crystals

Stability and Phase Transitions of Nontoxic γ-Cyclodextrin-K⁺ Metal-Organic Framework in Various Solvents

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1. PXRD Patterns

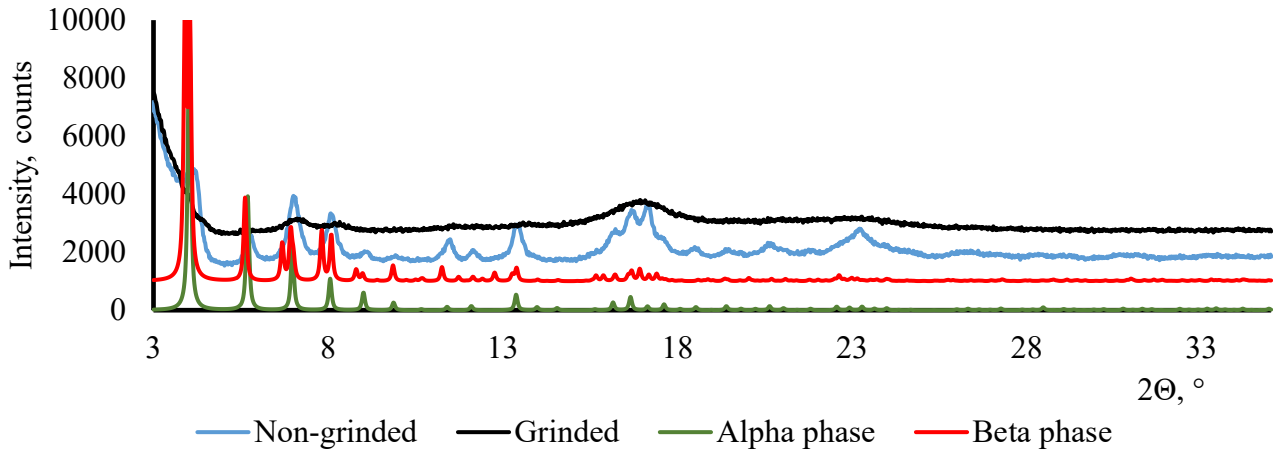

Figure S1. Powder pattern of γ-CD-MOF-α from 3 till 35 2Θ, °.

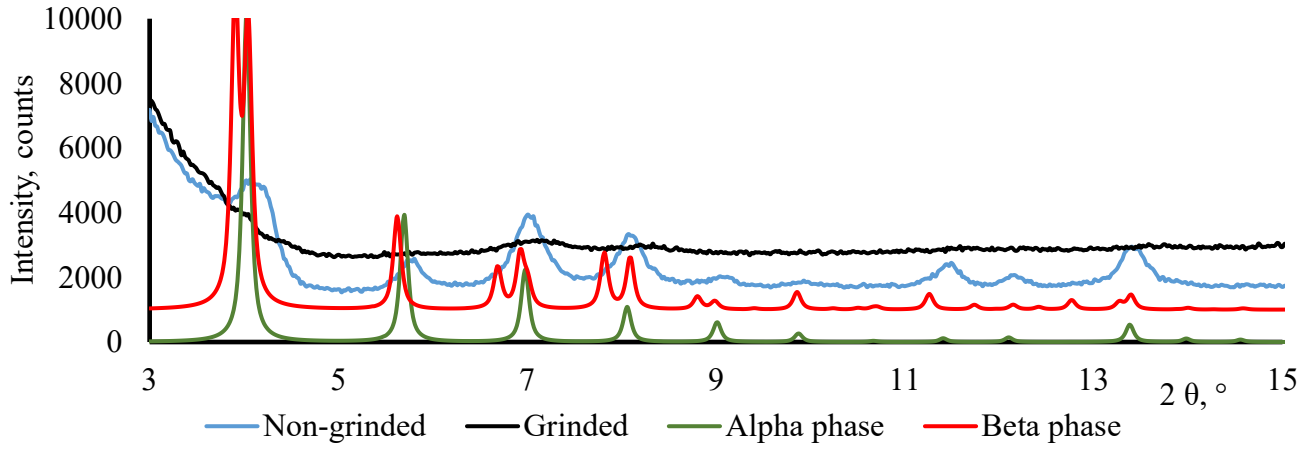

Figure S2. Powder pattern of γ-CD-MOF-α from 3 till 15 2 θ, °.

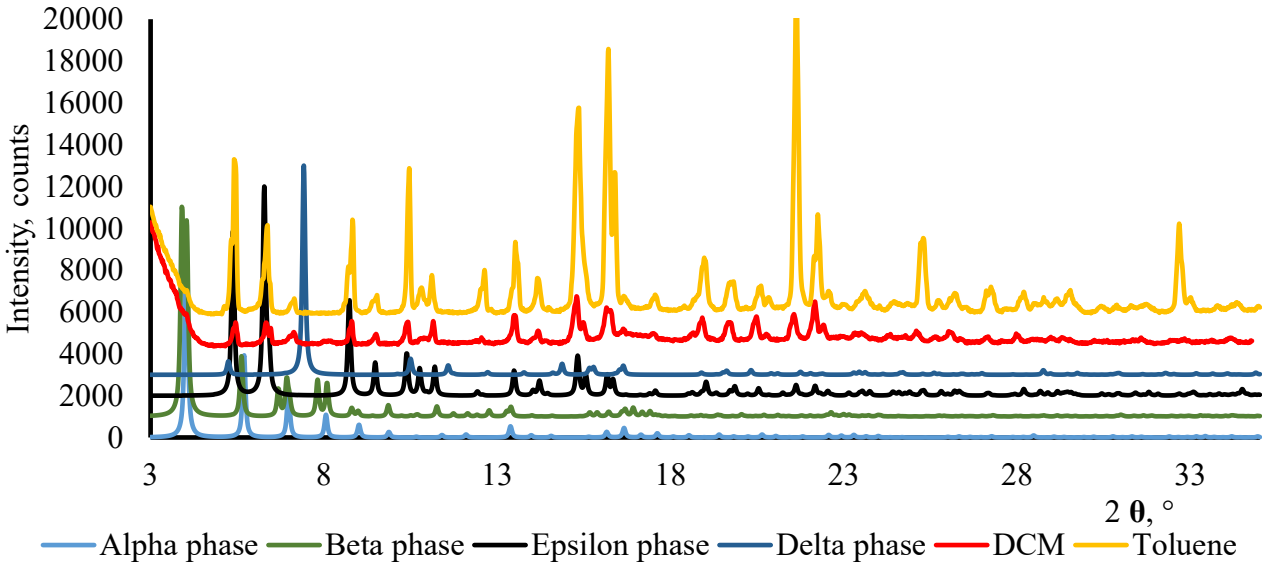

Figure S3. Powder pattern of γ-CD-MOF-1 in DCM and toluene from 3 till 35 2 θ, °.

