Supporting Information

Insight into the connecting roles of interaction synthons and water clusters within different transition metal coordination compounds of pyridine-2,5-dicarboxylic acid: experimental and theoretical studies

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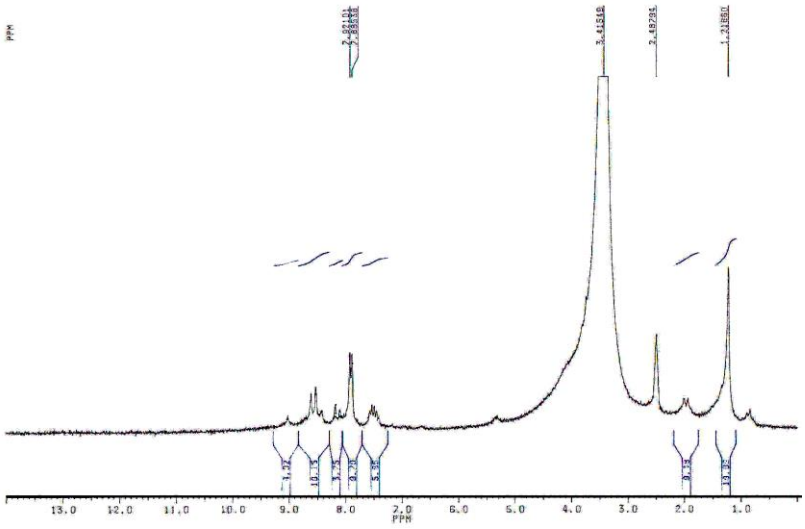


Figure S1. ^{1}H-NMR spectrum of compound **2**.

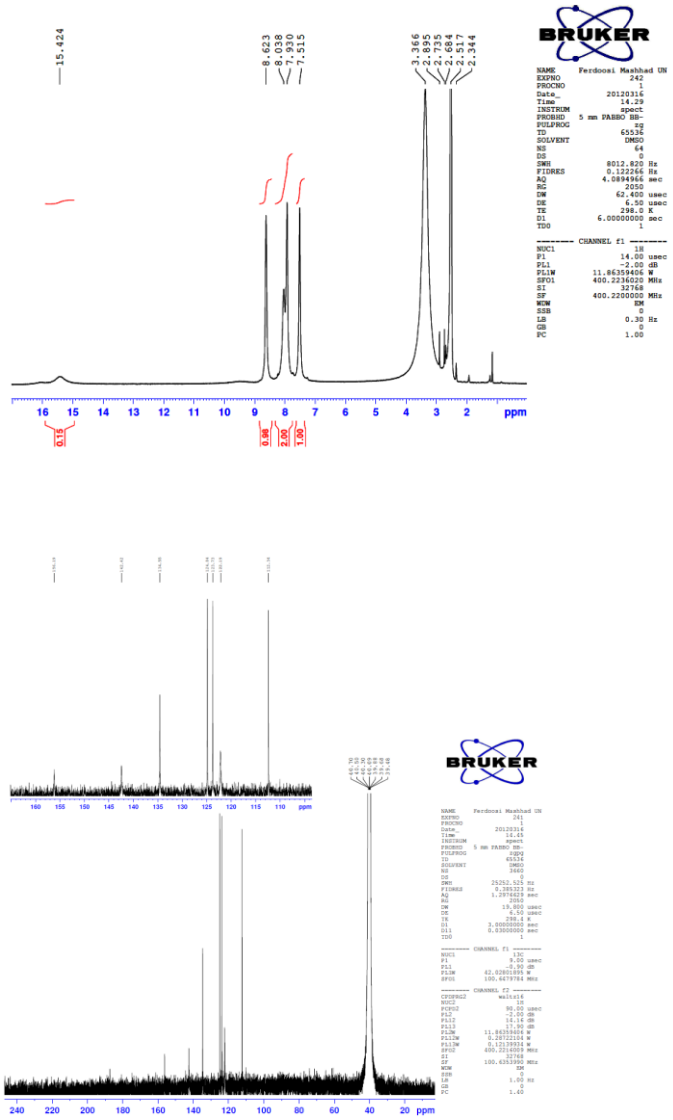


Figure S2. ^{1}H- and ^{13}C-NMR spectra of compound **3**.

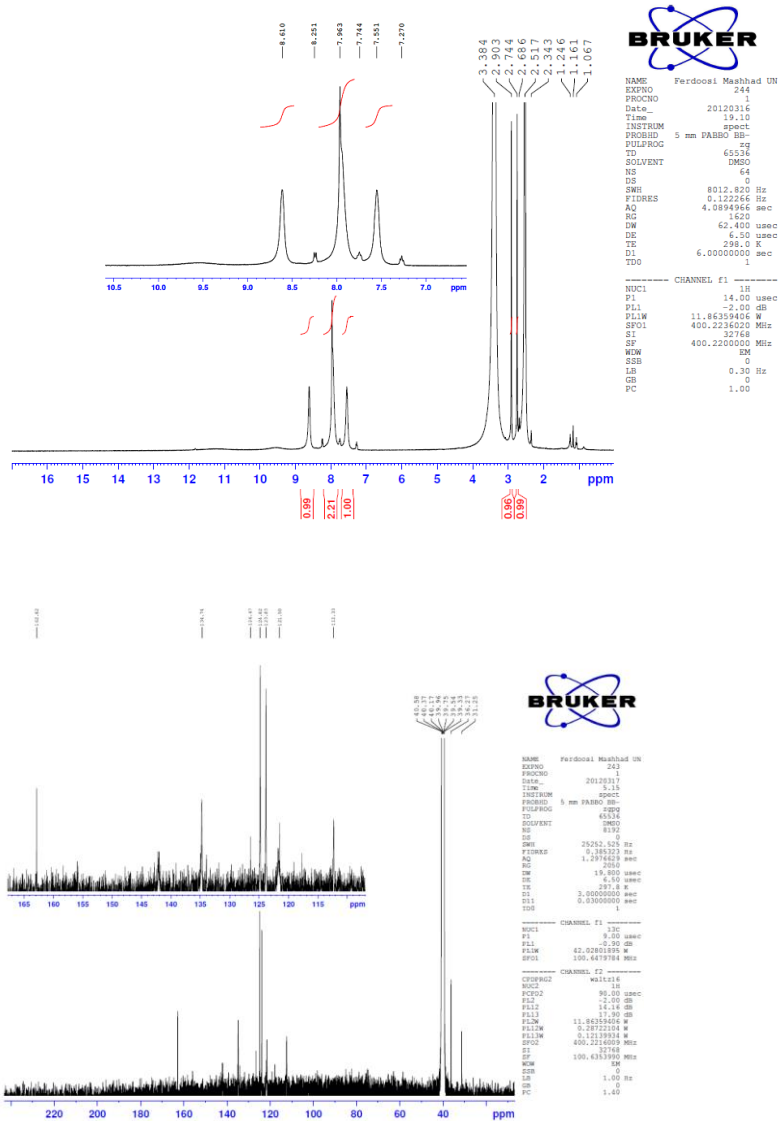


Figure S3. ^{1}H- and ^{13}C-NMR spectra of compound **4**.

