# *Supplementary Data for, Synthesis, Crystallization and Hirshfeld Surface Analysis of Transition Metal Carboxylate Pentapyridines*

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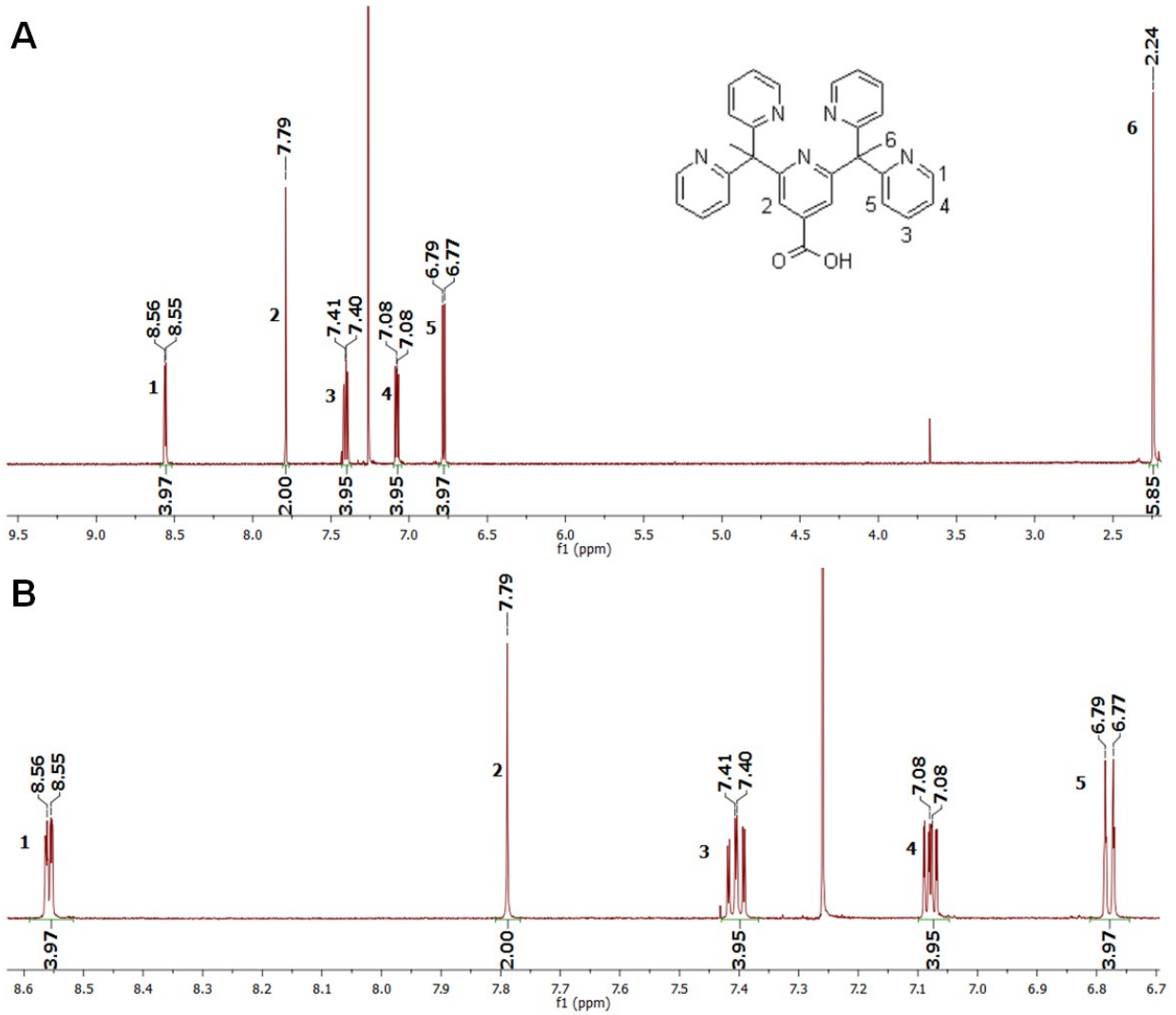
## Contents

**Results and Discussion**

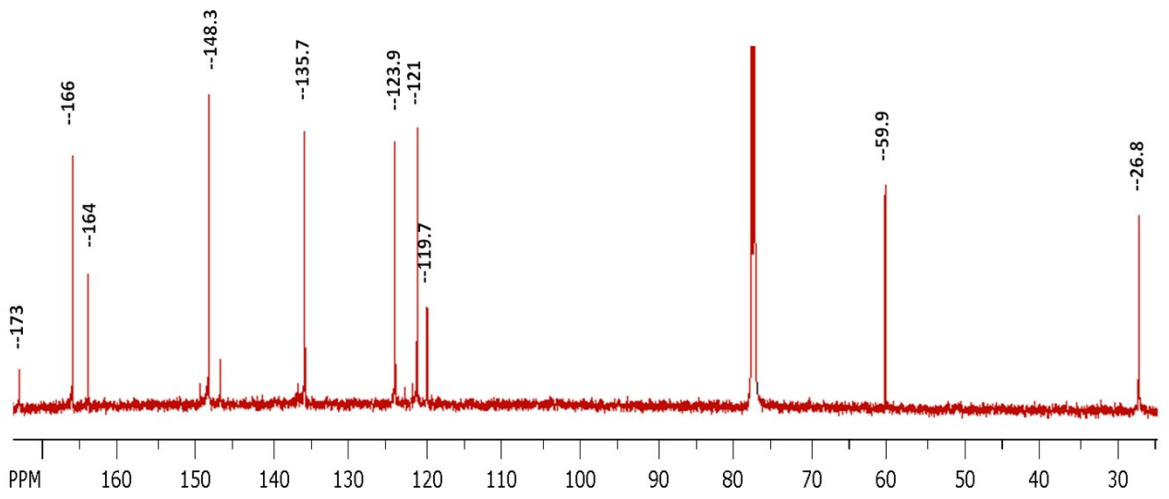
*Synthesis and Characterization*

NMR Spectroscopy




$^1$H NMR ($CDCl_3$, 500 MHz): δ = 8.56 (ddd, J = 4.86, 0.91 Hz, 4H), 7.79 (s, 2H), 7.40 (td, J=7.77, 1.92 Hz, 4H), 7.08 (dd, J = 4.86, 1.09 Hz, 4H), 6.78 (dt, J = 8.07,0.93 Hz, 4H), 2.24 (s, 6H)

**Figure S1: (A)** $^1$H NMR Spectra of Py5Me2COOH ligand in $d_3$-$CH_3Cl$ **(B)** $^1$H NMR Spectra of Py5Me2COOH ligand in $d_3$-$CH_3Cl$ zoom in of aromatics




$^{13}$C NMR ($CDCl_3$, 125.8 MHz): δ = 173 Q, 166.0 Q, 164 Q, 148.3 CH, 135.7 CH, 123.9 CH, 121.0 CH, 119.7 CH, 59.9 Q, 26.8 CH3

**Figure S2:** $^{13}$C NMR Spectra of Py5Me2COOH ligand in $d_3$-$CH_3Cl$

UV-Vis Spectroscopy

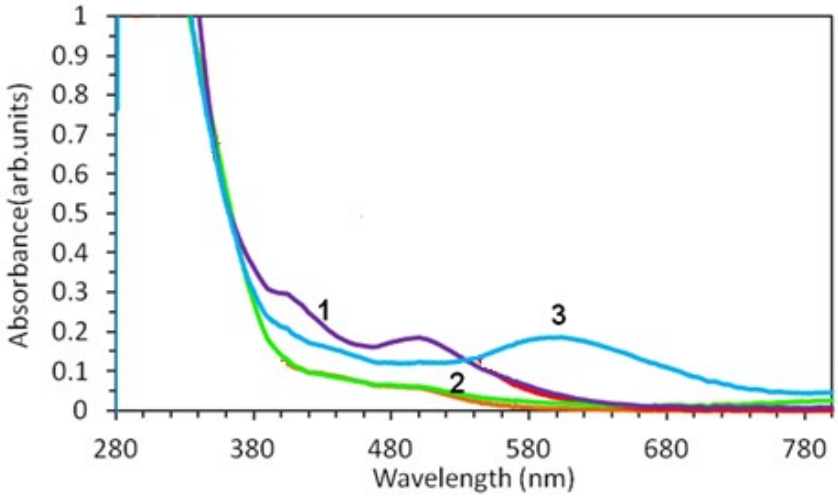



**Figure S3:** UV-Vis Spectrum in water of complexes **1**-**3**[~1mM]

High-Definition Mass Spectroscopy

| Observed Mass | Formula [M]+ | Calculated mass | Difference (ppm) | iFiT(norm)* |
|---|---|---|---|---|
| 695.0835 | C31H25N5O5F3SCo(59) | 695.0860 | -3.6 | 0.1 |
| 694.0900 | C31H25N5O5F3SNi(58) | 694.0882 | 2.6 | 4.3 |
| 550.1306 | C30H25N5O2Cu | 550.1304 | 0.4 | 0.0 |

*The iFit(norm) value is an estimation of how closely the measured isotope pattern fits the calculated isotope pattern. The closer the value to zero the closer the fit.

**Table S1:** Mass spectrometry values of complexes **1-3**

FT-IR Spectroscopy

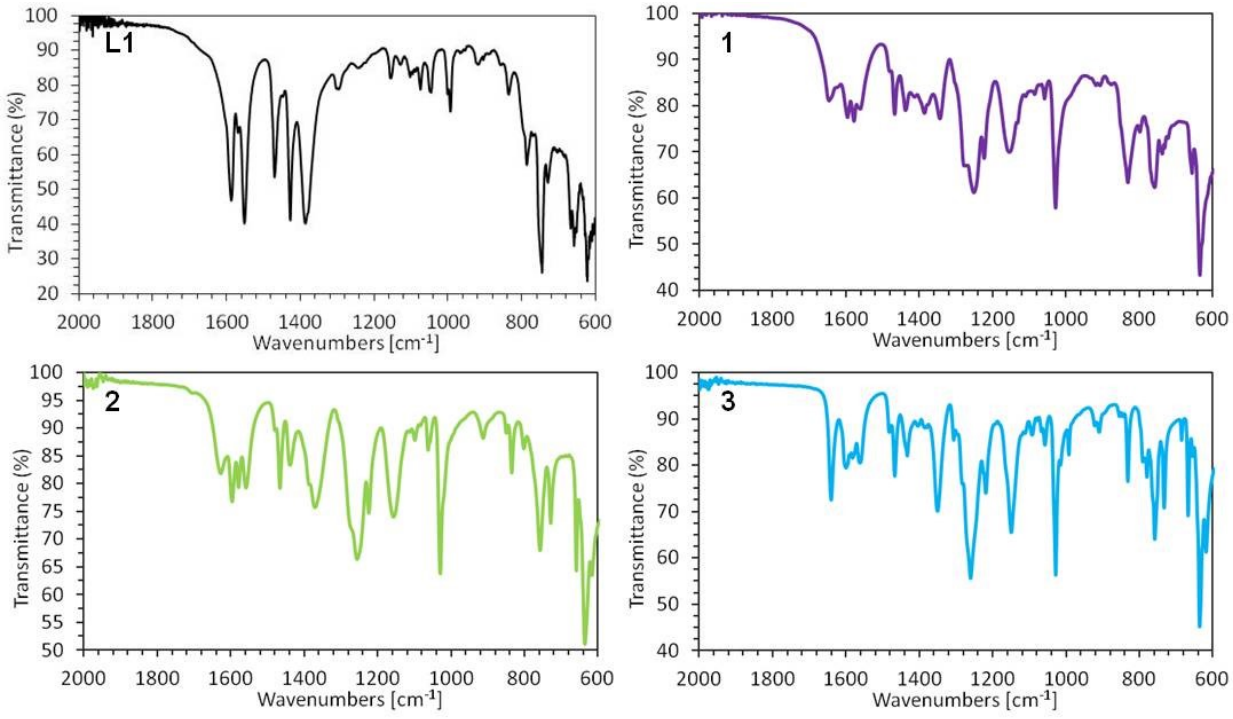
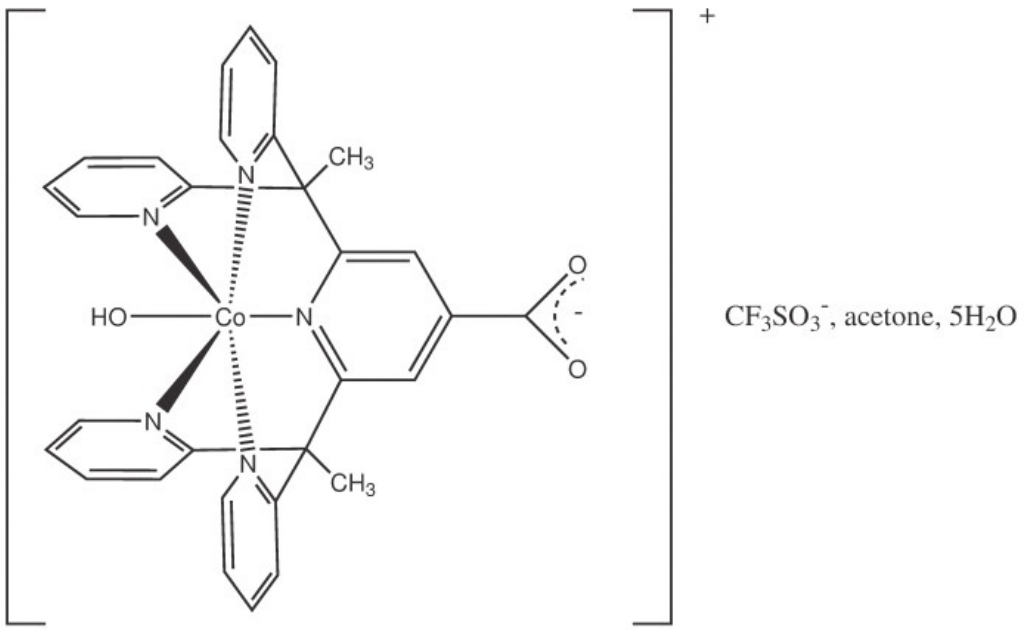



**Figure S4:** Infrared spectra of PyMe2COOH (**L1**) cobalt(**1**) nickel(**2**) and copper(**3**)

Structural Studies




**Scheme S1:** Formula for complex **1**

Crystallographic data for the structure were collected at 100(2) K on an Oxford Diffraction X calibur diffractometer fitted with Mo Kα radiation. Following analytical absorption corrections and solution by direct methods, the structure was refined against $F^2$ with full-matrix least-squares using the program SHELXL-2014[1].The water molecule and hydroxyl hydrogen atoms were located and refined with geometries restrained to ideal values. All remaining hydrogen atoms were added at calculated positions and refined by use of riding models with isotropic displacement parameters based on those of the parent atoms. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms.