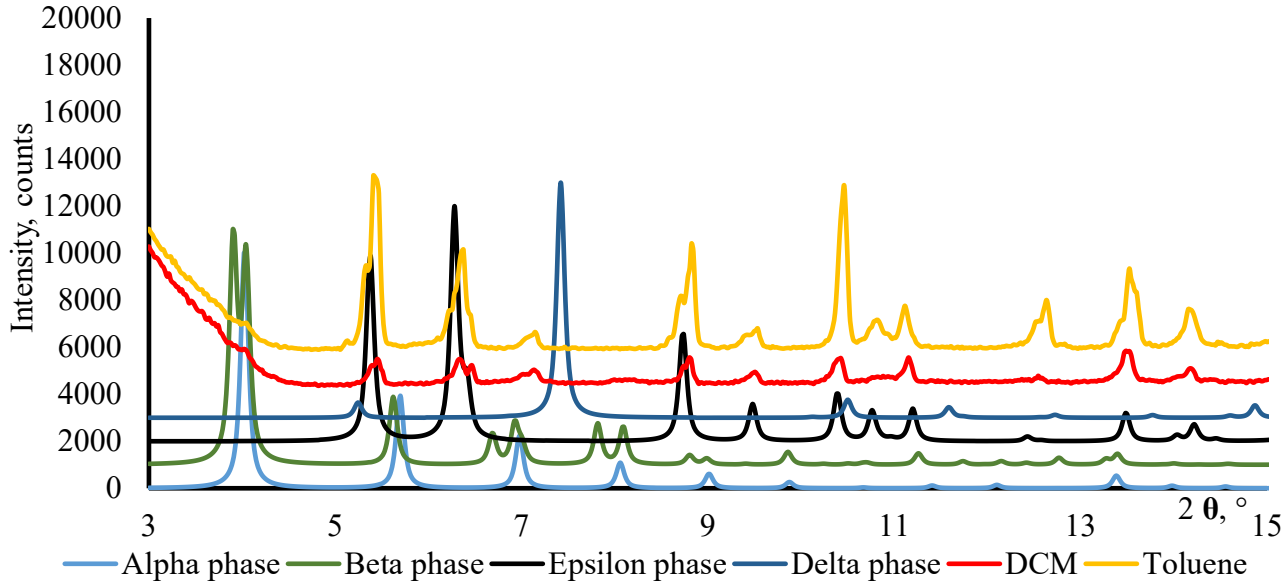

Figure S4. Powder pattern of γ-CD-MOF-1 in DCM and toluene from 3 till 15 2 θ, °.

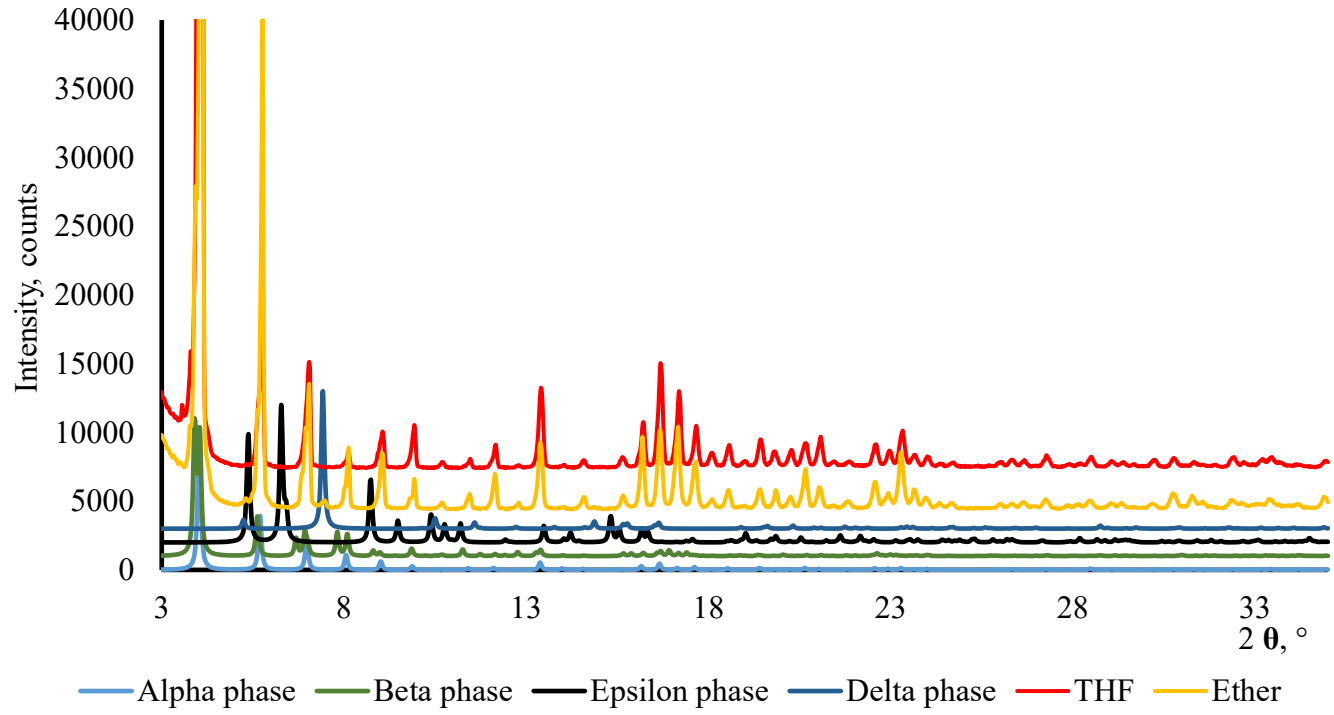

Figure S5. Powder pattern of γ-CD-MOF-1 in tetrahydrofuran (THF) and diethyl ether from 3 till 35 2 θ , °.