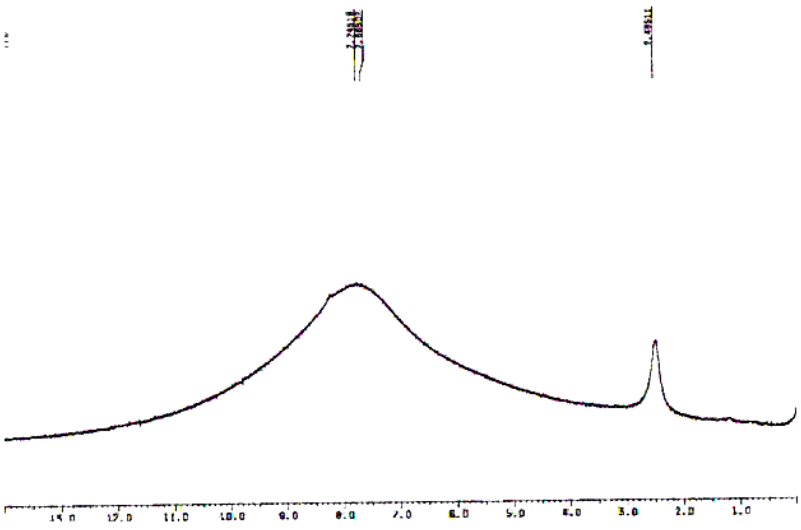


Figure S4. ^{1}H-NMR spectrum of compound **5**.

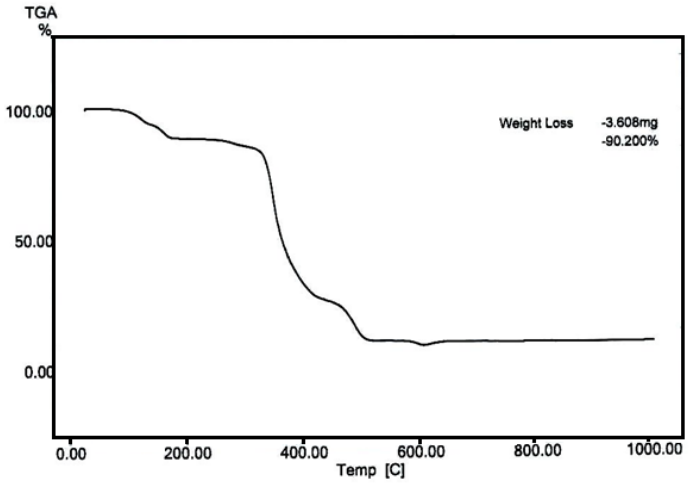


Figure S5. The TG curve of compound 2.

$(H9\text{-aacr})^{+}{}_2[Zn(py\text{-}2,5\text{-}dc)_2(H_2O)_2]\cdot 4H_2O$ (**2**)

A TGA analysis for compound, **2** was performed in the temperature range of 5-1000°C (Fig. S5). The TG curve shows that this compound exhibits three steps of weight loss. The first stages are related to removal of crystallization water molecules and coordinated water molecules in the range 110-160 ˚C (found: 11.35%, calcd: 12.09%), The second stage in the range 340-400 ˚C is related to the release of 9-aacr ligands and one py-2,5-dc ligand (found: 61.32%, calcd:62.02%). The third stage from 450 to 500 ˚C corresponds to the loss of second py-2,5-dc molecule (found: 18.08%, calcd: 18.46%). The final decomposition product is ZnO (found: 9.25%, calcd: 9.10%).

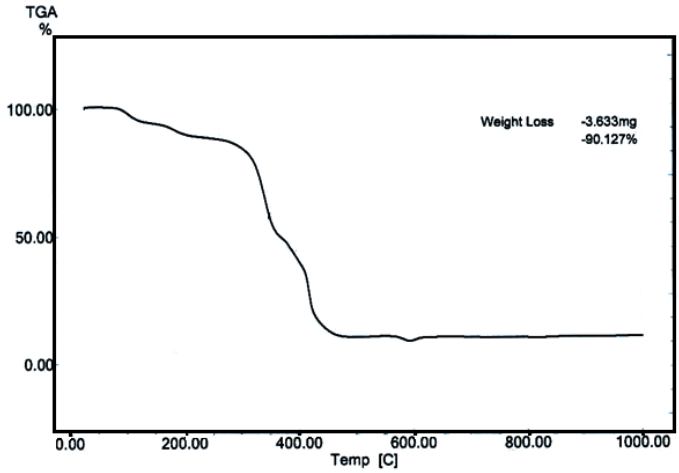


Figure S6. The TG curve of compound **3**.

(H9-aacr)$^{+}{}_2$[Ni(py-2,5-dc)$_2$(H_2O)$_2$]·4H_2O (**3**)

A thermogravimetric analysis for compound, **3**, was performed in the temperature range of 5-1000˚C (Fig. S6). The TG curve shows that this compound exhibits three steps of weight loss. The first stages are related to removal of two coordinated water and four non-coordinated water molecules in the range 95-190˚C (found: 11.39%, calcd: 12.20%). The second step between 300 and 400˚C is related to the release of the 9-aacr ligands (found: 39.97%, calcd: 44.06%). The third stage between 400 and 420˚C corresponds to the loss of py-2,5-dc molecules (found: 39.05%, calcd: 37.26%). The final decomposition product is NiO (found: 9.5%, calcd: 8.4%).

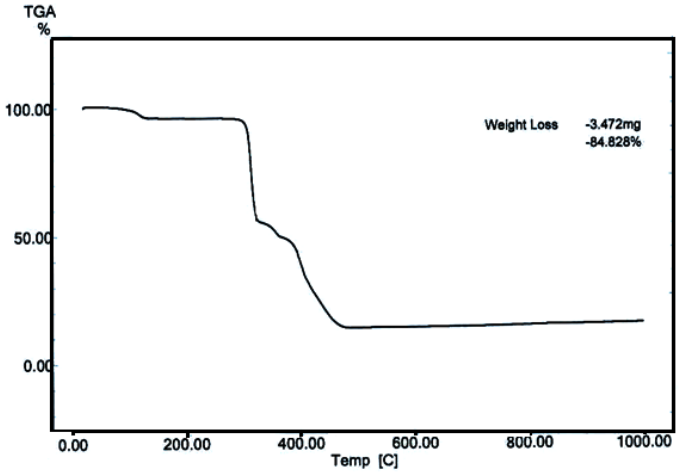


Figure S7. The TG curve of compound **4**.

(*H*9-aacr)$^{+}_{2}$[Cu(py-2,5-dc)$_2$(H$_2$O)]·H$_2$O·DMF (**4**)

The TG curve shows that this compound exhibits four steps of weight (Fig. S7). First step of decomposition of **4** from 100-150˚C are related to removal of coordinated and non-coordinated water molecules (found: 4.13%, calcd: 4.03%). The second step corresponds to the loss of two 9-aacr ligands in the range 315 ˚C (found: 41.00%, calcd: 43.71%). The third stage between 300 and 350˚C are related to the release of DMF molecule (found: 6.08%, calcd: 8.18%). The fourth stage between 350 and 400˚C corresponds to the loss of two py-2,5dc molecules (found: 35.06%, calcd: 35.82%). The final decomposition product is CuO and CO_2 (found: 13.79%, calcd: 13.83%).

