

Electronic Supplementary Information

Hirshfeld atom refinement of metal-organic frameworks for accurate positioning of hydrogen atoms and disorder analysis

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1. Preparation of single crystals of ZIF-2

1 mmol (68.1 mg) of imidazole¹ was dissolved in 3 mL of N,N-dimethylformamide (dmf) and the solution was placed in a 10 mL glass vial. After that, a solution of 0.5 mmol (110.7 mg) zinc acetate dihydrate dissolved in 2 mL of propylamine was carefully layered over the imidazole-dmf solution. Single crystals of zinc imidazolate, suitable for X-ray diffraction, were obtained by liquid diffusion after several days of storing the vial at room temperature.

2. Single crystal X-ray diffraction measurement

A good quality single-crystal of investigated compound was selected for X-ray diffraction experiments at 100(2) K. The crystal was mounted on a MiTeGen micro-mount using paratone-N-oil (Figure S1). Diffraction data were collected on an Agilent Technologies SuperNova Dual Source diffractometer equipped with an HyPix-6000HE hybrid pixel 2-dimensional detector with CuK α radiation ($\lambda = 1.54184$ Å) using CrysAlis Pro software.² During the measurement the crystal was positioned 55 mm from the detector. A total number of 882, 4112 and 8798 frames were collected at 0.5° intervals with a counting time of 0.05, 0.10 and 0.50 s, respectively. The analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid was applied.³ The lattice parameters were obtained by least-squares fit to the optimized setting angles of the reflections collected by using the CrysAlis CCD software². Data were reduced using the CrysAlis RED program.²



Figure S1. Selected single-crystal of investigated compound mounted on a MiTeGen micro-mount.

3. Details of fragmentation-based Hirshfeld atom refinement method

The refinement procedure starts by the fragmentation of ZIF-2 crystal structure into separate molecular fragments. In this case, seven distinct molecular fragments were defined, one representing the ZIF structure (shown in Figure 1 from main text). The remaining six fragments represent the three dmf molecules in the asymmetric unit, each present in two disordered configurations. The QM calculations were performed in Orca 5.03. Electron densities were computed for each fragment, initially using the PBE functional with cc-pVDZ basis set. The effect of the crystal field from the atoms surrounding the molecular fragments was simulated by adding multipole functions within a distance of 6 Å from every atom within the molecular fragment. To initially test the HAR method, PBE functional with cc-pVDZ

basis set were used. After each molecular wavefunction calculation, the resulting electron density was used by DiSCaMB⁴ to obtain aspherical atomic scattering factors for a standard least squares refinement in *OLEX2*,⁵ so that the atomic positional and thermal parameters are improved. All non-hydrogen atoms, as well as hydrogen atoms on the imidazolate rings were refined anisotropically, while the hydrogen atoms belonging to the dmf molecules were refined isotropically. Positions of imidazolate hydrogens were refined without restraints, while C-H bond lengths for the dmf hydrogens were restrained to 1.088 Å.

The QM-refinement steps were repeated in a loop until geometry convergence had been reached. Finally, the effect of using different QM methods (ie. Hartree-Fock or density functional theory with B3LYP and PBE) and four basis sets (6-31G, 6-311g, cc-pVDZ and cc-pVTZ) was tested via additional 11 structure refinements (Tables S2-S8).

4. Details of Hirshfeld atom refinement based on PAW densities with periodic boundary conditions

Hirshfeld atom refinement using aspherical atomic scattering factors obtained from periodic theoretical calculations was first implemented in the XHARPy library and for a few model structures, it was shown to yield positions and displacement parameters of hydrogen atoms as accurate as classical HAR with a cluster of charges simulating crystal environment.⁶ The XHARPy library uses the GPAW software^{7,8} to calculate densities derived from real-space projector augmented wave (PAW) densities with three-dimensional periodic boundary conditions. Only the valence electron density is subject to Hirshfeld partitioning, whereas the core density is assigned to the corresponding atom.

