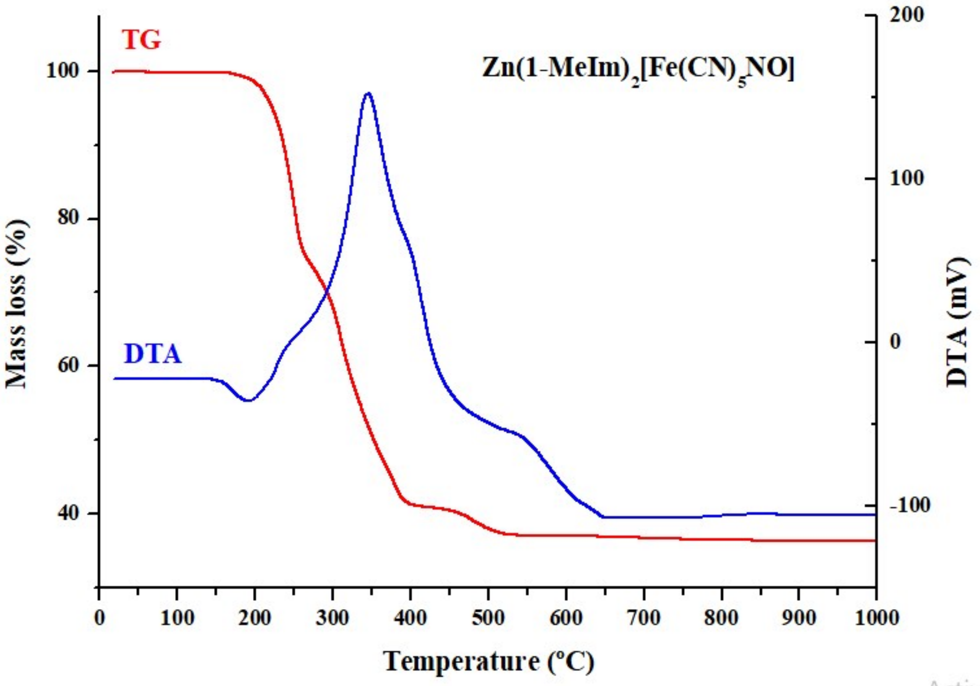


Figure S20. TG and DTA curves for the thermal decomposition of complex **5** in air.

