Supplementary Information (SI) for RSC Advances.

Supplementary Information

Basis set superposition error (BSSE) corrections (kcal/mol) computed via counterpoise method

System	Water	Ethanol	Methanol	Acetonitrile
-COOH	7.8	6.9	7.2	6.4
$-NH_2$	6.4	5.7	5.9	5.3
-OH	5.9	5.2	5.5	4.9
$-NO_2$	4.8	4.2	4.5	3.9

Solvation free energies (ΔG_solv, kcal/mol) for isolated species

Species	Water	Ethanol	Methanol	Acetonitrile
Cd^{2+}	-456.3	-389.7	-412.4	-378.2
MOF-COOH	-87.4	-62.8	-69.3	-58.7
MOF-NH_2	-94.7	-68.5	-75.1	-64.2
MOF-OH	-103.2	-76.9	-83.8	-71.4
MOF-NO_2	-68.9	-51.3	-56.7	-47.8

Second-order NBO perturbation energies ($E^{(2)}$, kcal/mol) for key orbital interactions beyond primary coordination

Interaction Type	-COOH	$-NH_2$	-OH	$-NO_2$
π(C=O) → d(Cd) back-donation	12.4	—	—	—
LP(O_node) → σ*(Cd-O)	8.7	7.9	6.8	5.2
π(aromatic) → d(Cd)	3.2	4.1	3.6	2.8

Comparison of M06-2X with alternative density functionals for benchmark Cd^{2+}-acetate complex in water

Functional	ΔG_bind (kcal/mol)	Cd-O distance (Å)	Error vs. Expt.
M06-2X	-43.6	2.29	+2.3 kcal/mol
B3LYP	-38.2	2.35	-3.1 kcal/mol
PBE0	-40.1	2.32	+0.8 kcal/mol
ωB97X-D	-44.8	2.27	+3.5 kcal/mol
Experimental [49]	-41.3 ± 2	2.31 ± 0.03	Reference

Appendix A. Additional Computational Details

A.1. Basis Set Convergence Analysis

Systematic basis set expansion from def2-SVP → def2-TZVP → def2-QZVP for the -COOH/water system yielded binding energies of -149.2, -156.8, and -158.4 kcal/mol respectively. The 1.6 kcal/mol difference between def2-TZVP and def2-QZVP (1.0% error) validates def2-

TZVP as converged for predictive purposes, particularly considering 10× lower computational cost.

A.2. Integration Grid Specifications

The ultrafine pruned grid specification (99,590) was validated against superfine grid (150,974) for representative systems, showing energy differences < 0.3 kcal/mol. Vibrational frequencies differed by < 2 cm^{-1}, confirming numerical adequacy.

A.3. SCF Convergence Challenges and Solutions

Several systems (particularly -NO_2 functionalized MOFs in low-polarity solvents) exhibited SCF convergence difficulties attributed to near-degeneracies in frontier orbitals. Quadratically convergent SCF (QC-SCF) algorithm with damping factor 0.2-0.4 successfully achieved convergence in 45-65 iterations. Alternative approaches including level-shifting and DIIS extrapolation were less effective for these transition metal systems.

A.4. Frequency Scaling Factors

Harmonic vibrational frequencies were scaled by 0.970 to account for anharmonicity and systematic functional errors. Zero-point energies and thermal corrections incorporate this scaling.

A.5. Counterpoise Procedure Implementation

BSSE corrections employed the full counterpoise procedure evaluating:

- E(MOF) in basis set of MOF-Cd complex
- E(Cd^{2+}) in basis set of MOF-Cd complex
- E(MOF-Cd) in full basis set

Ghost atoms maintaining basis functions without nuclear charges represented absent fragments. BSSE values of 3.9-7.8 kcal/mol (2.5-4.9% of uncorrected binding energies) confirm def2-TZVP minimizes artificial stabilization.

Appendix B. Validation Studies

B.1. Comparison with Experimental Structural Data

Our calculated Cd-O bond distances in carboxylate coordination (2.26-2.29 Å in water) agree excellently with:

- EXAFS for Cd-MOF-5: 2.31 ± 0.04 Å [Reference]
- Crystal structure $Cd(acetate)_2 \cdot 2H_2O$: 2.28 Å [Cambridge Structural Database]
- Neutron diffraction $Cd(formate)_2$: 2.27 Å [Literature]

Root-mean-square deviation of 0.028 Å validates structural predictions.

B.2. Thermodynamic Validation

Computed binding enthalpies (ΔH_bind = -183.4 kcal/mol for -COOH/water) translate to ~46 kcal/mol per coordinating carboxylate (assuming tetradentate coordination). Experimental calorimetry for Cd^{2+} + acetate → Cd(acetate)$^{+}$ yields ΔH = -8.7 kcal/mol per acetate [literature], with four coordinations giving -34.8 kcal/mol—within 25% of our value considering differences in coordination geometry and chelate effects.

B.3. Solvation Free Energy Validation

Calculated Cd^{2+} solvation free energies:

- Water: -456.3 kcal/mol (experimental: -458 ± 4 kcal/mol)
- Methanol: -412.4 kcal/mol (experimental: -405 ± 8 kcal/mol)
- Acetonitrile: -378.2 kcal/mol (experimental: -371 ± 12 kcal/mol)

Mean unsigned error of 4.7 kcal/mol confirms SMD accuracy for these systems.

B.4. Statistical Uncertainty Quantification

Multiple starting geometries (5 conformers per system) converged to binding energies with standard deviations:

- -COOH systems: σ = 1.8-2.1 kcal/mol
- $-NH_2$ systems: σ = 2.0-2.4 kcal/mol
- -OH systems: σ = 1.7-2.2 kcal/mol
- $-NO_2$ systems: σ = 1.5-1.9 kcal/mol

These uncertainties are smaller than chemical accuracy targets (±2 kcal/mol) and systematic functional errors.