Robust pyridylbenzoate metal-organic frameworks as sorbents for volatile solvents and gases

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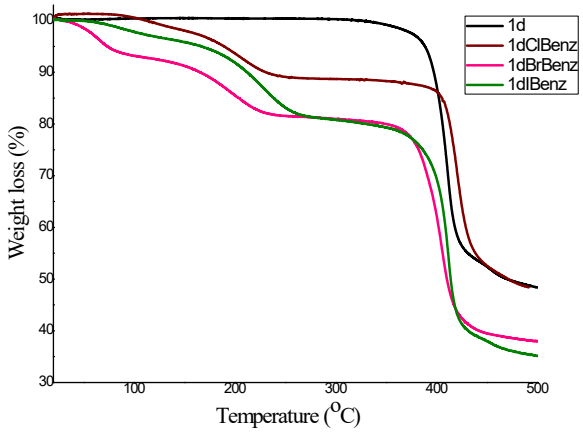
Supplementary material

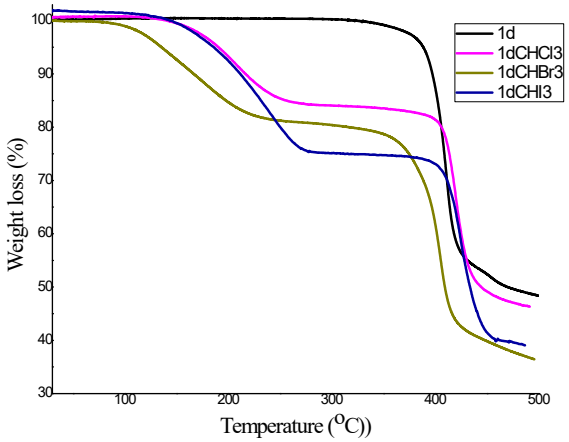
Figure S1: Sorption of VOCs (large vials) into the MOF adsorbents **1d** or **2d** in narrow vials. The examples shown here are ***1d*** *and iodomethane* (left) and ***1d*** *and iodobenzene* (right)

Table S1: Cell parameter of crystal from sorption of chlorinated solvents.

Compound	**1dCH_2Cl_2**	**1d$CHCl_3$**	**1dClBenz**
Formula	$C_{25}H_{18}Cl_2CoN_2O_4$	$C_{25}H_{16.83}Cl_3CoN_2O_4$	$C_{30}H_{21}ClCo\ N_2O_4$
Mass (g.mol^{-1})	540.24	574.52	567.89
Crystal size (mm)	0.16 x 0.20 x 0.34	0.11 x 0.21 x 0.33	0.10 x 0.13 x 0.20
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/(Å)	10.5973(11)	10.0048(16)	10.2944(16)
b/(Å)	15.3082(15)	16.371(3)	16.272(3)
c/(Å)	14.8848(15)	15.036(3)	15.248(3)
β/(°)	99.964(2)	97.402(3)	95.232(4)
V/(Å^3)	2378.3(4)	2442.3(7)	2543.6(7)
T/(K)	100	173	173
D (g·cm^{-3})	1.509	1.562	1.483
μ(Mo−Kα) (mm^{-1})	0.981	1.066	0.820
F(000)	1100	1163	1164
Range scanned, θ (°)	1.923-28.14	1.847-28.31	1.834-28.26
No. reflns collected	42669	42591	51772
No. unique reflns	5821	6062	6296
No. reflns with I≥ 2σ(I)	4338	4504	4493
Parameters/restraints	335/0	326/0	343/0
Goodness of fit, S	1.015	1.019	1.038
Final R indices (I≥ 2σ(I))	0.0696	0.0741	0.0550
Final wR2 (all data)	0.1092	0.1293	0.1386
Min,max e$^-$ density/(e Å^{-3})	0.646, -0.699	0.674, -0.946	1.282, -1.117



(a)



