A Zn-based MOF with honeycomb topology for highly efficient iodine uptake from vapor and liquid phases: synthesis, crystal structure, topology and dual-phase sorption performance

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Table S1. Selected bond lengths (Å) for **FV-Zn1.**

Bond	**d (Å)**
Zn1–O2	1.9670
Zn1–O6	1.9927
Zn1–O3	2.0804
Zn1–O5	2.2373
O1–C00C	1.2516
O2–C00C	1.2665
O3–C5	1.2585
O4–C5	1.2608
C00C–C2	1.5069
C2–C4	1.4028
C3–C4	1.3930
C4–C5	1.5065

Table S2. Selected bond angles (°) for **FV-Zn1.**

Angle (A–B–C)	∠ABC (°)
O1–C00C–C2	119.26
O1–C00C–O2	124.29
O2–C00C–C2	116.45
C00C–C2–C4	122.04
C2–C4–C3	119.30
C2–C4–C5	124.42
C3–C4–C5	116.27
O3–C5–C4	120.08
O3–C5–O4	124.69
O4–C5–C4	114.99
Zn1–O2–C00C	116.60
Zn1–O3–C5	132.61
O2–Zn1–O3	92.01
O2–Zn1–O5	90.69
O2–Zn1–O6	124.41
O3–Zn1–O5	173.70
O3–Zn1–O6	95.59
O5–Zn1–O6	87.56

Table S3. Kinetic parameters for iodine adsorption on **FV-Zn1.**

Kinetic model	Qe,exp (mg g^{-1})	Qe,cal (mg g^{-1})	Rate constant k	R^2
Pseudo-first-order	166.33	–	k_1 (min^{-1})	0.962
Pseudo-second-order	166.33	168.49	k_2 (g mg^{-1} min^{-1})	0.994

The crystallographically independent fragment of **FV-Zn1** consists of a single Zn(II) centre bound to a fragment of the benzene-1,2,4,5-tetracarboxylate ligand (tba) and coordinated oxygen donors. As shown in the asymmetric unit (**Fig. S1**), the aromatic ring (pink) bears a deprotonated carboxylate group that chelates/bridges to the Zn(II) ion (green) through its O atoms (red), while the remaining carboxylate groups of the linker are generated by symmetry in the extended structure. Together with additional O donors (from carboxylate and aqua ligands in the full coordination sphere), this gives a five-coordinate {ZnO_5} environment that propagates through **Zn–O–C–O–Zn** linkages to build up the three-dimensional framework of **FV-Zn1**.

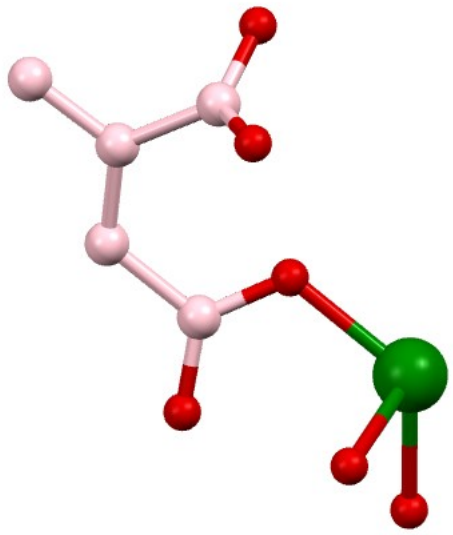

Fig. S1. Asymmetric unit of **FV-Zn1** showing the Zn(II) centre (green) coordinated to a fragment of the benzene-1,2,4,5-tetracarboxylate ligand (pink) through carboxylate O donors (red).

In **Fig. S2**. The 2D representation of **FV-Zn1** shows how the Zn(II) centres (blue spheres) are linked by the benzene-1,2,4,5-tetracarboxylate ligands (pink backbone, red O atoms) into an infinite zigzag array. Each linker bridges between two neighbouring Zn nodes through μ_2-carboxylate groups, giving a repeating Zn–carboxylate–aryl–carboxylate–Zn motif that extends along one crystallographic direction. These zigzag

chains constitute the basic inorganic–organic ribbons that further pack and cross-link to form the full three-dimensional framework of **FV-Zn1**.