The crystal data for **1** are summarized in Table S2 with the structure depicted in Fig S6. Selected coordination geometries are listed in Table S3 .The formula of **1** is shown in the scheme S1, with the hydrogen bonding shown in Figure S7,Geometrical details are shown in Table S4.

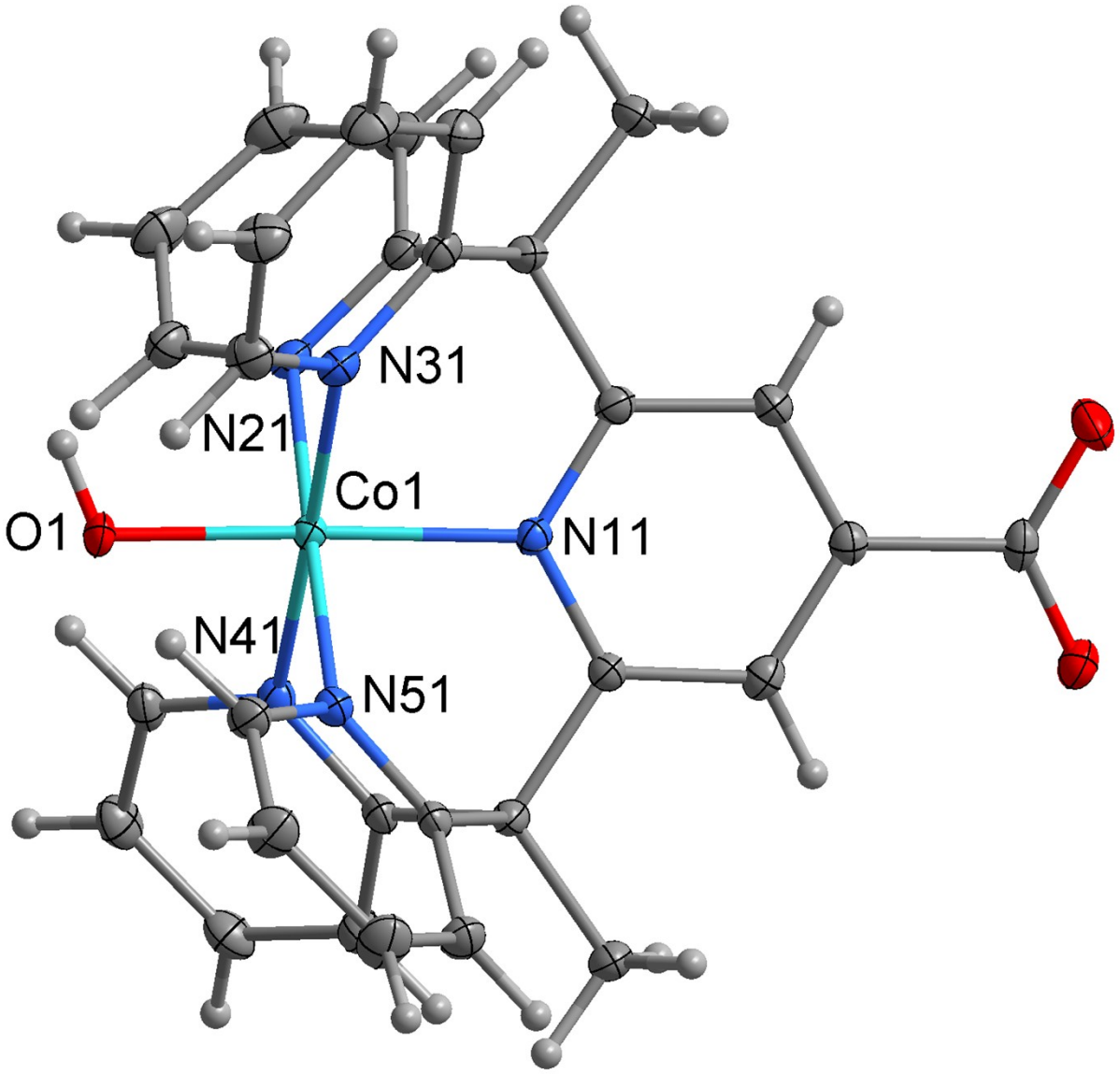



**Figure S5:** Crystal Structure of the complex **1** with thermal ellipsoids drawn at the 50% probability level.
Aqua, blue, grey, red and white spheres represent Co, N, C, O, H atoms, respectively.

**Table S2:** Crystal data and structure refinement for complex **1**

| | |
|---|---|
| Identification code | cocooh |
| Empirical formula | $C_{34}H_{41}CoF_3N_5O_{12}S$ |
| Formula weight | 859.71 |
| Temperature | 100(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | *Cc* |
| Unit cell dimensions | *a* = 16.7330(5) Å |
| *b* = 12.1818(3) Å | |
| *c* = 17.9613(5) Å | |
| β= 91.000(2)° | |
| Volume | 3660.64(17) $Å^3$ |
| *Z* | 4 |
| Density (calculated) | 1.560 $Mg/m^3$ |
| μ | 0.612 $mm^{-1}$ |
| Crystal size | 0.42 x 0.29 x 0.13 $mm^3$ |
| θ range for data collection | 2.268 to 32.179°. |
| Index ranges | -23<=h<=24, -18<=k<=13, -26<=l<=26 |
| Reflections collected | 19937 |
| Independent reflections | 10988 [*R*(int) = 0.0307] |
| Completeness to θ = 31.00° | 99.2 % |
| Absorption correction | Analytical |
| Max. and min. transmission | 0.937 and 0.826 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 10988 / 19 / 553 |
| Goodness-of-fit on $F^2$ | 1.031 |
| Final *R* indices [$I>2\sigma(I)$] | *R*1 = 0.0413, *wR*2 = 0.0885 |
| *R* indices (all data) | *R*1 = 0.0471, *wR*2 = 0.0927 |
| Absolute structure parameter | 0.001(6) |
| Largest diff. peak and hole | 0.637 and -0.342 $e.Å^{-3}$ |

**Table S3**: Selected bond lengths [Å] and angles [°] for complex **1**

| | |
|---|---|
| Co(1)-O(1) | 1.862(2) |
| Co(1)-N(51) | 1.971(3) |
| Co(1)-N(21) | 1.975(3) |
| Co(1)-N(11) | 1.975(2) |
| Co(1)-N(31) | 1.975(3) |
| Co(1)-N(41) | 1.985(3) |
| | |
| O(1)-Co(1)-N(51) | 89.05(10) |
| O(1)-Co(1)-N(21) | 92.24(10) |
| N(51)-Co(1)-N(21) | 178.55(11) |
| O(1)-Co(1)-N(11) | 178.26(11) |
| N(51)-Co(1)-N(11) | 89.46(10) |
| N(21)-Co(1)-N(11) | 89.23(10) |
| O(1)-Co(1)-N(31) | 90.90(10) |
| N(51)-Co(1)-N(31) | 97.12(11) |
| N(21)-Co(1)-N(31) | 83.52(11) |
| N(11)-Co(1)-N(31) | 90.18(10) |
| O(1)-Co(1)-N(41) | 87.86(10) |
| N(51)-Co(1)-N(41) | 82.81(10) |
| N(21)-Co(1)-N(41) | 96.57(11) |
| N(11)-Co(1)-N(41) | 91.06(10) |
| N(31)-Co(1)-N(41) | 178.76(12) |

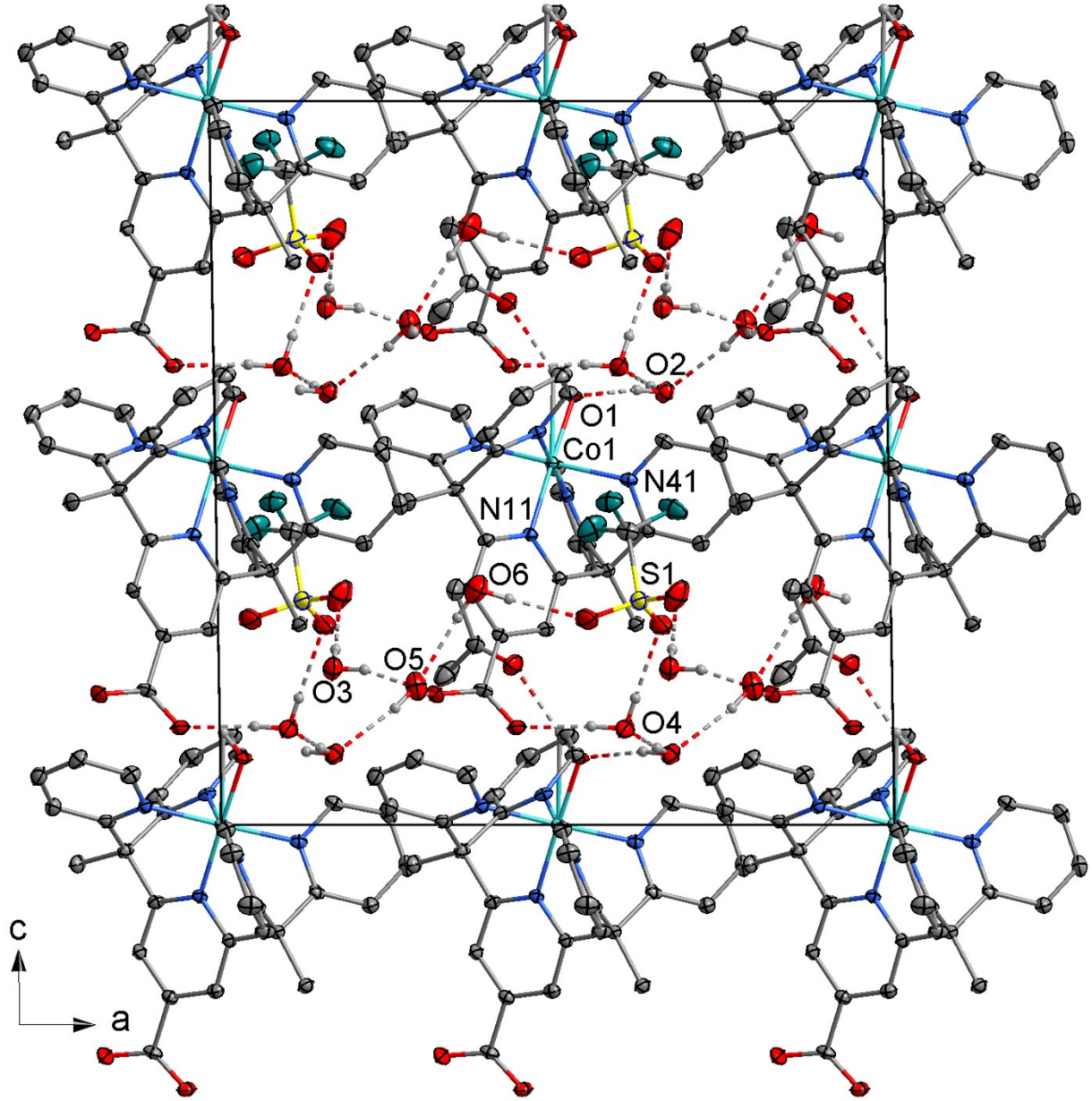


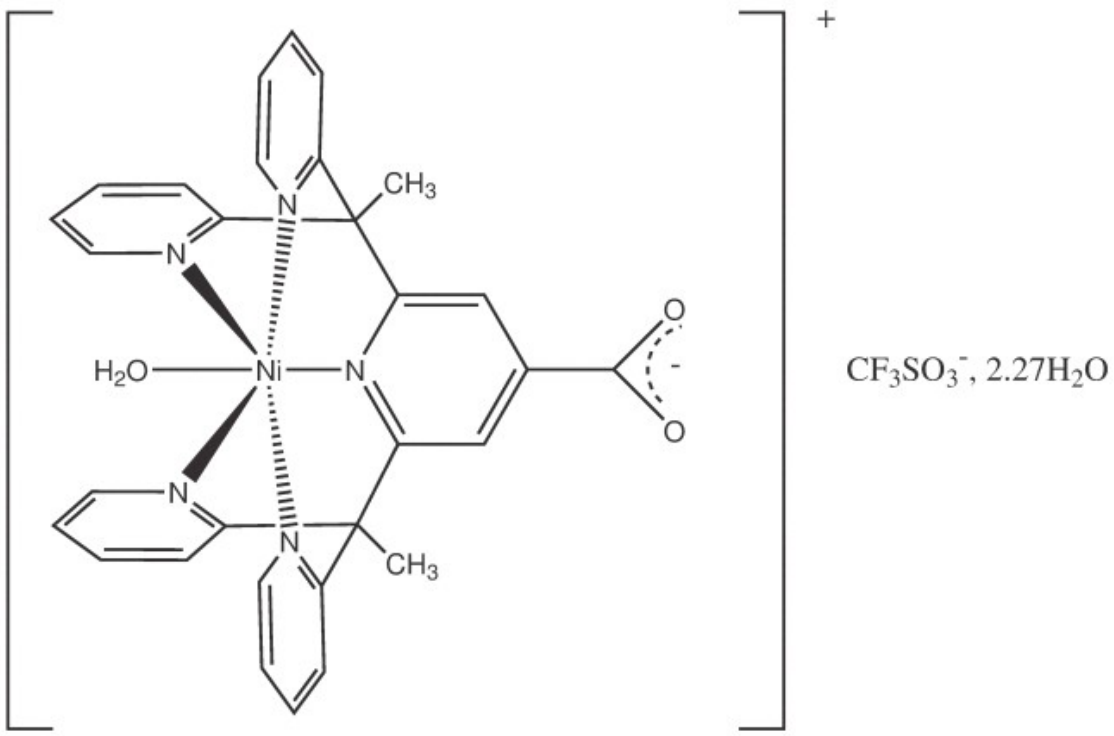

**Figure S6:** Unit cell contents of **1** projected along the b-axis showing the hydrogen bonds. Hydrogen atoms not involved in the hydrogen bonding have been omitted for clarity.