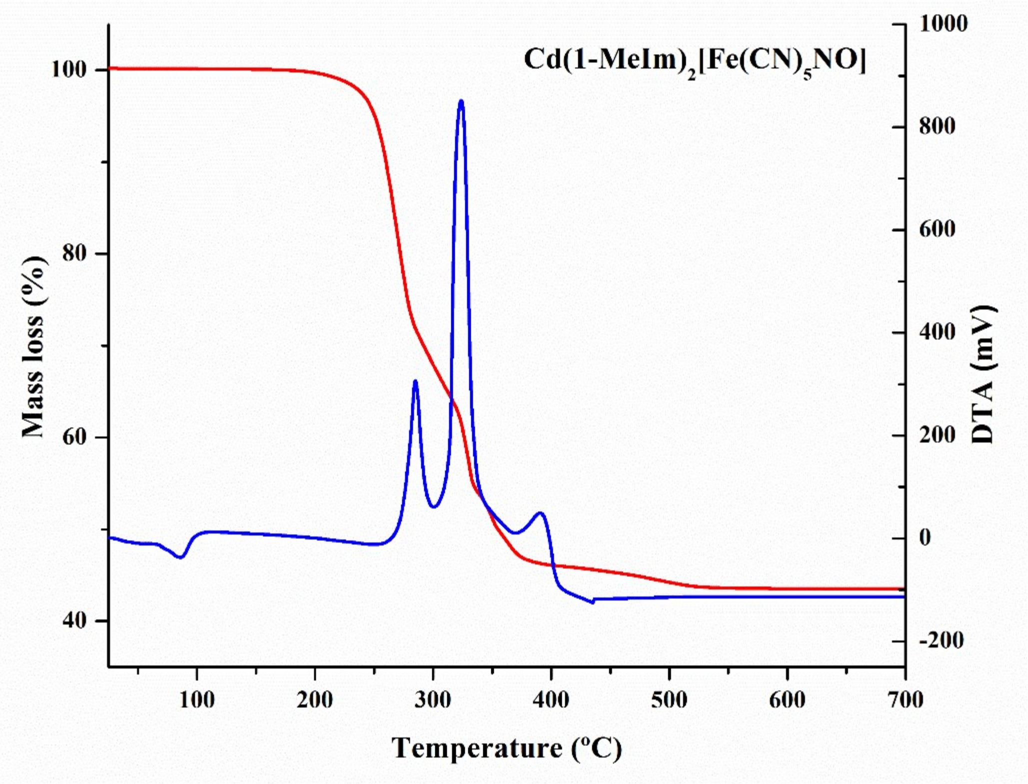


Figure S21. Cu 2p XPS spectrum of complex **3**. The copper spectrum consists of two main contributions assigned to Cu^{2+} (metal center linked to the two CN groups and four 1-MeIm ligands). On the lower-BE side, an intense peak appeared, which was assigned to $Cu^{1+}CN$. The intensity of the last one is proportional to the X-ray exposure time during the XPS experiment.

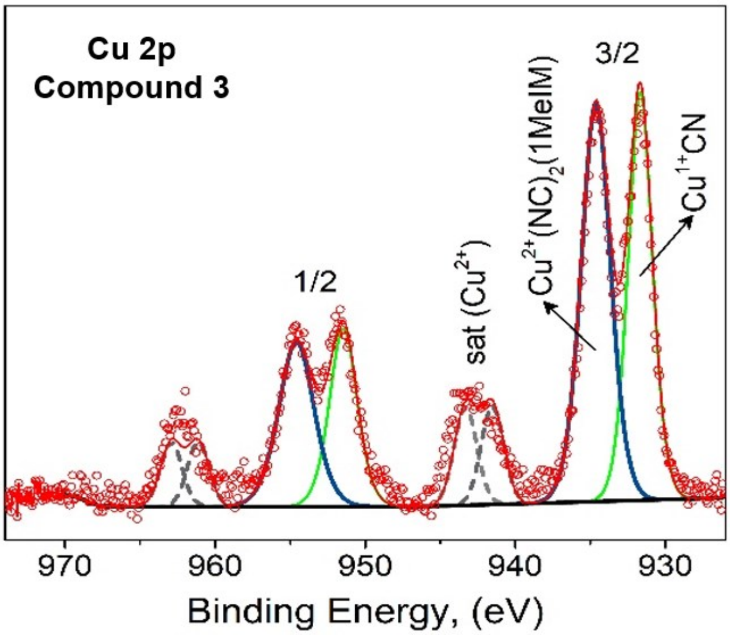


Figure S22. (Left) Mn 3s core-level region of complex **1**. The energy difference (ΔE) measured in Mn 3s (6.0 eV) is highly sensitive to the oxidation state of Mn^{2+}. (Right) Curve-Fitting results of Mn 2p spectrum.

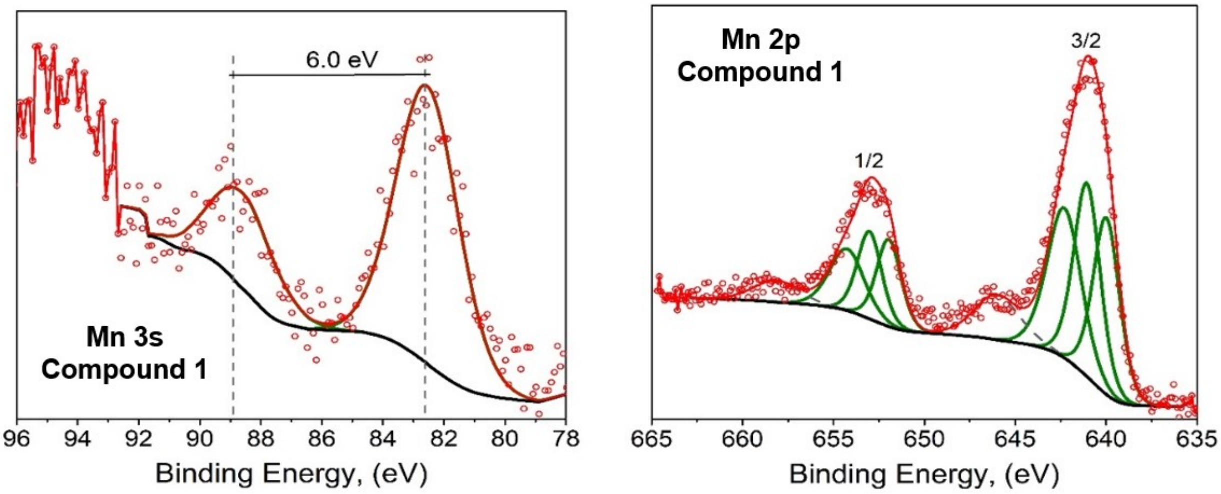


Figure S23. Inverse of magnetic susceptibility (χ) versus temperature curve to estimate the Curie-Weiss constant.

