The unique rht-MOF Platform, Ideal for Pinpointing the Functionalization and CO_2 Adsorption Relationship

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Materials and Methods.

- X-ray Powder Diffraction (XRPD) measurements were carried out at room temperature on a PANalytical X'Pert PRO diffractometer 45kV, 40mA for CuKα (λ = 1.5418 Å), with a scan speed of 0.02°/s and a step size of 0.008° in 2θ.

- Low pressure gas sorption measurements were performed on a fully automated micropore gas analyzer Autosorb-1C (Quantachrome Instruments) at relative pressures up to 1 atm. The cryogenic temperatures were controlled using a liquid argon bath at 87 K. The apparent surface areas of **rht**-MOF-7 were determined from the argon adsorption isotherm by applying the Brunauer-Emmett-Teller (BET) model using adsorption points in the pressure range of P/P_0 equal to 0.007 to 0.04. Pore size analyses were performed using a cylindrical NLDFT pore model system by assuming an oxidic (zeolitic) surface. The determination of the isosteric heats of adsorption (Q_{st}) for CO_2 was estimated by applying the Clausius-Clapeyron expression using the isotherms measured at 258, 273 and 298 K. In a typical experiment, **rht**-MOF-7 was activated by washing the as-synthesized crystals with 3 x 20 mL of DMF followed by solvent exchange in absolute ethanol for 7 days. 45-60 mg of activated sample was then transferred to a 6-mm sample cell, evacuated at room temperature for 46h (using a turbomolecular vacuum pump) and then gradually heated to 120^{o}C/16h and cooled to room temperature.

Preparation of 5,5',5''-(*s*-Triazine-2,4,6-triyltriimino)triisophthalic acid hexasodium salt, Na_6L.

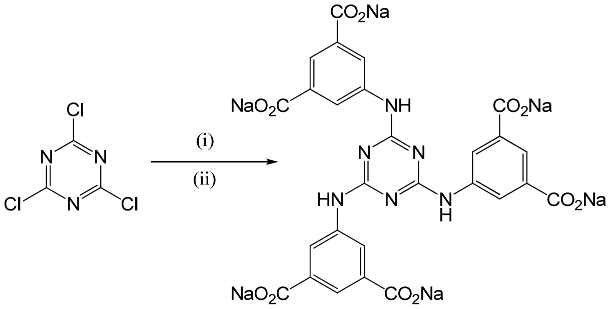

Figure S1. Schematic representation of the synthesis of Na_6L, which was synthesized according to a modified published procedure. [12]. Reagents and Conditions: (i) 5-aminoisophthatlic acid (5-NH_2bdc) / NaOH / $NaHCO_3$ / H_2O, Δ = 105°C for 24h, (ii) NaOH / H_2O, rt for 1h.

5-aminoisophthalic acid (9 g, 49.6 mmol, 4 eq.), H_2O (100 mL), and aqueous NaOH (5N, 20 mL) were combined in a 500-mL round bottom flask equipped with a stir bar. $NaHCO_3$ (4.2 g, 49.6 mmol) was then added to the solution and cooled to 10°C. A cyanuric chloride (2.28 g, 12.5 mmol, 1 eq.) solution in acetone (12.5 mL) was prepared and subsequently added dropwise. The solution was then heated to 105°C and refluxed for 24h. The solution was filtered and the filtrate isolated, concentrated to ~50 mL with a rotary evaporator, and diluted with EtOH (75 mL). This resulted in the formation of a white precipitate which was collected via filtration, washed with EtOH/H_2O (3:1, v/v), EtOH, and Et_2O. The solid was dried in an oven at 80°C to yield 14.69g of crude product.

The crude product was then added to a round bottom flask containing H_2O (120mL) and brought to a pH of 9-10 with aqueous NaOH (5N) while stirring. The solution was stirred for 1h and subsequently filtered. The filtrate was added to a stirred flask containing EtOH (150 mL). Lastly, the white precipitate was collected by filtration, washed with EtOH and dried to give 7.92 g (85%) of the final product.

Synthesis of $[Cu_3(L)_3(H_2O)_3]_n$, (rht-MOF-7).

A solution containing $Cu(BF_4)_2 \cdot 2.5H_2O$ (20.0 mg, 0.071 mmol), Na_6L (18 mg, 0.024 mmol), DMF (2 mL), and 0.6 mL 3M HNO_3 in DMF was prepared in a 20-mL scintillation vial. The solution was heated to 65°C for 7 days. Green polyhedral crystals were harvested and airdried (Yield: 18 mg, 88%). The as-synthesized material was determined to be insoluble in H_2O and common organic solvents.

