

Supplementary Information

Table S1 Select bond distance (Å) and angle (°) for the complexes **1-10**

Select bond distances (Å) and angles (°) for **1**

| | | | |
|----------------------|------------|---------------------|------------|
| Cu(1)-N(1) | 1.9997(17) | Cu(1)-N(1)#2 | 1.9997(17) |
| Cu(1)-Cl(1) | 2.2954(5) | Cu(1)-Cl(1)#2 | 2.2954(5) |
| N(1)-Cu(1)-N(1)#2 | 180.00(9) | N(1)-Cu(1)-Cl(1)#2 | 89.80(5) |
| N(1)#2-Cu(1)-Cl(1)#2 | 90.20(5) | N(1)-Cu(1)-Cl(1) | 90.20(5) |
| N(1)#2-Cu(1)-Cl(1) | 89.80(5) | Cl(1)#2-Cu(1)-Cl(1) | 180.0 |

Symmetry transformations used to generate equivalent atoms: #2 2-x, 1-y, -z

Select bond distances (Å) and angles (°) for **2**

| | | | |
|---------------------|----------|---------------------|----------|
| Cu(1)-N(1) | 2.009(2) | Cu(1)-N(1)#1 | 2.009(2) |
| Cu(1)-N(6)#2 | 2.045(2) | Cu(1)-N(6)#3 | 2.045(2) |
| N(1)-Cu(1)-N(1)#1 | 180.0 | N(1)-Cu(1)-N(6)#2 | 90.92(8) |
| N(1)#1-Cu(1)-N(6)#2 | 89.08(8) | N(1)-Cu(1)-N(6)#3 | 89.08(8) |
| N(1)#1-Cu(1)-N(6)#3 | 90.92(8) | N(6)#2-Cu(1)-N(6)#3 | 180.0 |

Symmetry transformations used to generate equivalent atoms: #1 -x, 1-y, 1-z; #2 -1+x, 1/2-y, 1/2+z; #3 1-x, 1/2+y, 1/2-z

Select bond distances (Å) and angles (°) for **3**

| | | | |
|---------------------|------------|---------------------|------------|
| Cu(1)-N(1) | 2.014(2) | Cu(1)-N(1)#1 | 2.0141(19) |
| Cu(1)-N(1)#2 | 2.014(2) | Cu(1)-N(1)#3 | 2.0141(19) |
| Cu(1)-O(5) | 2.423(3) | Cu(1)-O(5)#3 | 2.423(3) |
| N(1)-Cu(1)-N(1)#1 | 175.55(11) | N(1)-Cu(1)-N(1)#2 | 90.00(12) |
| N(1)#1-Cu(1)-N(1)#2 | 90.18(12) | N(1)-Cu(1)-N(1)#3 | 90.18(12) |
| N(1)#1-Cu(1)-N(1)#3 | 90.00(12) | N(1)#2-Cu(1)-N(1)#3 | 175.55(11) |

| | | | |
|---------------------|----------|---------------------|----------|
| N(1)-Cu(1)-O(5) | 92.22(5) | N(1)#1-Cu(1)-O(5) | 92.22(5) |
| N(1)#2-Cu(1)-O(5) | 87.78(5) | N(1)#3-Cu(1)-O(5) | 87.78(5) |
| N(1)-Cu(1)-O(5)#3 | 87.78(5) | N(1)#1-Cu(1)-O(5)#3 | 87.78(5) |
| N(1)#2-Cu(1)-O(5)#3 | 92.22(5) | N(1)#3-Cu(1)-O(5)#3 | 92.22(5) |
| O(5)-Cu(1)-O(5)#3 | 180.0 | | |

Symmetry transformations used to generate equivalent atoms: #1 5/4-x, y, 5/4-z; #2 x, 5/4-y, 5/4-z; #3 5/4-x, 5/4-y, z