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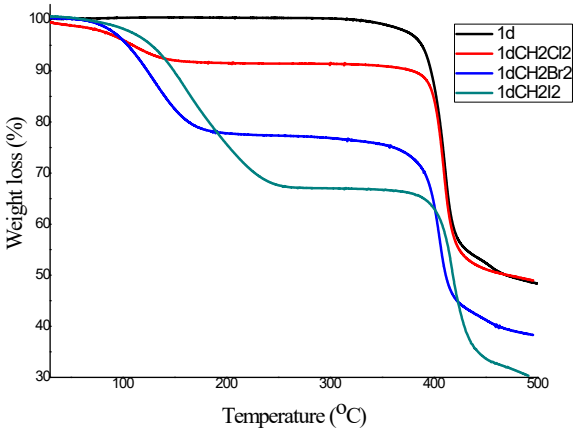
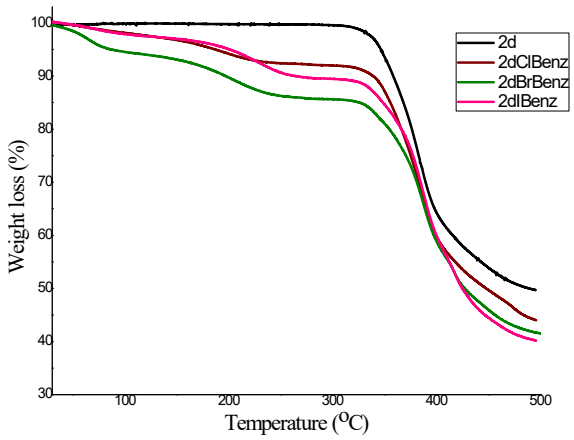
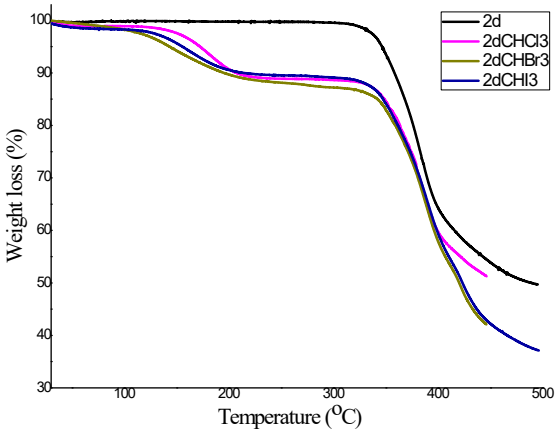


(c)

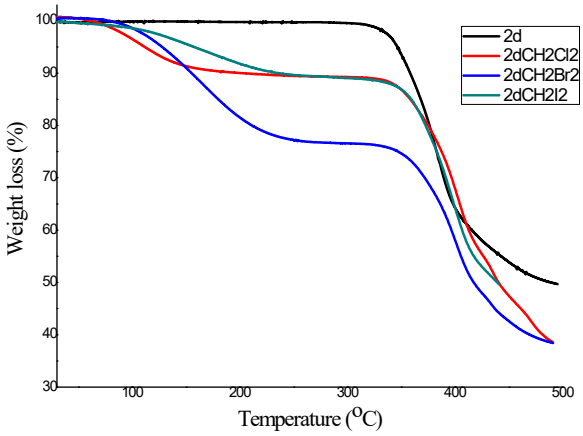
Fig S2 (ctd)



(d)



(e)



(f)

Figure S2. TGA showing sorption capacities for halogenated solvents for (a)-(c) **1d** and (d)-(f) **2d**