**Table S4:** Hydrogen bonds for **1** [Å and °]

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(1)-H(1)...O(102) | 0.84(6) | 2.07(6) | 2.905(3) | 171(6) |
| O(2)-H(2AO)...O(4)[1] | 0.85(2) | 1.94(2) | 2.788(4) | 177(4) |
| O(2)-H(2BO)...O(1) | 0.85(2) | 1.95(3) | 2.799(3) | 171(5) |
| O(3)-H(3AO)...O(11) | 0.84(2) | 1.92(3) | 2.743(4) | 163(5) |
| O(3)-H(3BO)...O(15)[2] | 0.84(2) | 2.06(3) | 2.894(4) | 173(5) |
| O(4)-H(4AO)...O(12) | 0.856(18) | 1.878(18) | 2.731(4) | 174(4) |
| O(4)-H(4BO)...O(14) | 0.835(18) | 1.995(19) | 2.829(4) | 178(5) |
| O(5)-H(5AO)...O(2)[3] | 0.82(2) | 2.00(3) | 2.806(4) | 170(5) |
| O(5)-H(5BO)...O(11) | 0.84(2) | 1.93(2) | 2.758(4) | 166(4) |
| O(6)-H(6AO)...O(13) | 0.88(2) | 2.02(3) | 2.885(5) | 170(5) |
| O(6)-H(6BO)...O(5) | 0.88(3) | 1.99(3) | 2.834(5) | 161(6) |
| C(45)-H(45)…O(11) | 0.95 | 2.358 | 3.230(4) | 152.5 |
| C(56)-H(56)…O(12) | 0.95 | 2.349 | 3.117(4) | 137.3 |

Symmetry transformations used to generate equivalent atoms:

[1] x,1-y,z+1/2, [2] x-1/2,y+1/2,z, [3] x-1/2,1/2-y,z-1/2




**Scheme S2:** Formula for complex **2**

The crystal data for **2** are summarized in Table S5 with the structure depicted in Fig.S8 where ellipsoids have been drawn at the 50% probability level. Selected coordination geometries are listed in Table S6 with hydrogen bonding geometries in Table S7. Hydrogen bonding is shown in Fig S9. The formula of **2** is shown in the scheme S2

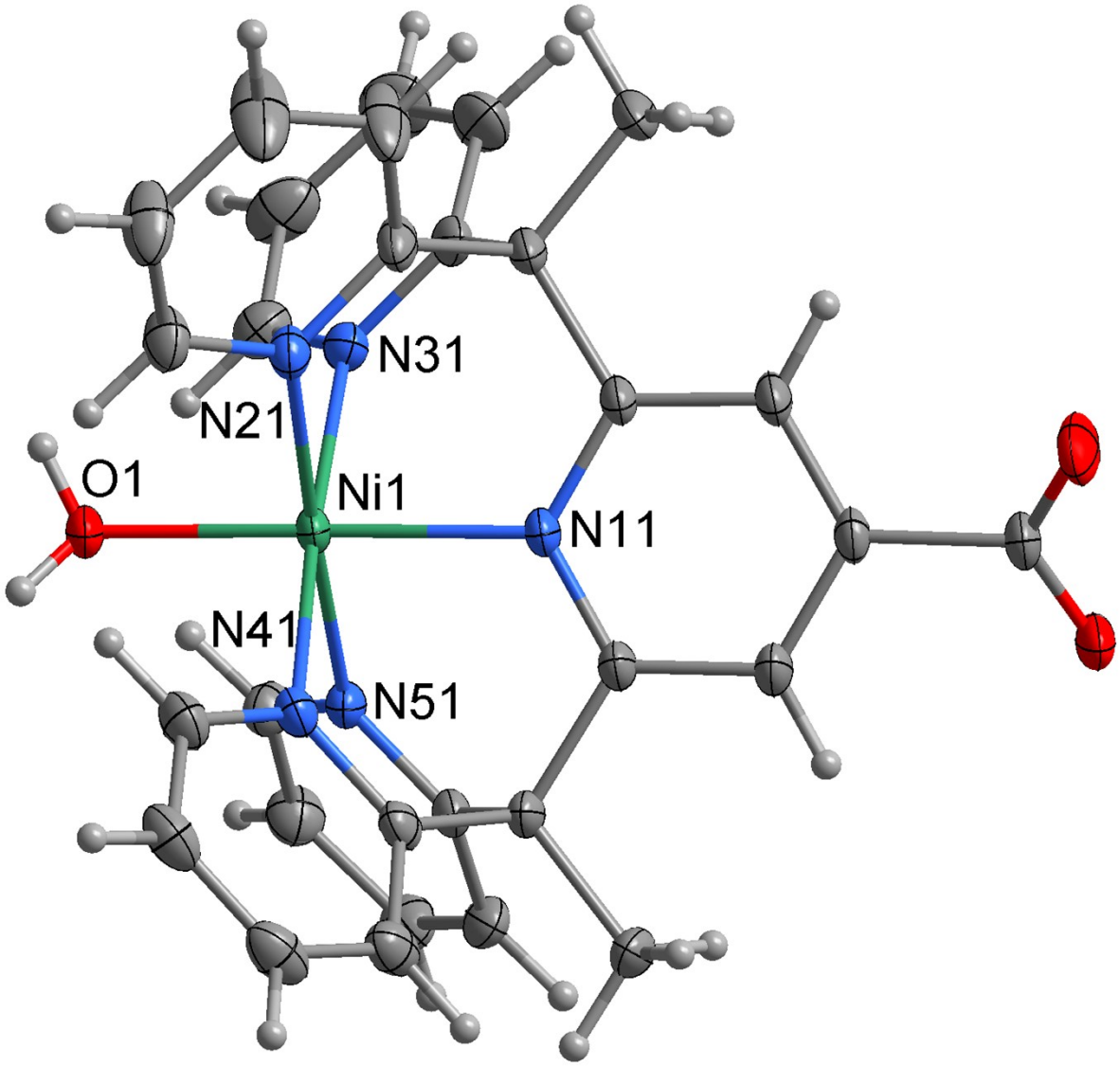



**Figure S7:** Crystal Structure of the complexes **2** with thermal ellipsoids drawn at the 50% probability level.
Green, blue, grey, red and white spheres represent Ni, N, C, O and H atoms, respectively.

Crystallographic data for the structure were collected at 150(2) K on an Oxford Diffraction Gemini diffractometer fitted with Mo Kα radiation. Following analytical absorption corrections and solution by direct methods, the structure was refined against $F^2$ with full-matrix least-squares using the program SHELXL-97.[1]The triflate anion is disordered over two sets of sites with occupancies refined to 0.728(3) and its complement. The solvent was modelled as water molecules. Water molecule O(1) was refined with full occupancy with the remainder refined with site occupancies assigned to match those of the disordered triflate anion after trial refinement and consideration of geometrical interactions. Hydrogen atoms for the coordinated water molecule and for the solvent water molecule O(1) were located and refined with geometries restrained to ideal values. Hydrogen atoms on the disordered water molecules O(3), O(4), and O(5) were not located. The remaining hydrogen atoms were added at calculated positions and refined by use of riding models with isotropic displacement parameters based on those of the parent atoms. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms.

**Table S5**: Crystal data and structure refinement for **2**

| | |
|---|---|
| Identification code | nicooh |
| Empirical formula | $C_{31}H_{30.54}F_3N_5NiO_{8.27}S$ |
| Formula weight | 753.23 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | P**Error!** |
| Unit cell dimensions | $a$ = 11.0416(3) Å |
| $b$ = 11.7979(4) Å | |
| $c$ = 14.2305(3) Å | |
| α= 104.917(2)° | |
| β= 98.643(2)° | |
| γ = 113.012(3)° | |
| Volume | 1581.79(8) Å$^3$ |
| $Z$ | 2 |
| Density (calculated) | 1.581 Mg/m$^3$ |
| μ | 0.758 mm$^{-1}$ |
| Crystal size | 0.36 x 0.24 x 0.12 mm$^3$ |
| θ range for data collection | 3.48 to 37.68°. |
| Index ranges | -18<=h<=18, -19<=k<=19, -24<=l<=23 |
| Reflections collected | 52816 |
| Independent reflections | 16092 [$R$(int) = 0.0406] |
| Completeness to θ = 37.00° | 98.9 % |
| Absorption correction | Analytical |
| Max. and min. transmission | 0.927 and 0.831 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 16092 / 25 / 549 |
| Goodness-of-fit on $F^2$ | 1.030 |
| Final $R$ indices [$I$>2σ($I$)] | $R$1 = 0.0475, $wR$2 = 0.1103 |
| $R$ indices (all data) | $R$1 = 0.0706, $wR$2 = 0.1221 |
| Largest diff. peak and hole | 1.040 and -0.561 e.Å$^{-3}$ |

**Table S6**: Selected bond lengths [Å] and angles [°] for **2**.

| | |
|---|---|
| Ni(1)-N(11) | 2.0452(10) |
| Ni(1)-O(1) | 2.0522(9) |
| Ni(1)-N(41) | 2.0899(12) |
| Ni(1)-N(31) | 2.0943(12) |
| Ni(1)-N(21) | 2.0965(12) |
| Ni(1)-N(51) | 2.1001(11) |
| N(11)-C(16) | 1.3474(17) |
| | |
| N(11)-Ni(1)-O(1) | 177.84(4) |
| N(11)-Ni(1)-N(41) | 87.31(4) |
| O(1)-Ni(1)-N(41) | 93.33(4) |
| N(11)-Ni(1)-N(31) | 88.95(4) |
| O(1)-Ni(1)-N(31) | 90.42(4) |
| N(41)-Ni(1)-N(31) | 176.24(4) |
| N(11)-Ni(1)-N(21) | 89.37(4) |
| O(1)-Ni(1)-N(21) | 92.58(4) |
| N(41)-Ni(1)-N(21) | 98.06(5) |
| N(31)-Ni(1)-N(21) | 81.54(5) |
| N(11)-Ni(1)-N(51) | 88.65(4) |
| O(1)-Ni(1)-N(51) | 89.37(4) |
| N(41)-Ni(1)-N(51) | 83.21(4) |
| N(31)-Ni(1)-N(51) | 97.06(4) |
| N(21)-Ni(1)-N(51) | 177.59(4) |

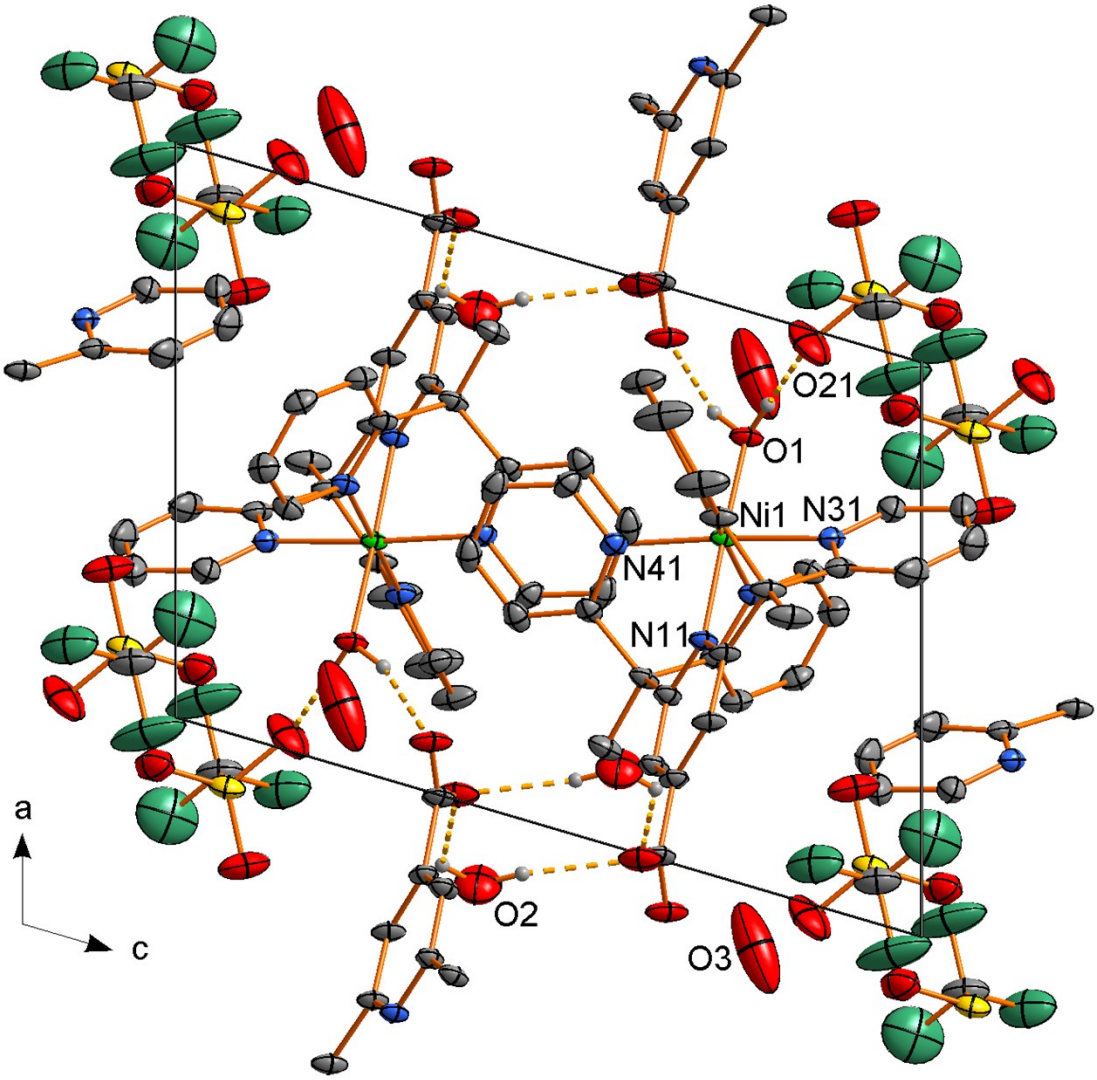



**Figure S8:** Unit cell contents of (**2**) projected along the b-axis showing the hydrogen bonds. Hydrogen atoms not involved in the hydrogen bonding have been omitted for clarity.