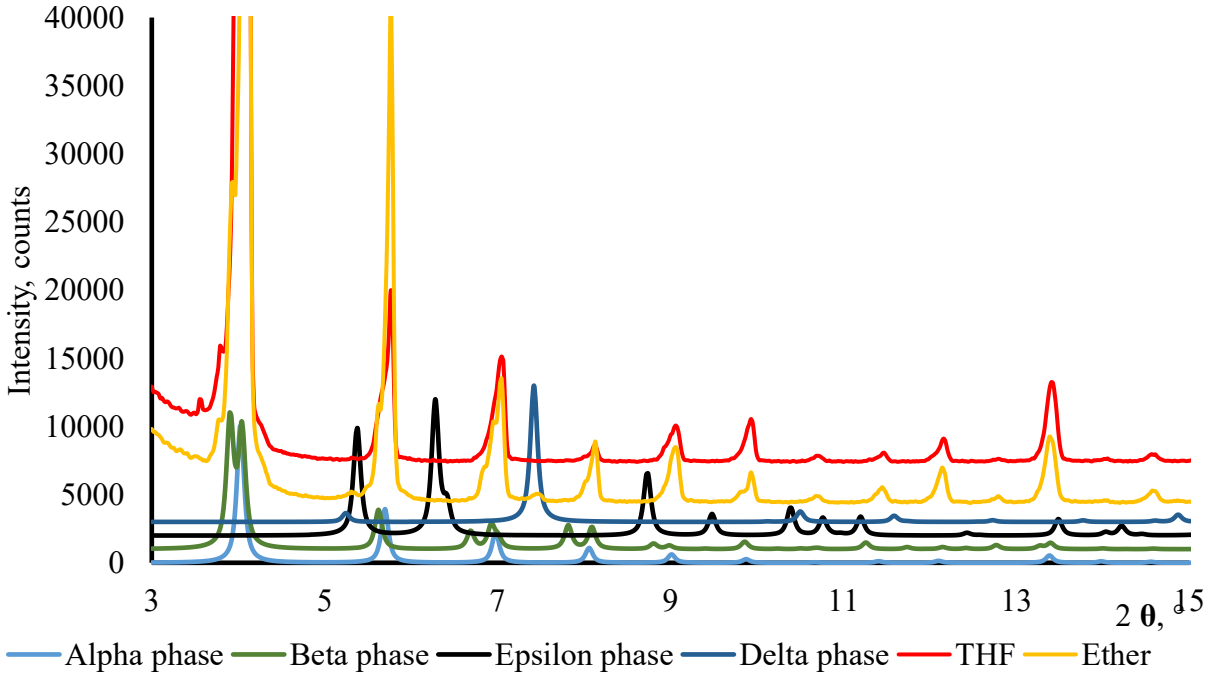

Figure S6. Powder pattern of γ-CD-MOF-1 in THF and diethyl ether from 3 till 15 2 θ, °.

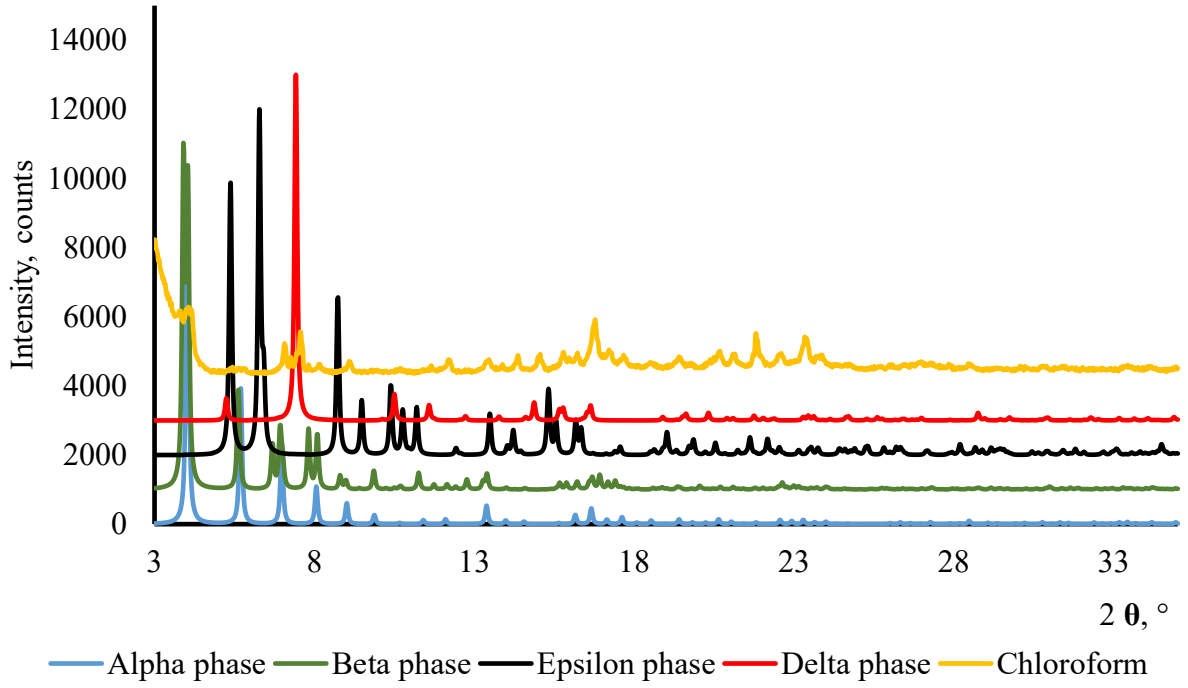

Figure S7. Powder pattern of γ-CD-MOF-1 in chloroform from 3 till 35 2 θ , °.