Select bond distances (Å) and angles (°) for **4**

| | | | |
|-------------------|------------|-------------------|------------|
| Cu(1)-O(3) | 1.961(3) | Cu(1)-O(1) | 1.964(3) |
| Cu(1)-O(4) | 1.974(2) | Cu(1)-O(2)#1 | 1.977(3) |
| Cu(1)-N(1) | 2.156(3) | | |
| O(3)-Cu(1)-O(1) | 89.78(12) | O(3)-Cu(1)-O(4) | 168.18(10) |
| O(1)-Cu(1)-O(4) | 88.11(11) | O(3)-Cu(1)-O(2)#1 | 89.89(12) |
| O(1)-Cu(1)-O(2)#1 | 167.92(11) | O(4)-Cu(1)-O(2)#1 | 89.75(12) |
| O(3)-Cu(1)-N(1) | 100.52(11) | O(1)-Cu(1)-N(1) | 98.90(12) |
| O(4)-Cu(1)-N(1) | 91.30(11) | O(2)#1-Cu(1)-N(1) | 93.03(12) |

Symmetry transformations used to generate equivalent atoms: #1 -x, 1-y, 1-z

Select bond distances (Å) and angles (°) for **5**

| | | | |
|-------------------|-----------|---------------------|------------|
| Ni(1)-N(1) | 2.065(3) | Ni(1)-O(1) | 2.056(4) |
| Ni(1)-N(1)#2 | 2.065(3) | Ni(1)-O(3) | 2.086(4) |
| Ni(1)-O(2) | 2.102(3) | Ni(1)-O(2)#2 | 2.102(3) |
| O(1)-Ni(1)-N(1)#2 | 91.48(12) | O(1)-Ni(1)-N(1) | 91.48(12) |
| N(1)#2-Ni(1)-N(1) | 95.11(19) | O(1)-Ni(1)-O(3) | 172.74(16) |
| N(1)#2-Ni(1)-O(3) | 93.41(12) | N(1)-Ni(1)-O(3) | 93.41(12) |
| O(1)-Ni(1)-O(2) | 85.56(12) | N(1)#2-Ni(1)-O(2) | 176.64(12) |
| N(1)-Ni(1)-O(2) | 86.58(13) | O(3)-Ni(1)-O(2) | 89.38(11) |
| O(1)-Ni(1)-O(2)#2 | 85.56(12) | N(1)#2-Ni(1)-O(2)#2 | 86.58(13) |

N(1)-Ni(1)-O(2)#2 176.64(12) O(3)-Ni(1)-O(2)#2 89.38(11)
 O(2)-Ni(1)-O(2)#2 91.59(17)

Symmetry transformations used to generate equivalent atoms: #2 x, 3/2-y, z

Select bond distances (Å) and angles (°) for **6**

| | | | |
|----------------------|------------|-----------------------|------------|
| Ni(1)-N(1) | 2.1249(17) | Ni (1)-N(1) #2 | 2.1249(17) |
| Ni (1)-N(1)#3 | 2.1249(17) | Ni (1)-N(6)#4 | 2.1103(17) |
| Ni (1)- N(6)#5 | 2.1104(17) | Ni (1)- N(6)#6 | 2.1104(17) |
| Ni (2)-N(7) | 2.1033(18) | Ni (2)-N(7)#7 | 2.1033(18) |
| Ni (2)-N(7)#8 | 2.1034(18) | Ni (2)-N(7)#9 | 2.1034(18) |
| Ni (2)- N(7)#10 | 2.1034(18) | Ni (2)- N(7)#11 | 2.1034(18) |
| | | | |
| N(6)#4-Ni(1)-N(6)#5 | 90.77(7) | N(6)#4-Ni(1)-N(6)#6 | 90.77(7) |
| N(6)#5-Ni(1)-N(6)#6 | 90.77(7) | N(6)#4-Ni(1)-N(1)#2 | 88.65(7) |
| N(6)#5-Ni(1)-N(1)#2 | 177.77(6) | N(6)#6-Ni(1)-N(1)#2 | 91.39(6) |
| N(6)#4-Ni(1)-N(1)#3 | 91.39(6) | N(6)#5-Ni(1)-N(1)#3 | 88.66(7) |
| N(6)#6-Ni(1)-N(1)#3 | 177.77(6) | N(6)#4-Ni(1)-N(1) | 177.76(6) |
| N(6)#5-Ni(1)-N(1) | 91.39(6) | N(6)#6-Ni(1)-N(1) | 88.65(7) |
| N(1)#2-Ni(1)-N(1)#3 | 89.20(7) | N(1)#2-Ni(1)-N(1) | 89.21(7) |
| N(1)#3-Ni(1)-N(1) | 89.21(7) | N(7)#8-Ni(2)-N(7)#9 | 180.0 |
| N(7)#8-Ni(2)-N(7)#7 | 91.45(7) | N(7)#9-Ni(2)-N(7)#7 | 88.55(7) |
| N(7)#8-Ni(2)-N(7) | 88.55(7) | N(7)#9-Ni(2)-N(7) | 91.45(7) |
| N(7)#7-Ni(2)-N(7) | 180.0 | N(7)#8-Ni(2)-N(7)#11 | 91.45(7) |
| N(7)#9-Ni(2)-N(7)#11 | 88.55(7) | N(7)#7-Ni(2)-N(7)#11 | 88.55(7) |
| N(7)-Ni(2)-N(7)#11 | 91.45(7) | N(7)#8-Ni(2)-N(7)#10 | 88.55(7) |
| N(7)#9-Ni(2)-N(7)#10 | 91.45(7) | N(7)#7-Ni(2)-N(7)#10 | 91.45(7) |
| N(7)-Ni(2)-N(7)#10 | 88.55(7) | N(7)#11-Ni(2)-N(7)#10 | 180.00(8) |