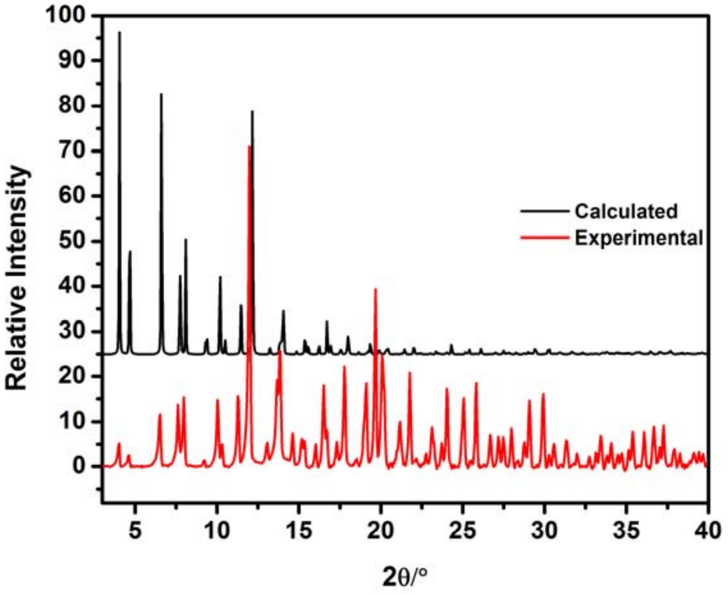

Figure S2. Experimental and calculated powder X-ray diffraction (PXRD) patterns for **rht**-MOF-7, indicating the phase purity of the as-synthesized samples.

Table S1. Structural data for **rht**-MOF-1 and **rht**-MOF-7.

	UC[a]	d[b] (g/cm^3)	FV[c] (%)	PV[d] (cm^3/g)	Cavity dimensions								
					tcz			**rdo-a**			**tcu**		
					id[e] (Å)	ap[f] (Å)		id (Å)	ap (Å)		id (Å)	ap (Å)	
						□	△		▭	□		▭	△
rht-MOF-1	a=44.459	0.702	76.4	1.1	15.9	6.8	4.1	**20.2**	7.4x 7.5	6.8	12.1	7.4x 7.5	4.1
rht-MOF-7	a=26.6700 c=38.0416	0.836	70.5	0.894	15.7	6.8	4.1	**17.8**	6.4x 9.8	6.8	10.4	6.4x 9.2	4.1

a = unit cell; b = density; c = free volume; d = pore volume; e = internal diameter; f = aperture