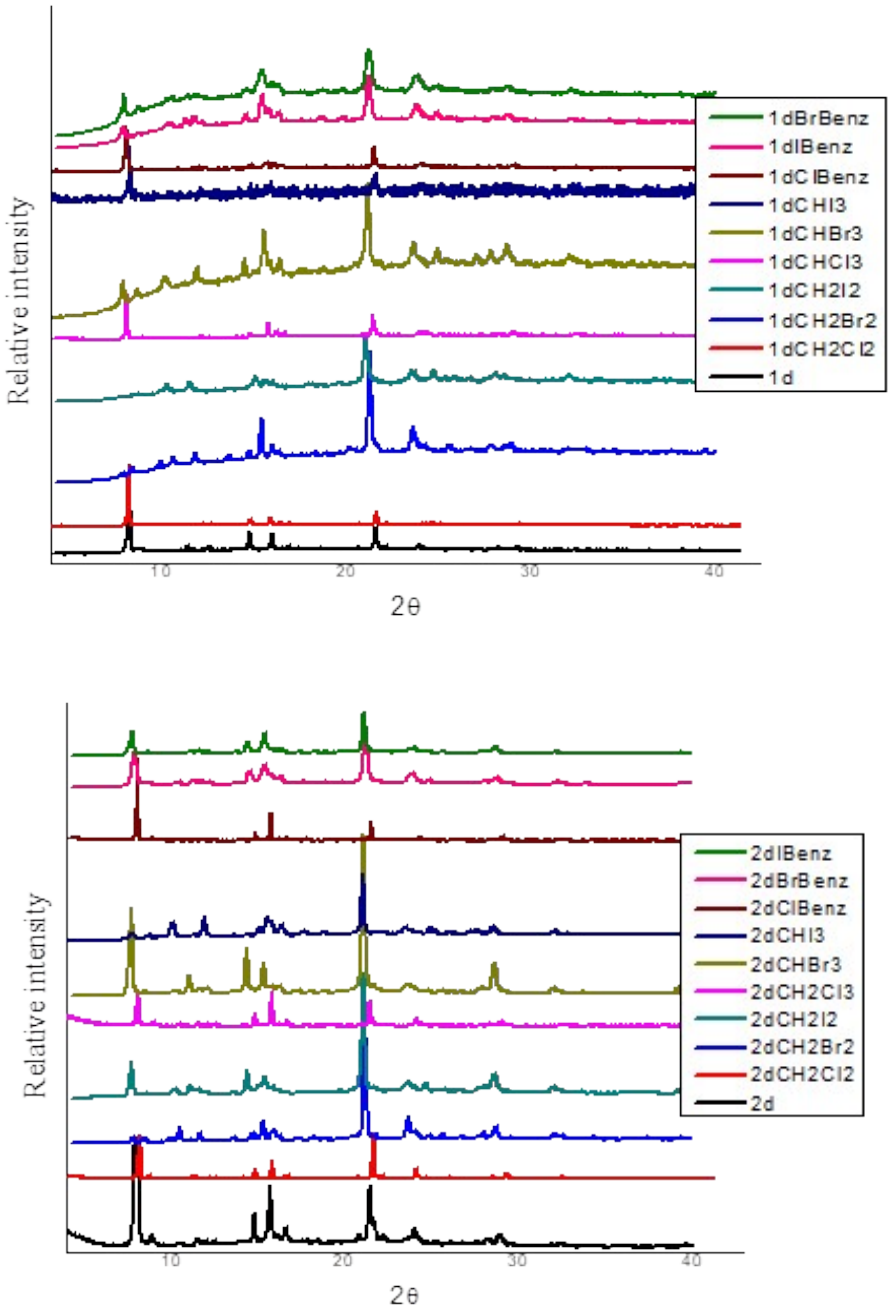


Figure S3. PXRD of sorption products of halogenated solvents for (top) **1d** and (bottom) **2d**

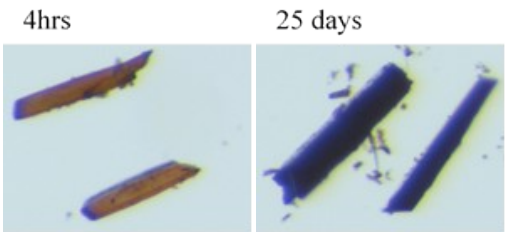


Figure S4. Colour changes are evident on adsorption of iodine to form **1dI_2**

Table S5. Void volumes in crystal structures

	Void volume per unit cell (Å^3)
1dCH_2Cl_2	457
1d$CHCl_3$	621
1dClBenz	730
1dI_2	644
1d	481
1dI_2d	445