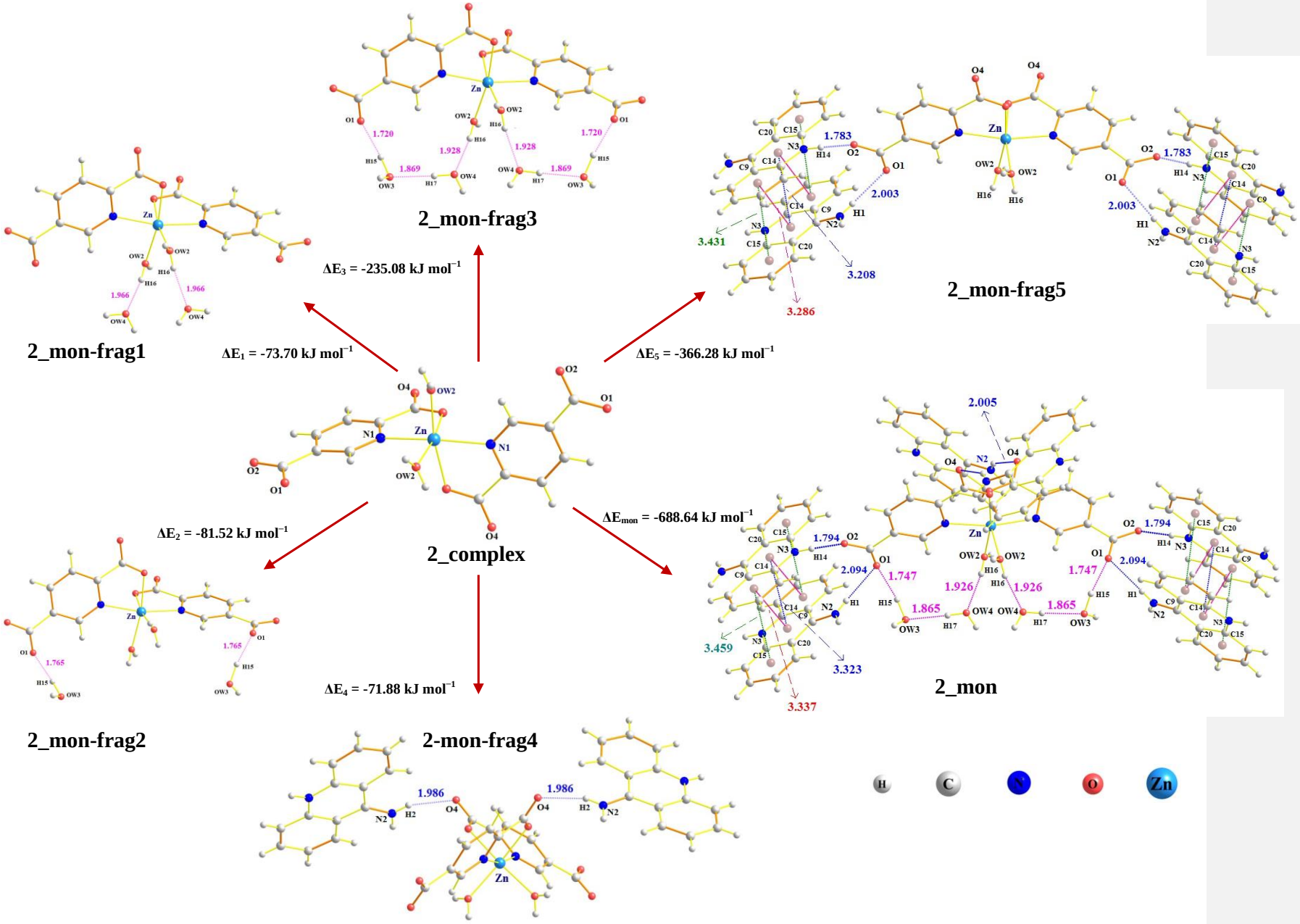
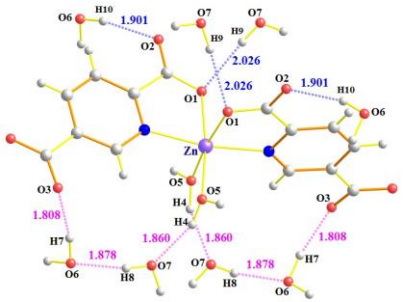
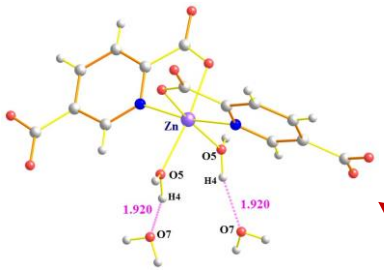


Figure S8. The Formation energy of **2_mon** starting from the $[Zn(py\text{-}2,5\text{-}dc)_2(H_2O)_2]^{2-}$ metal complex (**2_complex**).



