Supporting Information

Sorption discrimination between secondary alcohol enantiomers by chiral alkyl-dicarboxylate MOFs

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After adjustment of the approach given in ref.[1] (by inclusion of the factor of 12), the deviation (*D*) of the metal coordination from perfectly octahedral can be estimated as

$$D = \frac{\frac{\sum|\theta - 90|}{12}}{90} \times 100\%,$$

where θ are the values of the twelve *cis*-angles in the MD_6 chromophore.

Alternatively, an RMS value can be used:

$D = \frac{\sqrt{\frac{\sum(\theta - 90)^2}{12}}}{90} \times 100$, which gives 4.2 % for the Co^{II} ion in **1**.

Table S1. The values of Co–O(water)–Co angles in aqua- and diaqua- bridged Co^{II} complexes.

Compound [a]	Angle Co-O(water)-Co, °	Ref.
$Et_4N[Co_2(AcO)_5(\mu\text{-}OH_2)(py)_2]$	112.9(2)	2
$[Co_2(\mu\text{-}OH_2)_2(\mu\text{-}O_2CAr^{Tol})_2(O_2CAr^{Tol})_2(py)_2]$	84.9	3
$[Co_2(\mu\text{-}OH_2)_2(\mu\text{-}O_2CAr^{Tol})_2(O_2CAr^{Tol})_2(THF)_2]$	85.4	3
$[Co_2(\mu\text{-}OH_2)_2(\mu\text{-}O_2CAr^{Tol})_2(O_2CAr^{Tol})_2$ (N,N-Bn_2en)$_2$]	84.3	3
$[Co_2(\mu\text{-}OH_2)_2(\mu\text{-}O_2CAr^{Tol})_2(O_2CAr^{Tol})_2(py)_2]$	92.1	3
$[Co_2(\mu\text{-}OH_2)_2(H_2O)_2][Co(H_2O)_3]_4[Re_6Se_8(CN)_6]_3\cdot 44H_2O$	99.4	4
$[Co_2(\mu\text{-}OH_2)_2(H_2O)_2][Re_6S_8(CN)_6]\cdot 12H_2O$	101.0	4
$Co_2(O_2CFcCO_2)_2(2,2'\text{-bpy})_2(\mu\text{-}OH_2)_2\cdot CH_3OH\cdot 2H_2O$	100.8	5
$[Co_2(\mu\text{-}OAc)_2(\mu\text{-}OH_2)_2(tmen)_2][OTf]_2$	86.6	6
$Co(\mu\text{-}OH_2)_2[Au(CN)_2]_2$	*ca*. 100 [b]	7
$((tmen)Co(\mu\text{-}H_2O)(O_2CFcCO_2)_2$	113.5	8

a) AcO^- = acetate, py = pyridine, $Ar^{Tol}CO_2H$ = 2,6-di(p-tolyl)benzoic acid, THF = tetrahydrofuran, N,N-Bn_2en = *N,N*-dibenzylethylenediamine, HO_2CFcCO_2H = 1,1'-ferrocenedicarboxylic acid, 2,2'-bpy = 2,2'-bipyridine, tmen = N,N,N',N'-tetramethylethylenediamine, OTf^- = trifluoromethanesulfonate;

b) single crystal structure of $Co(\mu\text{-}OH_2)_2[Au(CN)_2]_2$ was not determined; estimation based on single crystal X-ray structure of Ni^{II} analogue, $Ni(\mu\text{-}OH_2)_2[Au(CN)_2]_2$, for which the angle Ni-O(water)-Ni is 100.6°.[9]

Table S2. Optical spectroscopic data (*d-d* transitions in visible region) for selected Co^{II} coordination polymers with octahedral and tetrahedral Co^{II} coordination. Arrows in column 2 indicate spectral changes upon transformation of O_h Co^{II} into T_d Co^{II} due to chemical reaction of the coordination polymer (exposure to some reagent)