The ZIF-2 structure is a challenging case for XHARPy at its current level of development due to disorder and the presence of heavy metal atoms. Since disorder is not implemented in periodic HAR yet, we decided to exclude from refinement the minor disorder component. Using a two k-point grid (the (2, 1, 1) Monkhorst-Pack grid including Γ point) for the first Brillouin zone integration was possible only with the help of high performance computing. The functional employed was PBE. Real space grid spacing was 0.16 Å and the applied convergence criterion for density was 10^{-7} . To overcome technical problems, XHARPy was used to obtain aspherical atomic scattering factors saved in a .tsc file, which was subsequently passed to OLEX2 for a least squares refinement of atomic positions and displacement parameters. Similarly as for fragmentation based HAR, the C-H bonds in the solvent molecules were restrained to the average neutron value of 1.088 Å and the hydrogen atoms were refined isotropically. The positions and ADPs of hydrogen atoms in the imidazolate framework were freely refined. Calculations of atomic scattering factors with periodic boundary conditions followed by least squares refinement were repeated iteratively. Periodic HAR was terminated after 16 cycles since during the last 6 cycles the maximum parameter shift oscillated between 0.063 and 0.067 of the parameter standard uncertainty.

5. Periodic DFT calculations

Periodic DFT calculations were performed in plane-wave DFT code CASTEP20.⁹ The input structure files were prepared using cif2cell software.¹⁰ Given that dmf molecules are disordered in the experimental

crystal structure, and the periodic DFT calculation requires the structural model to be fully ordered, we prepared two separate models: one containing all dmf molecules in the orientation from the major disorder component, and the other corresponding to the minor disordered component. These two structural models were then geometry-optimized and the final geometries were compared with the experimental structures refined by HAR method (see Table S1).

The crystal structures were optimized with respect to atom positions, subject to the symmetry constraints of the *Pbca* space group. The unit cell parameters were fixed at their experimental values. The calculations were performed using the PBE¹¹ functional, combined with Grimme D3¹² dispersion correction. The plane-wave basis set was truncated at 800 eV cutoff. The 1st electronic Brillouin zone was sampled with a $2\pi \times 0.05 \text{ \AA}^{-1}$ k-point grid. Convergence criteria were set with respect to maximum energy change per atom (2×10^{-5} eV), maximum force on atom (0.05 eV \AA^{-1}) and maximum atom displacement (0.001 \AA). The energies of the optimized structures corresponding to the major and minor disorder component are shown in Table S1.

Table S1. Comparison of the energies for the periodic DFT-optimized structures representing the major and minor components of the disorder of dmf molecules. The energy difference between two configurations is $5.818 \text{ kJ mol}^{-1}$ per formula unit, which contains three dmf molecules, or $1.939 \text{ kJ mol}^{-1}$ per dmf molecule.

dmf disorder component	Energy per unit cell / eV	Energy per formula unit / eV	Relative energy per formula unit / kJ mol^{-1}
Major	-94267.205	-5891.700	0.000
Minor	-94266.240	-5891.640	5.818

6. Comparison of Hirshfeld atom refinement parameters with different QM methods.

Table S2. Summary of all refined imidazolate C-H bond lengths at each given QM method and basis set using DiSCaMB software, by standard independent atom model (IAM) or by periodic HAR method using XHARPy software⁶ with the choice of inclusion of disordered dmf molecules, as well as those calculated by periodic DFT. The population standard deviation values are shown in the brackets.