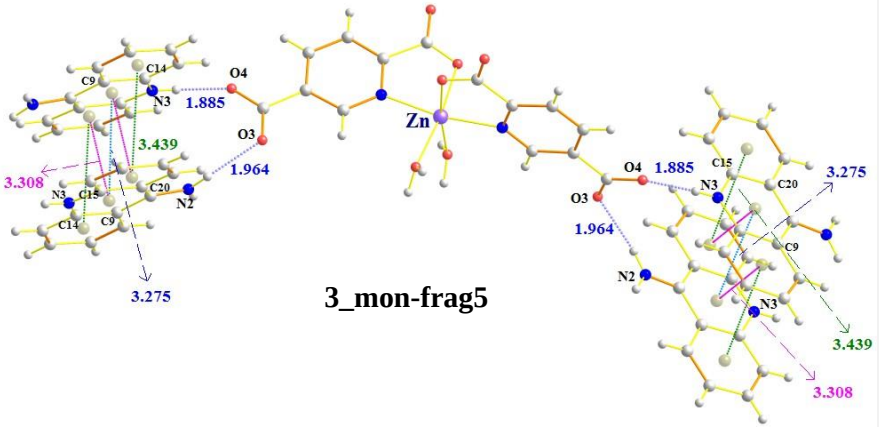
3_mon-frag3

ΔE_3 = -380.56 kJ mol^{-1}



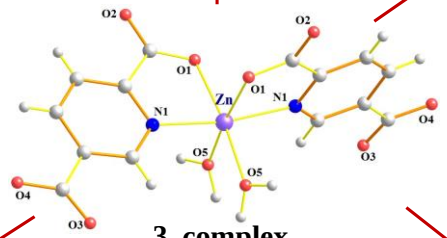
ΔE_1 = -74.64 kJ mol^{-1}

3_mon-frag1



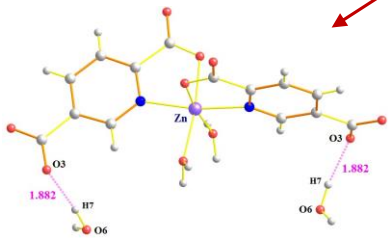
ΔE_5 = -405.70 kJ mol^{-1}

3_mon-frag5



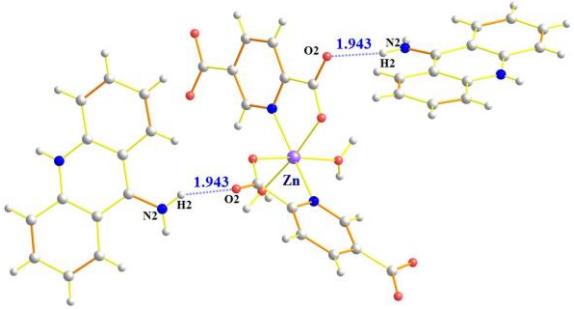
3_complex

ΔE_2 = -76.56 kJ mol^{-1}



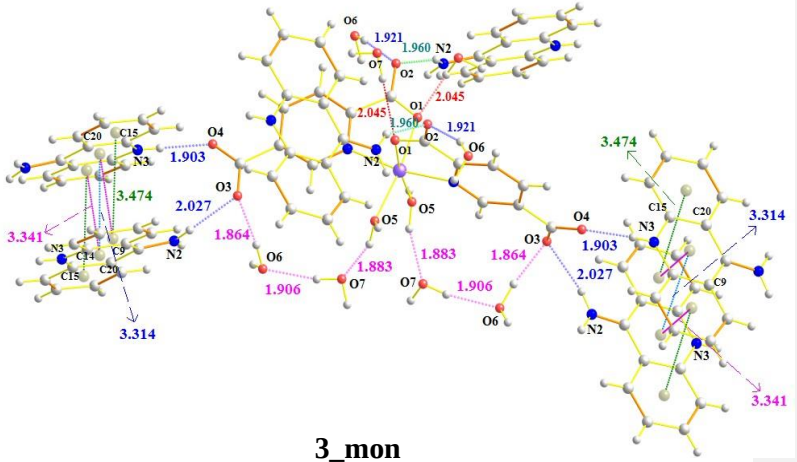
3_mon-frag2

ΔE_4 = -73.74 kJ mol^{-1}



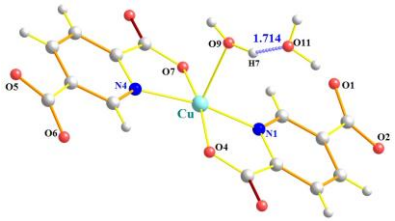
3_mon-frag4

ΔE_{mon}= -860.42 kJ mol^{-1}



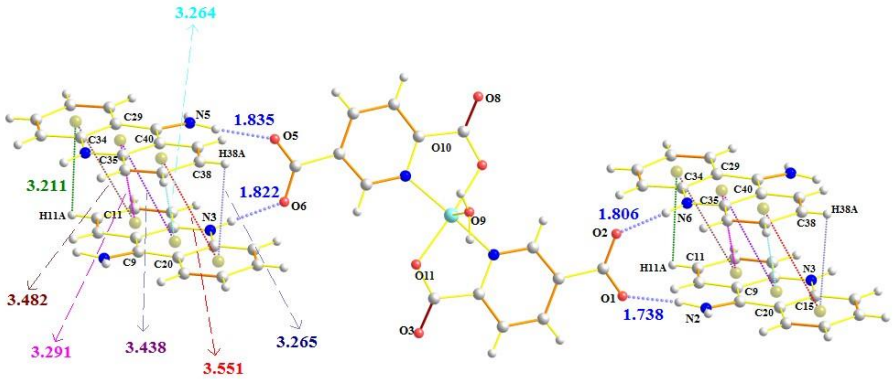
3_mon

Figure S9. The Formation energy of 3_mon starting from the $[Ni(py\text{-}2,5\text{-}dc)_2(H_2O)_2]^{2-}$ metal complex (**3_complex**).