Complex [a)]	Bands in visible region assigned to *d-d* transitions, λ, nm		Ref.
	Co^{II} in octahedral environment	Co^{II} in tetrahedral environment	
$\{[Co_2(H_2O)_4][Re_6S_8(CN)_6]\cdot 10H_2O\}_n$	434, 500		4
$\{[Co_2(H_2O)_4][Re_6S_8(CN)_6]\cdot 10H_2O\}_n$ upon exposure to $(C_2H_5)_2O$ (Tranformation Oh Co^{II} into Td Co^{II})	→	540, 570, 596 ($^4A_2 \rightarrow {}^4T_1(P)$ and $^4A_2 \rightarrow {}^4T_1(F)$)	
$\{[Co(H_2O)_3]_4[Co_2(H_2O)_4][Re_6Se_8(CN)_6]_3.44 H_2O\}_n$ upon exposure to $(C_2H_5)_2O$ (Tranformation Oh Co^{II} into Td Co^{II})	460		4
$\{[Co(H_2O)_3]_4[Co_2(H_2O)_4][Re_6Se_8(CN)_6]_3.44 H_2O\}_n$	→	650	
$[(TTB)_2CoBr_2(MeOH)(DMF)]_n$	475		10
$[(TTB)_2CoBr_2(MeOH)(DMF)]_n + COCl_2 \rightarrow [(TTB)_2CoCl_2]_n$ (Tranformation Oh Co^{II} into Td Co^{II})	→	670 ($^4A_2 \rightarrow {}^4T_1(P)$)	
$[Co(m\text{-}dtab)Cl_2]_n$		613, 653, 719 ($^4A_2 \rightarrow {}^4T_1(P)$ and $^4A_2 \rightarrow {}^4T_1(F)$)	11
$[Co(m\text{-}dtab)Br_2]_n$		650, 680, 746 ($^4A_2 \rightarrow {}^4T_1(P)$ and $^4A_2 \rightarrow {}^4T_1(F)$)	11
$[Co_4O(bdpb)_3]_n$		610, 1000	12
$Co[O_2C(CH_2)_3CO_2]_n$		1302 ($^4A_2(F) \rightarrow {}^4T_1(F)$) 826, 572, 526 ($^4A_2(F) \rightarrow {}^4T_1(P)$)	13
$\{[Co(BPB)]\cdot 3DMF\}_n$		570, 1040	14
$[\{Co(2,2'\text{-bipy})_2(LH_4)\}(LH_2)]_n$	475 (sh), 500, 525 (sh)[b)]		15
$[Co(OOC(CH_2)_{14}COO)(H_2O)_2]_n$	543 ($^4T_{1g} \rightarrow {}^4T_{1g}(P)$), 714 ($^4T_{1g} \rightarrow {}^4A_{2g}$)		16

Table S2 *(continued)*. Optical spectroscopic data (*d-d* transitions in visible region) for selected Co^{II} coordination polymers with octahedral and tetrahedral Co^{II} coordination. Arrows in column 2 indicate spectral changes upon transformation of O_h Co^{II} into T_d Co^{II} due to chemical reaction of the coordination polymer (exposure to some reagent)

Complex [a]	Bands in visible region assigned to *d-d* transitions, λ, nm		Ref.
	Co^{II} in octahedral environment	Co^{II} in tetrahedral environment	
$[Co(H_2cit)(H_2O)]_n$	532 ($^4T_{1g}$ (F) →$^4T_{1g}$(P)), 680 ($^4T_{1g}$(F) → $^4A_{2g}$(F))		17
$\{[Co(H_2O)_4]_n[Co_2(Hcit)_2(H_2O)_4]\cdot 6H_2O\}_n$	520 ($^4T_{1g}$ (F) →$^4T_{1g}$(P))		17
$\{(NH_4)_2[Co_2(Hcit)_2(H_2O)_2]\}_n$	520 ($^4T_{1g}$ (F) →$^4T_{1g}$(P))		17

[a] TTB = 1,2,4,5-tetra(2H-tetrazole-5-yl)-benzene, m-dtab = the dithioamide of 1,3-benzenedicarboxylic acid, H_2bdpb = 1,4-bis[(3,5-dimethyl)-pyrazol-4-yl]benzene, H_2BPB = 1,4-bis(4'-pyrazolyl)benzene, 2,2'-bipy = 2,2'-bipyridine, H_4L = p-xylylenediphosphonic acid, H_4cit = citric acid, H_4cit = citric acid, H_4cit = citric acid