Symmetry transformations used to generate equivalent atoms : #2 -y+1, x-y+1, z; #3 -x+y, -x+1, z;
 #4 x+1/3, y+2/3, z-1/3; #5 -y+1/3, x-y+2/3, z-1/3; #6 -x+y+1/3, -x+2/3, z-1/3; #7 -x, -y, -z; #8 -y,
 x-y, z; #9 y, -x+y, -z; #10 -x+y, -x, z; #11 x-y, x, -z.

Select bond distances (Å) and angles (°) for **7**

| | | | |
|---------------------|------------|---------------------|------------|
| Ni(1)-N(1)#4 | 2.1043(13) | Ni(1)-N(1)#5 | 2.1043(13) |
| Ni(1)-N(1)#6 | 2.1043(13) | Ni(1)-N(1)#7 | 2.1043(13) |
| Ni(1)-N(1)#8 | 2.1043(13) | Ni(1)-N(1) | 2.1043(13) |
| N(1)#4-Ni(1)-N(1) | 180.00(9) | N(1)#4-Ni(1)-N(1)#5 | 89.87(5) |
| N(1)-Ni(1)-N(1)#5 | 90.13(5) | N(1)#4-Ni(1)-N(1)#6 | 90.13(5) |
| N(1)-Ni(1)-N(1)#6 | 89.87(5) | N(1)#5-Ni(1)-N(1)#6 | 90.13(5) |
| N(1)#4-Ni(1)-N(1)#7 | 90.13(5) | N(1)-Ni(1)-N(1)#7 | 89.87(5) |
| N(1)#5-Ni(1)-N(1)#7 | 180.00(8) | N(1)#6-Ni(1)-N(1)#7 | 89.87(5) |
| N(1)#4-Ni(1)-N(1)#8 | 89.87(5) | N(1)-Ni(1)-N(1)#8 | 90.13(5) |
| N(1)#5-Ni(1)-N(1)#8 | 89.87(5) | N(1)#6-Ni(1)-N(1)#8 | 180.00(13) |
| N(1)#7-Ni(1)-N(1)#8 | 90.13(5) | | |

Symmetry transformations used to generate equivalent atoms : #4 -x, -y -z; #5 x-y, x, -z; #6 -y, x-y, z; #7 -x+y, -x, z; #8 y, -x+y, -z.