Table S6. Unit cell parameters as crystals are taken through a sequence of drying and solvent sorption.*

Compound	**1d**	**1dI_2**	**1dI_2d**	**1dI_2****	**1dI_2d****	**1dI_2dDMF****
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/(Å)	10.3931(14)	10.114(3)	10.4014(11)	10.21	10.14	9.49
b/(Å)	16.027(2)	16.501(4)	16.1330(17)	16.89	16.07	17.84
c/(Å)	14.996(2)	14.700(4)	14.6878(15)	14.73	14.38	14.63
β/(°)	98.243(2)	97.159(4)	98.482(2)	96.9	97.7	92.12
V/(Å^3)	2472.2(6)	2434.3(11)	2437.7(4)	2524	2323	2475

* **1dI_2** prepared on exposing **1d** on iodine in 25 days, was submerged into methanol in vial for four days and methanol was refreshed two times to form **1dI_2d**. The latter was again submerged in DMF in vial to form **1dI_2d_DMF.**

** Only a cell check done, hence the data is not as precise as for those crystals where full refinement was carried out.

Table S7. Properties of halogenated VOCs used in sorption experiments[a]

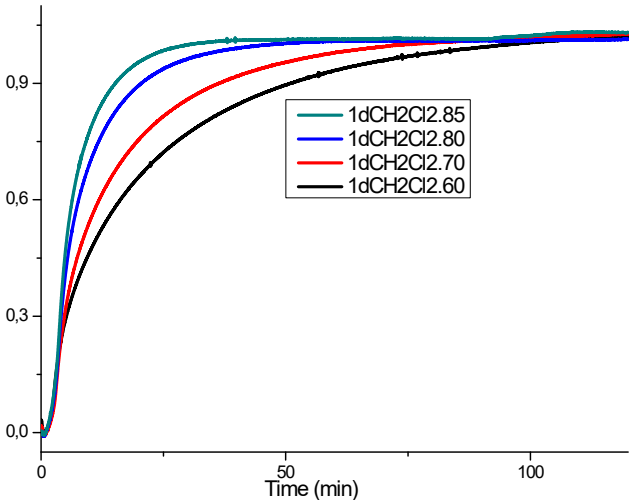
Guest molecules	**Boiling point (°C)**	**Density (g cm^{-3})**	**Solvent molecular volume (A^3)[b]**
CH_2Cl_2	39.6	1.33	106
CH_2Br_2	97.0	2.5	115
CH_2I_2	181	3.32	134
$CHCl_3$	61.2	1.49	133
$CHBr_3$	149.1	2.89	145
CHI_3	121	4.01	163
Chlorobenzene	132	1.11	168
Bromobenzene	156	1.5	173
Iodobenzene	188	1.83	185
Iodine		4.93	85

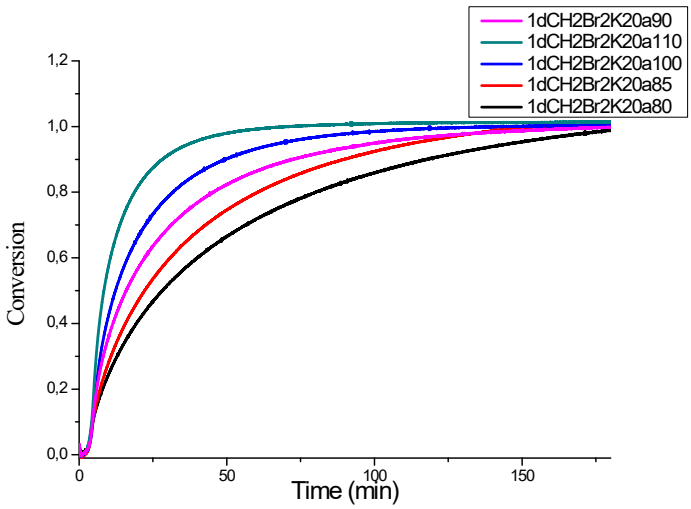
[a] Density and boiling point taken from pubchem.ncbi.nlm.nih.gov

[b] Molecular volume of solvent $= \frac{Molecular\ Weight}{N_A \times Density}$

Table S8: Selected torsion angles.