[b] sh = shoulder

Table S3. Optical spectroscopic data (*d-d* transitions in visible region) for selected Co^{II} coordination compounds with octahedral and trigonal-bipyramidal Co^{II} coordination. Arrow in column 2 indicates spectral changes upon transformation of Co^{II} due to dehydration

Complex [a]	Bands in visible region assigned to *d-d* transitions, λ, nm		Ref.
	Co^{II} in octahedral environment	Co^{II} in trigonal-bipyramidal environment	
$[Co(phen)(HO_3P\text{-}C_2H_4\text{-}PO_3H)(H_2O)_2]_n$	534 ($^4T_{1g} \rightarrow {}^4T_{1g}(P)$), 468 (sh)		18
$[Co(phen)(HO_3P\text{-}C_2H_4\text{-}PO_3H)]_n$	→	468 (sh), 504, 534, 624 ($^4A_2(F) \rightarrow {}^4E(F)$)	
$(Tp^{Np})Co\text{-}C_2O_4\text{-}Co(Tp^{Np})$		460, 526 (sh)	19

[a] phen = 1:10-phenantroline, Tp^{Np} = tris(3-neopentylpyrazolyl)borate

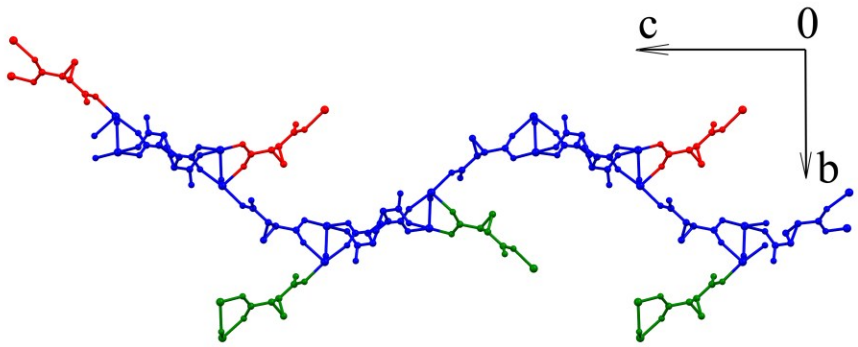


Fig. S1. View of 2D layer in **1**·5py. Colours correspond to the scheme used in Fig. 2 in the main text. Projection along *a* axis.

