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Supplementary Information for

Simple lattice model of surface-confined metal-organic networks consisting of linear nitrogen-bearing molecules and transition metals

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Details of DFT calculations

We have parametrized the developed lattice model using density functional theory (DFT) within the framework of the GGA/rPBE approximation in the Orca software package. Def2-TZVP basis set and DFT-D4 corrections were used. The threshold for the electronic optimization has been set to 10^{-8} Ha, and geometry optimizations were considered finished when the energy difference was below 5×10^{-6} Ha. All calculations were performed under vacuum conditions with the total charge of the system equal to zero. We considered the following molecules: 1,4-dicyanobenzene (DCB), 4,4′-(1,4-phenylene)dipyridine (BPyB) and deprotonated 4,9-diaminoperylene quinone-3,10-diimine (DPDI). These molecules are allowed to form coordination bonds with Cu and Fe atoms. We have calculated the energy of coordination motifs with the number of coordinated molecules from 2 to 6. In the case of four or more molecules, we performed constrained optimization, in which the geometric centers of the benzene rings of the molecules were fixed in one plane. In our calculations the energy of each configuration corresponds to the optimal distance between the linker molecule and the metal atom in vacuum.

Further, we have determined the potential energy E of configurations with N coordinated molecules by subtracting the optimal energy of molecules (E_{Mol}) and metal atom (E_{Me}) from the total energy (E_{tot}) of the configuration:

$$E_N = E_N^{tot} - N \cdot E_{Mol} - E_{Me}$$

The energy w of coordination bonding and the energy ε of intermolecular interactions were calculated from the expression:

$$E_N = N \cdot w + N \cdot \varepsilon_N$$

Since the energy ε_2 of intermolecular interactions in the two-fold configuration of our model is equal to zero, the energy w of the coordination interaction can be found as:

$$w = \frac{E_2}{2}$$

The results of DFT calculations are presented in Tables 1 and 2.

Table 1 – Results of DFT calculations of the potential energy of configurations with 2-6 coordinated molecules. The color highlights the energy w of coordination interaction.

Number of molecules in configuration	Potential energy of configurations E, kJ/mol			
	Cu		Fe	
	total	per molecule	total	per molecule
DCB				

2	-242.2457106	-121.1228553	-293.2434725	-146.6217362
3	-301.6521141	-100.5507047	-405.3498697	-135.1166232
4	-296.0540581	-74.01351454	-439.9862687	-109.9965672
5	-369.0417888	-73.80835776	-435.8280859	-87.16561719
6	-251.8806714	-41.98011191	-405.5149565	-67.58582608
BPyB				
2	-261.9387364	-130.9693682	-297.4341963	-148.7170982
3	-340.0416122	-113.3472041	-431.0877236	-143.6959079
4	-388.8003538	-97.20008844	-528.5787663	-132.1446916
5	-320.2342069	-64.04684139	-457.5142122	-91.50284245
6	-274.7168181	-45.78613636	-399.1686497	-66.52810828
DPDI				
2	-655.8894106	-327.9447053	-951.2505894	-475.6252947
3	-744.6011114	-248.2003705	-1239.824008	-413.2746693
4	-753.0570782	-188.2642695	-1087.752903	-271.9382258
5	-	-	-	-
6	-	-	-	-

Table 2 – The energy ε of intermolecular interactions in configurations with 2-6 coordinated molecules.

Number of molecules in configuration	Energy of intermolecular interactions ε per molecule, kJ/mol	
	Cu	Fe
DCB		
2	0	0
3	20.57215061	11.50511299
4	47.10934076	36.62516905
5	47.31449754	59.45611904
6	79.14274339	79.03591015
BPyB		
2	0	0
3	17.62216416	5.021190287
4	33.76927977	16.57240659
5	66.92252682	57.21425572
6	85.18323185	82.18898988
DPDI		
2	0	0
3	79.74433483	62.3506254
4	139.6804358	203.6870689
5	-	-
6	-	-

The dependences of E and ε on the number of molecules in the configuration have been approximated by linear functions:

$$\frac{E/N}{|w|} = -1 + \frac{k}{|w|} \cdot (N-2), N \geq 2$$

$$\frac{\varepsilon/N}{|w|} = \frac{k}{|w|} \cdot (N-2), N \geq 2$$

The values of the $k/|w|$ parameter of the linear functions for each system are presented in Table 3.

Table 3 – Values of the $k/|w|$ parameter of the linear function.

System	k/|w| value
DCB-Cu	0.16
DCB-Fe	0.13
BPyB-Cu	0.16
BPyB-Fe	0.10
DPDI-Cu	0.23
DPDI-Fe	0.20