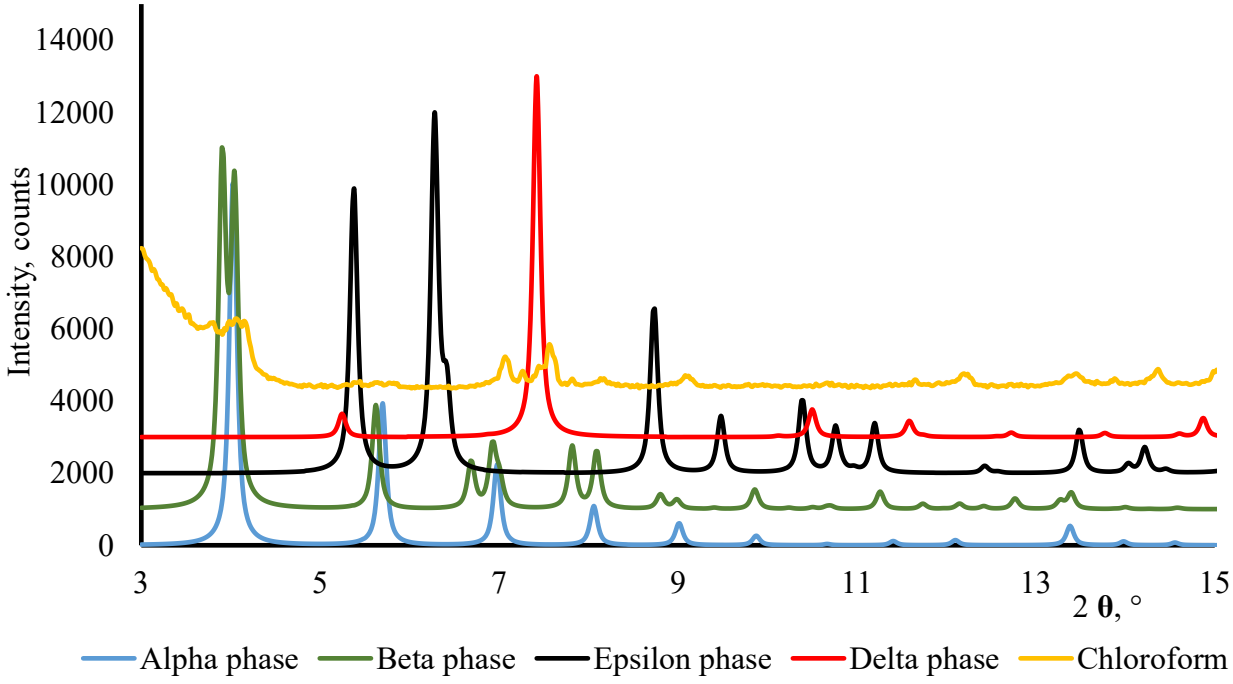

Figure S8. Powder pattern of γ-CD-MOF-1 in chloroform from 3 till 15 2 θ , °.

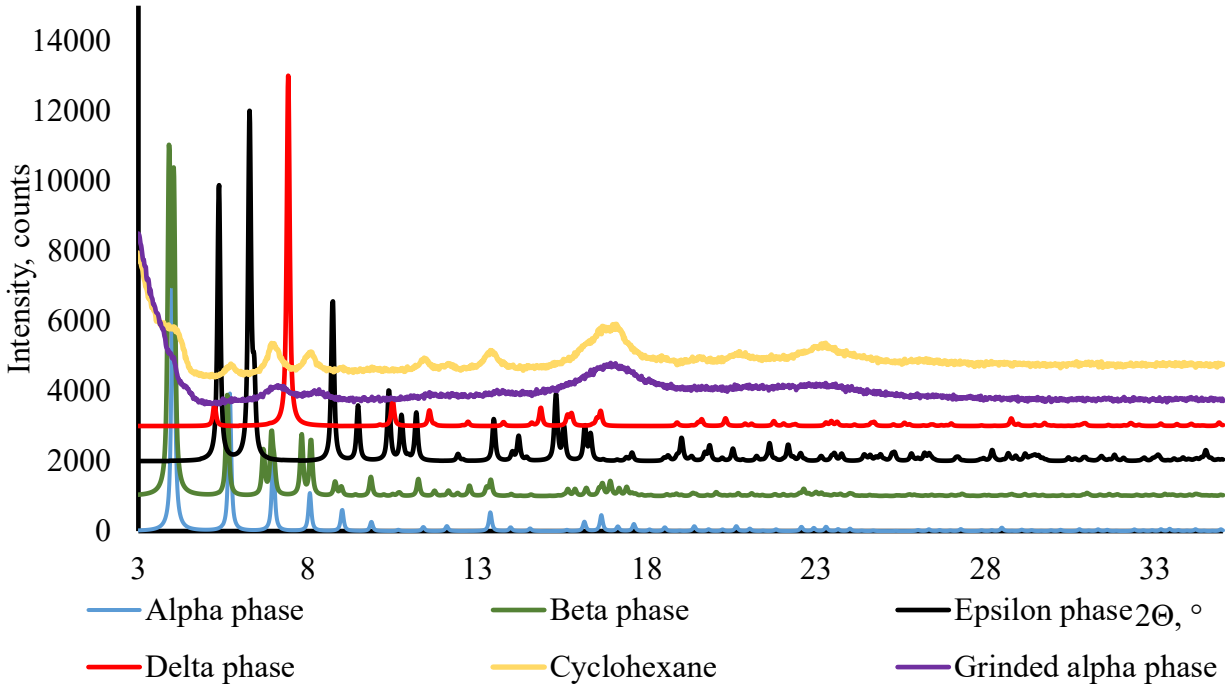

Figure S9. Powder pattern of γ-CD-MOF-1 in cyclohexane from 3 till 35 2 θ , °.

2. ^{1}H NMR Spectra for Solubility Studies of γ-CD-MOF in Various Solvents

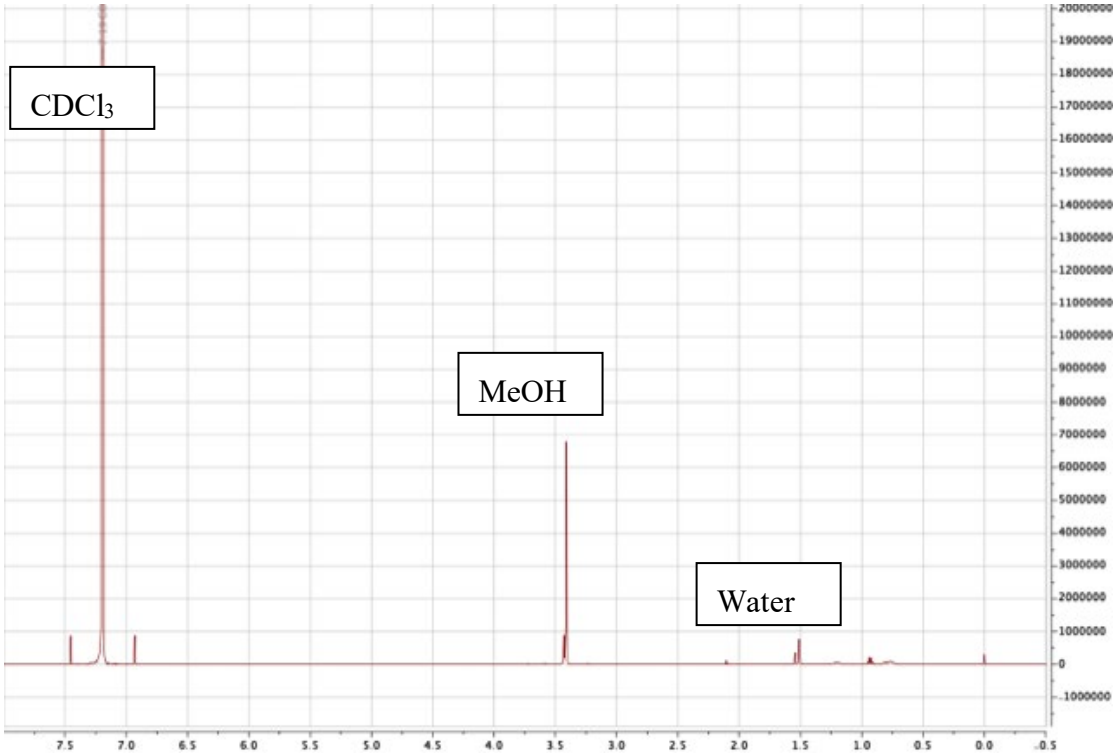

Figure S10. 400 MHz FT-NMR of $CDCl_3$-d solution after crystals of γ-CD-MOF-1 α-phase were immersed for 24 h.