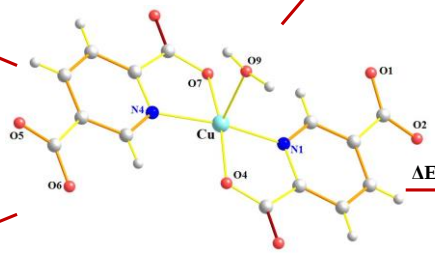
4_mon-frag1

ΔE_1 = -41.88 kJ mol^{-1}



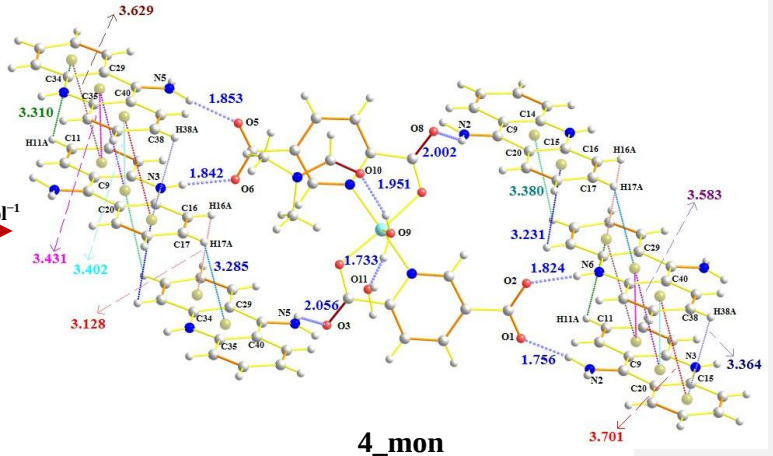
4_mon-frag3

ΔE_3 = -475.14 kJ mol^{-1}



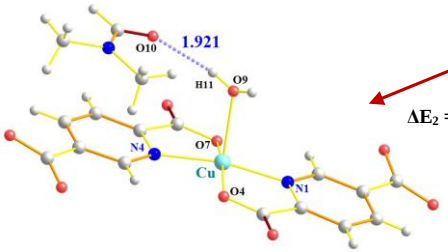
4_complex

ΔE_{mon} = -654.01 kJ mol^{-1}



4_mon

ΔE_2 = -37.20 kJ mol^{-1}



4_mon-frag2

ΔE_4 = -338.07 kJ mol^{-1}

4_mon-frag4

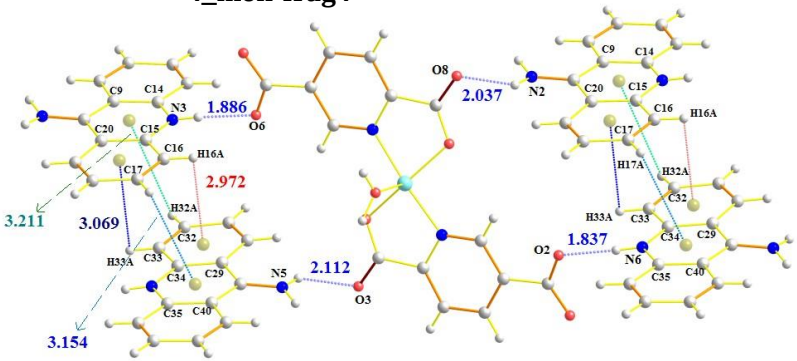
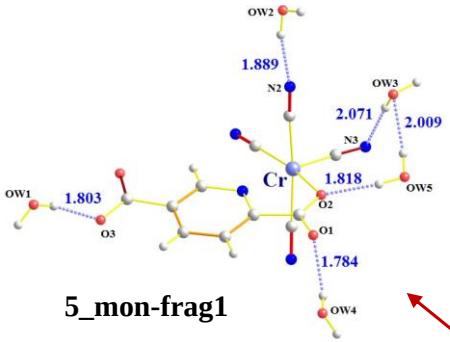
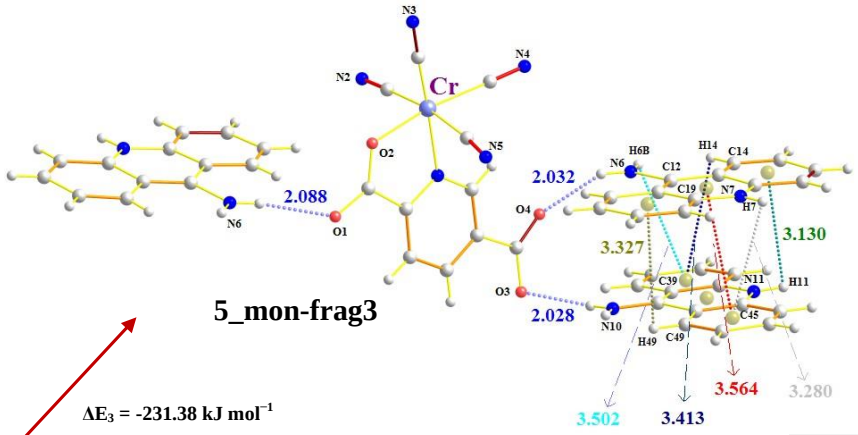


Figure S10. The Formation energy of **4_mon** starting from the $[Cu(py\text{-}2,5\text{-}dc)_2(H_2O)]^{2-}$ metal complex (**4_complex**).



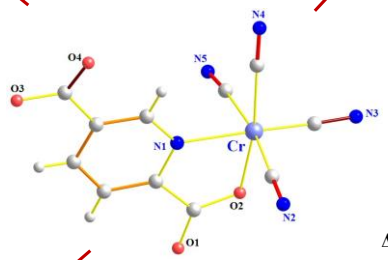
5_mon-frag1

ΔE_1 = -227.93 kJ mol^{-1}

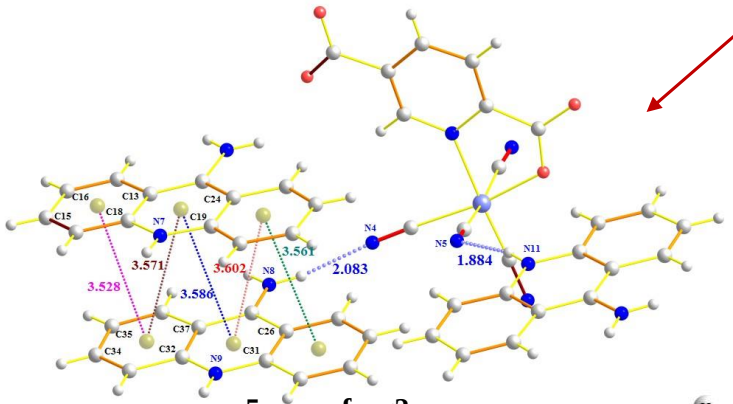


5_mon-frag3

ΔE_3 = -231.38 kJ mol^{-1}

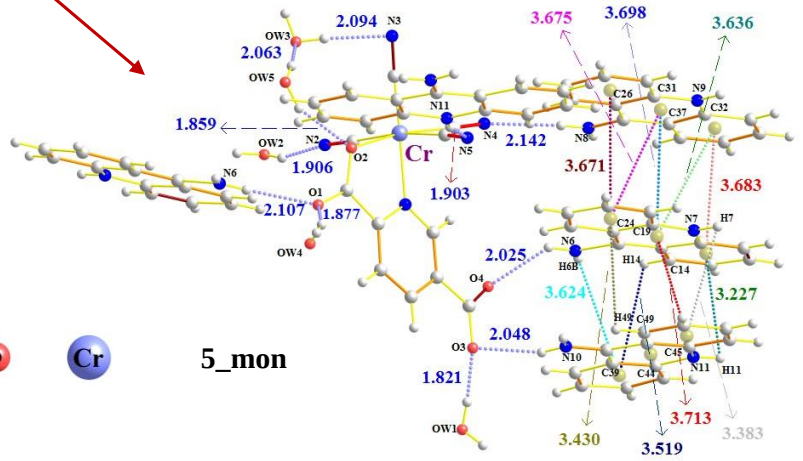


ΔE_2 = -171.23 kJ mol^{-1}



5_mon-frag2

ΔE_{mon} = -608.99 kJ mol^{-1}



5_mon

H C N O Cr

Figure S11. The Formation energy of **5_mon** starting from the $[Cr(CN)_4(py\text{-}2,5\text{-}dc)]^{3-}$ metal complex (**5_complex**)

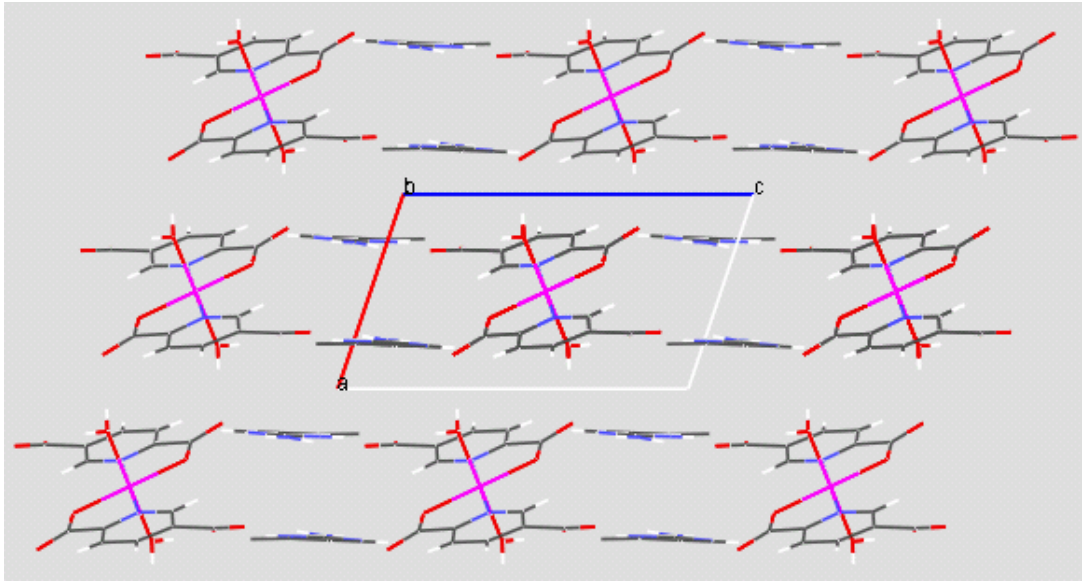


Figure S12. Crystal packing diagram of compound **1** showing a columnar distribution of the anionic and cationic fragments.