Select bond distances (Å) and angles (°) for **8**

| | | | |
|---------------------|------------|-------------------|------------|
| Co(1)-O(5) | 2.070(2) | Co(1)-O(1) | 2.107(2) |
| Co(1)-N(1)#2 | 2.107(2) | Co(1)-N(1) | 2.107(2) |
| Co(1)-O(4)#2 | 2.1375(18) | Co(1)-O(4) | 2.1375(18) |
| O(5)-Co(1)-O(1) | 172.20(10) | O(5)-Co(1)-N(1)#2 | 91.59(7) |
| O(1)-Co(1)-N(1)#2 | 93.68(7) | O(5)-Co(1)-N(1) | 91.59(7) |
| O(1)-Co(1)-N(1) | 93.68(7) | N(1)#2-Co(1)-N(1) | 94.87(11) |
| O(5)-Co(1)-O(4)#2 | 85.13(7) | O(1)-Co(1)-O(4)#2 | 89.42(7) |
| N(1)#2-Co(1)-O(4)#2 | 86.83(7) | N(1)-Co(1)-O(4)#2 | 176.35(7) |
| O(5)-Co(1)-O(4) | 85.13(7) | O(1)-Co(1)-O(4) | 89.42(7) |
| N(1)#2-Co(1)-O(4) | 176.35(7) | N(1)-Co(1)-O(4) | 86.83(7) |
| O(4)#2-Co(1)-O(4) | 91.29(10) | | |

Symmetry transformations used to generate equivalent atoms: #2 x, -y+1/2, z

Select bond distances (Å) and angles (°) for **9**

| | | | |
|---------------------|------------|-----------------------|------------|
| Co(1)-N(7) | 2.093(2) | Co(1)-N(7)#1 | 2.093(2) |
| Co(1)-N(1) | 2.158(3) | Co(1)-N(1)#1 | 2.158(3) |
| Co(1)-N(6)#1 | 2.1375(18) | Co(1)-N(6) | 2.1375(18) |
| N(7)-Co(1)-N(7)#1 | 180.000(1) | N(7) #1-Co(1)-N(6) #1 | 89.86(13) |
| N(7) -Co(1)-N(6)#1 | 90.14(13) | N(7)#1-Co(1)-N(6) | 90.14(13) |
| N(7) -Co(1)-N(6) | 89.86(13) | N(6)#1-Co(1)-N(6) | 180.000(1) |
| N(7)#1-Co(1)-N(1) | 91.12(12) | N(7)-Co(1)-N(1) | 88.88(12) |
| N(6)#1-Co(1)-N(1) | 86.83(11) | N(6)-Co(1)-N(1) | 93.17(11) |
| N(7)#1-Co(1)-N(1)#1 | 88.88(12) | N(7)-Co(1)-N(1) #1 | 91.12(12) |
| N(6)#1-Co(1)-N(1)#1 | 93.17(11) | N(6)-Co(1)-N(1)#1 | 86.83(11) |
| N(1)-Co(1)-N(1)#1 | 180.00(16) | | |

Symmetry transformations used to generate equivalent atoms: #1 2-x, -y, 2-z

Select bond distances (Å) and angles (°) for **10**

| | | | |
|---------------------|------------|---------------------|------------|
| Co(1)-O(1)#4 | 2.0801(16) | Co(1)-O(1) | 2.0801(16) |
| Co(1)-N(1)#4 | 2.161(2) | Co(1)-N(1) | 2.161(2) |
| Co(1)-N(7) | 2.167(2) | Co(1)-N(7)#4 | 2.167(2) |
| Co(2)-O(6) | 2.088(2) | Co(2)-O(6)#5 | 2.088(2) |
| Co(2)-O(3)#5 | 2.1273(18) | Co(2)-O(3) | 2.1273(18) |
| Co(2)-N(5)#5 | 2.136(3) | Co(2)-N(5) | 2.136(3) |
| O(1)#4-Co(1)-O(1) | 180.000(1) | O(1)#4-Co(1)-N(1)#4 | 94.23(7) |
| O(1)-Co(1)-N(1)#4 | 85.77(7) | O(1)#4-Co(1)-N(1) | 85.77(7) |
| O(1)-Co(1)-N(1) | 94.23(7) | N(1)#4-Co(1)-N(1) | 180.000(1) |
| O(1)#4-Co(1)-N(7) | 93.43(7) | O(1)-Co(1)-N(7) | 86.57(7) |
| N(1)#4-Co(1)-N(7) | 93.46(8) | N(1)-Co(1)-N(7) | 86.54(8) |
| O(1)#4-Co(1)-N(7)#4 | 86.57(7) | O(1)-Co(1)-N(7)#4 | 93.43(7) |
| N(1)#4-Co(1)-N(7)#4 | 86.54(8) | N(1)-Co(1)-N(7)#4 | 93.46(8) |