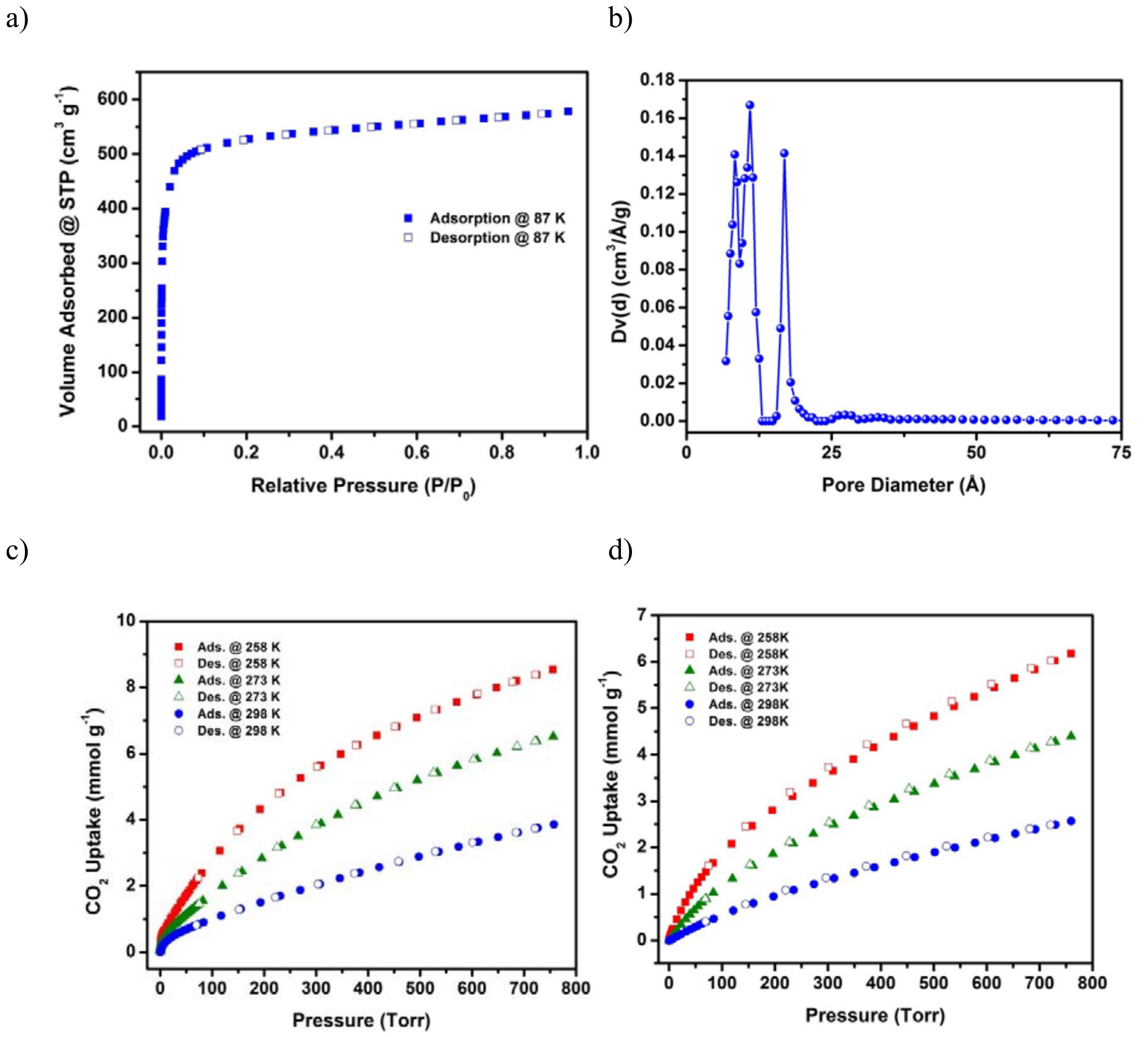

Figure S3. a) Argon sorption isotherm for **rht**-MOF-7. b) Pore size distribution for **rht**-MOF-7 determined from the Ar sorption isotherm @ 87K. c) CO_2 sorption isotherms for **rht**-MOF-7. d) CO_2 sorption isotherms for **rht**-MOF-1.

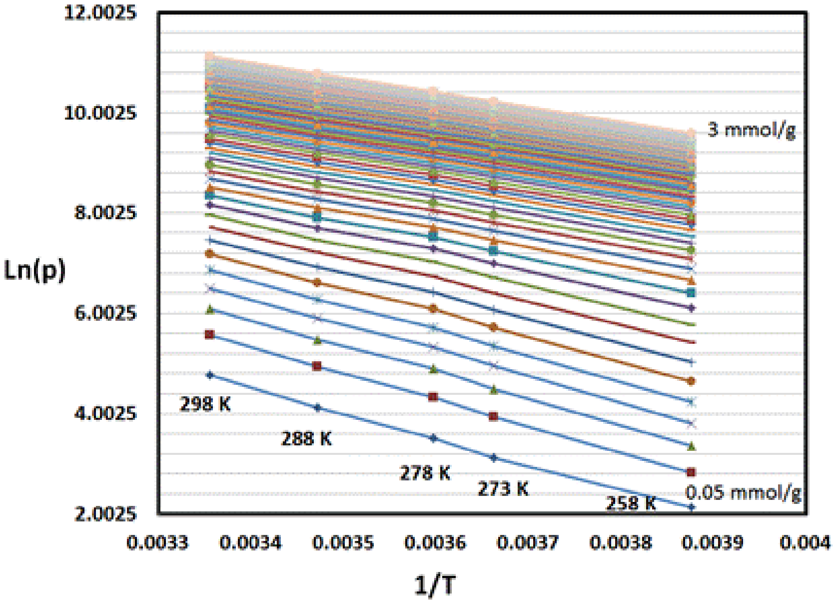

Figure S4. CO_2 adsorption isosters for **rht**-MOF-7.