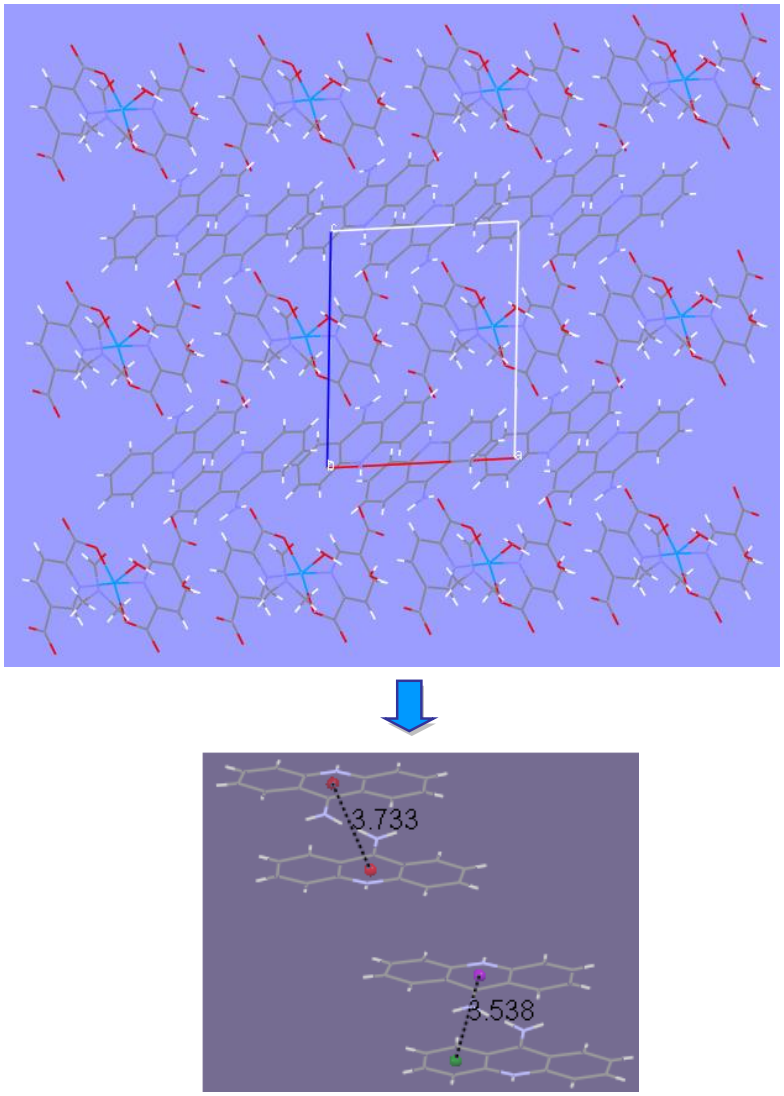


Figure S13. Crystal Packing diagram of the compound **4** and π–π stacking interactions between cationic species centers of (*H*9-aacr)$^{+}$.

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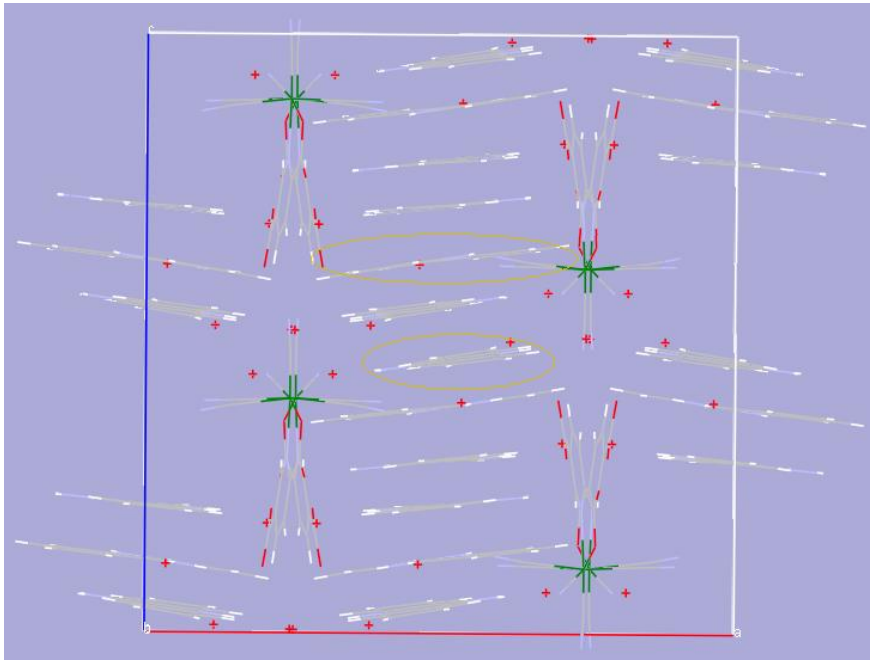

Figure S14. Crystal packing diagram of compound **5** (water molecules omitted) and schematic image of π–π stacking interactions between $(H9\text{-aacr})^{+}$ cationic units viewed along the *b* axis.

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Table S1. Selected experimental and calculated bond lengths (Å) and angles (°) for compounds **1**–**5**.