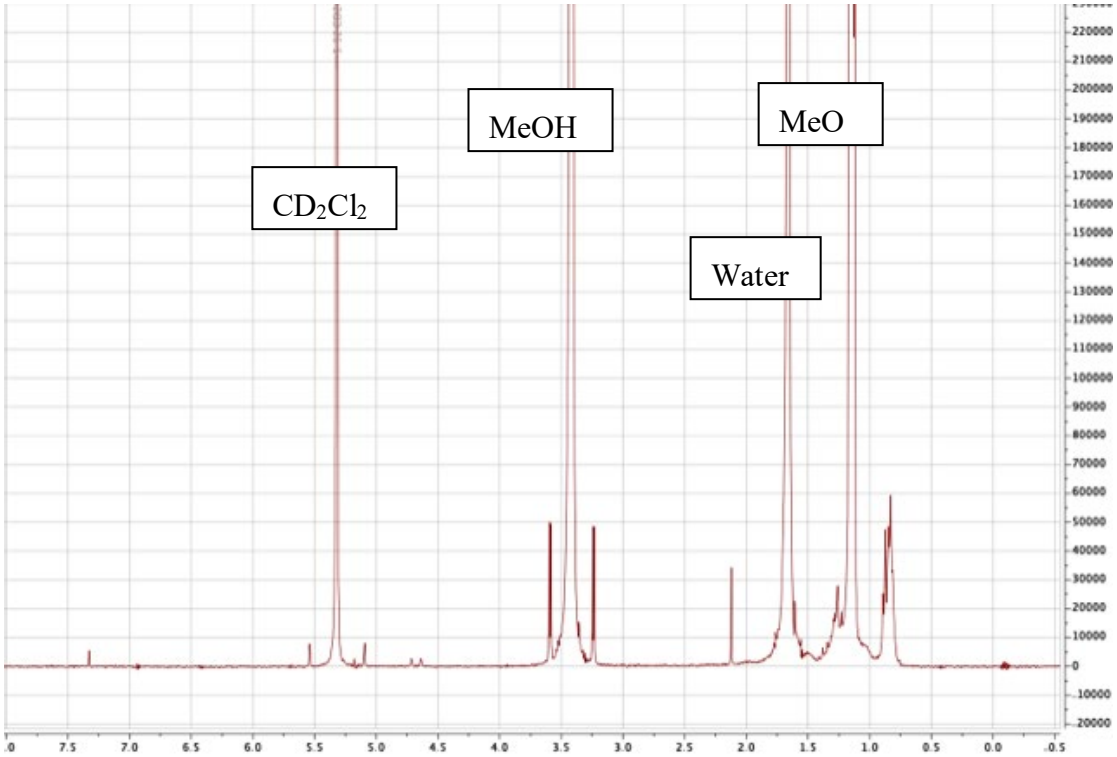

Figure S11. 400 MHz FT-NMR of CD_2Cl_2-d_2 solution after crystals of γ-CD-MOF-1 α-phase were immersed for 24 h.

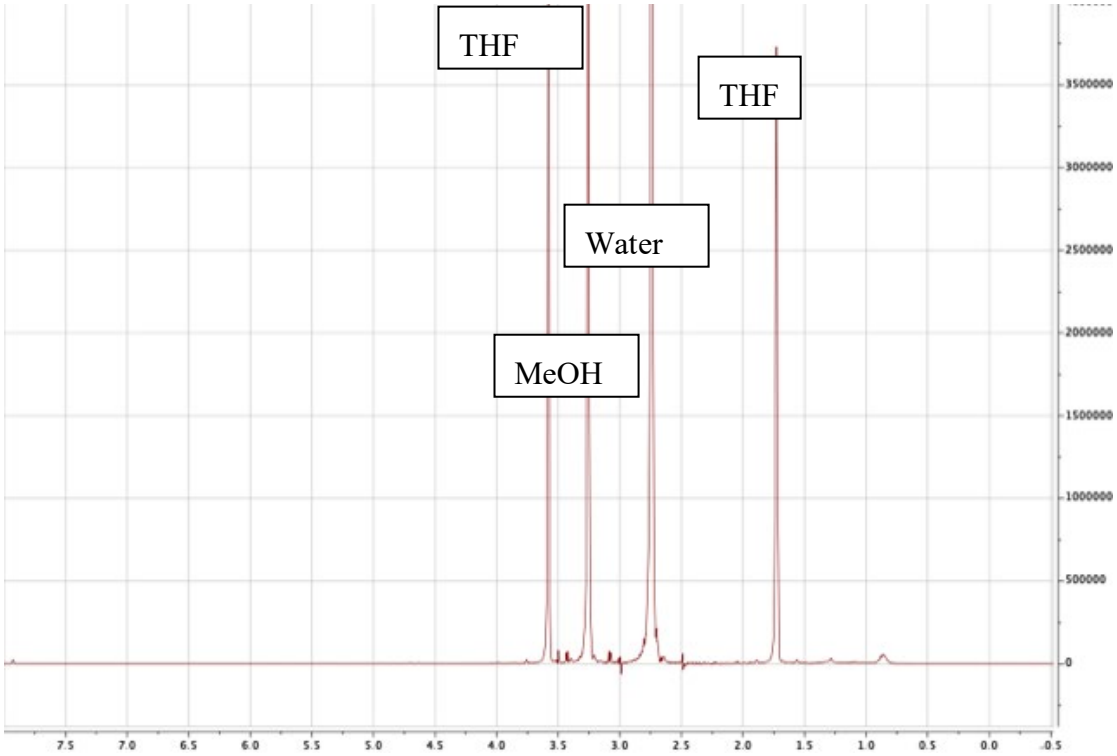

Figure S12. 400 MHz FT-NMR of THF-d_8 solution after crystals of γ-CD-MOF-1 α-phase were immersed for 24 h.