QM method	Disordered dmf	Basis set	C2-H2	C6-H6	C10-H10	C11-H11	C23-H23	C24-H24	C25-H25	C26-H26	C27-H27	C28-H28	C29-H29	C30-H30
PBE - DiSCaMB	yes	6-31G	1.066(17)	1.074(16)	1.074(17)	1.060(19)	1.075(19)	1.081(19)	1.069(17)	1.06(2)	1.096(17)	1.090(18)	1.070(16)	1.080(15)
	yes	6-311G	1.063(17)	1.070(16)	1.069(17)	1.051(19)	1.070(19)	1.075(19)	1.063(17)	1.061(18)	1.092(17)	1.084(18)	1.065(16)	1.075(15)
	yes	cc-pVDZ	1.076(17)	1.086(16)	1.086(16)	1.067(19)	1.086(19)	1.085(19)	1.080(17)	1.07(2)	1.107(17)	1.102(18)	1.073(16)	1.087(15)
	yes	cc-pVTZ	1.078(17)	1.088(16)	1.086(16)	1.067(19)	1.088(19)	1.084(19)	1.081(17)	1.07(2)	1.109(17)	1.100(18)	1.077(15)	1.090(15)
HF - DiSCaMB	yes	6-31G	1.062(17)	1.072(16)	1.071(17)	1.060(19)	1.073(19)	1.077(19)	1.067(17)	1.06(2)	1.094(17)	1.089(18)	1.069(16)	1.078(15)
	yes	6-311G	1.061(17)	1.068(16)	1.065(17)	1.051(19)	1.065(19)	1.073(19)	1.062(17)	1.059(18)	1.090(17)	1.083(18)	1.065(16)	1.074(15)
	yes	cc-pVDZ	1.076(17)	1.083(16)	1.086(16)	1.064(19)	1.086(19)	1.085(19)	1.080(17)	1.07(2)	1.108(17)	1.100(18)	1.073(17)	1.087(15)
	yes	cc-pVTZ	1.078(17)	1.086(16)	1.086(17)	1.066(19)	1.086(19)	1.084(19)	1.083(17)	1.07(2)	1.110(17)	1.099(18)	1.077(15)	1.091(16)
B3LYP - DiSCaMB	yes	6-31G	1.061(17)	1.066(16)	1.063(17)	1.054(19)	1.068(19)	1.070(19)	1.060(17)	1.06(2)	1.092(19)	1.085(18)	1.063(17)	1.074(15)
	yes	6-311G	1.058(17)	1.063(16)	1.059(17)	1.052(19)	1.066(17)	1.068(19)	1.058(17)	1.06(2)	1.089(17)	1.081(18)	1.060(16)	1.071(15)
	yes	cc-pVDZ	1.074(17)	1.079(16)	1.081(17)	1.071(19)	1.084(19)	1.07(2)	1.079(17)	1.07(2)	1.106(19)	1.096(18)	1.068(17)	1.085(16)
	yes	cc-pVTZ	1.077(17)	1.083(16)	1.083(17)	1.073(19)	1.088(19)	1.08(2)	1.082(17)	1.07(2)	1.112(19)	1.097(18)	1.072(17)	1.089(17)
IAM	yes	N/A	0.937(19)	0.954(18)	0.942(17)	0.93(2)	0.96(2)	0.94(2)	0.921(17)	0.95(2)	0.962(17)	0.966(19)	0.937(17)	0.938(17)
DFT	major		1.084	1.085	1.086	1.084	1.083	1.083	1.088	1.081	1.086	1.084	1.085	1.084
	minor		1.084	1.085	1.087	1.084	1.083	1.084	1.087	1.081	1.085	1.084	1.086	1.084
PBE - DiSCaMB	no	cc-pVTZ	1.07(4)	1.09(3)	1.06(3)	1.09(5)	1.08(3)	1.04(4)	1.09(3)	1.06(3)	1.11(4)	1.03(4)	1.08(4)	1.10(3)
IAM	no	N/A	0.93(3)	0.94(3)	0.89(3)	0.97(4)	0.96(4)	0.90(4)	0.93(3)	0.94(3)	0.97(3)	0.92(3)	0.92(3)	0.95(3)
PBE - XHARPy	no	real-space PAW	1.07(4)	1.08(3)	1.06(3)	1.08(5)	1.08(3)	1.03(5)	1.08(4)	1.06(4)	1.11(4)	1.02(4)	1.08(4)	1.09(3)

Table S3. Crystal data and structure refinement details, shared for all HAR calculations. For geometry analysis and refinement statistics for different QM methods and basis sets see Tables S4-S8.