Compound 1	**Experimental**	**Calculated**		**Experimental**	**Calculated**
Zn−O(1)	2.0733(16)	2.0526	N(1^{i})−Zn−N(1)	180.000(1)	178.12
Zn−N(1)	2.1086(19)	2.0882	O(1)−Zn−OW(1)	90.99(7)	87.32
Zn−OW(1)	2.1671(17)	2.1453	N(1)−Zn−OW(1)	91.51(7)	90.37
O(1^{i})−Zn−O(1)	180.000(1)	175.26	O(1)−Zn−OW(1^{i})	89.01(7)	88.30
O(1)−Zn−N(1^{i})	100.55(7)	98.36	N(1)−Zn−OW(1^{i})	88.49(7)	90.28
O(1)−Zn−N(1)	79.45(7)	74.67	OW(1)−Zn−OW(1^{i})	180.0	179.04
Compound 2					
Zn−OW(1)	2.095(2)	2.107	O(3^{i})−Zn−O(3)	88.45(11)	89.70
Zn−O(3)	2.1140(19)	2.095	OW(1)−Zn−N(1)	91.90(8)	90.43
Zn−N(1)	2.136(2)	2.127	O(3^{i})−Zn−N(1)	92.74(8)	93.72
OW(1^{i})−Zn−OW(1)	90.37(14)	88.56	O(3)−Zn−N(1)	78.45(8)	75.08
OW(1^{i})−Zn−O(3)	91.40(9)	95.06	OW(1)−Zn−N(1^{i})	96.71(8)	92.33
OW(1)−Zn−O(3)	170.33(7)	167.39	OW(1)−Zn−N(1)	91.90(8)	91.03
Compound 3					
Ni−O(1)	2.0679(18)	2.0582	O(1) −Ni−OW(1)	172.67(7)	173.22
Ni−N(1)	2.080(2)	2.0588	N(1) −Ni−OW(1)	92.41(8)	89.03
Ni−OW(1)	2.081(2)	2.0590	O(1) −Ni−OW(1^{i})	90.96(8)	91.36
O(1)−Ni−O(1^{i})	88.47(10)	87.60	N(1) −Ni−OW(1^{i})	94.64(8)	95.58
O(1)−Ni−N(1^{i})	92.47(8)	91.90	OW(1) −Ni−OW(1^{i})	90.53(12)	88.46
O(1)−Ni−N(1)	80.31(8)	79.55	O(1) −Ni−OW(1)	172.67(7)	173.87
Compound 4					
Cu−O(4)	1.959(3)	1.977	N(1)−Cu−N(4)	168.58(11)	172.45
Cu−O(7)	1.960(3)	1.982	O(4)−Cu−OW(1)	98.90(10)	99.37
Cu−N(1)	1.972(3)	1.985	O(7)−Cu−OW(1)	94.02(10)	97.52
Cu−N(4)	1.975(3)	1.982	N(1)−Cu−OW(1)	99.12(10)	97.20
Cu−OW(1)	2.204(2)	2.216	N(4)−Cu−OW(1)	92.30(10)	95.16
O(4)−Cu−O(7)	166.96(10)	165.30			
O(4)−Cu−N(1)	83.69(11)	85.49			
O(7)−Cu−N(1)	96.10(11)	92.82			
O(4)−Cu−N(4)	94.51(11)	93.87			
O(7)−Cu−N(4)	83.10(11)	84.91			
Compound 5					
Cr(01)–C(9)	1.683(5)	1.667	C(9)–Cr(01)–N(1)	174.6(2)	177.18
Cr(01)–O(2)	1.959(4)	1.940	O(2)–Cr(01)–N(1)	79.06(16)	82.90
Cr(01)–C(8)	2.048(7)	2.028	C(8)–Cr(01)–N(1)	87.8(2)	86.22
Cr(01)–C(10)	2.065(7)	2.047	C(10)–Cr(01)–N(1)	92.3(2)	92.06
Cr(01)–C(11)	2.076(6)	2.057	C(11)–Cr(01)–N(1)	84.25(19)	86.57
Cr(01)–N(1)	2.100(4)	2.083	C(9)–Cr(01)–O(2)	96.6(2)	93.35
C(9)–Cr(01)–C(8)	95.3(2)	97.13			
O(2)–Cr(01)–C(8)	88.4(2)	85.10			
C(9)–Cr(01)–C(10)	91.9(2)	92.82			
O(2)–Cr(01)–C(10)	171.15(19)	173.49			
C(9)–Cr(01)–C(11)	93.2(2)	96.64			
O(2)–Cr(01)–C(11)	87.2(2)	90.38			
C(8)–Cr(01)–C(11)	171.5(2)	175.50			
C(10)–Cr(01)–C(11)	90.1(2)	92.24			

[1]Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1. [2]Symmetry code: (i) −*x*+1, *y*, −*z*+3/2. [3]Symmetry code: (i) −*x*, *y*, −*z*−1/2.

Table S2. The Non-Covalent Interactions Distances (Å), Angles (º), and Binding Energies (kcal mol^{-1}) of **1_mon** to **5_mon** calculated with B3LYP-D/ triple—ζ 6-311+G(*d*, *p*).

Interactions	d(H···A)	< (DHA)	Binding Energy	Interactions	d(H···A)	< (DHA)	Binding Energy
1_mon							
N_4–H_4···O_2	1.891	170.63	37.73	N_3–H_6···O_4	1.773	175.43	40.24
N_4–H_5···O_3	1.767	177.11	40.38				
2_mon							
N_2–H_1···O_1	2.094	155.67	33.57	OW_4–H_{17}···OW_3	1.865	177.28	39.04
N_3–H_{14}···O_2	1.794	173.20	40.56	$\pi_{C15\text{-}C20}$···$\pi_{C9\text{-}C14}$	3.495	180.00	20.83
N_2–H_2···O_4	2.005	149.51	36.31	$\pi_{C8\text{-}N3}$···$\pi_{C9\text{-}C14}$	3.337	180.00	21.82
OW_3–H_{15}···O_1	1.747	161.34	41.07	$\pi_{N3\text{-}C15}$···$\pi_{N3\text{-}C15}$	3.323	180.00	20.66
OW_2–H_{16}···OW_4	1.926	176.70	37.81				
3_mon							
N_3–H_3···O_4	1.903	173.26	38.26	O_7–H_9···O_1	2.045	176.31	35.61
N_2–H_1···O_3	2.027	154.30	35.92	O_7–H_8···O_6	1.906	169.14	38.20
N_2–H_2···O_2	1.960	151.32	37.15	$\pi_{C15\text{-}C20}$···$\pi_{C9\text{-}C14}$	3.474	180.00	20.96
O_5–H_4···O_7	1.883	155.29	38.67	$\pi_{N3\text{-}C15}$···$\pi_{C9\text{-}C14}$	3.341	180.00	21.79
O_6–H_7···O_3	1.864	168.75	39.06	$\pi_{N3\text{-}C15}$··· $\pi_{N3\text{-}C15}$	3.314	180.00	21.97
O_6–H_{10}···O_2	1.921	154.94	37.90				
4_mon							
N_6–H_4···O_2	1.824	173.80	39.92	C_{17}–H_{17A}···$\pi_{N6\text{-}C34}$	3.285	100.25	22.16
N_2–H_3···O_1	1.756	160.35	41.46	C_{33}–H_{33A}···$\pi_{C15\text{-}C20}$	3.231	88.37	22.53
N_5–H_5···O_5	1.853	164.62	39.29	C_{16}–H_{16A}···$\pi_{C29\text{-}C34}$	3.128	87.12	23.26
N_3–H_1···O_6	1.842	173.74	39.53	C_{32}–H_{32A}··· $\pi_{N3\text{-}C15}$	3.380	101.44	21.54
N_5–H_6···O_3	2.056	146.03	35.40	C_{38}–H_{38A}··· $\pi_{C15\text{-}C20}$	3.364	77.20	21.75
N_2–H_2···O_8	2.002	146.22	36.37	C_{11}–H_{11A}··· $\pi_{C293\text{-}C34}$	3.310	85.17	22.83
O_9–H_{11}···O_{10}	1.951	166.39	37.32	$\pi_{C35\text{-}C40}$···$\pi_{C15\text{-}C20}$	3.701	180.00	19.67