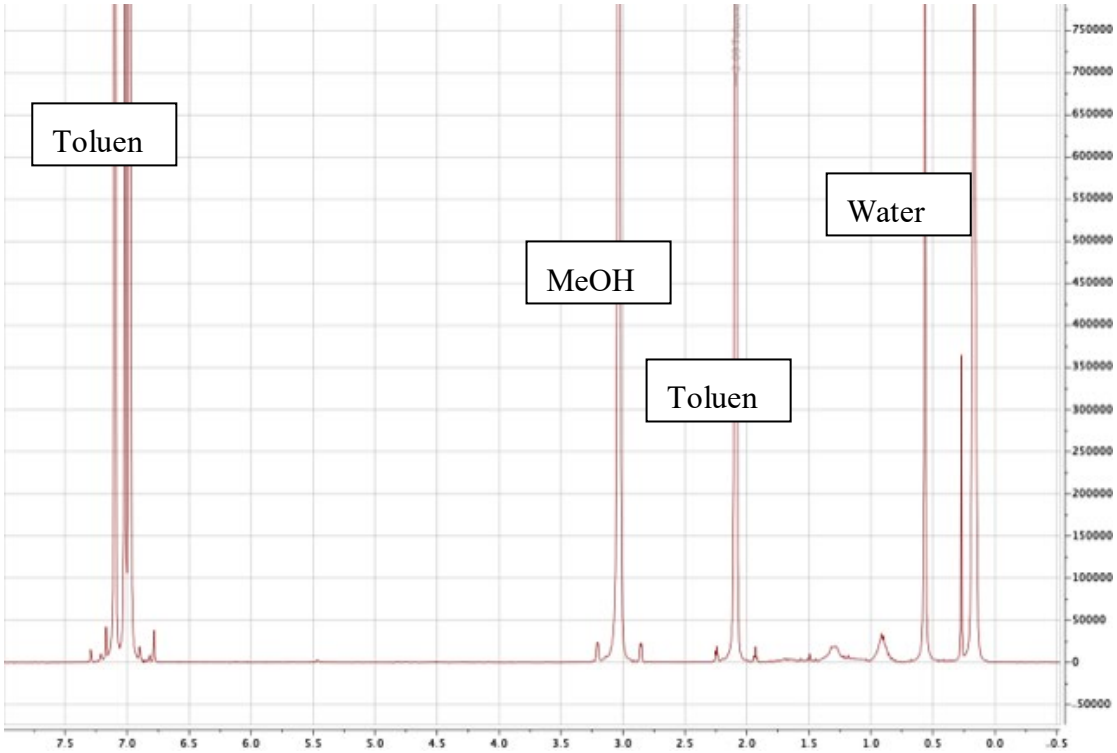

Figure S13. 400 MHz FT-NMR of toluene-d_8 solution after crystals of γ-CD-MOF-1 α-phase were immersed for 24 h.

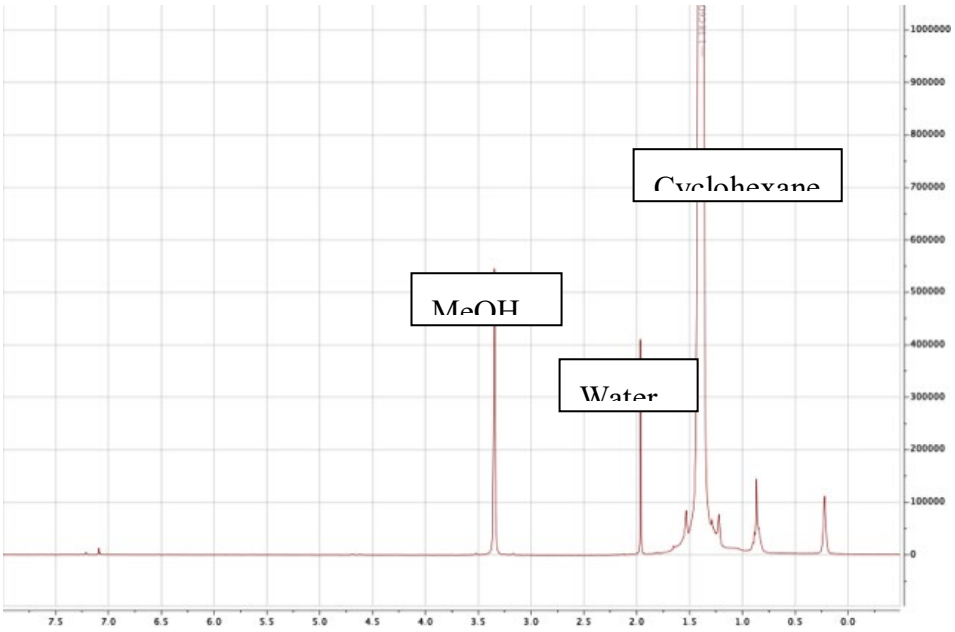

Figure S14. 400 MHz FT-NMR of cycloheaxane-d_{12} solution after crystals of γ-CD-MOF-1 α-phase were immersed for 24 h.

3. ^{1}H NMR Solubility Experiments for γ-Cyclodextrin in Deuterated Solvents

Sample preparation for the γ-cyclodextrin solubility experiment in selected solvents: 20 mg of the γ-cyclodextrin dissolved in 1 mL of DMSO-d_6. After that 100 μL of the obtained solution diluted with 0.5 mL of the selected solvent (Toluene-d_8; THF-d_8: DCM-d_2; $CDCl_3$). After a precipitate was formed, the obtained solution was filtered and the ^{1}H NMR spectrum recorded. Cyclohexane was not used because it is immiscible with DMSO.