Empirical formula	$C_{12}H_{12}N_8Zn_2 (C_3H_7NO)_3$
Formula weight	618.36
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	<i>Pbca</i>
a / Å	9.63356(3)
b / Å	24.09227(7)
c / Å	24.40968(8)
$\alpha / ^\circ$	90
$\beta / ^\circ$	90
$\gamma / ^\circ$	90
Volume / Å ³	5665.35(3)
Z	8
$\rho_{\text{calc}} / \text{g/cm}^3$	1.450
μ / mm^{-1}	2.445
F(000)	2560
Crystal size / mm ³	0.30 x 0.28 x 0.22
Radiation	CuK α ($\lambda = 1.5406 \text{ \AA}$)
Θ range for data collection / °	4.504 to 50.246
Index ranges	$-12 \leq h \leq 12, -30 \leq k \leq 30, -31 \leq l \leq 30$
Reflections collected	159869
Independent reflections	6081

Table S4. General refinement statistics of using a given QM method and basis set with DiSCaMB software, the standard IAM or periodic HAR method with XHARPy software are summarized here (PBE method with cc-pVTZ is used as a reference). The effects of including disordered dmf molecules are also considered. $R1(I>2 \text{ sigma})$ is the regression coefficient of the least squares fit for the atomic positions to the experimental electron density, $R1(\text{all } I)$ and wR_2 is the discrepancy factor, gof is the goodness of fit and max/min peak is the maximum/minimum atomic peak heights.

QM method	CCDC deposition number	Disordered dmf	Basis set	$R1(I>2 \text{ sigma})$	$R1(\text{all } I)$	$wR_2(I>2 \text{ sigma})$	gof	Residual density / electrons \AA^{-3}	
								peak	hole
PBE - DiSCaMB	2248339	yes	6-31G	0.0224	0.0229	0.0566	1.0946	0.1752	-0.3216
	2248338	yes	6-311G	0.0225	0.023	0.0566	1.0954	0.1805	-0.3235
	2248340	yes	cc-pVDZ	0.0221	0.0226	0.0557	1.0768	0.1721	-0.3164
HF - DiSCaMB	2248333	yes	6-31G	0.0219	0.0225	0.0559	1.0822	0.1864	-0.3043
	2248332	yes	6-311G	0.0219	0.0224	0.0557	1.0785	0.1861	-0.2931
	2248334	yes	cc-pVDZ	0.0216	0.0222	0.0551	1.0662	0.177	-0.3032
	2248335	yes	cc-pVTZ	0.0217	0.0222	0.0551	1.0672	0.1792	-0.3001
B3LYP - DiSCaMB	2248320	yes	6-31G	0.0223	0.0228	0.0565	1.0935	0.1774	-0.3174
	2248319	yes	6-311G	0.0224	0.0229	0.0565	1.0932	0.1814	-0.3187
	2248321	yes	cc-pVDZ	0.0219	0.0225	0.0555	1.0747	0.17	-0.3106
	2248322	yes	cc-pVTZ	0.0220	0.0226	0.0555	1.0742	0.1766	-0.3280
IAM	2263423	yes	N/A	0.0275	0.0280	0.0723	1.0475	0.3000	-0.4457
IAM	2263462	no	N/A	0.0434	0.0441	0.1241	1.0368	1.6194	-0.6543
PBE - DiSCaMB	2263454	no	cc-pVTZ	0.0419	0.0426	0.1201	1.0251	1.6409	-0.813
PBE - XHARPy	2263422	no	real-space PAW	0.0418	0.0426	0.1225	1.0444	1.6578	-0.8149

Table S5. Statistics for comparison of imidazolate C-H bond lengths, using various QM methods and basis sets with DisCaMB software, IAM or periodic HAR method with XHARPy software. The effects of inclusion of disordered dmf molecules are also investigated. PBE method with cc-pVTZ refinement was used as the reference for bond lengths. $|R_x - R_r|$ is the average absolute bond length difference compared to the reference bond length; sd is the population standard deviation; wRMSD(ΔR) is the weighted root mean squared deviant of the imidazolate C-H bond lengths; $R_x - R_r$ is the average bond length difference compared to the reference bond length; R_x / R_r is the average bond length ratio compared to the reference bond length and finally R_x are the averaged bond lengths.