**Table S7:** Hydrogen bonds for **2** [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(1)-H(1AO)...O(12)[1] | 0.854(15) | 1.883(17) | 2.7100(14) | 163(2) |
| O(1)-H(1BO)...O(21) | 0.828(15) | 1.841(16) | 2.660(4) | 170(3) |
| O(1)-H(1BO)...O(31) | 0.828(15) | 1.893(18) | 2.700(9) | 165(2) |
| O(2)-H(2AO)...O(11) | 0.851(13) | 2.116(9) | 2.915(2) | 156(3) |
| O(2)-H(2BO)...O(11)[2] | 0.824(16) | 2.29(3) | 2.826(2) | 123(2) |
| C(43)-H(43)…O(12) | 0.950 | 2.454 | 3.338(2) | 154.7 |
| C(26)-H(26)…O(11) | 0.950 | 2.445 | 3.322(3) | 153.3 |
| C(45)-H(45)…O(2) | 0.950 | 2.458 | 3.209(3) | 135.9 |
| C(54)-H(54)…O(22) | 0.950 | 2.345 | 3.292(8) | 174.8 |
| C(61)-H(61C)…O(4) | 0.980 | 2.432 | 3.360(8) | 157.7 |
| C(5)-H(56)…O(23) | 0.950 | 2.470 | 3.322(2) | 149.2 |
| C(24)-H(24)…O(5) | 0.950 | 2.395 | 3.130(6) | 133.9 |
| C(15)-H(15)…O(5) | 0.950 | 2.510 | 3.032(7) | 114.7 |

Symmetry transformations used to generate equivalent atoms:

[1] x+1,y,z ; [2] -x,1-y,1-z

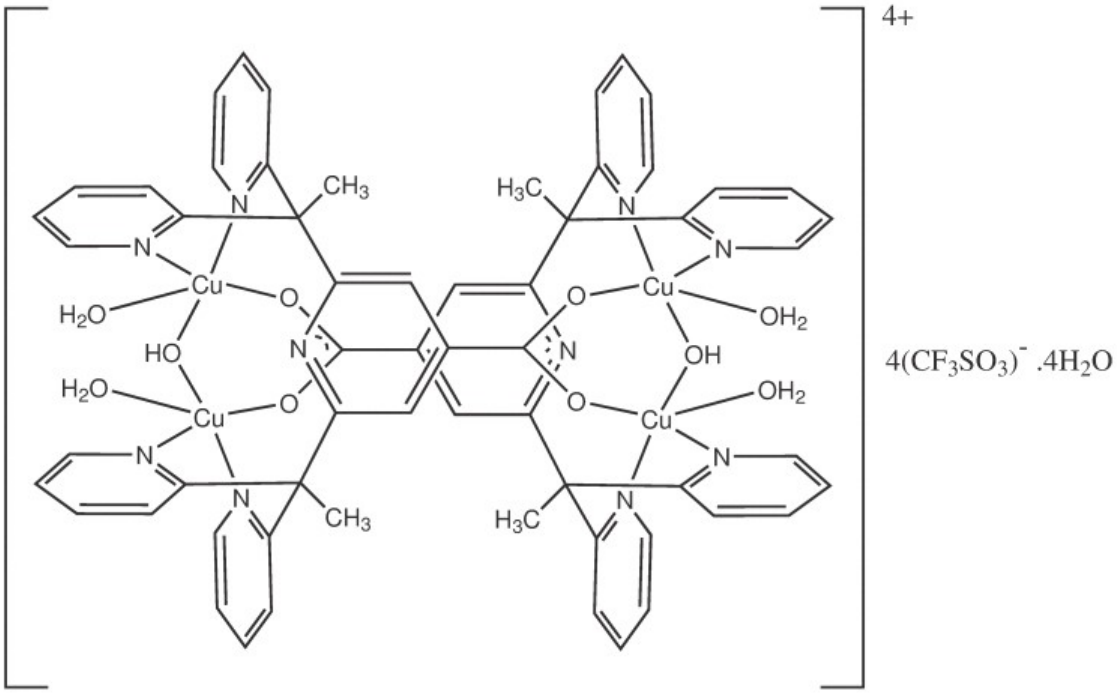
**Table S8:** π - π stacking interactions of compound **2**[a]

| D-H...A | d(H...A) | d(D...A) |
|---|---|---|
| Cg(1)...Cg(1) | 5.671 | 3.715 |
| Cg(2)...Cg(2) | 3.644 | 3.554 |
| Cg(3)...Cg(3) | 4.051 | 4.324 |

**Table S9:** Geometrical parameters [Å and °] for the C-H… π interactions for compound **2**[a]

| D-H...A | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|
| C(44)-H(44)...Cg(4) | 2.883 | 3.571 | 130.16 |
| C(34)-H(34)...Cg(5) | 3.132 | 3.649 | 115.94 |
| C(33)-H(33)...Cg(4) | 3.192 | 3.853 | 128.26 |
| C(21)-H(23)...Cg(3) | 3.450 | 3.824 | 106.05 |

[a] Cg(1), Cg(2), Cg(3), Cg(4)and Cg(5), are the ring centroids of the pyridine rings N21,N31,N41,N51and N11 respectively.




**Scheme S3:** Formula for complex **3**

The crystal data for **3** are summarized in Table S10 with the structure depicted in Figs. S10 and S11. Selected coordination geometries are listed in Table S11 with hydrogen bonding geometries listed in Table S12.Hydrogen bonding is shown in Fig.S12. The formula for complex **3** is shown in scheme S3.

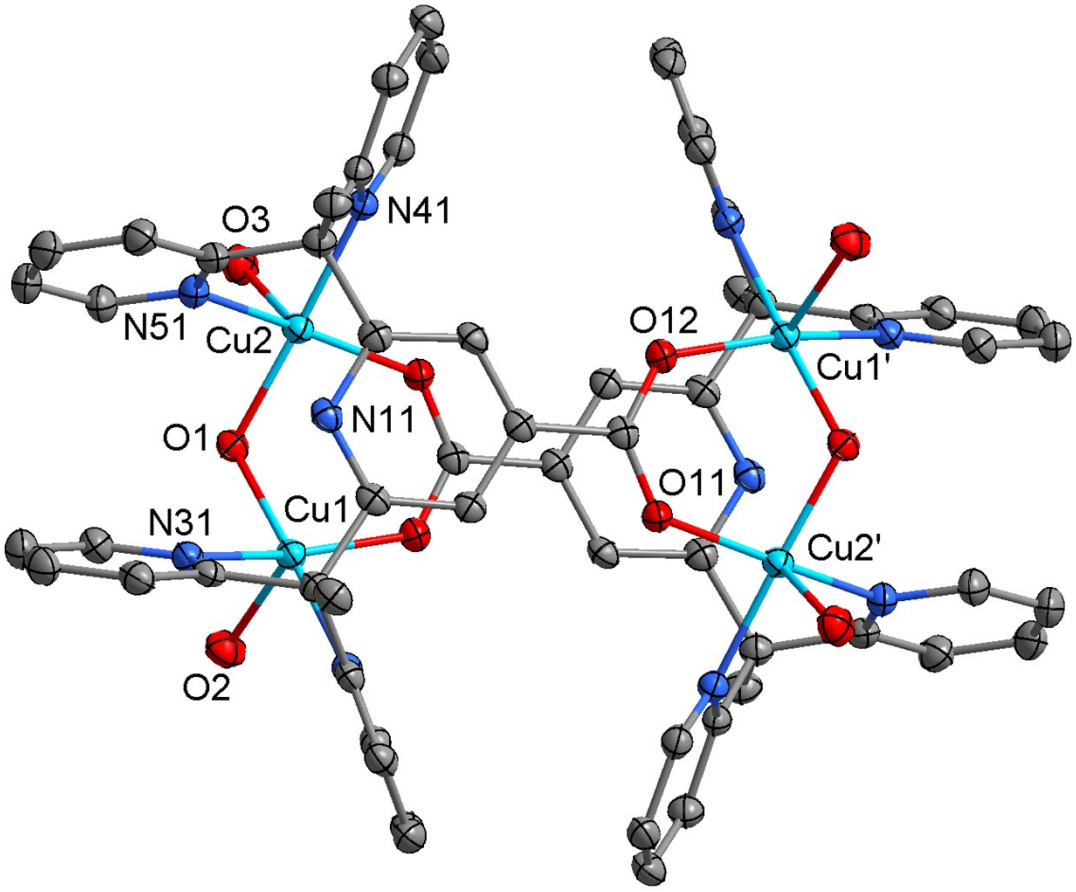


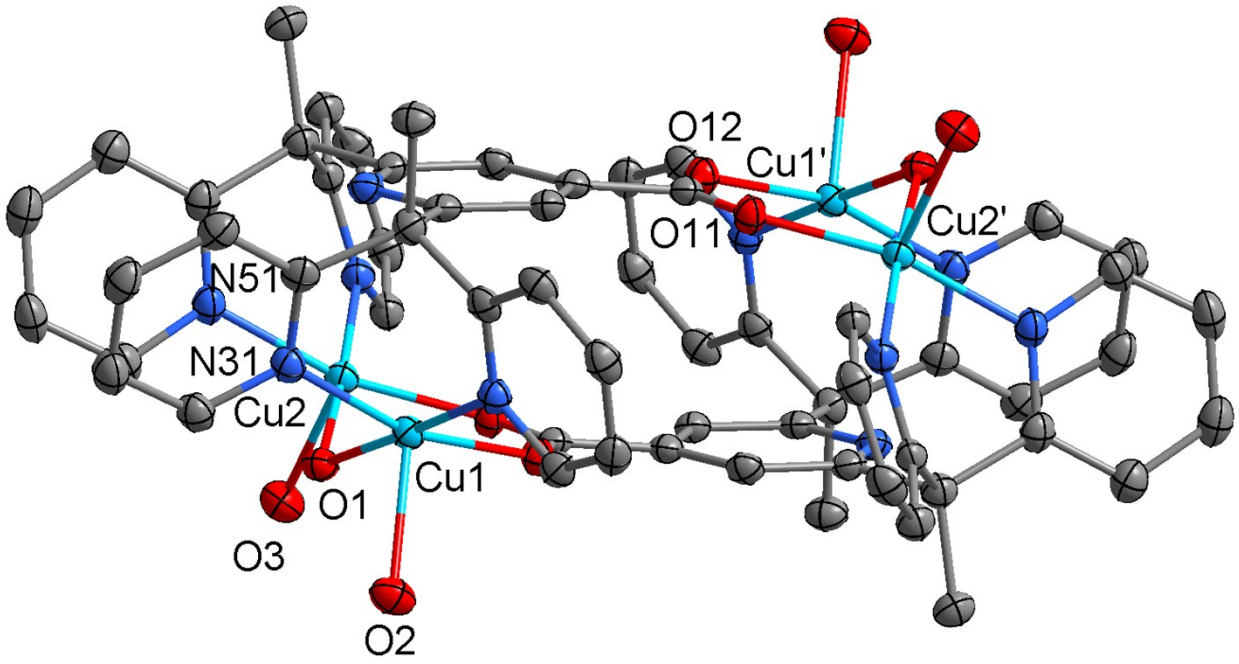

**Figure S9:** Crystal Structure of the complexes **3** with thermal ellipsoids drawn at the 50% probability level.

Aqua, blue, grey, red and white spheres represent Cu,N,C,O,H atoms, respectively; hydrogen atoms have been omitted for clarity. Structure of the cation of (**3**) projected approximately onto the plane of the central ring. Hydrogen atoms have been omitted for clarity. The primes refer to the atoms generated by the inversion centre.

**Figure S10:** Crystal Structure of the complexes **3** with thermal ellipsoids drawn at the 50% probability level.

Aqua, blue, grey, red and white spheres represent Cu, N,C, O, H atoms, respectively; hydrogen atoms have been omitted for clarity. Structure of the cation of (3) projected oblique to that given

in Fig S09. Hydrogen atoms have been omitted for clarity. The primes refer to the atoms generated by the inversion centre.




Crystallographic data for the structure were collected at 120(2) K on an Oxford Diffraction Gemini diffractometer fitted with Cu Kα radiation Following analytical absorption corrections and solution by direct methods, the structure was refined against $F^2$ with full-matrix least-squares using the program SHELXL-97.[1]Water molecule and hydroxyl hydrogen atoms were refined with geometries restrained to ideal values. The remaining hydrogen atoms were added at calculated positions and refined by use of riding models with isotropic displacement parameters based on those of the parent atoms. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms.

**Table S10**: Crystal data and structure refinement for **3**

| | |
|---|---|
| Identification code | cucooh |
| Empirical formula | $C_{64}H_{66}Cu_4F_{12}N_{10}O_{26}S_4$ |
| Formula weight | 2001.67 |
| Temperature | 120(2) K |
| Wavelength | 1.54178 Å |
| Crystal system | Triclinic |
| Space group | *P***Error!** |
| Unit cell dimensions | *a* = 12.5531(4) Å |
| *b* = 13.0741(4) Å | |
| *c* = 14.6993(5) Å | |
| α= 68.163(3)° | |
| β= 65.870(3)° | |
| γ = 64.215(3)° | |
| Volume | 1926.33(11) $Å^3$ |
| *Z* | 1 |
| Density (calculated) | 1.725 $Mg/m^3$ |
| μ | 3.279 $mm^{-1}$ |
| Crystal size | 0.36 x 0.10 x 0.06 $mm^3$ |
| θ range for data collection | 3.39 to 67.39°. |
| Index ranges | -15<=h<=14, -15<=k<=15, -17<=l<=17 |
| Reflections collected | 38901 |
| Independent reflections | 6854 [*R*(int) = 0.0385] |
| Completeness to θ = 67.39° | 98.9 % |
| Absorption correction | Analytical |
| Max. and min. transmission | 0.833 and 0.531 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 6854 / 13 / 579 |
| Goodness-of-fit on $F^2$ | 1.044 |
| Final *R* indices [$I>2\sigma(I)$] | *R*1 = 0.0373, *wR*2 = 0.0984 |
| *R* indices (all data) | *R*1 = 0.0447, *wR*2 = 0.1057 |
| Largest diff. peak and hole | 0.675 and -0.307 $e.Å^{-3}$ |

**Table S11:** Selected bond lengths [Å] and angles [°] for **3**

| | |
|---|---|
| Cu(1)-O(1) | 1.9080(18) |
| Cu(1)-O(12)[1] | 1.9959(17) |
| Cu(1)-N(21) | 2.001(2) |
| Cu(1)-N(31) | 2.026(2) |
| Cu(1)-O(2) | 2.2379(19) |
| Cu(2)-O(1) | 1.9077(17) |
| Cu(2)-O(11)[1] | 1.9843(17) |
| Cu(2)-N(51) | 2.003(2) |
| Cu(2)-N(41) | 2.016(2) |
| Cu(2)-O(3) | 2.233(2) |
| Cu(1)-Cu(2) | 3.1991(5) |
| O(1)-Cu(1)-O(12)[1] | 93.13(7) |
| O(1)-Cu(1)-N(21) | 177.24(8) |
| O(12)[1]-Cu(1)-N(21) | 89.57(8) |
| O(1)-Cu(1)-N(31) | 90.54(8) |
| O(12)[1]-Cu(1)-N(31) | 163.18(8) |
| N(21)-Cu(1)-N(31) | 86.70(9) |
| O(1)-Cu(1)-O(2) | 89.69(7) |
| O(12)[1]-Cu(1)-O(2) | 95.85(8) |
| N(21)-Cu(1)-O(2) | 90.60(8) |
| N(31)-Cu(1)-O(2) | 100.58(8) |
| O(1)-Cu(2)-O(11)[1] | 93.32(7) |
| O(1)-Cu(2)-N(51) | 88.99(8) |
| O(11)[1]-Cu(2)-N(51) | 164.36(8) |
| O(1)-Cu(2)-N(41) | 174.83(8) |
| O(11)[1]-Cu(2)-N(41) | 90.11(8) |
| N(51)-Cu(2)-N(41) | 86.67(9) |
| O(1)-Cu(2)-O(3) | 91.46(8) |
| O(11)[1]-Cu(2)-O(3) | 95.40(8) |
| N(51)-Cu(2)-O(3) | 100.01(8) |
| N(41)-Cu(2)-O(3) | 92.07(8) |
| Cu(1)-O(1)-Cu(2) | 113.9(1) |