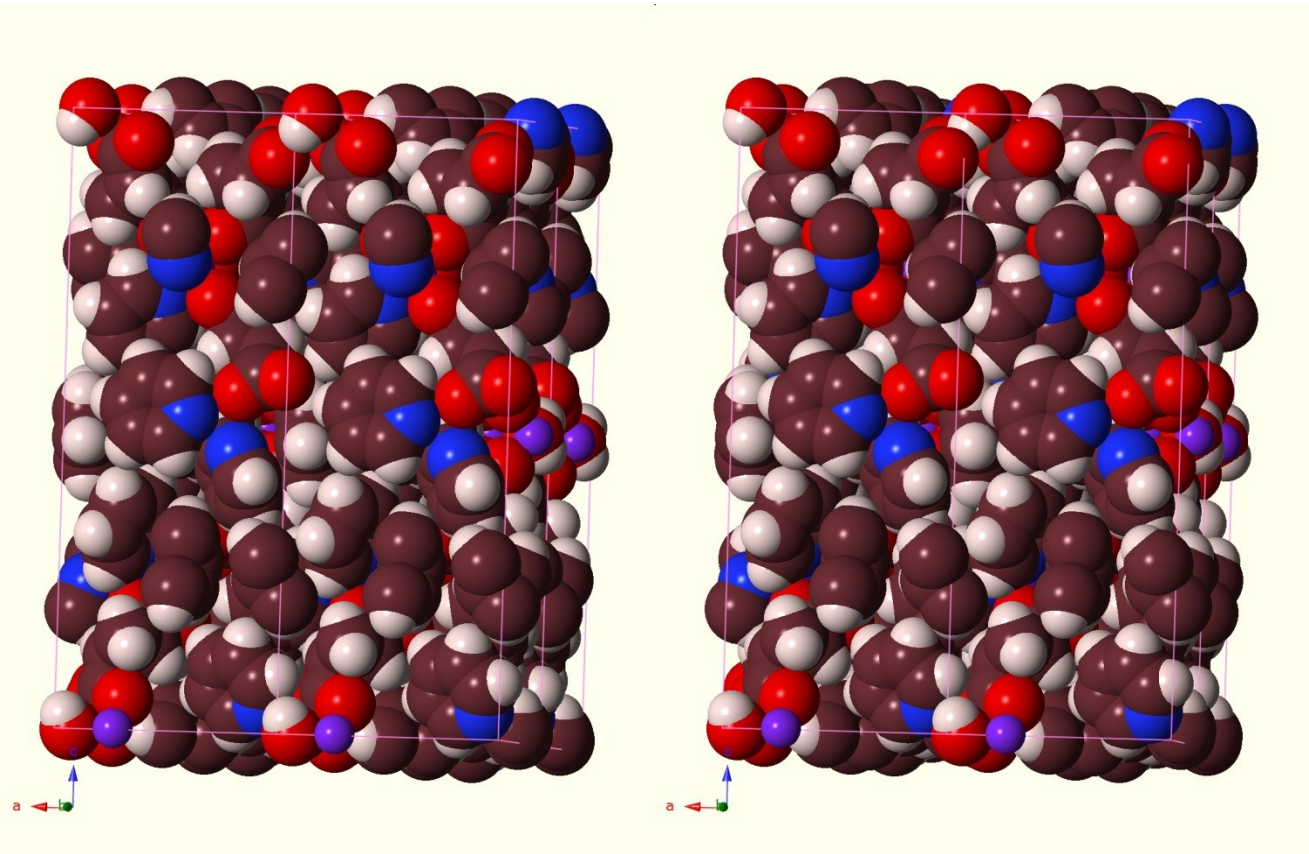
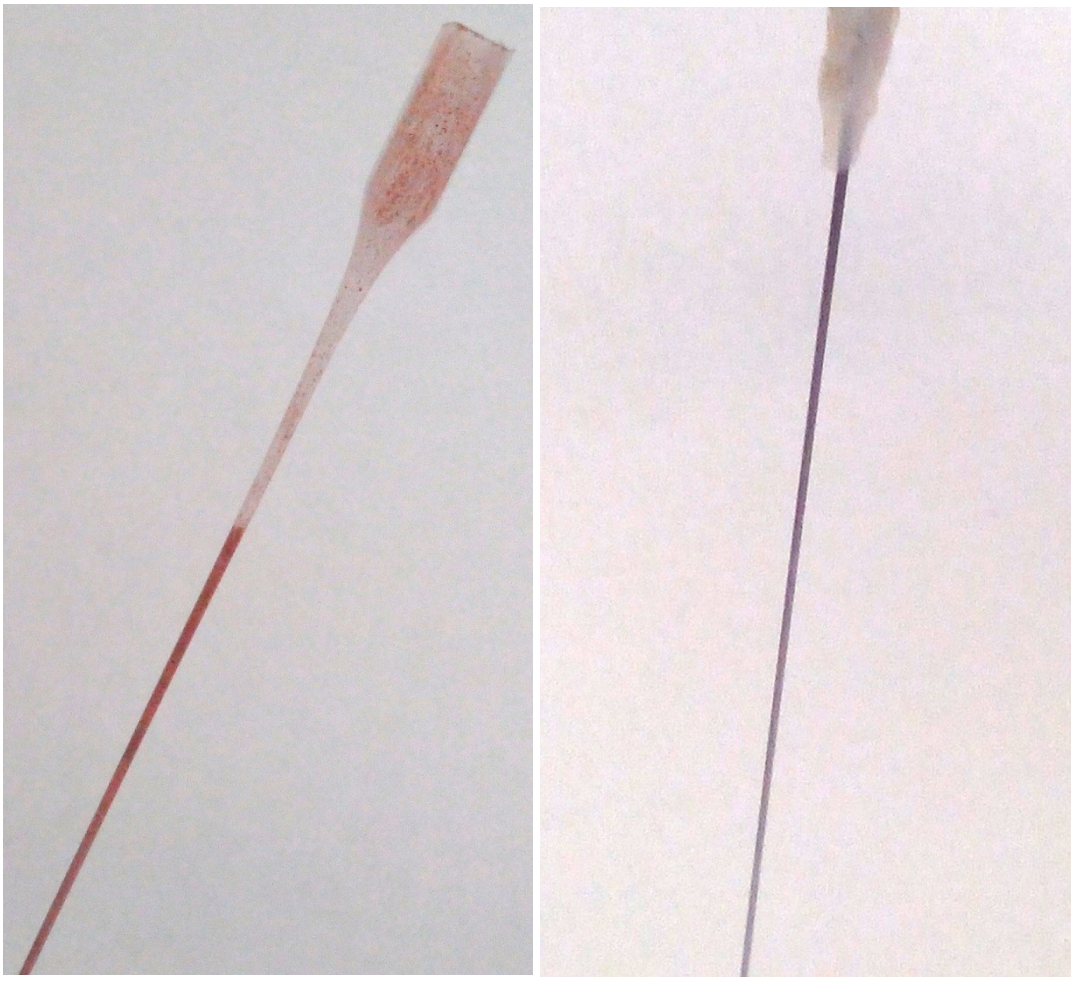