QM method	Disordered dmf	Basis set	$ R_x - R_r $	sd	wRMSD(ΔR)	$R_x - R_r$	R_x / R_r	R_x
PBE - DiSCaMB	yes	6-31G	0.0105	0.0063	0.5046	-0.0105	0.9904	1.0742
	yes	6-311G	0.0146	0.0063	0.6966	-0.0146	0.9865	1.0701
	yes	cc-pVDZ	0.0014	0.0064	0.0764	-0.0011	0.9990	1.0836
HF - DiSCaMB	yes	6-31G	0.0174	0.0064	0.8165	-0.0174	0.9840	1.0673
	yes	6-311G	0.0203	0.0064	0.9481	-0.0203	0.9813	1.0644
	yes	cc-pVDZ	0.0051	0.0066	0.2572	-0.0049	0.9955	1.0798
	yes	cc-pVTZ	0.0028	0.0066	0.1384	-0.0014	0.9987	1.0833
B3LYP - DiSCaMB	yes	6-31G	0.0124	0.0063	0.5911	-0.0124	0.9886	1.0723
	yes	6-311G	0.0167	0.0063	0.7950	-0.0167	0.9846	1.0680
	yes	cc-pVDZ	0.0018	0.0064	0.1033	-0.0015	0.9987	1.0832
	yes	cc-pVTZ	0.0008	0.0064	0.0482	0.0004	1.0004	1.0851
IAM	yes	N/A	0.1394	0.0071	5.7981	-0.1394	0.8715	0.9453
IAM	no	N/A	0.1506	0.0104	4.3199	-0.1506	0.8612	0.9341
PBE - DiSCaMB	no	cc-pVTZ	0.0184	0.0108	0.6713	-0.0113	0.9897	1.0734
PBE - XHARPy	no	real-space PAW	0.0172	0.0111	0.6472	-0.0148	0.9865	1.0699

Table S6. Statistics for comparison of anisotropic imidazolate hydrogen atoms with different QM methods and basis sets using DiSCaMB software or periodic HAR method using XHARPy software with or without disorder of dmf molecules (using PBE method with cc-pVTZ as a reference for ADP values). $|\Delta U_{ij}|$ is the average absolute difference of ADP tensor components; $wRSMD(\Delta U_{ij})$ is the weighted root mean square deviation for components of ADP tensor; U_{ijx}/U_{ijr} is the average ratio of ADP tensor components; S_{12} is the ADP similarity index; V_x/V_r is the ratio of X-ray to reference thermal ellipsoids; sigma is the population standard deviation of the averaged ADP tensor components; and $|\Delta U_{ij}|/|U_{ij}|$ is the ration of average absolute difference of ADP tensor components to average absolute value of ADP tensor components.

QM method	Disordered dmf	Basis set	$ \Delta U_{ij} $	$wRSMD(\Delta U_{ij})$	U_{iix}/U_{iir}	S_{12}	V_x/V_r	sigma	$ \Delta U_{ij} / U_{ij} $
PBE - DiSCaMB	Yes	6-31G	0.0023	0.1973	0.9378	3.7649	0.5158	0.0113	0.0631
	Yes	6-311G	0.0023	0.2090	0.9421	4.5640	0.4842	0.0111	0.0637
	Yes	cc-pVDZ	0.0020	0.1551	0.9464	0.1978	0.8647	0.0114	0.0586
HF - DiSCaMB	Yes	6-31G	0.0030	0.2285	0.9744	0.7509	1.1128	0.0113	0.0778
	Yes	6-311G	0.0030	0.2294	0.9712	0.6656	1.0993	0.0112	0.0787
	Yes	cc-pVDZ	0.0061	0.4622	1.0485	4.2725	1.7618	0.0117	0.1627
	Yes	cc-pVTZ	0.0051	0.3935	1.0906	3.6159	1.9750	0.0118	0.1363
B3LYP - DiSCaMB	Yes	6-31G	0.0020	0.1689	0.9567	1.8150	0.6406	0.0113	0.0559
	Yes	6-311G	0.0020	0.1790	0.9599	2.1188	0.6113	0.0111	0.0549
	Yes	cc-pVDZ	0.0020	0.1547	0.9727	0.3573	1.0386	0.0115	0.0573
	Yes	cc-pVTZ	0.0009	0.0682	1.0283	0.1449	1.1863	0.0114	0.0234
PEB - DisCaMB	No	cc-pVTZ	0.0152	0.7439	1.0482	12.4895	1.0292	0.0224	0.3963
PBE - XHARPy	No	real-space PAW	0.0157	0.7432	1.0920	12.0769	1.1290	0.1290	0.4141

Table S7. Statistics for averaged non-hydrogen atom ADP comparisons using various QM methods and basis sets using DiSCaMB software or periodic HAR method using XHARPy software with the choice of disordered dmf molecules (PBE method with cc-pVTZ refinement is the reference for ADP values). $|U_{ijx} - U_{ijr}|$ is the average absolute difference of ADP tensor components; $wRSMD(\Delta U_{ij})$ is the weighted root mean square deviation for components of ADP tensor and U_{ijx}/U_{ijr} is the average ration of ADP tensor components.

