Supporting Information

to the paper entitled

Supramolecular Assemblies Involving Anion−π and Lone Pair−π Interactions: Experimental Observation and Theoretical Analysis

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Table S1. Crystal data and structure refinement for compounds **1** and **2**.

Compound	**1**	**2**
Formula	$C_{26}H_{36}N_8O_{18}Cl_2Ni$	$C_{26}H_{36}N_8O_{10}P_2F_{12}Ni$
Mw (g mol^{-1})	878.22	969.28
Crystal system	Triclinic	Triclinic
Space group	*P*ī (No. 2)	*P*ī (No. 2)
a/ Å	7.0471(12)	7.0459(10)
b/ Å	11.314(2)	11.8570(17)
c/ Å	11.747(2)	11.8501(17)
α	86.321(3)º	84.482(2)º
β	83.933(3)º	84.484(2)º
γ	72.684(3)º	72.251(2)º
F(000)	454	494
V/ Å^3	888.6(3)	936.2(2)
Z	1	1
T/*K*	100	100
Theta min-max [˚]	1.9 to 26.4	2.4 to 26.4
λ (Mo Kα)/ Å	0.71073	0.71073
μ (Mo Kα)/ mm^{-1}	0.787	0.728
Crystal Size [mm^3]	0.40 × 0.45 × 0.50	0.20 × 0.45 × 0.50
*R*1, $I > 2\sigma(I)$ (all)	0.0340	0.0292
w*R*2, $I > 2\sigma(I)$ (all)	0.0791	0.0783
S (GOF)	0.97	1.04
Total reflections	7093	7510
Independent reflections (R_{int})	3571 (0.049)	3768 (0.014)
Observed data [$I > 2\sigma(I)$]	2921	3573
Min. and max. resd. dens. [e/ Å^3]	−0.38, 0.56	−0.36, 0.51

Table S2. Selected bond lengths (Å) and angles (deg) for **1**.

Ni(1)–O(1)	2.0137(15)	O(4)–C(3)	1.283(3)
Ni(1)–O(4)	2.0051(15)	O(3)–C(3)	1.232(2)
Ni(1)–O(5)	2.0949(18)	C(1)–C(2)	1.513(3)
O(1)–C(1)	1.275(3)	C(2)–C(3)	1.522(3)
O(2)–C(1)	1.247(3)		
O(1)–Ni(1)–O(4)	90.81(6)	Ni(1)–O(4)–C(3)	128.39(13)
O(1)–Ni(1)–O(5)	94.38(7)	O(4)–C(3)–O(3)	123.10(19)
O(1)–Ni(1)–O(4)$^{\#}$	89.19(6)	C(1)–C(2)–C(3)	120.11(18)
O(1)–Ni(1)–O(5)$^{\#}$	85.62(7)	O(1)–C(1)–O(2)	122.22(19)
O(4)–Ni(1)–O(5)	91.96(6)	O(4)–C(3)–C(2)	119.38(18)
O(4)–Ni(1)–O(5)$^{\#}$	88.05(6)	O(1)–C(1)–C(2)	119.05(19)
Ni(1)–O(1)–C(1)	127.11(13)	O(4)–C(3)–C(2)	119.38(18)

Symmetry code: # = 2−x, 1−y, 2−z

Table S3. Selected bond lengths (Å) and angles (deg) for **2**

Ni(1)–O(1)	2.0218(12)	O(4)–C(3)	1.2841(19)
Ni(1)–O(4)	1.9971(11)	O(3)–C(3)	1.2344(19)
Ni(1)–O(5)	2.0878(14)	C(1)–C(2)	1.520(2)
O(1)–C(1)	1.2704(19)	C(2)–C(3)	1.525(2)
O(2)–C(1)	1.253(2)		
O(1)–Ni(1)–O(4)	91.10(5)	Ni(1)–O(4)–C(3)	129.30(10)
O(1)–Ni(1)–O(5)	94.56(5)	O(4)–C(3)–O(3)	123.00(15)
O(1)–Ni(1)–O(4)$^{\#}$	88.90(5)	C(1)–C(2)–C(3)	120.20(14)
O(1)–Ni(1)–O(5)$^{\#}$	85.44(5)	O(1)–C(1)–O(2)	122.02(14)
O(4)–Ni(1)–O(5)	92.03(5)	O(4)–C(3)–C(2)	120.08(13)
O(4)–Ni(1)–O(5)$^{\#}$	87.97(5)	O(1)–C(1)–C(2)	120.05(13)
Ni(1)–O(1)–C(1)	127.52(10)	O(4)–C(3)–C(2)	120.08(13)