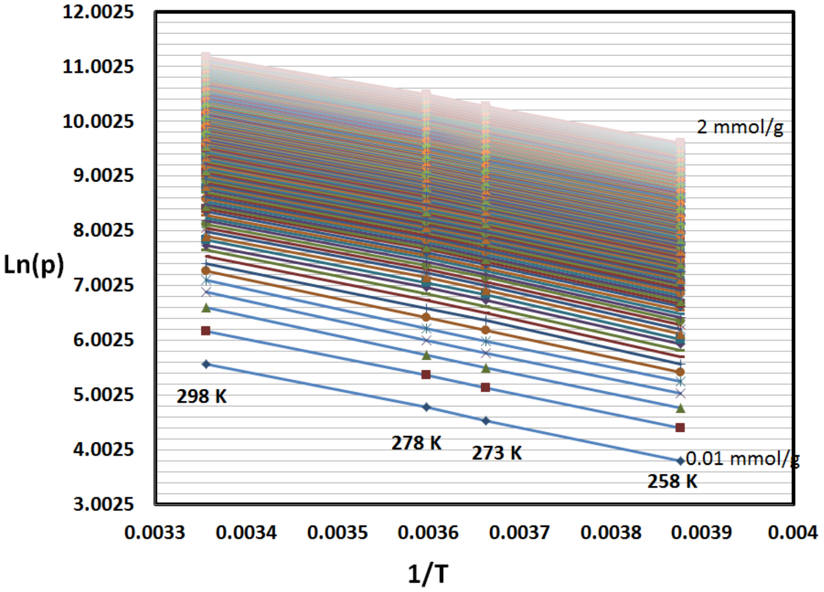

Figure S5. CO_2 adsorption isosters for **rht**-MOF-1.

CO_2 **Adsorption** Q_{st} **Analysis on rht**-MOF-7 **using Multi-Site Langmuir model (MSL)**

Equation for MSL: $n = n_{sat1}{*}b_1p/1+b_1p + n_{sat2}{*}b_2p/1+b_2p + \ldots + n_{sati}{*}b_ip/1+b_ip$

Equation in the case of dual site Langmuir model (DSL): $q = n_{sat1}{*}b_1p/1+b_1p + n_{sat2}{*}b_2p/1+b_2p$
Where n_{sat1} and b_1 are the saturation capacity and the affinity parameters on site 1, respectively, and n_{sat2} and b_2 are the analogous parameters on site 2.

Table S2. Dual site Langmuir parameters for CO_2 adsorption on **rht**-MOF-7.

	Parameters	Temperatures / K				
		258	273	278	288	298
Adsorption Site 1	n_{sat1}	0.4724	0.43668	0.43546	0.46339	0.46627
	b_1	0.01419	0.00522	0.00342	0.00165	8.52E-04
Adsorption Site 2	n_{sat2}	12.81583	12.86082	13.09387	13.93269	14.34703
	b_2	1.67E-05	9.05E-06	7.24E-06	4.62E-06	3.12E-06

The parameters, extracted from the best DSL fit (Table S2), were used to recalculate the adsorption isotherms and the evolution of the isosteric heat of adsorption (Q_{st}) for each site using the Clausius–Clapeyron equation. The results are shown in Figures S6-S9.

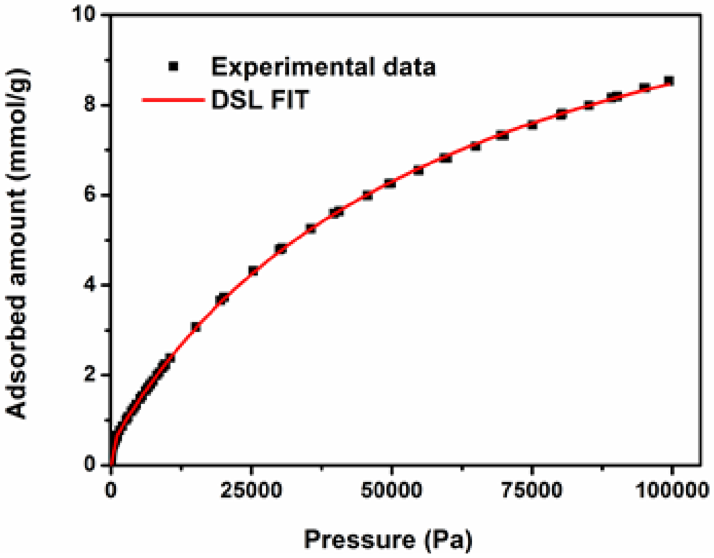

Figure S6. Example of dual site Langmuir fit for CO_2 adsorption isotherms at 258 K for **rht**-MOF-7.