QM method	Disordered		$ U_{ijx} - U_{ijr} $	$wRSMD(\Delta U_{ij})$	U_{ijx}/U_{ijr}
	dmf	Basis set			
PBE - DiSCaMB	Yes	6-31G	0.0007	0.6558	1.0154
	Yes	6-311G	0.0007	0.6522	1.0259
	Yes	cc-pVDZ	0.0003	0.3180	0.9993
HF - DiSCaMB	Yes	6-31G	0.0008	0.6925	0.9948
	Yes	6-311G	0.0009	0.7284	0.9902
	Yes	cc-pVDZ	0.0010	0.7527	0.9605
	Yes	cc-pVTZ	0.0011	0.8050	0.9537
B3LYP - DiSCaMB	Yes	6-31G	0.0006	0.6537	1.0113
	Yes	6-311G	0.0006	0.6220	1.0220
	Yes	cc-pVDZ	0.0004	0.3686	0.9893
	Yes	cc-pVTZ	0.0002	0.1597	0.9914
PBE - DiSCaMB	No	cc-pVTZ	0.0005	0.9025	0.9683
PBE - XHARPy	No	real-space PAW	0.0005	0.7765	0.9704

Table S8. Maximum discrepancies of anisotropic imidazolate hydrogen atoms for each QM method and basis set using DiSCaMB software or by periodic HAR method using XHARPy software with the choice disordered dmf molecules, using PBE method with cc-pVTZ refinement as the reference ADPs. $|U_x - U_r|$ is the average absolute difference of ADP tensor components; S_{12} is the ADP similarity index and min/max V_x/V_r is the maximum/minimum ratio of X-ray thermal ellipsoids to reference thermal ellipsoids.

QM method	Disordered dmf	Basis set	$ U_x - U_r $	atom	wRMSD	atom	S_{12}	atom	min V_x/V_r	atom	max V_x/V_r	atom
PBE - DiSCaMB	Yes	6-31G	0.0028	H23	0.2413	H10	14.6246	H10	0.1971	H10	0.7347	H24
	Yes	6-311G	0.0031	H26	0.2856	H26	15.7841	H28	0.1795	H28	0.7112	H24
	Yes	cc-pVDZ	0.0031	H25	0.2291	H25	0.4993	H30	0.7557	H30	0.9430	H29
HF - DiSCaMB	Yes	6-31G	0.0057	H11	0.3352	H11	2.7395	H6	0.8271	H25	1.6041	H6
	Yes	6-311G	0.0060	H11	0.3505	H11	2.5604	H6	0.8426	H25	1.5780	H6
	Yes	cc-pVDZ	0.0095	H24	0.5704	H24	7.1525	H23	1.3151	H24	2.3711	H28
	Yes	cc-pVTZ	0.0078	H24	0.4908	H26	7.1519	H23	1.4635	H24	2.6402	H28
B3LYP - DiSCaMB	Yes	6-31G	0.0026	H23	0.2133	H10	7.5502	H10	0.3433	H10	0.7985	H6
	Yes	6-311G	0.0028	H11	0.2330	H26	5.6810	H28	0.3970	H28	0.7826	H6
	Yes	cc-pVDZ	0.0029	H24	0.2033	H25	0.6382	H28	0.8957	H30	1.1858	H28
	Yes	cc-pVTZ	0.0012	H26	0.0906	H26	0.4011	H23	1.0958	H24	1.3259	H28
PBE - DiSCaMB	No	cc-pVTZ	0.0334	H28	1.3069	H28	34.8436	H30	0.0353	H30	1.9253	H2
PBE - XHARPy	No	real- space PAW	0.0328	H28	1.2445	H28	23.7639	H28	0.1001	H30	2.1440	H2

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