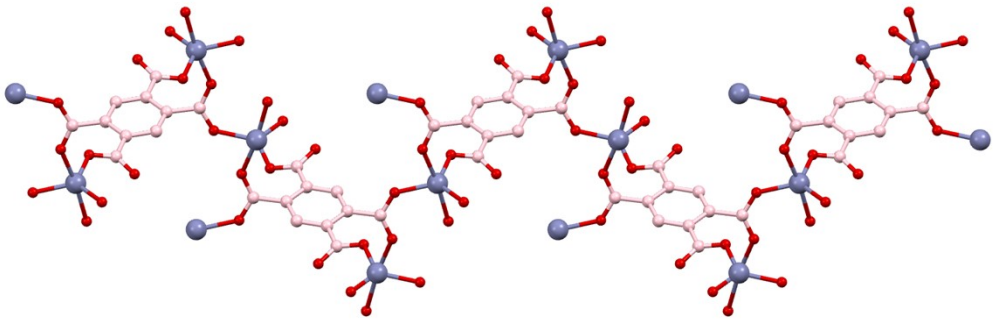

Fig. S2. Zigzag Zn–carboxylate chains in **FV-Zn1**, showing Zn(II) nodes (blue) bridged by benzene-1,2,4,5-tetracarboxylate linkers (pink/red) into an extended 1D motif.

The benzene-1,2,4,5-tetracarboxylate ligand in **FV-Zn1** acts as a rigid tetratopic linker. As shown in the binding-mode illustration, each of the four carboxylate groups is deprotonated and coordinates in a **μ_2-κO:κO′** bridging fashion, with the two oxygen atoms of each –COO^- group binding to two different Zn(II) centres (indicated by the green spheres). In this way the aromatic core remains essentially planar while the four carboxylate "arms" radiate outwards to connect neighbouring ZnO_5 units, allowing the ligand to stitch multiple metal nodes together and propagate the extended Zn–carboxylate framework of **FV-Zn1**. **Fig. S3**

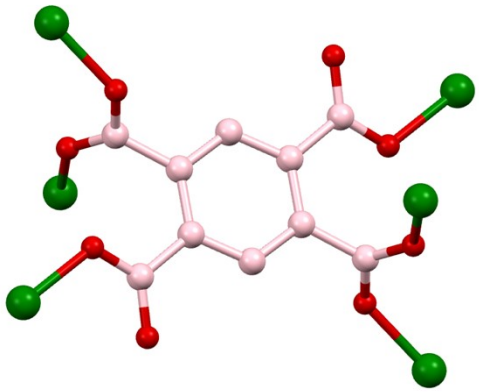

Fig. S3. Binding mode of the benzene-1,2,4,5-tetracarboxylate ligand in **FV-Zn1**, showing each carboxylate group acting as a μ_2-κO:κO′ bridge between neighbouring Zn(II) centres (green).

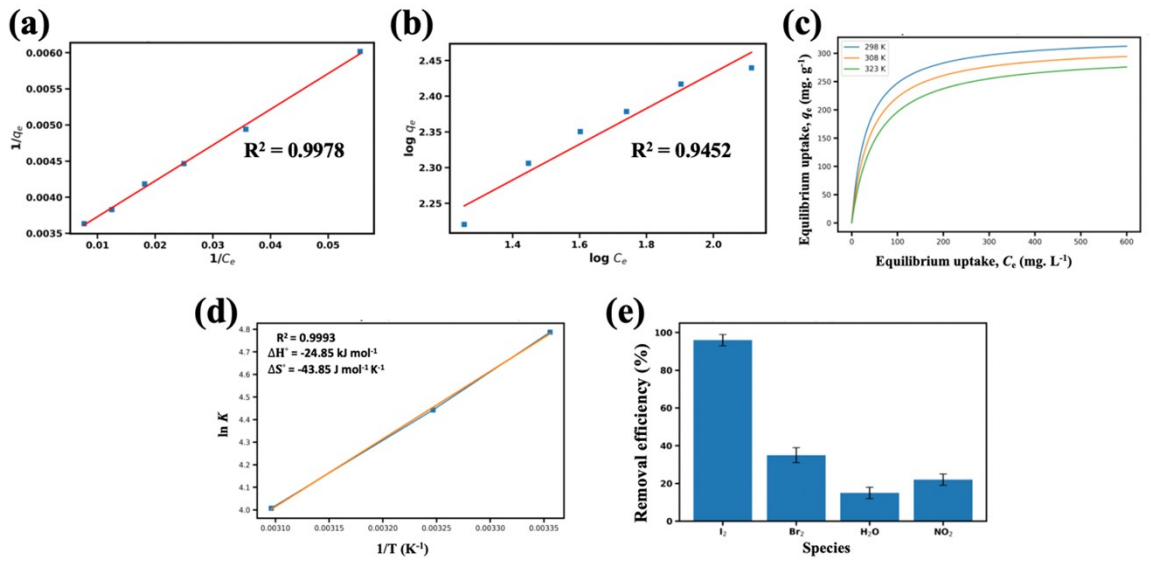

Fig. S4. (a) Langmuir isotherm plot, **(b)** Freundlich isotherm plot, **(c)** variable-temperature adsorption isotherms (298–323 K), **(d)** van't Hoff plot for thermodynamic parameters, and **(e)** competing-species selectivity for iodine uptake by **FV-Zn1**.