Fig. S2: Space-filling inverse stereoview along the b-axis, demonstrating the absence of channels or significant voids in **1**·5Py.



(a) (b)

Fig. S3. Digital images of glass capillaries filled with air-dried samples of **1** (a) and **1'** (b), used for powder X-ray diffraction experiments.

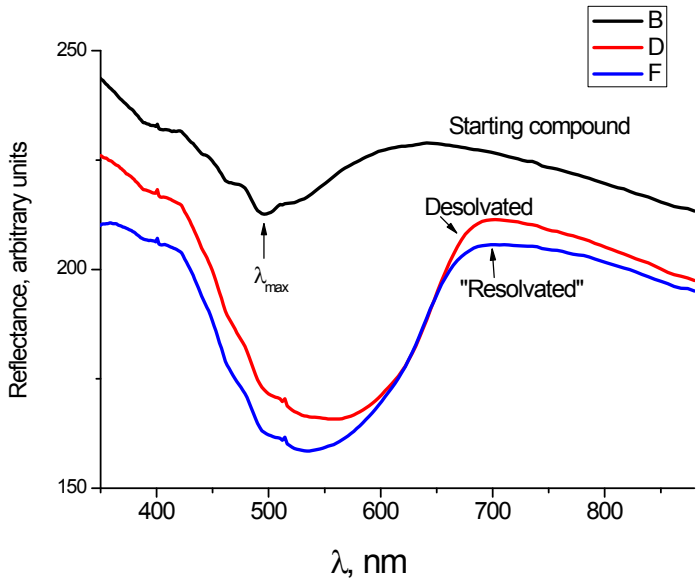
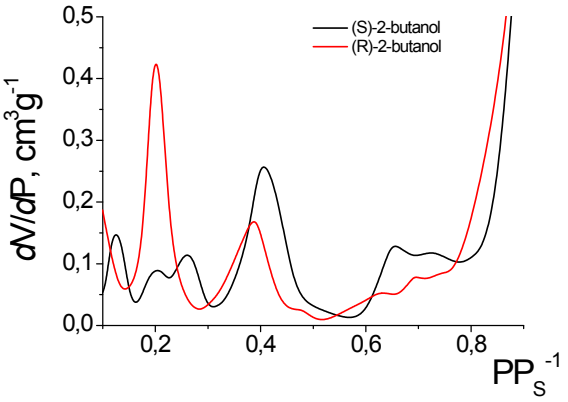
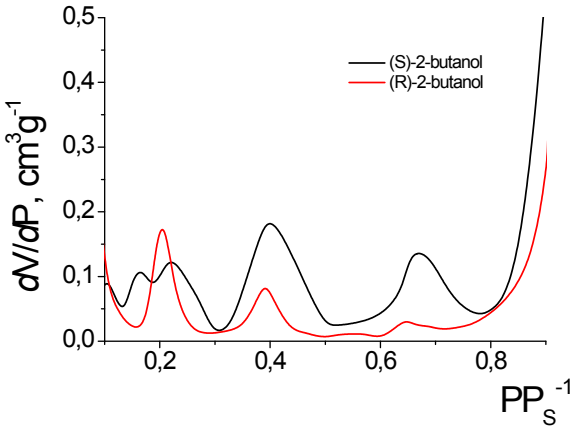