| | | | |
|---------------------|-----------|---------------------|------------|
| N(7)-Co(1)-N(7)#4 | 180.0 | O(6)-Co(2)-O(6)#5 | 180.000(1) |
| O(6)-Co(2)-O(3)#5 | 88.87(8) | O(6)#5-Co(2)-O(3)#5 | 91.13(8) |
| O(6)-Co(2)-O(3) | 91.13(8) | O(6)#5-Co(2)-O(3) | 88.87(8) |
| O(3)#5-Co(2)-O(3) | 180.0 | O(6)-Co(2)-N(5)#5 | 88.45(10) |
| O(6)#5-Co(2)-N(5)#5 | 91.55(10) | O(3)#5-Co(2)-N(5)#5 | 87.18(9) |
| O(3)-Co(2)-N(5)#5 | 92.82(9) | O(6)-Co(2)-N(5) | 91.55(10) |
| O(6)#5-Co(2)-N(5) | 88.45(10) | O(3)#5-Co(2)-N(5) | 92.82(9) |
| O(3)-Co(2)-N(5) | 87.18(9) | N(5)#5-Co(2)-N(5) | 180.000(1) |

Symmetry transformations used to generate equivalent atoms: #4 -x,-y,-z+2; #5 -x,-y+1,-z+1

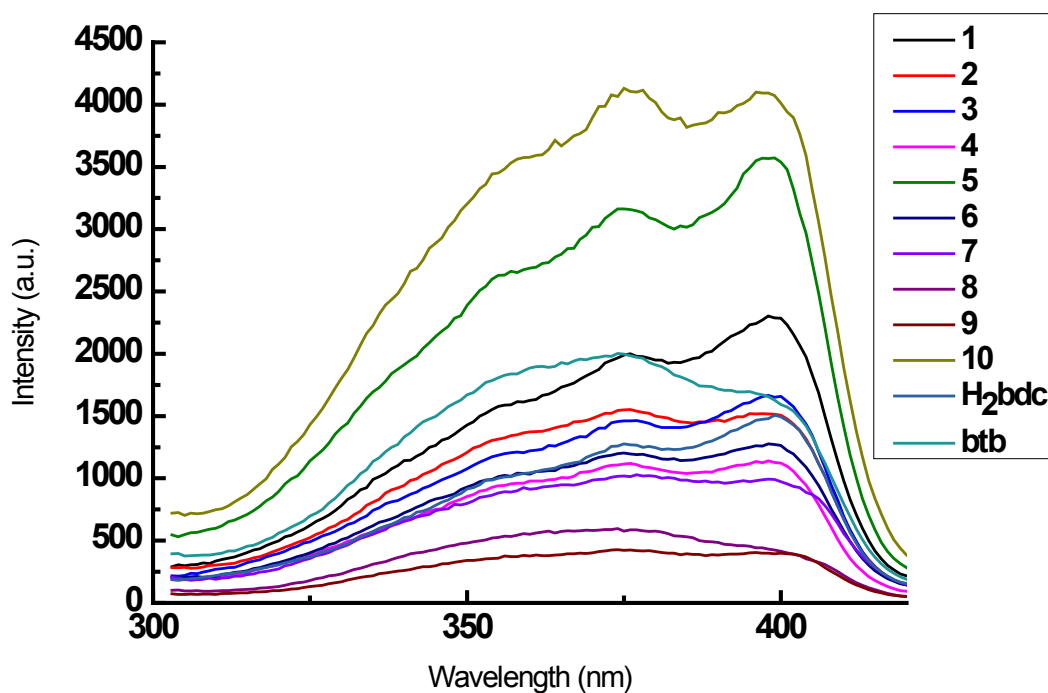


Fig. S1 The excitation spectra of the complexes and free ligands in solid state at room temperature. The excitation spectra were measured at the emission (λ_{max} , 433 nm for btb, 431 nm for H₂bdc, 430 nm for **1**, 430 nm for **2**, 431 nm for **3**, 430 nm for **4**, 429 nm for **5**, 431 nm for **6**, 432 nm for **7**, 430 nm for **8**, 430 nm for **9** and 431 nm for **10**).