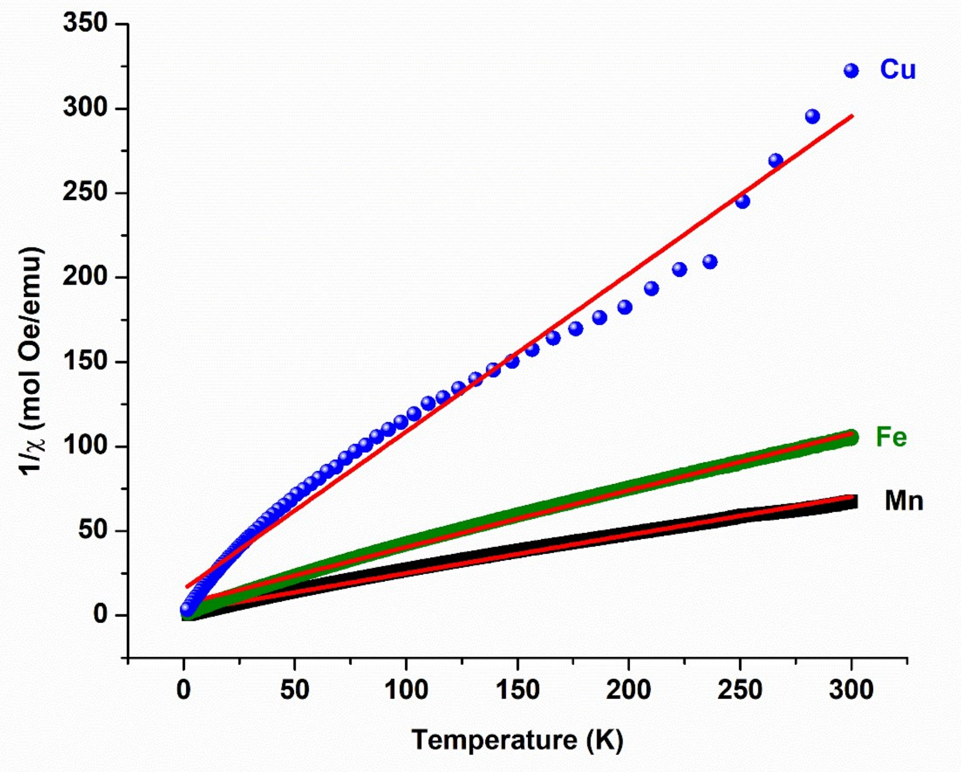


Table S1. Refined atomic fractional coordinates and displacement parameters (B_{iso}, Å^2) for Fe(1-MeIm)$_2$[Fe(CN)$_5$NO].

atom	site	x	y	z	Biso
Fe	4e	0.478(2)	0.243(2)	0.749(4)	0.018(3)
Fe1	2b	1/2	1/2	1/2	0.018(3)
Fe2	2d	1/2	0	1/2	0.018(3)
C1	4e	0.493(6)	0.336(2)	0.658(2)	0.021(3)
N1	4e	0.504(3)	0.390(6)	0.605(3)	0.021(3)
C2	4e	0.430(3)	0.155(3)	0.652(5)	0.021(3)
N2	4e	0.415(4)	0.101(7)	0.597(4)	0.021(3)
C3	4e	0.425(5)	0.153(4)	0.837(4)	0.021(3)
N3	4e	0.402(5)	0.098(4)	0.889(4)	0.021(3)
C4	4e	0.497(6)	0.334(4)	0.846(3)	0.021(3)
N4	4e	0.512(4)	0.387(7)	0.900(4)	0.021(3)
C5	4e	0.251(4)	0.272(4)	0.735(4)	0.021(3)
N5	4e	0.119(6)	0.290(3)	0.728(3)	0.021(3)
N	4e	0.671(6)	0.221(6)	0.761(7)	0.021(3)
O	4e	0.803(2)	0.209(2)	0.769(3)	0.021(3)
C11	4e	0.826(3)	0.487(4)	0.399(4)	0.023(3)
C12	4e	0.955(6)	0.434(6)	0.394(7)	0.023(3)
C13	4e	0.825(4)	0.386(6)	0.503(4)	0.023(3)
C14	4e	1.074(6)	0.300(3)	0.482(5)	0.023(3)
N11	4e	0.739(6)	0.456(4)	0.466(5)	0.023(3)
N12	4e	0.955(5)	0.371(3)	0.460(5)	0.023(3)
C21	4e	0.164(3)	-0.102(4)	0.437(4)	0.023(3)
C22	4e	0.016(6)	-0.090(5)	0.391(4)	0.023(3)
C23	4e	0.154(4)	0.031(3)	0.391(4)	0.023(3)
C24	4e	-0.126(7)	0.042(4)	0.311(3)	0.023(3)
N21	4e	0.250(5)	-0.026(5)	0.436(3)	0.023(3)
N22	4e	0.010(5)	-0.005(4)	0.362(2)	0.023(3)