Fig. S4. Diffuse reflectance spectra for samples **1**, **1'** and **1''** resolvated by 2-butanol.

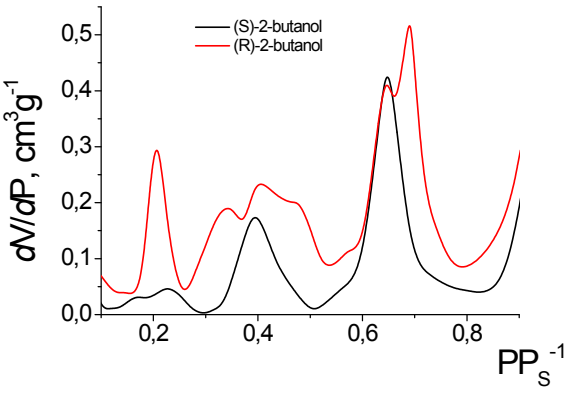
The band at λ_{max} = 495 nm in the spectrum of **1**·3.5py·2.5H_2O is assignable as the $^4T_{1g}$ → $^4T_{1g}$(P) transition of Co^{II} ion in a distorted octahedral donor set, and the one at 560 nm in the spectrum of **1''** as the $^4A_2$ (F) —> $^4T_1$(P) transition in a tetrahedral environment.



(a)



(b)



(c)

Fig. S5. First-derivative isotherms for 2-butanol enantiomer sorption by **1'** (a), **2'** (b) and **3'** (c) from the gas phase at 303 K.

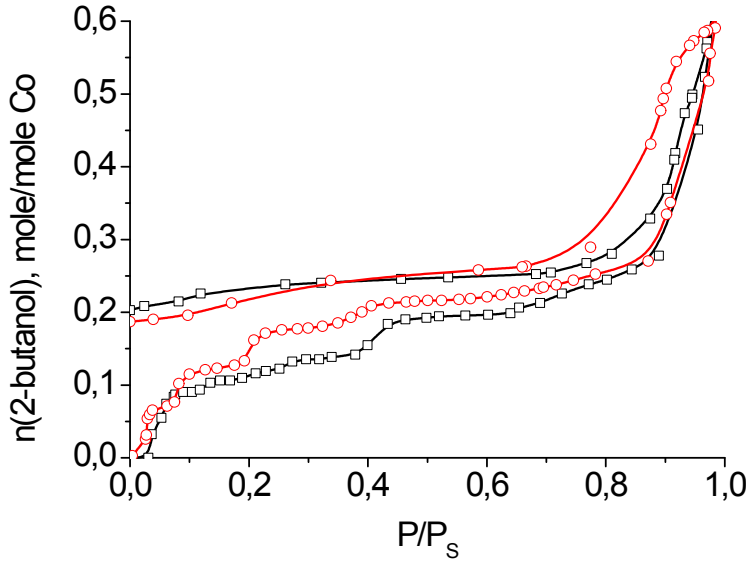


Fig. S6. Isotherms for sorption of the pure 2-butanol optical isomers by **1'** from the gas phase at 303 K, expressed as moles of butanol per mole of Co^{II} ions. □: (S)-2-butanol, ○: (R)-2-butanol.

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