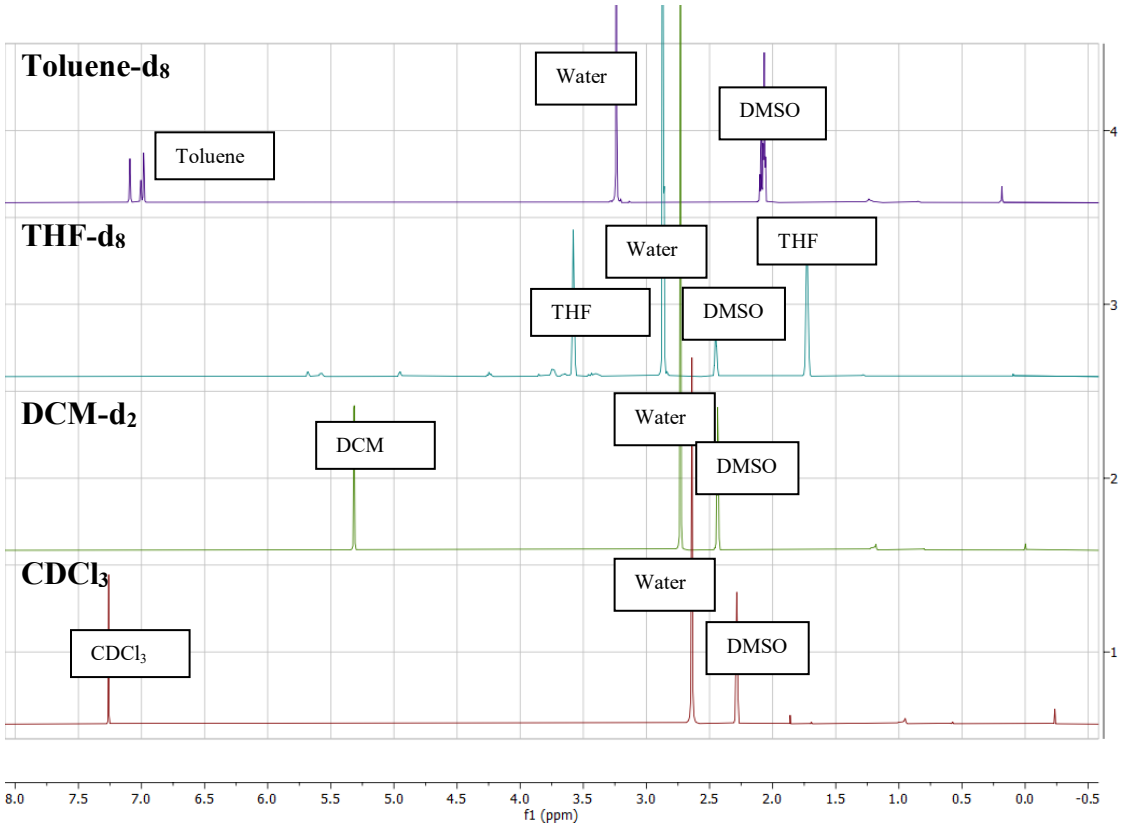

Figure S15. 400 MHz ^{1}H NMR of the γ-cyclodextrin dissolved in DMSO-d_6 and diluted by the indicated solvent.

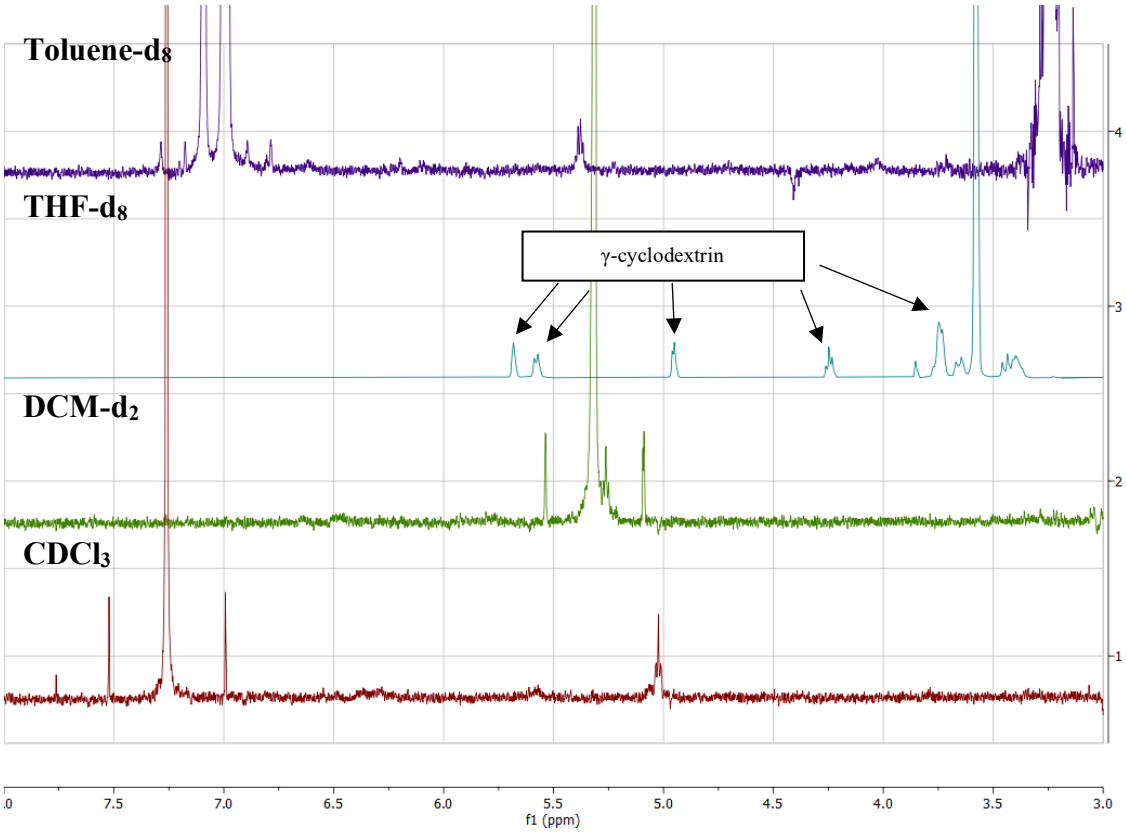

Figure S16. 400 MHz ^{1}H NMR of the γ-cyclodextrin dissolved in DMSO-d$_6$ solution and diluted by the indicated solvent: region from 3.0 till 8.0 ppm.

4. Crystallographic Data and Lattice Parameters

Table S1. Full crystal data and structure refinement for ε-, ε·tol-, and δ-phases.