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

**Table S12:** Hydrogen bonds for **3** [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(1)-H(1)...O(5) | 0.827(18) | 1.994(19) | 2.811(3) | 169(3) |
| O(2)-H(2AO)...O(5) | 0.823(18) | 2.01(2) | 2.802(3) | 160(3) |
| O(5)-H(5AO)...O(23)[1] | 0.856(18) | 2.022(19) | 2.877(3) | 177(3) |
| O(3)-H(3BO)...O(4) | 0.825(18) | 1.906(18) | 2.716(3) | 167(3) |
| O(2)-H(2BO)...O(21) | 0.824(18) | 2.057(18) | 2.871(3) | 170(3) |
| O(3)-H(3AO)...O(31) | 0.823(18) | 2.047(18) | 2.868(3) | 175(4) |
| O(5)-H(5BO)...O(32) | 0.858(18) | 2.024(19) | 2.861(3) | 165(4) |
| O(4)-H(4BO)...O(22)[2] | 0.855(19) | 2.04(2) | 2.829(3) | 152(4) |
| O(4)-H(4AO)...O(23)[1] | 0.862(18) | 2.04(2) | 2.875(4) | 162(4) |

Symmetry transformations used to generate equivalent atoms:

[1] 1-x,1-y,1-z ; [2] x+1,y-1,z

**Table S13:** π - π stacking interactions of compound **3**[a]

| D-H...A | Cg-Cg | d(D...A) |
|---|---|---|
| Cg(1)...Cg(1) | 3.711 | 3.715 |
| Cg(2)...Cg(2) | 4.411 | 3.554 |

**Table S14:** Geometrical parameters (Å,º) for the C-H… π interactions for compound **3**[a]

| D-H...A | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|
| C(24)-H(24)...Cg(3) | 3.348 | 4.060 | 133.34 |
| C(34)-H(34)...Cg(4) | 3.043 | 3.538 | 142.24 |

[a] Cg(1), Cg(2), Cg(3)and Cg(4), are the ring centroids of the pyridine rings N21,N51,N31 and N41 respectively.

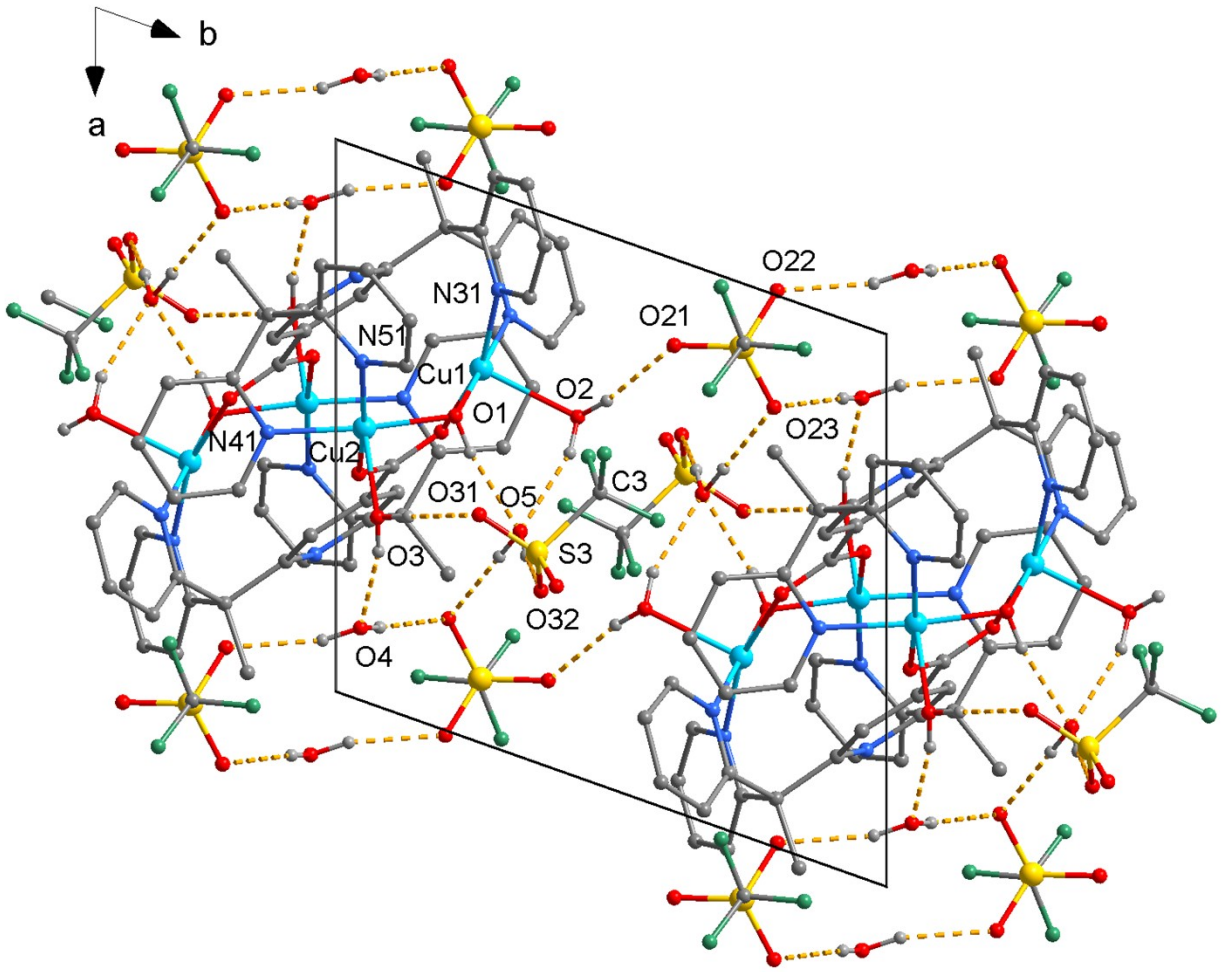



**Figure S11:** Unit cell contents of (**3**) projected along the *c*-axis showing the hydrogen bonds. Hydrogen atoms not involved in the hydrogen bonding have been omitted for clarity.

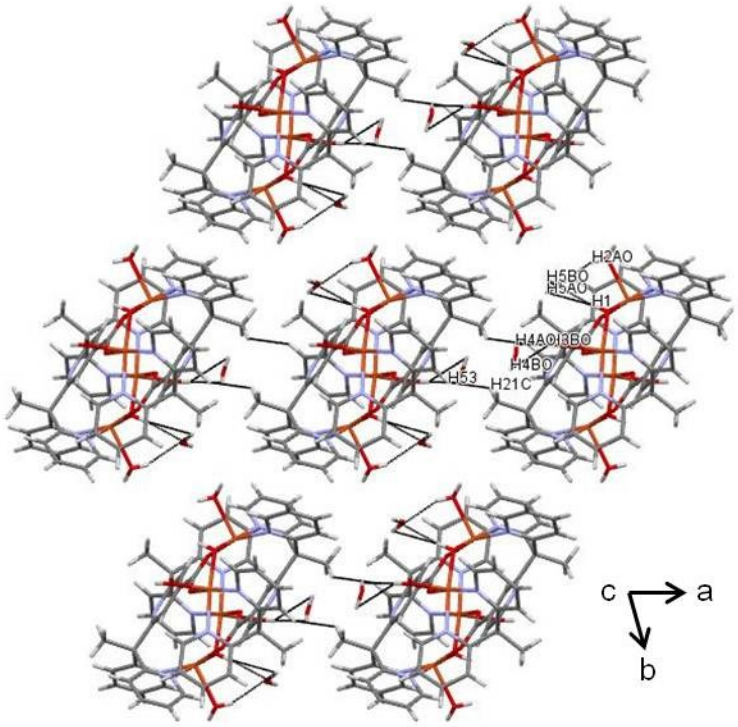



**Figure S12:** Packing diagram of **3** with short H…H contacts highlighted in black.

**Table S15:**.Short H…H contacts for **3** [Å].

| D-H...A | d(H...A) |
|---|---|
| O(3)-H3BO... H4BO | 2.48(4) |
| O(3)- H3BO... H4AO | 2.36(4) |
| O(2)- H2AO... H5AO | 2.60(4) |
| O(1)- H1... H5AO | 2.45(4) |
| O(1)- H1... H5BO | 2.45(6) |
| C(53)- H53... H21C | 2.619 |

**Table S16:** π - π stacking interactions of compound **4**[a]

| D-H...A | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|
| Cg(4)...Cg(4) | 4.385 | | |
| Cg(2)...Cg(2) | 3.810 | | |
| Cg(3)...Cg(3) | 5.042 | | |
| Cg(5)...Cg(5) | 4.541 | | |

[a] Cg(1), Cg(2), Cg(3), Cg(4)and Cg(5), are the ring centroids of the pyridine rings N5,N3,N1,N4and N18 respectively.

**Table S17:** Geometrical parameters [Å and °].for the C-H…π interactions for compound **4**[a]

| D-H...A | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|
| C(16)-H(16)...Cg(2) | 3.005 | 3.715 | 133.35 |
| C(22)-H(22)...Cg(1) | 3.225 | 3.554 | 102.81 |
| C(7)-H(7C)...Cg(5) | 3.392 | 4.293 | 155.31 |