Table S4. Isotherm and thermodynamic parameters for iodine adsorption on **FV-Zn1**

Model	**Parameter**	**Value**
Langmuir (298 K)	q_{max} (mg g^{-1})	**310.33**
	K_L (L mg^{-1})	**0.0649**
	R^2	**0.9978**
Freundlich (298 K)	K_F	**85.47**
	n	**3.99**
	R^2	**0.9452**
Thermodynamics (van't Hoff)	ΔH° (kJ mol^{-1})	**−24.85**
	ΔS° (J mol−1 K^{-1})	**−43.85**
	ΔG∘ at 298 K (kJ mol^{-1})	**−11.78**

Table S5. Coordinates of **FV-Zn1**

Atom	x(Å)	y(Å)	z(Å)
Zn	-4.826987	-1.847158	0.470931
O	-2.095881	-2.527897	-0.393832
O	-3.199883	-0.747486	0.359789
O	-3.103937	1.767934	-1.126693
O	-2.433370	2.406434	0.903592
O	-4.794403	-2.167343	-1.743115
H	-4.542082	-2.981675	-1.914122
H	-4.176157	-1.668522	-2.097762
O	-4.834744	-3.829685	0.672005
H	-4.624355	-4.198383	-0.088040
H	-5.646696	-4.101303	0.828882
C	-2.161710	-1.314981	-0.092131
C	-0.942207	-0.446352	-0.262599
C	0.149049	1.701940	-0.382258
H	0.098088	2.650694	-0.372502
C	-1.019976	0.954198	-0.261525
C	-2.303504	1.735795	-0.156127
O	2.545798	3.167612	-0.387076
O	3.649800	1.387200	-1.140697
O	3.553853	-1.128220	0.345785
O	2.883286	-1.766720	-1.684500
C	2.611627	1.954695	-0.688777
C	1.392124	1.086066	-0.518309
C	0.300868	-1.062225	-0.398651
H	0.351828	-2.010980	-0.408406
C	1.469893	-0.314483	-0.519384
C	2.753421	-1.096081	-0.624781
Zn	3.326861	-0.718341	2.372786
O	3.294278	-0.398156	4.586832
H	3.041957	0.416177	4.757839
H	2.676032	-0.896976	4.941479
O	3.334618	1.264186	2.171712
H	3.124230	1.632885	2.931757
H	4.146571	1.535805	2.014835
Zn	-2.876945	1.358055	-3.153694
Zn	4.193673	-3.141527	-2.235682
Zn	5.276903	2.486872	-1.251840
Zn	-3.743756	3.781241	1.454774
O	1.699758	-1.818012	2.483928
O	-5.053979	-1.437278	2.497932
O	5.034825	-1.711995	2.453577
O	-6.534950	-0.853503	0.390140

Table S6. Coordinates of **I_2@FV-Zn1** (mode1).

Atom	x(Å)	y(Å)	z(Å)
Zn	4.879770	1.955382	-0.939866
O	2.162130	1.636760	-2.027557
O	3.227259	1.293790	-0.102849
O	3.067858	-1.313044	1.210612
O	2.389842	0.062204	2.831841
O	4.846811	0.264592	-2.404695
H	4.612813	0.563784	-3.186856
H	4.215935	-0.293497	-2.187080
O	4.934139	3.193946	-2.499965
H	4.729669	2.756197	-3.224145
H	5.752710	3.459982	-2.629652
C	2.200919	1.235482	-0.842655
C	0.961037	0.642270	-0.224954
C	-0.180085	-0.600415	1.499543
H	-0.151072	-1.104760	2.304292
C	1.006359	-0.113502	0.955869
C	2.271808	-0.466214	1.693216
O	-2.610131	-1.358021	2.688464
O	-3.675259	-1.015050	0.763755
O	-3.515858	1.591784	-0.549705
O	-2.837842	0.216535	-2.170935
C	-2.648919	-0.956743	1.503561
C	-1.409038	-0.363530	0.885860
C	-0.266239	0.874177	-0.840786
H	-0.296928	1.383500	-1.643386
C	-1.454359	0.392242	-0.294963
C	-2.719809	0.744954	-1.032310
Zn	-3.291280	3.073712	0.893108
O	-3.258320	4.764502	2.357937
H	-3.024322	4.465311	3.140098
H	-2.627444	5.322592	2.140322
O	-3.345648	1.835149	2.453207
H	-3.141178	2.272898	3.177388
H	-4.164220	1.569112	2.582894
Zn	2.843279	-2.794973	-0.232202
Zn	-4.117977	0.514341	-3.648628
Zn	-5.327771	-1.676643	1.600772
Zn	3.669977	-0.235602	4.309534
O	-1.638768	3.735305	0.056091
O	5.104349	3.437311	0.502948
O	-4.975482	3.704125	0.070272
O	6.563973	1.324970	-0.117030
I	-0.630126	-2.988486	0.056504
I	0.560911	-1.555153	-2.023841

Table S7. Coordinates of **I_2@FV-Zn1** (mode2).