Parameter	ε	ε·Tol	δ
Radiation		Cu Kα (λ = 1.54184)	
Crystal system	Orthorhombic	Orthorhombic	Tetragonal
Space group	*I*222	*I*222	*I*4
a/Å	15.7898(1)	15.8765(1)	23.8093(2)
b/Å	20.2381(1)	20.1735(1)	23.8093(2)
c/Å	28.1282(2)	28.1409(2)	15.2630(1)
Volume/Å^3	8988.5(1)	9013.1(1)	8652.3(2)
Z	8	8	8
ϱ_{calc}g/cm^3	1.122	1.245	1.112
μ/mm^{-1}	1.498	1.603	1.717
F(000)	3194	3416	3008
Crystal size/mm^3	0.12 × 0.07 × 0.04	0.23 × 0.13 × 0.12	0.10 × 0.07 × 0.05
Temperature/K	170(2)	150(1)	170(2)
2Θ max. for data collection/°	150	156	150
Reflections collected	23669	49173	21231
Independent reflections	8457 [R_{int} = 0.0214]	9525 [R_{int} = 0.0232]	7069 [R_{int} = 0.0718]
Data/restraints/parameters	8278/4/471	9491/0/478	6777/2/437
Goodness-of-fit on F^2	1.028	1.054	1.035
Final *R* indexes [$I > 2\sigma(I)$]	R_1 = 0.0718, wR_2 = 0.2109	R_1 = 0.0779, wR_2 = 0.2343	R_1 = 0.0736, wR_2 = 0.2120
Final *R* indexes [all data]	R_1 = 0.0725, wR_2 = 0.2127	R_1 = 0.0780, wR_2 = 0.2345	R_1 = 0.0754, wR_2 = 0.2147
Largest diff. peak/hole/eÅ^{-3}	1.83/–0.56	1.25/–0.97	0.87/–0.84
Flack's *x* parameter	0.03(1)	0.04(2)	0.07(2)

5. Crystallographic Data Collected over Time

Table S2. Measured lattice parameter of γ-CD-MOF-1 in dichloromethane (DCM).

	DCM-1				**DCM-2**			
	Time, Days							
	3	**6**	**9**	14	3	6	9	14
a, Å	15.78	15.78	15.69	15.86	30.97	15.78	15.69	15.78
b, Å	20.23	20.26	20.27	20.27	30.97	20.26	20.27	20.38
c, Å	28.13	28.13	28.13	28.11	30.97	28.13	28.13	28.37
α, °	90	90	90	90	90	90	90	90
β, °	90	90	90	90	90	90	90	90
γ, °	90	90	90	90	90	90	90	90
V, Å^3	8982	8992	9016	8956	29704	8992	8992	9123
Space group	I222	I222	I222	I222	I432	I222	I222	I222

Table S3. Measured lattice parameter of γ-CD-MOF-1 in chloroform.

	Chloroform-1				**Chloroform-2**			
	Time, Days							
	3	**6**	**9**	14	3	6	9	14
a, Å	30.97	30.97	42.77	30.99	30.98	43.72	42.91	42.91
b, Å	30.97	30.97	42.91	30.99	30.98	43.72	42.91	42.91
c, Å	30.97	30.97	28.20	30.99	30.98	27.16	28.19	28.12
α, °	90	90	90	90	90	90	90	90
β, °	90	90	90	90	90	90	90	90
γ, °	90	90	120	90	90	120	120	120
V, Å^3	29688	29688	44850	29761	29773	45145	45054	44846
Space group	I432	I432	R32	I432	I432	R32	R32	R32

Table S4. Measured lattice parameter of γ-CD-MOF-1 in THF.

	THF-1				**THF-2**			
	Time, Days							
	3	**6**	**9**	14	3	6	9	14
a, Å	30.99	30.87	43.67	30.87	30.99	43.78	43.69	30.86
b, Å	30.99	30.99	43.67	30.87	30.99	43.80	43.69	30.86
c, Å	30.99	30.97	26.77	30.87	30.99	26.84	26.82	30.86
α, °	90	90	90	90	90	90	90	90
β, °	90	90	90	90	90	90	90	90
γ, °	90	90	120	90	90	120	120	90
V, Å3	29762	29655	44253	29432	29762	44912	44362	29408
Space group	I432	I432	R32	I432	I432	R32	R32	I432

Table S5. Measured lattice parameter of γ-CD-MOF-1 in toluene.

	Toluene-1				**Toluene-2**			
	Time, Days							
	3	**6**	**9**	14	3	6	9	14
a, Å	30.99	23.55	15.78	15.86	30.99	32.96	15.87	15.87
b, Å	30.99	23.75	20.23	20.20	30.99	33.48	20.20	20.20
c, Å	30.99	22.88	28.10	28.20	30.99	22.91	28.20	28.20
α, °	90	90	90	90	90	90	90	90
β, °	90	90	90	90	90	90	90	90

γ, °	90	90	90	90	90	90	90	90
V, Å^3	29762	12801	8970	9032	29762	25283	9037	9037
Space group	I432		I222	I222	I432		I222	I222

Table S6. Measured lattice parameter of γ-CD-MOF-1 in cyclohexane.

	Cyclohexane-1				**Cyclohexane-2**			
	Time, Days							
	3	**6**	**9**	14	3	6	9	14
a, Å	30.99	43.67	43.79	43.67	30.99	43.79	43.79	43.31
b, Å	30.99	43.67	43.79	43.67	30.99	43.79	43.79	43.31
c, Å	30.99	26.84	26.86	26.77	30.99	26.86	26.86	26.84
α, °	90	90	90	90	90	90	90	90
β, °	90	90	90	90	90	90	90	90
γ, °	90	120	120	120	90	120	120	120
V, Å^3	29762	44453	44662	44253	29762	44662	44662	44123
Space group	I432	R32	R32	R32	I432	R32	R32	R32

Table S7. Measured lattice parameter of γ-CD-MOF-1 in methyl tert-butyl ether (MTBE).

	MTBE-1				**MTBE-2**			
	Time, Days							
	3	**6**	**9**	14	3	6	9	14
a, Å	30.99	30.99	30.97	30.91	30.99	30.99	30.99	30.92
b, Å	30.99	30.99	30.97	30.91	30.99	30.99	30.99	30.92
c, Å	30.99	30.99	30.97	30.91	30.99	30.99	30.99	30.92
α, °	90	90	90	90	90	90	90	90
β, °	90	90	90	90	90	90	90	90
γ, °	90	90	90	90	90	90	90	90
V, Å^3	29762	29762	29704	29580	29762	29762	29762	29560
Space group	I432	I432	I432	I432	I432	I432	I432	I432

Table S8. Measured lattice parameter of γ-CD-MOF-1 in diethyl ether.

	Diethyl Ether-1				**Diethyl Ether-2**			
	Time, Days							
	3	**6**	**9**	14	3	6	9	14
a, Å	30.99	43.79	23.81	23.81	30.99	43.79	23.81	23.81
b, Å	30.99	43.79	23.81	23.81	30.99	43.79	23.81	23.81
c, Å	30.99	26.86	15.26	15.26	30.99	26.86	15.26	15.26
α, °	90	90	90	90	90	90	90	90
β, °	90	90	90	90	90	90	90	90
γ, °	90	120	90	90	90	120	90	90
V, Å^3	29762	44662	8652	8652	29762	44662	8652	8652
Space group	I432	R32	I4	I4	I432	R32	I4	I4

DCM—dichloromethane

THF—tetrahydrofuran

MTBE—methyl tert-butyl ether