Compound	**1d**	**1dI_2**	**1dI_2d**	**1dCH_2Cl_2**	**1d$CHCl_3$**	**1dClBenz**
34pba:						
C3A-C4A-C8A-C12A	157.3(4)	139.5(4)	153.8(3)	156.5(3)	135.0(3)	-138.8(3)
C3A-C4A-C8A-C121	145.6(4)	179.6(4)	-153.8(3)			
O1A-C1A-C2A-C7A	-178.8(4)		178.7(3)	174.8(3)	-179.1(2)	177.8(3)
44pba:						
C4B-C5B-C8B-C12B	154.47(4)	163.0(4)	-166.6(3)	-159.0(3)	151.7(3)	157.0(3)
C4B-C5B-C8B-C121	-172.1(4)		160.7(3)			
O1B-C1B-C2B-C7B	-157.2(4)	-179.4(4)	154.4(3)	162.2(3)	-171.5(3)	-177.9(3)
O1B-C1B-C2B-C71	155.1(4)		-161.3(3)			





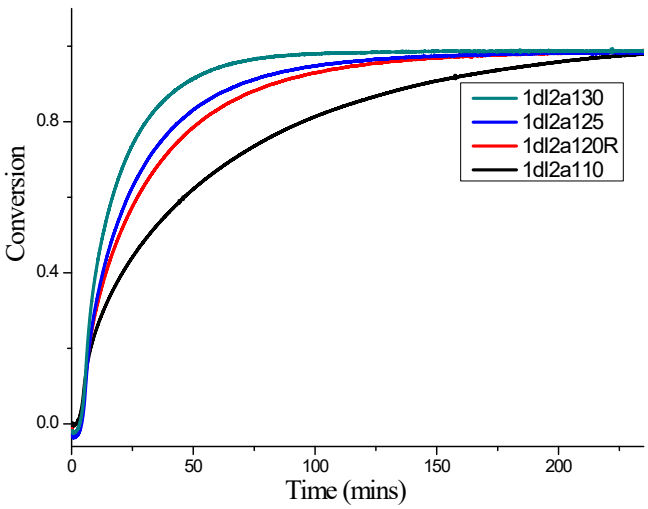
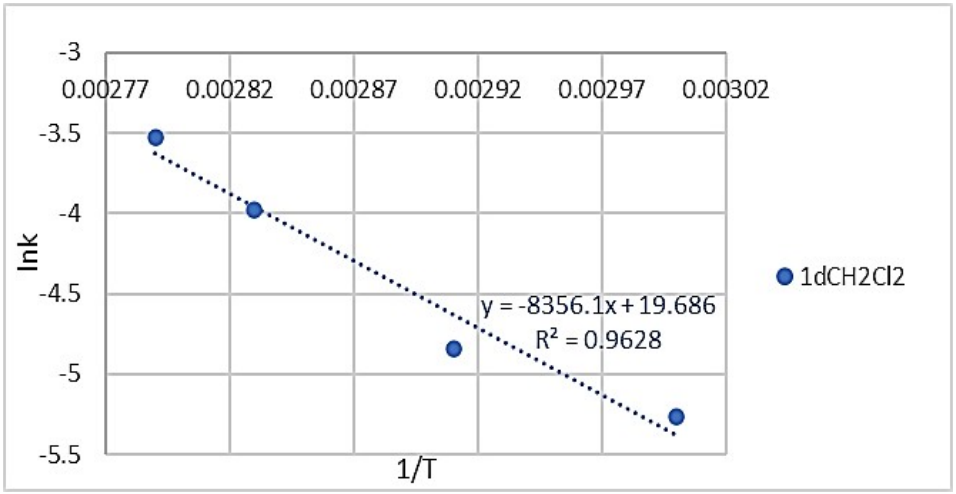
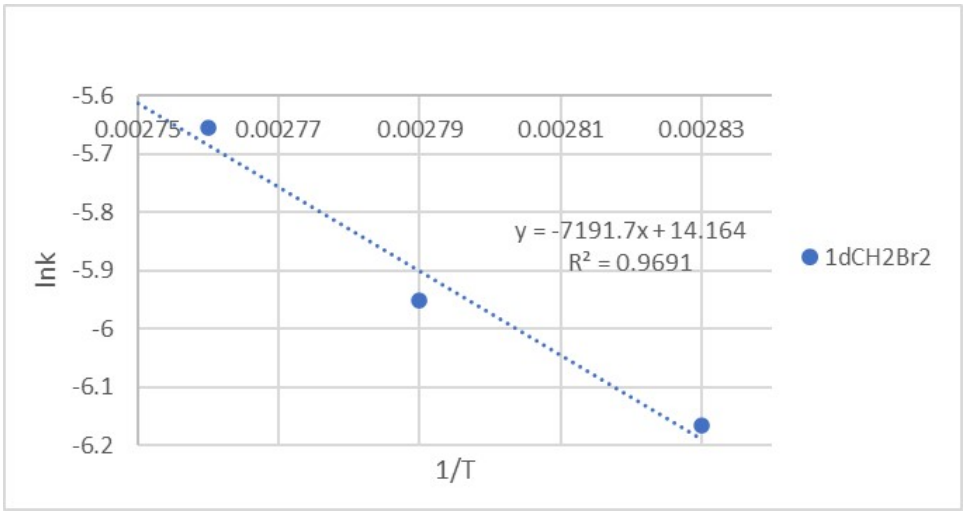