Hirshfeld Surface Studies

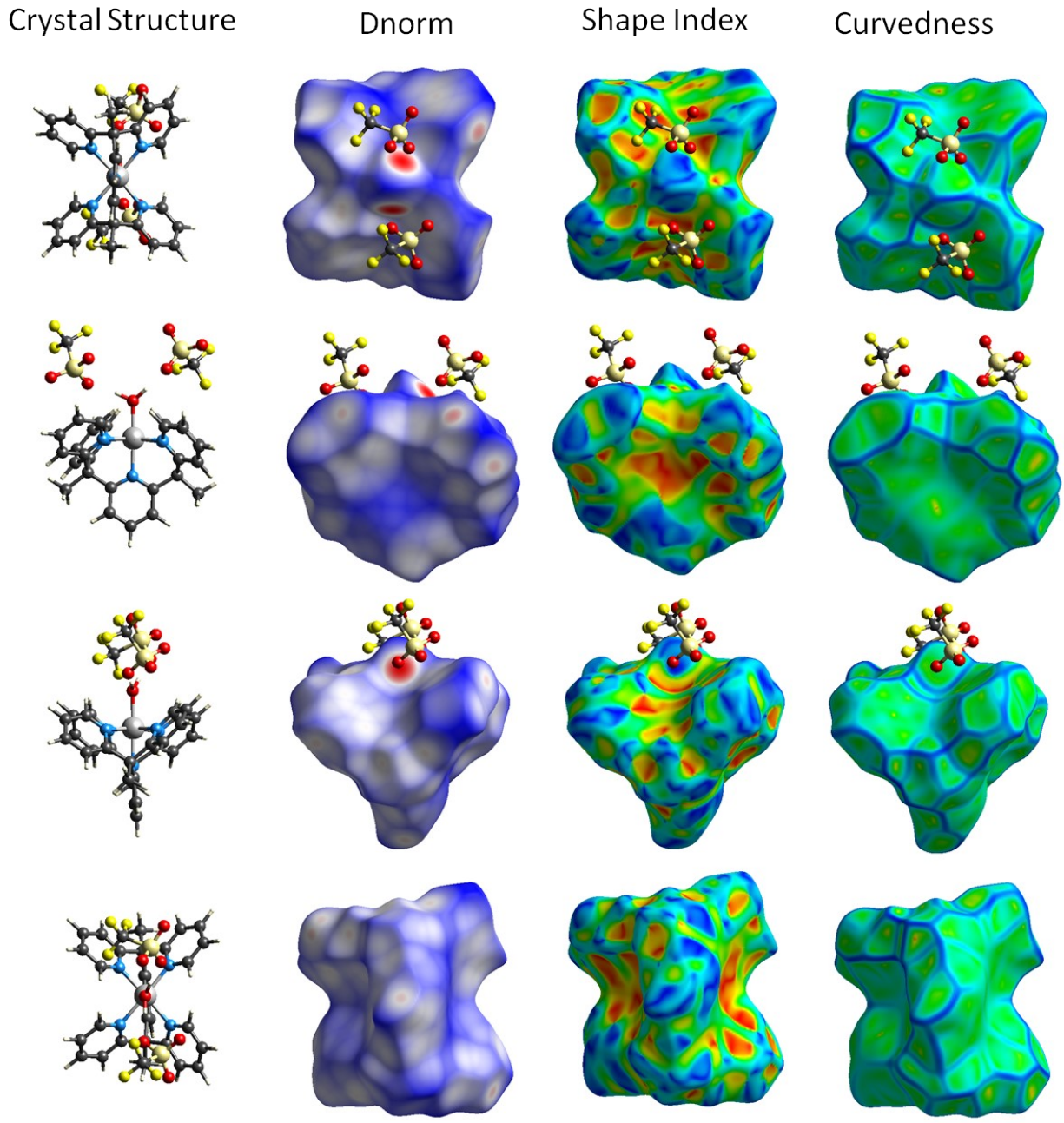



**Figure S13:** Hirshfeld surface of **4** mapped with $d_{norm}$, Shape Index and Curvedness function.

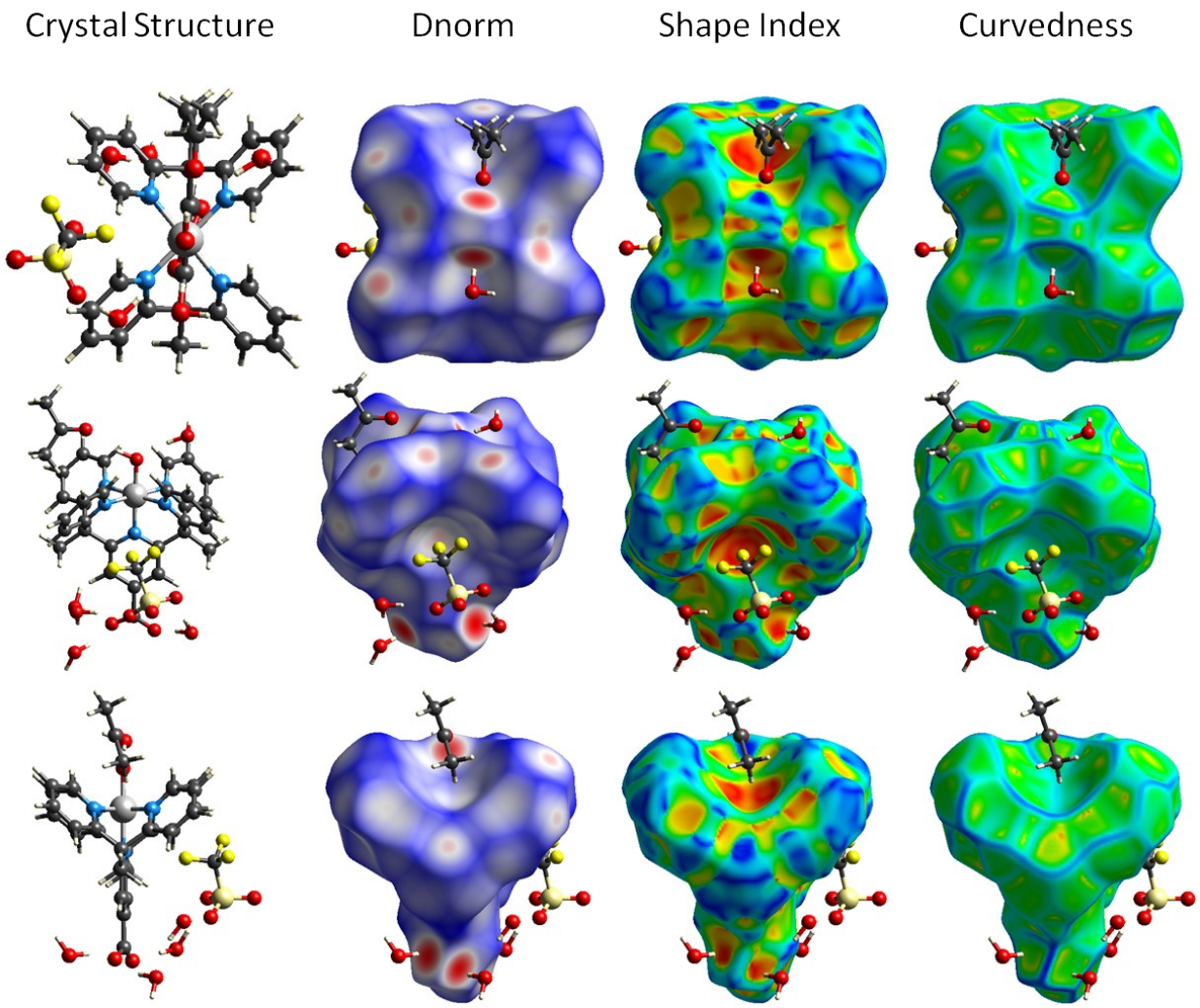



**Figure S14:** Hirshfeld surface of **1** mapped with $d_{norm}$, Shape Index and Curvedness function.

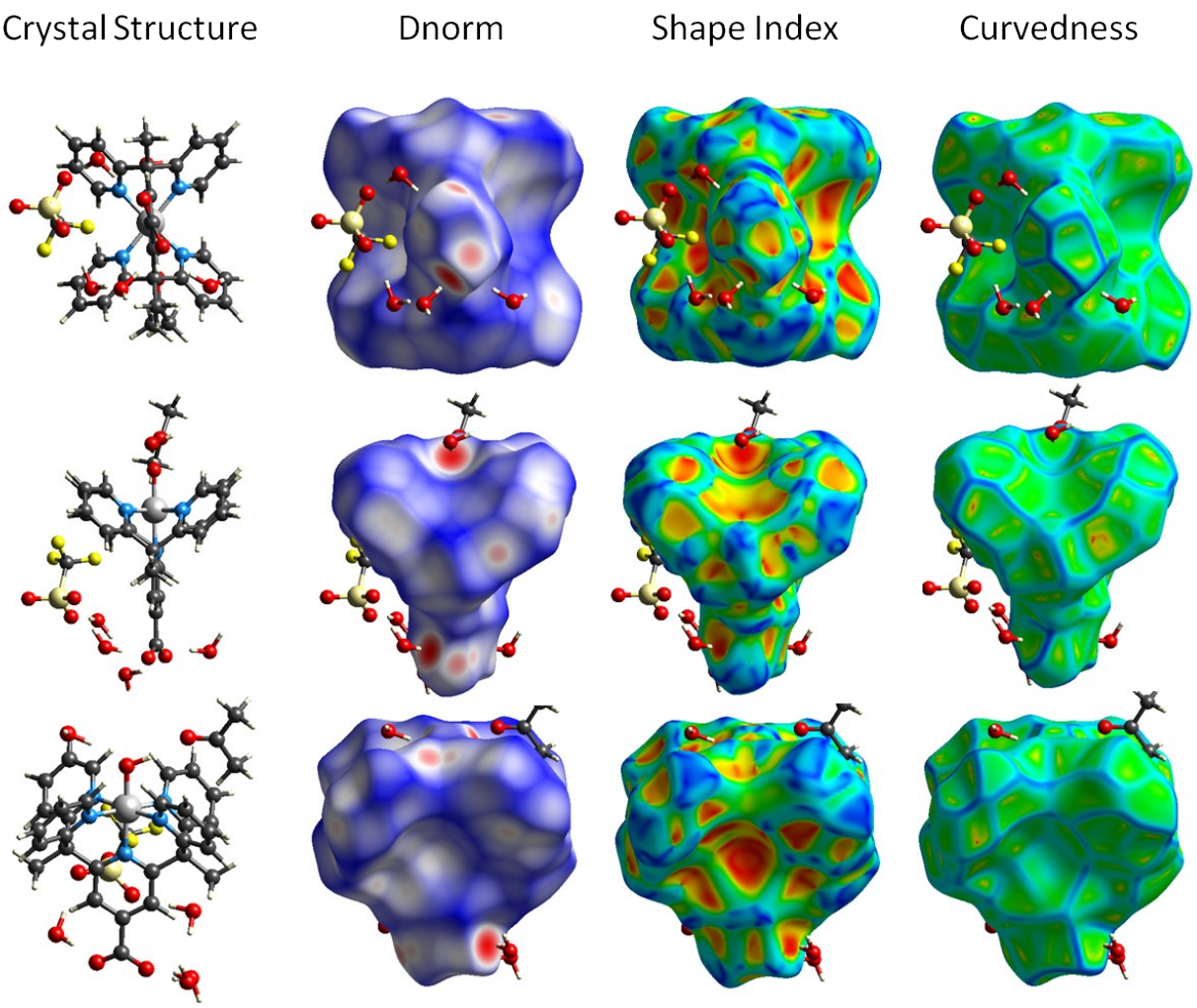



**Figure S14:** Hirshfeld surface of **1** mapped with $d_{norm}$, Shape Index and Curvedness function.

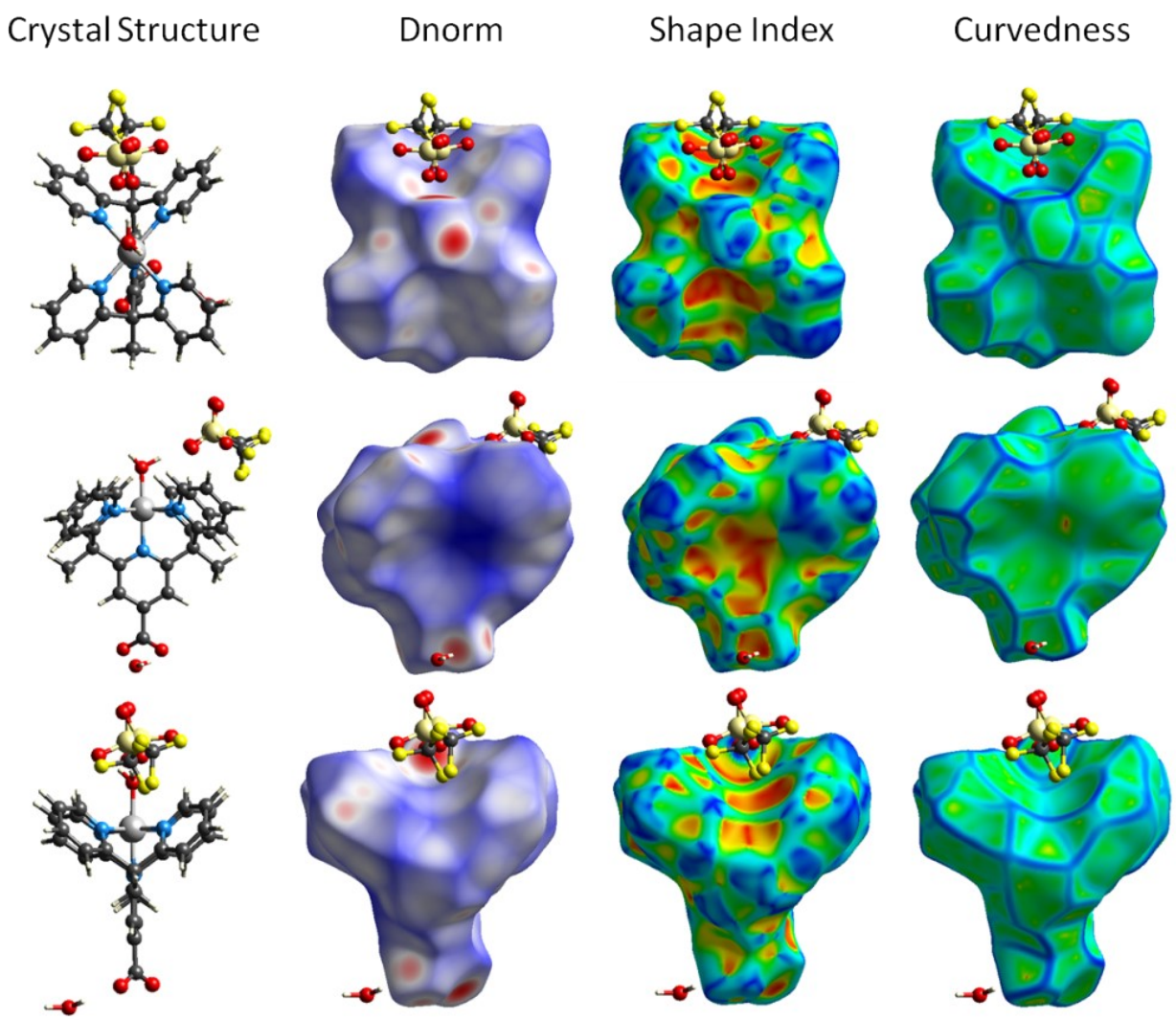



**Figure S15:** Hirshfeld surface of **2** mapped with $d_{norm}$, Shape Index and Curvedness function.

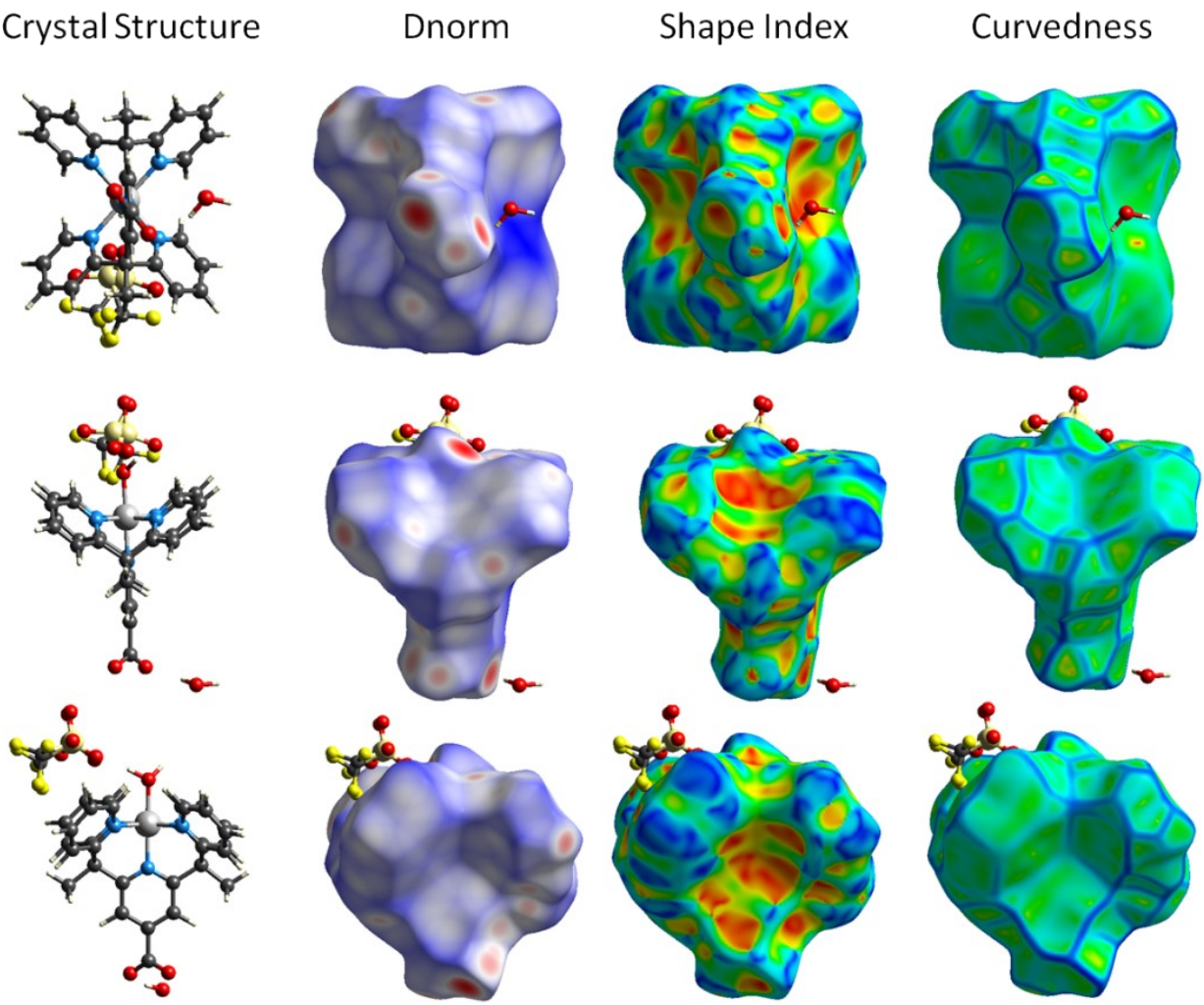



**Figure S15:** Hirshfeld surface of **2** mapped with $d_{norm}$, Shape Index and Curvedness function.

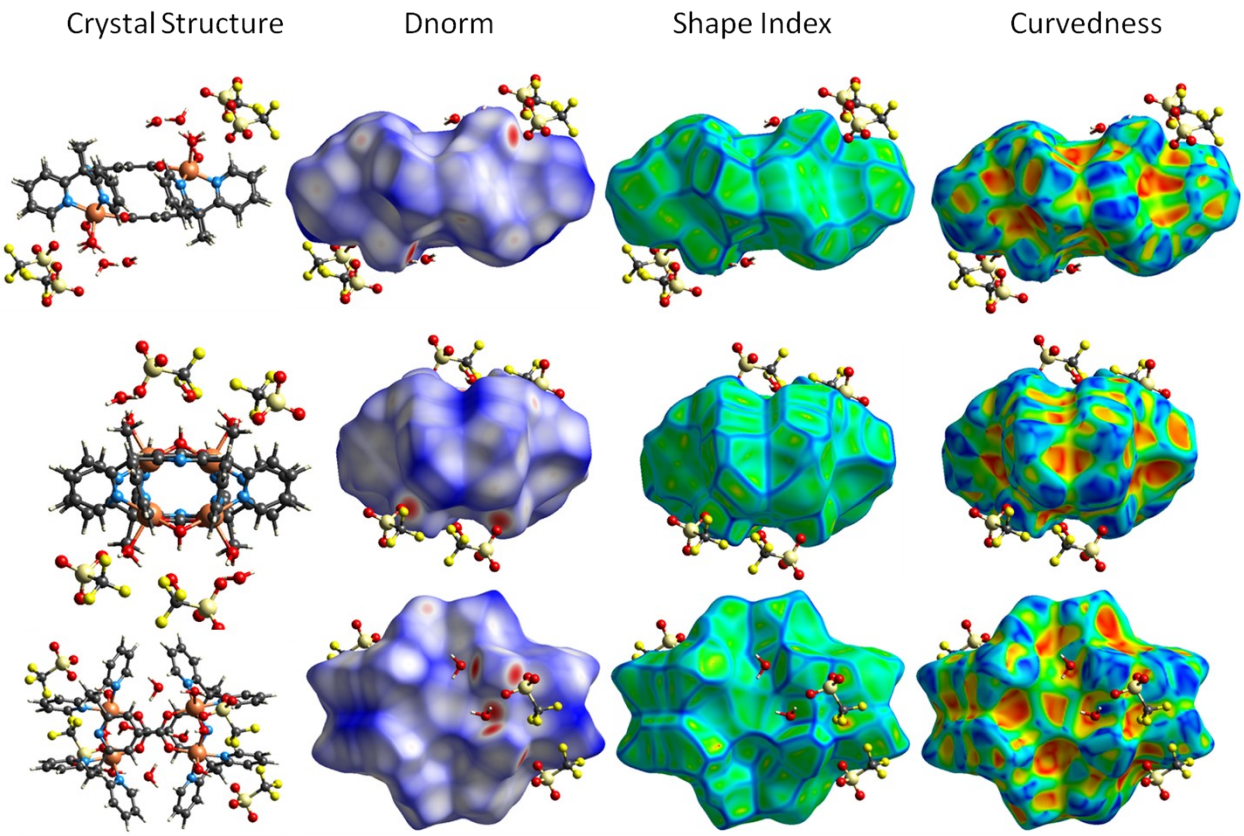



**Figure S16:** Hirshfeld surface of **3** mapped with $d_{norm}$, Shape Index and Curvedness function.

2D fingerprint plots