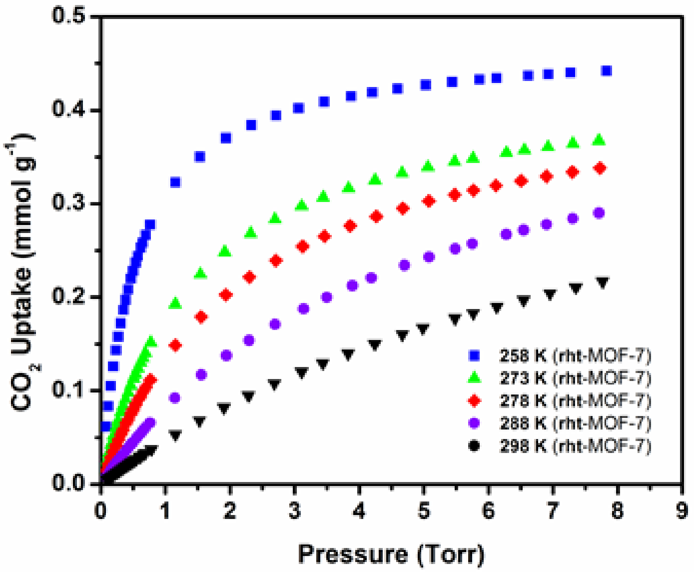

Figure S7. Adsorption isotherms branch in **rht**-MOF-7 calculated using the dual site Langmuir model based on site 1 parameters (effect of the amine/triazine nitrogen atoms).

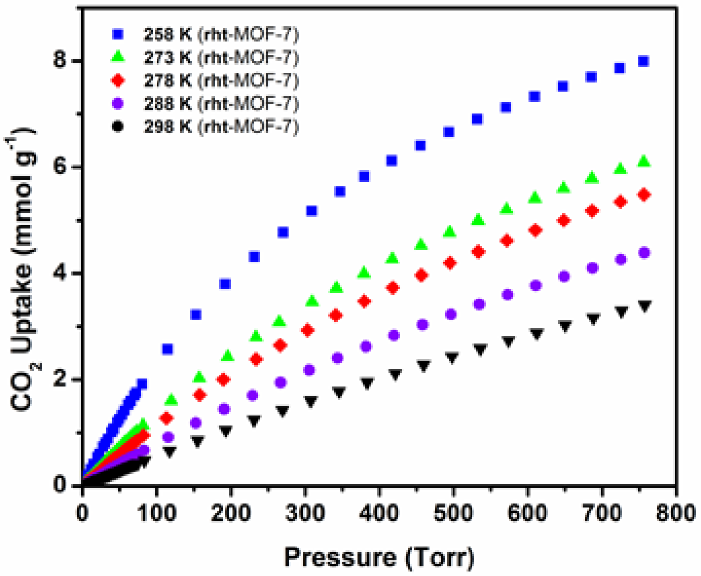

Figure S8. Adsorption isotherms branch as seen by dual site Langmuir model for site 2 (effect of the pore size).

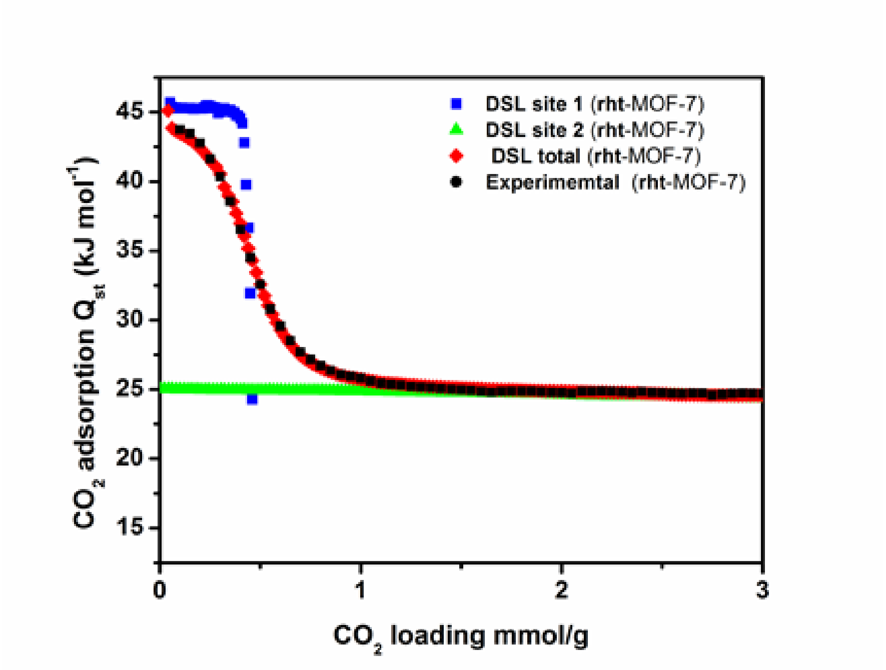

Figure S9. Q_{st} analysis for **rht**-MOF-7 using the dual site Langmuir model.