Symmetry code: # = 2−x, 1−y, 2−z

Figure S1. Schematic representation of the reaction pathways used to determine the dimerization energies E_1 and E_2 for monomers A) **M5** and B) **M6**. The two noncovalent forces (H-bonding and lp–π interactions) responsible for the formation of the dimers **D5** and **D6** are indicated.

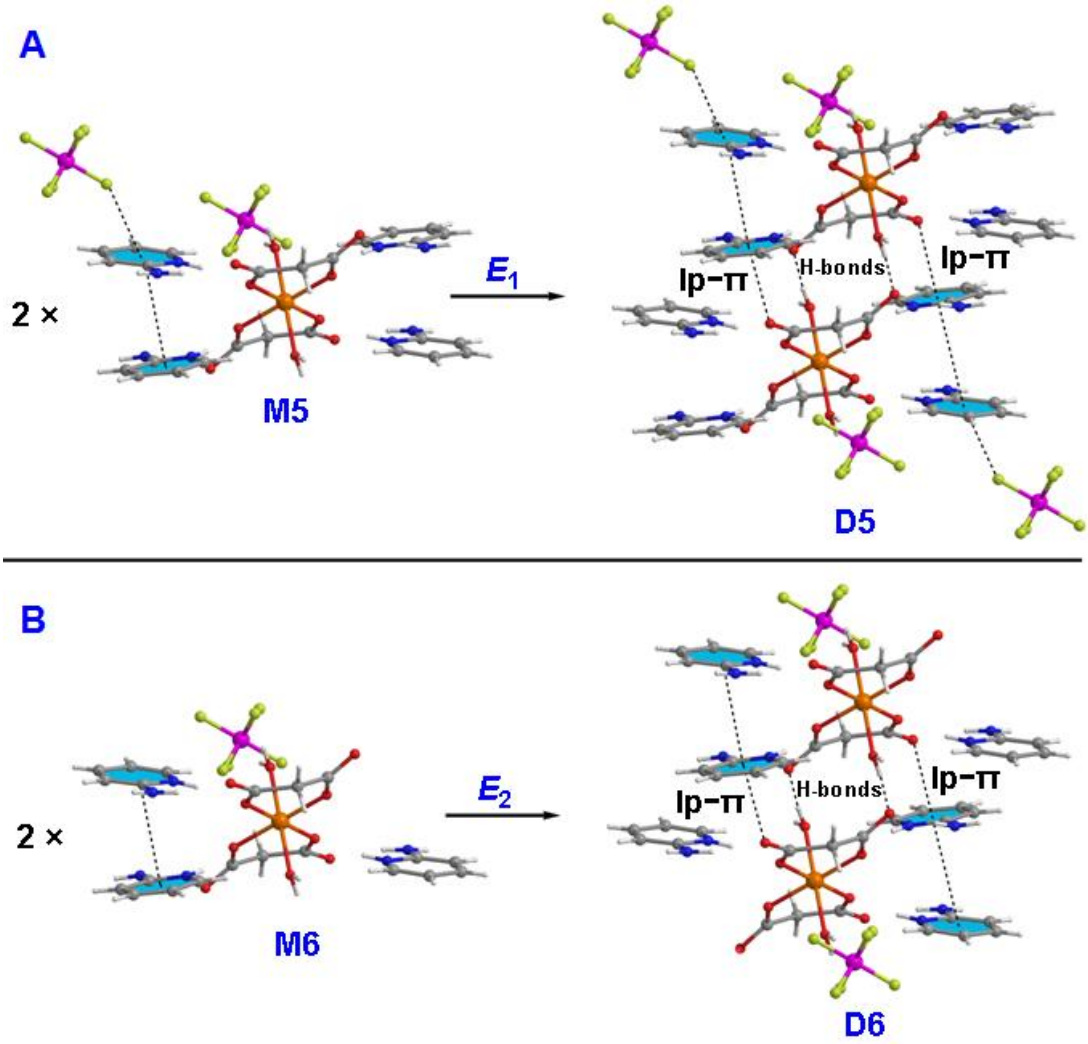