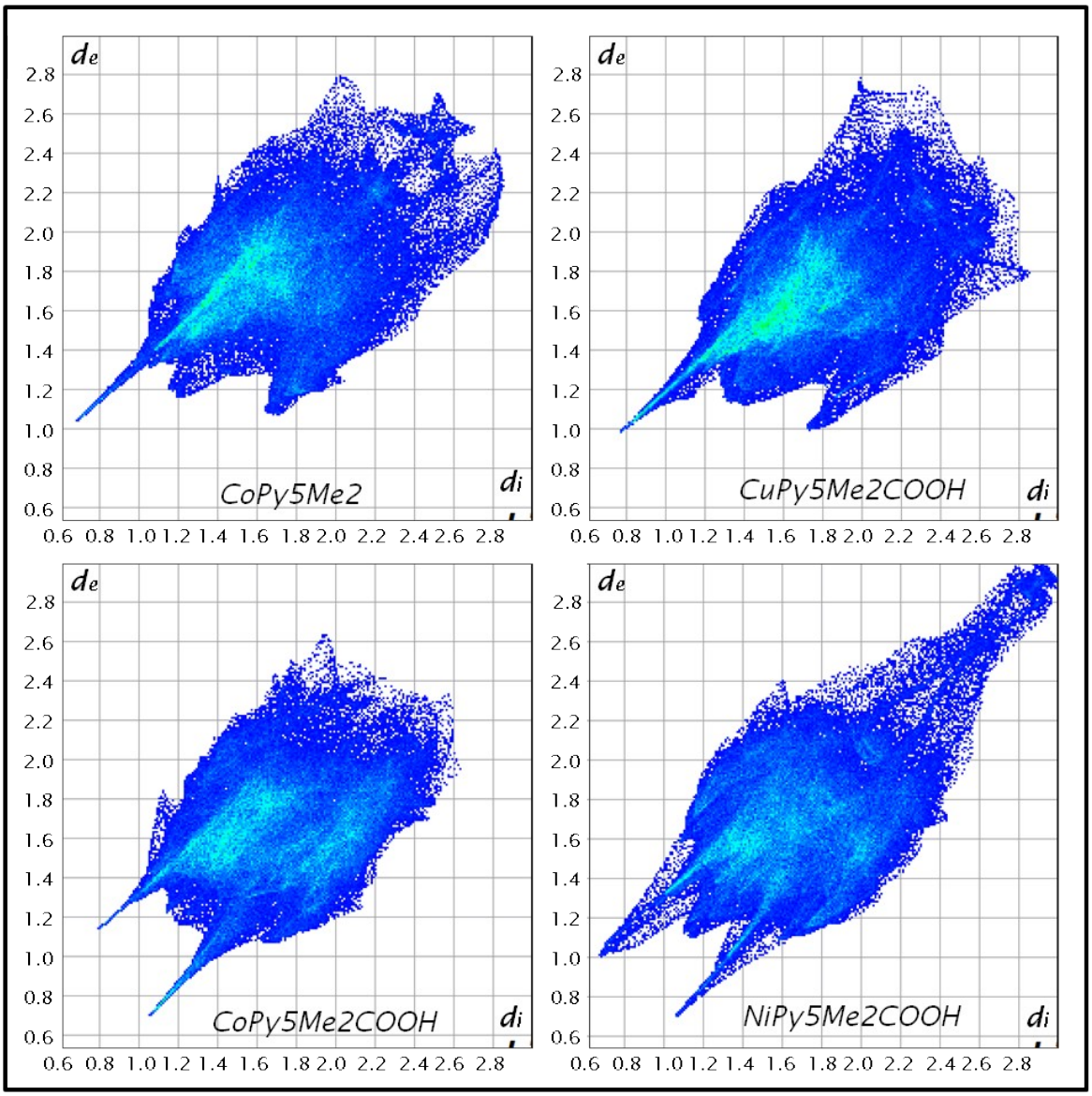
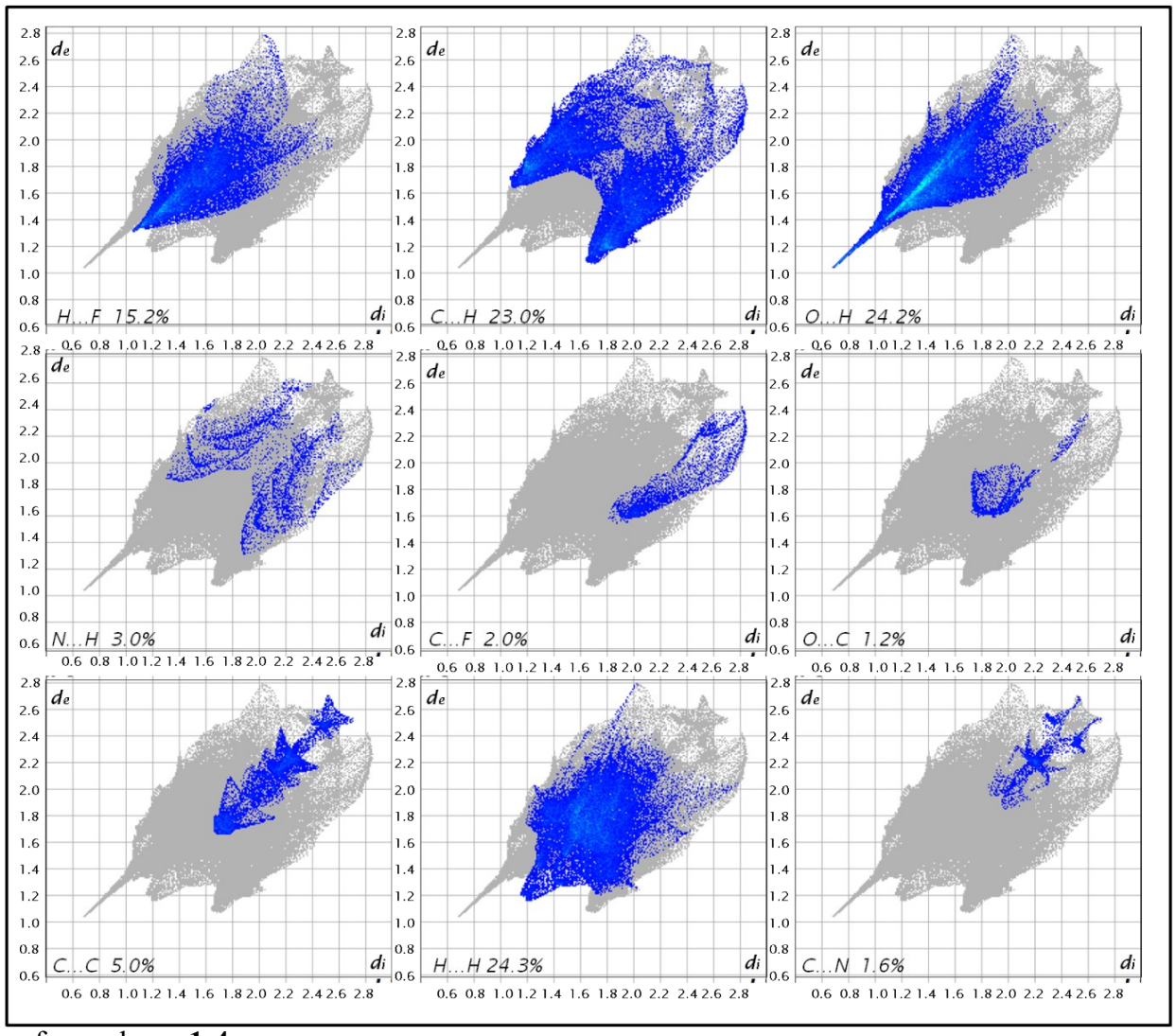



**Figure S17:** 2D Fingerprint plots of complexes **1-4**

| Contact Type | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| H…F | 3.7 | 5.2 | 21.3 | 15.2 |
| C…H | 17.4 | 20.7 | 11.2 | 23.0 |
| O…H | 28.0 | 31.5 | 25.1 | 24.2 |
| N…H | 1.8 | 2.7 | 2.1 | 3.0 |
| C…F | 6.0 | 2.6 | 1.0 | 2.0 |
| O…C | 2.6 | 1.6 | 3.0 | 1.2 |
| C…C | 0.2 | 5.6 | 2.0 | 5.0 |
| H…H | 38.6 | 26.5 | 33.4 | 24.3 |
| C…N | 0 | 2.0 | 0.4 | 1.6 |

**Table S18**: Percentage contributions of different intermolecular contacts to the Hirshfeld surface




of complexes **1-4**

**Figure S18:** 2D fingerprint plot of **4** resolved/decomposed into type contacts, revealing the percentage of contribution of the contact to the total Hirshfeld surface area.