Table S2. Calculated inter-atomic distances (in Å) and bond angles (in °) from the refined structure; $Fe(MeIm)_2[Fe(CN)_5NO]$.

Bond distance (Å)	Angles (°)	
$Fe(1\text{-}MeIm)_2[Fe(CN)_5NO]$		
Fe1-N1 = 2.217(1)	N2-Fe2-N2^{a} = 180.0	C3-Fe-C1 = 170.85(3)
Fe1-N3 = 2.245(1)	N2-Fe2-N4^{b} = 93.04(3)	C3-Fe-C4 = 90.99(3)
Fe1-N11 = 2.218(2)	N2-Fe2-N4^{c} = 86.96(2)	C3-Fe-C5 = 85.76(3)
Fe2-N2 = 2.231(1)	N2-Fe2-N21 = 91.38(3)	C3-Fe-C2 = 88.15(3)
Fe2-N4 = 2.210(1)	N2-Fe2-N21^{a} = 88.62(3)	C1-Fe-C4 = 89.22(3)
Fe2-N21 = 2.218(2)	N21-Fe2-N2^{a} = 88.62(3)	C1-Fe-C5 = 85.14(4)
Fe-C1 = 1.923(1)	N21-Fe2-N4^{b} = 91.41(3)	C1-Fe-C2 = 90.51(3)
Fe-C2 = 1.917(1)	N21-Fe2-N4^{c} = 88.59(3)	C4-Fe-C5 = 85.51(4)
Fe-C3 = 1.923(1)	N21-Fe2-N21^{a} = 180.0	C4-Fe-C2 = 172.87(3)
Fe-C4 = 1.933(1)	N4^{b}-Fe2-N2^{a} = 86.96(2)	C5-Fe-C2 = 87.37(4)
Fe-C5 = 1.937(2)	N4^{b}-Fe2-N21^{a} = 88.59(3)	N1-C1-Fe = 179.51(5)
Fe-N = 1.645(2)	N4^{b}-Fe2-N4^{c} = 180.0	N2-C2-Fe = 174.21(5)
C1-N1 = 1.123(1)	N21^{a}-Fe2-N2^{a} = 91.38(3)	N3-C3-Fe = 176.57(5)
C2-N2 = 1.124(1)	N21^{a}-Fe2-N4^{c} = 91.41(3)	N4-C4-Fe = 178.33(5)
C3-N3 = 1.136(1)	N2^{a}-Fe2-N4^{c} = 93.04(3)	N5-C5-Fe = 178.60(8)
C4-N4 = 1.110(1)	N1-Fe1-N1^{d} = 180.0	O-N-Fe = 178.31(8)
C5-N5 = 1.126(1)	N1-Fe1-N11^{d} = 90.12(3)	C1-N1-Fe1 = 174.64(5)
N-O = 1.111(1)	N1-Fe1-N11 = 89.88(3)	C2-N2-Fe2 = 155.11(4)
N11-C11 = 1.361(1)	N1-Fe1-N3^{c} = 89.48(2)	C3-N3-Fe1 = 149.04(4)
C11-C12 = 1.341(1)	N1-Fe1-N3^{e} = 90.52(2)	C4-N4-Fe2 = 170.65(5)
C12-N12 = 1.338(1)	N11-Fe1-N1^{d} = 90.12(3)	Fe1-N11-C11 = 129.41(5)
N12-C13 = 1.338(1)	N11-Fe1-N3^{c} = 85.27(3)	N11-C11-C12 = 110.24(6)
C13-N11 = 1.329(1)	N11-Fe1-N3^{e} = 94.73(3)	C11-C12-N12 = 107.63(5)
C14-N12 = 1.457(1)	N11-Fe1-N11^{d} = 180.0	C12-N12-C13 = 106.00(5)
N21-C21 = 1.337(1)	N1^{d}-Fe1-N3^{c} = 90.52(2)	N12-C13-N11 = 112.53(6)
C21-C22 = 1.344(1)	N1^{d}-Fe1-N3^{e} = 89.48(2)	C13-N11-Fe1 = 126.74(5)
C22-N22 = 1.331(1)	N1^{d}-Fe1-N11^{d} = 89.88(3)	C14-N12-C12 = 127.04(5)
N22-C23 = 1.337(1)	N11^{d}-Fe1-N3^{c} = 94.73(3)	C14-N12-C13 = 126.95(6)
C23-N21 = 1.299(1)	N11^{d}-Fe1-N3^{e} = 85.27(3)	Fe2-N21-C21 = 128.90(5)
C24-N22 = 1.467(1)	N3^{c}-Fe1-N3^{e} = 180.0	N21-C21-C22 = 110.57(6)
	N-Fe-C3 = 95.50(4)	C21-C22-N22 = 106.22(5)
	N-Fe-C1 = 93.61(4)	C22-N22-C23 = 106.53(5)
	N-Fe-C4 = 93.34(4)	N22-C23-N21 = 112.01(6)
	N-Fe-C5 = 178.32(6)	C23-N21-Fe2 = 126.41(5)
	N-Fe-C2 = 93.78(4)	C24-N22-C22 = 127.44(5)
		C24-N22-C23 = 126.00(6)