Figure S2. Schematic representation of the reaction used to determine the dimerization energies E_3 and E_4 for monomers A) **M7** and B) **M8**. The two noncovalent forces (H-bonding and lp–π interactions) responsible for the formation of the dimers **D7** and **D8** are indicated.

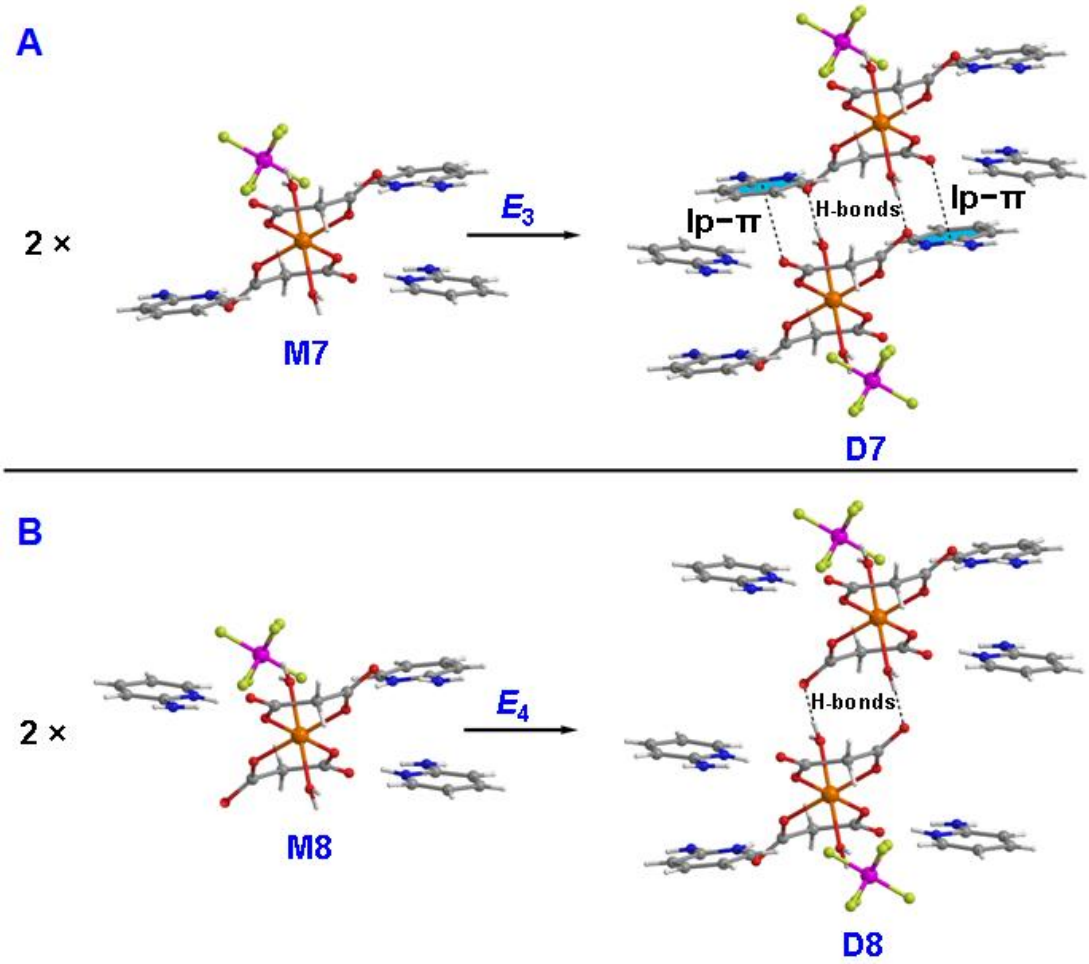

Figure S3. TG plots of compounds **1** and **2**.