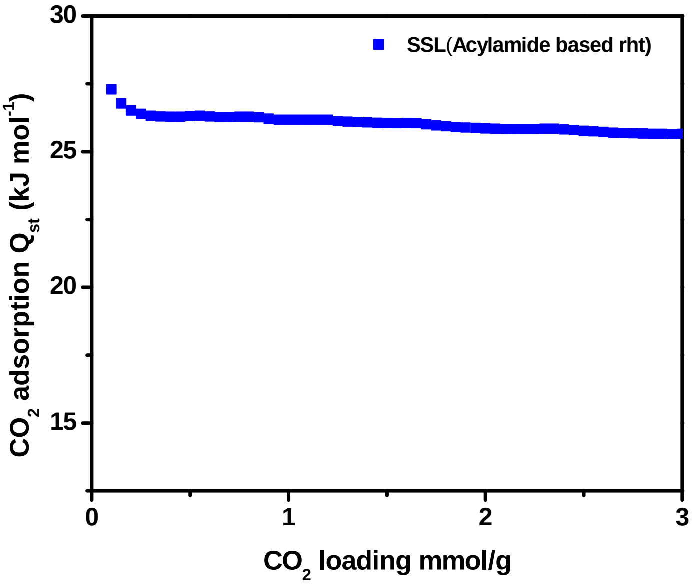

Figure S10. Q_{st} of CO_2 adsorption for the acylamide-based **rht**-MOF determined using the SSL (Raw data from [11]).

Table S3. Dual site Langmuir parameters for CO_2 adsorption on acylamide based **rht**[a]

	Parameters	Temperature / K	
		273	298
Adsorption Site 1	n_{sat1}	10.88265	13.37589
	b_1	0.00807	0.00247
Adsorption Site 2	n_{sat2}	10.88265	13.37589
	b_2	0.00807	0.00247

[a] Raw data from [11]

Table S4. Crystal data and structure refinement for compound **rht**-MOF-7

Identification code	**rht**-MOF-7
Empirical formula	C27 H12 Cu3 N6 O15
Formula weight	851.05
Temperature	100(2) K
Wavelength	1.54178 A
Crystal system, space group	Tetragonal, I4/m
Unit cell dimensions	a = 26.6700(3) A alpha = 90 deg.
	b = 26.6700(3) A beta = 90 deg.
	c = 38.0416(10) A gamma = 90 deg.
Volume	27058.6(8) A^3
Z, Calculated density	16, 0.836 Mg/m^3
Absorption coefficient	1.445 mm^-1
F(000)	6768
Crystal size	0.10 x 0.10 x 0.10 mm
Theta range for data collection	2.02 to 65.45 deg.
Limiting indices	-29<=h<=26, -29<=k<=21, -42<=l<=42
Reflections collected / unique	44425 / 10968 [R(int) = 0.1105]
Completeness to theta = 65.45	92.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8689 and 0.8689
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10968 / 3 / 466
Goodness-of-fit on F^2	0.998
Final R indices [I>2sigma(I)]	R1 = 0.0552, wR2 = 0.1162
R indices (all data)	R1 = 0.0944, wR2 = 0.1239
Largest diff. peak and hole	1.159 and -0.607 e.A^-3

The single crystal X-ray diffraction data were collected using a Bruker-AXS SMART-APEXII CCD diffractometer using CuKα (λ = 1.54178 Å). Indexing was performed using APEX2 [1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01 [2]. Absorption correction was performed by multi-scan method implemented in SADABS [3]. Space groups were determined using XPREP implemented in APEX2 [1]. Structures were solved using SHELXS-97 (Patterson methods), expanded using Fourier methods, and refined using SHELXL-97 (full-matrix least-squares on F2) contained in APEX2 [1] and WinGX v1.70.01 [4,5,6,7] program packages. Hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(-CH,-CH_2). The contribution of highly disordered anions / solvent molecules was treated as diffuse using the Squeeze procedure implemented in the Platon program [8, 9]. The central (organic core) part of the organic ligand for **rht**-MOF-7 was disordered. Disordered parts of the structures were refined using restraints.

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