^{a}) 1-x, -y, 1-z; ^{b})1-x, -0.5+y, 1.5-z; ^{c}) x, 0.5-y, -0.5+z; ^{d}) 1-x, 1-y, 1-z; ^{e}) 1-x, 0.5+y, 1.5-z

Table S3. Selected bond lengths (Å) and angles (º) around the metal centers for **1-5**

	1	**2**	**5**	**4**		**3**	
[Fe(CN)$_5$NO]							
Fe-C1	1.945(6)	1.92(5)	1.941(5)	1.948(6)		1.936(3)	
Fe-C2	1.936(4)	1.92(7)	1.940(4)	1.929(6)		1.945(3)	
Fe-N	1.653(4)	1.64(5)	1.663(4)	1.643(5)		1.644(2)	
C1-Fe-C5	85.3(2)	85(2)	85.3(2)	84.9(2)		85.1(1)	
C2-Fe-C5	87.7(2)	88(2)	87.5(2)	84.9(2)		89.8(1)	
C2-Fe-N	93.5(2)	93(4)	93.4(2)	93.0(2)		96.3(1)	
C1-Fe-N	93.5(2)	94(3)	93.9(2)	94.6(2)			
M(1-MeIm)$_2$N$_4$*						***Cu(1-MeIm)$_4$N$_2$***	
M1-N1	2.2413(3)	2.2224(6)	2.3486(1)	Zn-N1	2.1862(2)	Cu1-N1	2.4245(1)
M1-N3	2.2658(3)	2.2437(6)	2.4094(1)	Zn-N2	2.1796(2)	Cu1-N11	2.0315(1)
M2-N2	2.2569(3)	2.2239(6)	2.3744(1)	Zn-N3	2.2206(2)	Cu1-N13	2.0298(1)
M2-N4	2.2347(3)	2.2198(6)	2.3491(1)	Zn-N4	2.2619(2)	Cu2-N3	2.7450(1)
M1-N11	2.2348(3)	2.2178(6)	2.2844(1)	Zn-N11	2.1090(2)	Cu2-N23	1.9946(1)
M2-N21	2.2273(3)	2.2211(6)	2.2687(1)	Zn-N21	2.1015(2)	Cu2-N21	2.0138(1)
N11-M1-N1	89.88(1)	89.82(6)	89.76(1)	N1-Zn-N11	89.67(1)	N1-Cu1-N11	90.07(1)
N3-M1-N1	89.51(1)	89.43(3)	89.98(1)	N11-Zn-N2	89.99(1)	N13-Cu1-N1	90.96(1)
N21-M2-N2	91.46(1)	88.80(5)	89.41(1)	N1-Zn-N3	88.16(1)	N11-Cu1-N13	90.46(1)
N4-M2-N2	87.13(1)	87.04(3)	85.82(1)	N1-Zn-N21	91.35(1)	N3-Cu2-N23	87.78(1)

* *M* = Mn, Fe and Cd for complexes **1**, **2** and **5**, respectively.