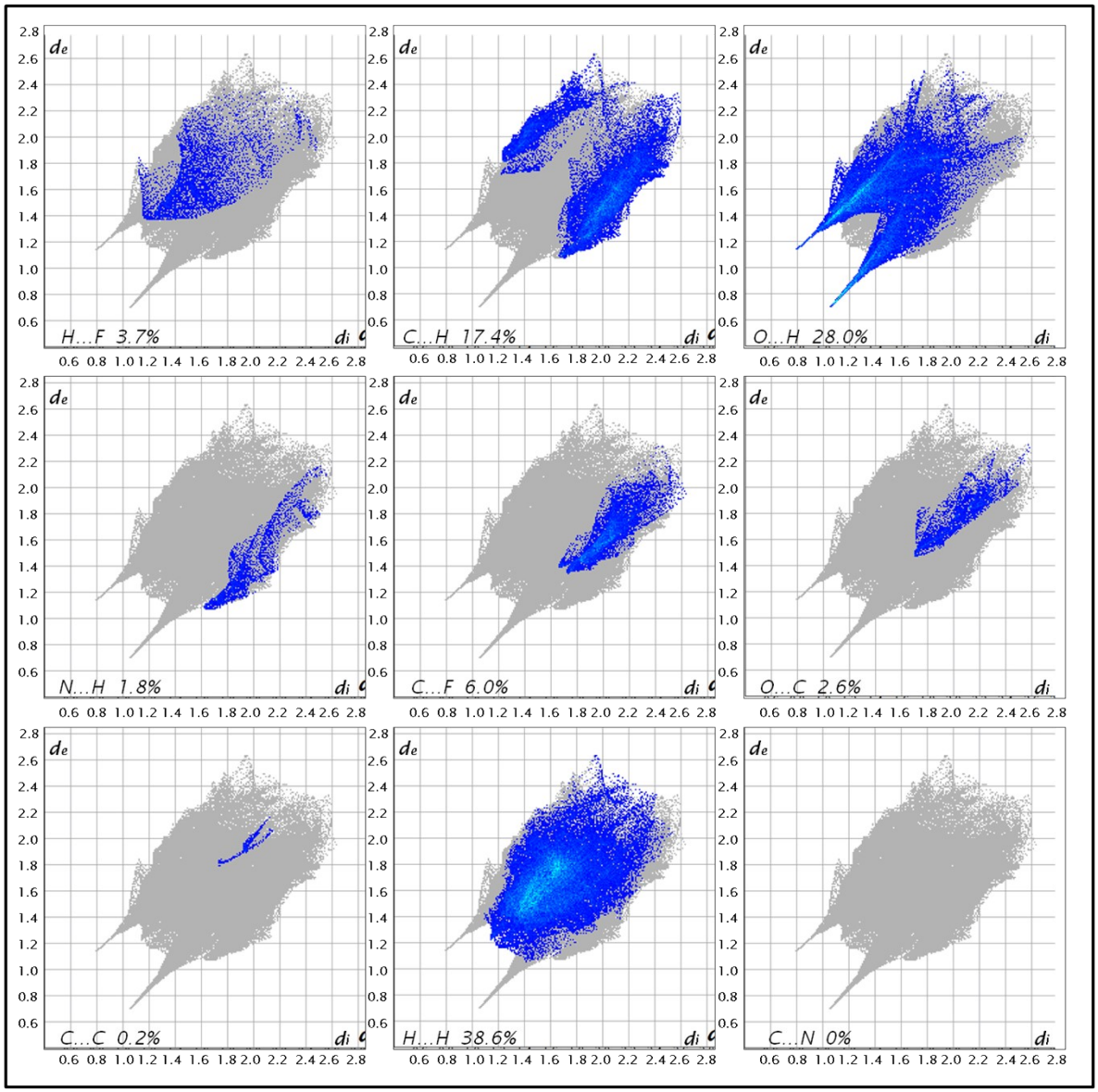

de
di
H...F 3.7%
C...H 17.4%
O...H 28.0%
N...H 1.8%
C...F 6.0%
O...C 2.6%
C...C 0.2%
H...H 38.6%
C...N 0%
0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4 2.6 2.8

**Figure S19:** 2D fingerprint plot of **1** resolved/decomposed into type contacts, revealing the percentage of contribution of the contact to the total Hirshfeld surface area.

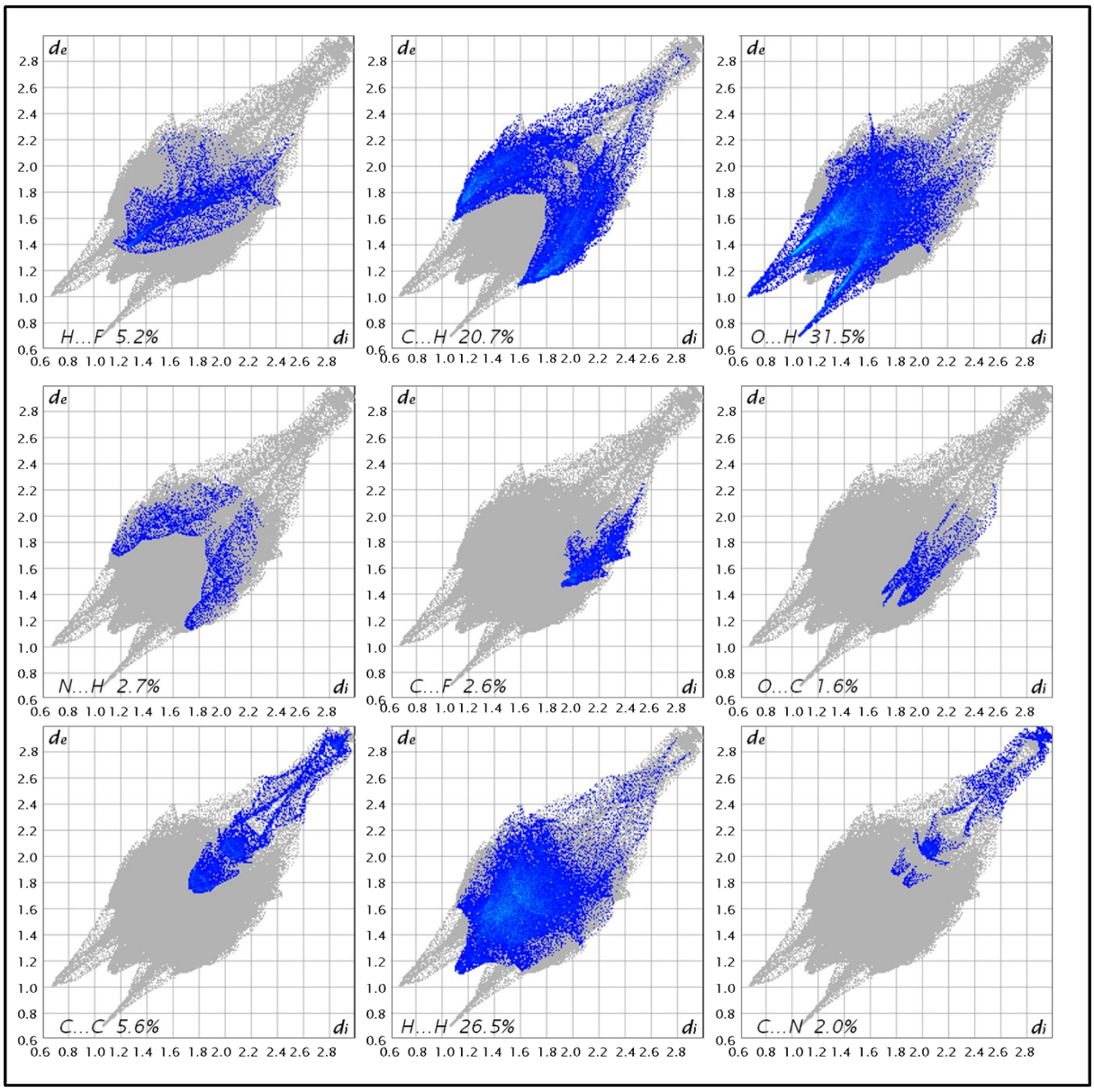



**Figure S20:** 2D fingerprint plot of **2** resolved/decomposed into type contacts, revealing the percentage of contribution of the contact to the total Hirshfeld surface area.

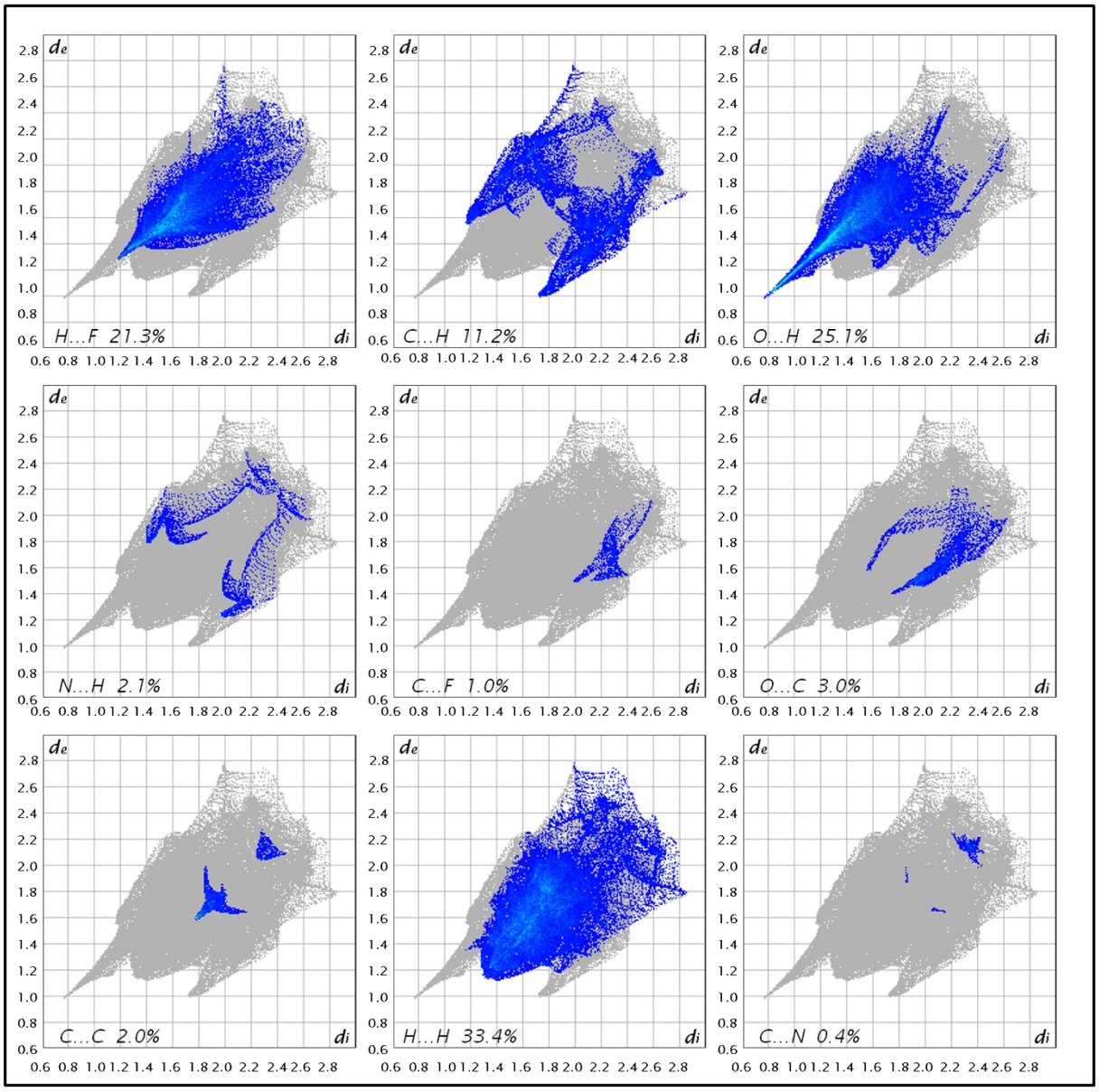



**Figure S21:** 2D fingerprint plot of **3** resolved/decomposed into type contacts, revealing the percentage of contribution of the contact to the total Hirshfeld surface area.

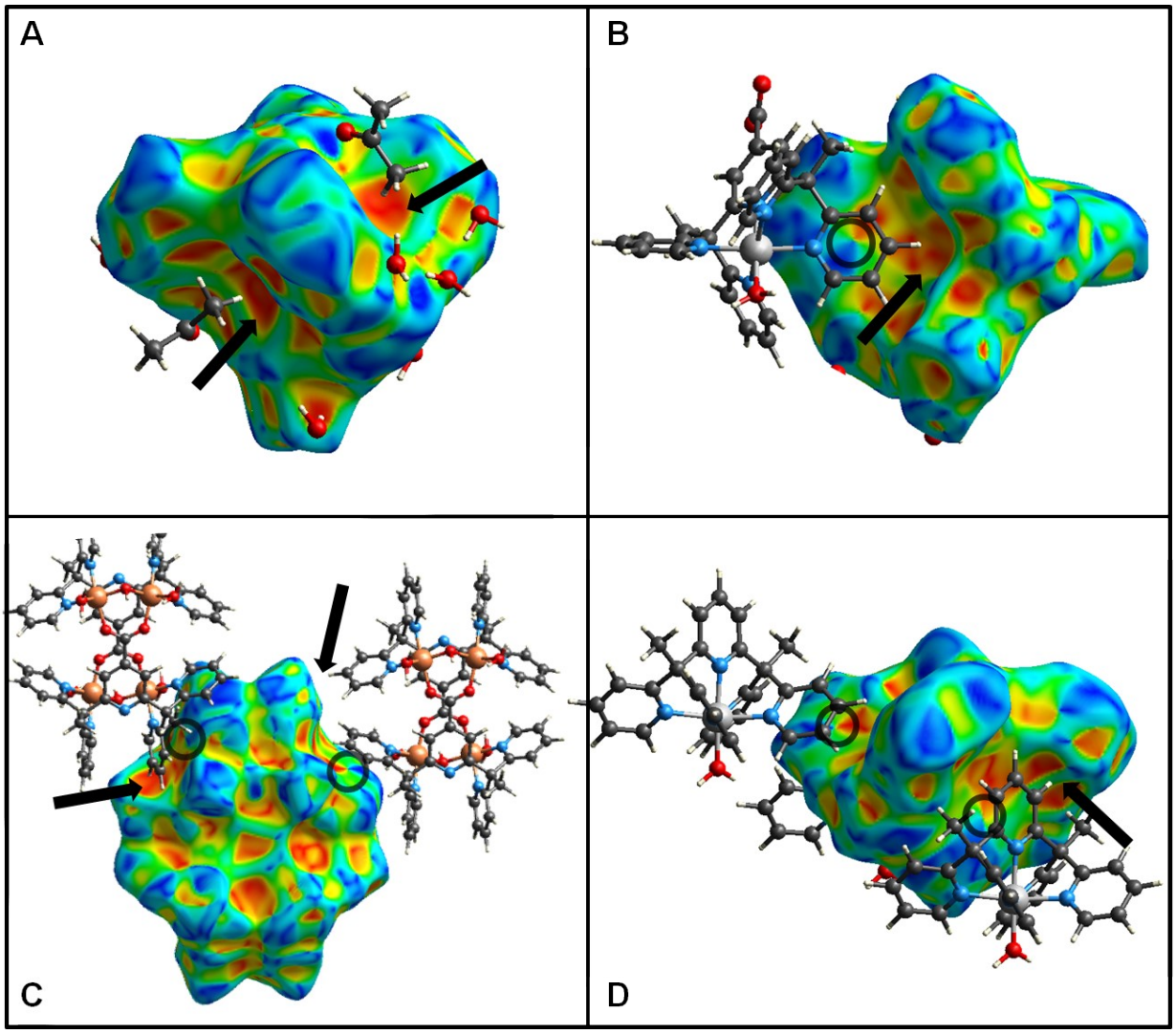



**Figure S22:** Hirshfeld surfaces mapped with shape index of **1**(A), **2**(B), **3**(C) and **4**(D). C…H contacts are shown by the arrow. "bow-tie" patterns indicating C…C contacts are circled.

1. Sheldrick G: **A short history of SHELX**. *Acta Crystallographica Section A* 2008, **64**(1):112-122.