Supporting Information For

Syntheses and structural characterizations of di-substituted alkylimido hexamolybdates: An insight on bi-alkylimido functionalization

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1. Computation details

All the calculations presented in this work were carried out with the GAUSSIAN-03 programs package. The structures of each stationary point was fully optimized using the B3LYP method, in combination with the LANL2DZ basis set for molybdate atoms and the 6-31G(d) basis set for rest atoms. To characterize the nature of the stationary points and give the thermal correction to Gibbs free energy, vibrational frequencies of each stationary point were calculated at the same level of theory. The minimum-energy path (MEP) was obtained using intrinsic reaction coordinate (IRC) calculations to confirm the connection of each transition state with the designated equilibrium species.[S1]

In addition, the solvent effect of acetonitrile on the functionalization of hexamolybdate has also been considered. A single point energy calculation was performed by using the integral equation formulism within the polarized continuum model (IEF-PCM)[S2] with the Bondi atomic radii for the united atom topological model at the B3LYP level based on each optimized geometry, with the LANL2DZ basis set for molybdate atoms and the 6-31+G(d, p) basis set for rest atoms denoted as IEFPCM-B3LYP/BS1. The dielectric constant of acetonitrile used in calculations is the default value of the GAUSSIAN-03 program.

2. Hydrogen Bonding

Table S1 Summary of Hydrogen Bonding in Compound **2**

D-H···A	d_{DH}	d_{AH}	d_{DA}	< DHA
C4-H4C···O12	0.96	2.90	3.803(12)	157.5
C7-H7A···O26	0.96	2.81	3.541(12)	133.5
C12-H12C···O21	0.96	2.87	3.803(15)	164.5
C11-H11B···O35	0.96	2.61	3.553(13)	168.0
C16-H16C···O3	0.96	2.80	3.745(11)	169.2
C15-H15B···O8	0.96	2.61	3.560(11)	170.7

Table S2 Summary of Hydrogen Bonding in Compound **3**

D-H···A	d_{DH}	d_{AH}	d_{DA}	< DHA
C1-H1···O3	1.00	2.83	3.72(2)	148.6
C3-H3B···O3	0.99	2.83	3.75(3)	154.4
C5-H5A···O3	0.99	2.93	3.81(3)	149.2

3. References

S1 C. Gonzalez, H. B. Schlegel, *J. Chem. Phys.* **1989**, *90*, 2154.

S2 M. T. Cancès, B. Mennucci, J. Tomasi, *J. Chem. Phys.* **1997**, *107*, 3032; b) M. Cossi, V. Barone, B. Mennucci, J. Tomasi, *Chem. Phys. Lett.* **1998**, *286*, 253; c) B. Mennucci, J.Tomasi, *J. Chem. Phys.* **1997**, *106*, 5151.