Table S4. Binding energy values and curve-fitting parameters resulting from the C 1s spectra recorded from complexes **1-3**.

Compound	***1***			***2***			***3***		
Assignation	**BE (eV)**	**FWHM (eV)**	**Atomic %**	**BE (eV)**	**FWHM (eV)**	**Atomic %**	**BE (eV)**	**FWHM (eV)**	**Atomic %**
$\mathrm{CN}_{\text{non-linked}}$	283.8	1.7	8.9	283.8	1.4	8.0	283.8	1.4	42.1
$\mathrm{CN}_{\text{linked(eq)}}$	284.1	1.7	44.7	284.2	1.4	40.2	284.2	1.4	9.3
$\mathrm{CN}_{\text{linked(ex)}}$	-	-	-	-	-	-	284.4	1.4	9.3
C_{adv}	284.8	1.7	32.1	284.8	1.4	27.4	284.8	1.4	24.9
$\mathrm{CH_3\text{-}N_{ring}}$	285.2	1.7	3.6	285.2	1.4	4.4	285.2	1.4	3.5
$\mathrm{C_{ring}\text{-}N\text{-}T}$	285.6	1.7	10.6	285.8	1.4	13.2	285.7	1.4	10.2
CuCN	-	-	-	-	-	-	285.8	1.4	0.8
C=O	-	-	-	287.8	1.5	6.8	-	-	-
T π-π*	290.8	1.8	-	~290.9	-	-	290.9	1.5	-

Table S5. Binding energy values and curve-fitting parameters resulting from the N 1s spectra recorded from complexes **1-3**.

Compound	***1***			***2***			***3***		
Assignation	**BE (eV)**	**FWHM (eV)**	**Atomic %**	**BE (eV)**	**FWHM (eV)**	**Atomic %**	**BE (eV)**	**FWHM (eV)**	**Atomic %**
$\mathrm{N1s\text{-}CN_{non\text{-}linked}}$	397.2	1.5	12.0	397.3	1.4	11.6	397.0	1.4	28.9
$\mathrm{N1s\text{-}CN_{linked}}$	397.8	1.5	60.0	397.9	1.5	58.1	397.7	1.4	23.1
$\mathrm{N1s\text{-}CN_{linked(axial)}}$	-	-	-	-	-	-	398.3	1.4	23.1
N1s-CuCN	-	-	-	-	-	-	398.9	1.4	2.7
$\mathrm{N1s\text{-}N_{ring}\text{-}CH_3}$	399.6	1.5	12.3	399.7	1.5	13.3	399.8	1.4	9.8
$\mathrm{N1s\text{-}N_{ring}\text{-}M}$	400.0	1.5	12.3	400.1	1.5	13.3	400.2	1.4	9.8
N1s-NO	402.5	1.5	3.4	402.5	1.5	3.8	402.5	1.5	2.5

Table S6. Binding energy values and curve-fitting parameters resulting from the Cu 2p spectrum recorded from Cu(II) complex **3**.

Compound 3	***BE, eV***		***FWHM, eV***		***Atom. %***	
Cu 2p	**2p3/2**	**2p1/2**	**2p3/2**	**2p1/2**	**2p3/2**	**2p1/2**
Cu2p-CuCN	931.7	951.5	1.9	2.2	30.3	15.6
Cu2p-$Cu^{2+}(NC)_x$	934.6	954.6	2.3	2.8	35.8	18.4
Cu2p-sat (Cu^{2+})	941.5	961.1	-	-	-	-
Cu2p-sat (Cu^{2+})	943.3	962.9	-	-	-	-

Table S7. Binding energy values and curve-fitting parameters resulting from the Mn 2p spectrum recorded from Mn(II) complex **1**.

Compound 1	***BE, eV***		***FWHM, eV***		***Atom. %***	
Mn 2p	**2p3/2**	**2p1/2**	**2p3/2**	**2p1/2**	**2p3/2**	**2p1/2**
Mn2p-Mn2+ (1)	640.0	652.0	1.7	1.6	20.8	10.5
Mn2p-Mn2+ (2)	641.1	653.0	1.7	1.6	22.8	11.5
Mn2p-Mn2+ (3)	642.3	654.3	2.2	2.2	22.8	11.5
Mn2p-sat	646.0	658.2	2.9	2.9	0.0	0.0
Mn 3s	82.5	6.0 Δ_{BE}	2.4	2.4	74.3	25.7