O_9–H_7···O_{11}	1.733	150.43	42.01	$\pi_{C35\text{-}C40}$···$\pi_{N3\text{-}C15}$	3.402	180.00	21.40
$\pi_{N6\text{-}C34}$···$\pi_{C9\text{-}C14}$	3.431	180.00	21.22	$\pi_{N6\text{-}C34}$···$\pi_{N3\text{-}C15}$	3.583	180.00	20.32
$\pi_{C29\text{-}C34}$···$\pi_{C9\text{-}C14}$	3.629	180.00	20.06				
5_mon							
N_8–H_{8B}···N_4	2.142	153.22	33.85	$\pi_{C32\text{-}C37}$···$\pi_{C13\text{-}C18}$	3.683	180.00	19.77
N_6–H_{6A}···O_4	2.025	140.74	35.94	$\pi_{C32\text{-}C37}$···$\pi_{N7\text{-}C19}$	3.636	180.00	19.70
N_{10}–H_{10A}···O_3	2.048	154.29	35.55	$\pi_{N9\text{-}C31}$···$\pi_{C19\text{-}C24}$	3.713	180.00	19.61
N_{11}–H_{11}···N_5	1.903	167.62	38.24	$\pi_{C26\text{-}C31}$···$\pi_{C19\text{-}C24}$	3.671	180.00	19.75
N_6–H_{6B}···O_1	2.107	163.92	34.56	$\pi_{C45\text{-}C50}$···$\pi_{N7\text{-}C19}$	3.675	180.00	19.81
OW_1–H···O_3	1.821	159.03	39.98	$\pi_{N9\text{-}C31}$···$\pi_{N7\text{-}C19}$	3.698	180.00	19.42
OW_2–H···N_2	1.906	172.13	38.21	N_{11}–H_{11}···$\pi_{C13\text{-}C18}$	3.227	165.20	22.49
OW_4–H···O_1	1.877	166.78	38.79	N_7–H_7···$\pi_{C45\text{-}C50}$	3.383	159.83	21.52
OW_5–H···O_2	1.859	164.90	39.16	C_{14}–H_{14}···$\pi_{C39\text{-}C44}$	3.519	168.38	20.69
OW_3–H···N_3	2.094	157.45	34.77	C_{49}–H_{49}··· $\pi_{C19\text{-}C24}$	3.430	169.47	21.23
OW_5–H···OW_3	2.063	168.53	35.29	N_6–H_{6B}···$\pi_{C39\text{-}C44}$	3.624	175.39	20.08

Table S3. The Non-Covalent Interactions Distances (Å), Angles (º), and Binding Energies (kcal mol^{-1}) of **1_CN** to **3_CN**, and **2_WCN** to **5_WCN** calculated with B3LYP-D/ triple—ζ 6-311+G(*d*, *p*).

Interactions	d(H···A)	< (DHA)	Binding Energy	Interactions	d(H···A)	< (DHA)	Binding Energy
1_CN							
N_4–H_4···O_2	1.910	162.24	37.70	N_3–H_6···O_4	1.791	176.20	40.27
N_4–H_5···O_3	1.749	176.81	40.89	$\pi_{N1\text{-}C6}$···$\pi_{N1\text{-}C6}$	3.493	180.00	20.22
O_5–H_{10}···O_4	1.826	173.47	40.52	C_4–H_2··· $\pi_{N1\text{-}C6}$	3.348	77.39	21.32
O_5–H_9···O_2	1.928	177.56	38.53				
2_CN							
OW_2–H_{12}···O_2	1.954	167.22	37.26	$\pi_{C15\text{-}C20}$···$\pi_{C9\text{-}C14}$	3.487	180.00	21.14
N_2–H_1···O_1	2.124	155.67	34.28	$\pi_{C8\text{-}N3}$···$\pi_{C9\text{-}C14}$	3.328	180.00	22.05
N_3–H_{14}···O_2	1.830	171.24	39.79	$\pi_{N3\text{-}C15}$···$\pi_{N3\text{-}C15}$	3.315	180.00	21.91
N_2–H_2···O_4	2.035	150.51	35.78				
2_WCN							
OW_3–H_{15}···O_1	1.726	166.87	40.48	OW_3–H_{18}···O_4	1.937	159.30	37.59
OW_2–H_{16}···OW_4	1.903	163.47	36.70	OW_2–H_{12}···O_2	1.968,1.947	156.28	36.97,38.04
OW_4–H_{17}···OW_3	1.837	177.12	37.90	$\pi_{N1\text{-}C6}$···$\pi_{N1\text{-}C6}$	3.498	180.00	20.81
OW_4–H_{19}···O_3	2.104	171.50	34.61				

3_CN							
N_3–H_3···O_4	1.922	174.64	37.88	$\pi_{N1\text{-}C6}$···$\pi_{N1\text{-}C6}$	3.561	180.00	20.45
N_2–H_1···O_3	2.050	153.27	35.51	$\pi_{C15\text{-}C20}$···$\pi_{C9\text{-}C14}$	3.439	180.00	21.17
N_2–H_2···O_2	1.981	148.15	36.75	$\pi_{N3\text{-}C15}$···$\pi_{C9\text{-}C14}$	3.308	180.00	22.01
O_5–H_5···O_4	1.876,1.952	171.39	38.81,37.30	$\pi_{N3\text{-}C15}$··· $\pi_{N3\text{-}C15}$	3.281	180.00	22.19
3_WCN							
O_5–H_5···O_4	1.953	174.27	37.28	O_7–H_9···O_1	2.024	177.32	35.28
O_5–H_4···O_7	1.869	157.12	38.03	O_7–H_8···O_6	1.882	169.03	37.84
O_6–H_7···O_3	1.859	167.29	38.73	$\pi_{N1\text{-}C6}$···$\pi_{N1\text{-}C6}$	3.316	180.00	21.72
O_6–H_{10}···O_2	1.920	155.75	37.53	C_4–H_{4A}···$\pi_{N1\text{-}C6}$	3.856	65.92	16.38
4_WCN							
O_9–H_7···O_{11}	1.708	150.94	43.64	O_{11}–H_{12}···O_1	1.856	159.23	40.83
5_WCN							
OW_1–H···N_4	2.038	161.44	35.70	OW_5–H···O_2	1.980	161.43	36.48
OW_5–H···OW_1	1.983	169.97	36.81	N_8–H_{8A}···OW_5	2.209	162.75	32.46
OW_1–H···OW_5	2.048	160.68	33.85	OW_3–H···N_3	2.133	173.83	33.83
OW_1–H···O_3	1.839	159.89	39.59	OW_2–H···N_2	2.011	176.30	35.90
N_{10}–H_{10B}···OW_2	2.040	151.61	34.78	N_8–H_{8B}···N_4	2.078	154.32	34.74
OW_2–H···OW_3	1.969	171.16	36.27	N_7–H_7···OW_4	1.827	168.50	39.35
OW_3–H···OW_2	1.966	170.25	36.82	OW_4–H···O_1	1.945	170.78	36.98
OW_5–H···OW_3	2.108	169.29	33.32	OW_4–H···O_4	1.812	177.42	39.67

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