Atom	x(Å)	y(Å)	z(Å)
Zn	4.402468	-1.052576	1.612603
O	2.064365	0.682719	1.174214
O	2.613039	-1.457920	0.903562
O	2.206991	-2.754011	-1.685153
O	1.093768	-4.113270	-0.309453
O	4.798823	0.328427	-0.102423
H	4.762887	1.151809	0.174701
H	4.151486	0.264368	-0.680068
O	4.813797	0.473536	2.826149
H	4.815170	1.214419	2.369027
H	5.629397	0.397299	3.120492
C	1.812080	-0.482906	0.794485
C	0.475202	-0.779553	0.165581
C	-1.028121	-2.187965	-1.090090
H	-1.189468	-2.986255	-1.579504
C	0.241615	-1.952003	-0.568166
C	1.287410	-2.996085	-0.860837
O	-3.655687	-2.737969	-1.918350
O	-4.204362	-0.597330	-1.647699
O	-3.798313	0.698760	0.941017
O	-2.685090	2.058020	-0.434683
C	-3.403402	-1.572344	-1.538621
C	-2.066524	-1.275698	-0.909717
C	-0.560873	0.134237	0.341007
H	-0.401854	0.931005	0.835368
C	-1.832938	-0.103247	-0.175970
C	-2.878732	0.940834	0.116701
Zn	-3.997199	-0.715119	2.454175
O	-4.393554	-2.096123	4.169201
H	-4.357618	-2.919504	3.892077
H	-3.746217	-2.032063	4.746846
O	-4.408528	-2.241231	1.240629
H	-4.409901	-2.982114	1.697751
H	-5.224128	-2.164994	0.946286
Zn	2.405876	-1.340131	-3.198311
Zn	-3.554244	3.820119	-0.209766
Zn	-5.993790	-1.002674	-2.356739
Zn	1.962922	-5.875369	-0.534370
O	-2.207770	-0.309775	3.163216
O	4.203582	-2.466456	3.125761
O	-5.434692	0.525368	3.007186
O	5.839961	-2.293063	1.059592
I	2.372646	2.328824	-0.809348
I	1.705549	4.957015	-0.139691

Table S8. Coordinates of **I_2@FV-Zn1** (mode3).

Atom	x(Å)	y(Å)	z(Å)
Zn	-6.482659	-1.691054	0.369672
O	-3.769619	-2.455326	-0.482067
O	-4.812288	-0.654123	0.308589
O	-4.598543	1.895785	-1.105078
O	-3.929355	2.450611	0.950100
O	-6.434436	-1.950728	-1.852000
H	-6.212169	-2.769369	-2.042972
H	-5.792578	-1.467174	-2.185195
O	-6.570931	-3.676528	0.514600
H	-6.365520	-4.032051	-0.253045
H	-7.394872	-3.919976	0.654272
C	-3.791549	-1.249591	-0.147037
C	-2.536758	-0.425620	-0.278691
C	-1.360434	1.680191	-0.324933
H	-1.374170	2.629583	-0.288995
C	-2.559403	0.976343	-0.238990
C	-3.812446	1.805008	-0.126541
O	1.091959	3.049216	-0.260439
O	2.134628	1.248012	-1.051095
O	1.920883	-1.301895	0.362573
O	1.251695	-1.856721	-1.692605
C	1.113889	1.843481	-0.595468
C	-0.140902	1.019510	-0.463815
C	-1.318839	-1.085248	-0.422912
H	-1.303490	-2.035694	-0.453510
C	-0.118258	-0.382453	-0.503515
C	1.134785	-1.211119	-0.615964
Zn	1.684331	-0.939732	2.397552
O	1.636107	-0.680058	4.619224
H	1.413840	0.138583	4.810196
H	0.994250	-1.163611	4.952418
O	1.772603	1.045743	2.252623
H	1.567192	1.401266	3.020269
H	2.596543	1.289191	2.112951
Zn	-4.361991	1.533621	-3.140057
Zn	2.513937	-3.266598	-2.267062
Zn	3.804999	2.284943	-1.112177
Zn	-5.191597	3.860488	1.524557
O	0.013960	-1.976662	2.458634
O	-6.719211	-1.328890	2.404651
O	3.350732	-2.002206	2.470167
O	-8.149060	-0.628579	0.297057
I	6.908875	0.630258	-0.229703
I	4.368237	-0.456013	0.177756