Figure S5. Isothermal desorption curves





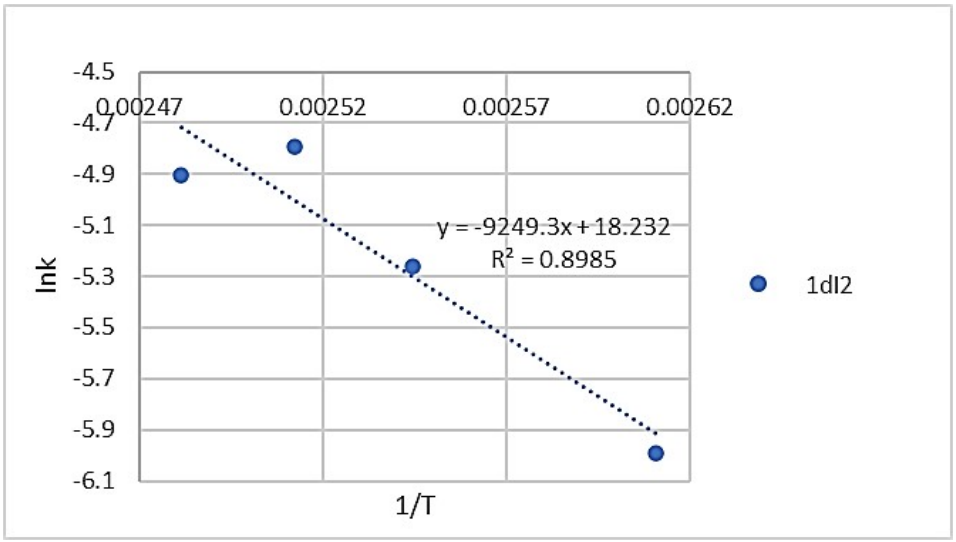


Figure S6: Arrhenius plots for desorption in CH_2Cl_2, CH_2Br_2, and I_2