Supplementary Information for

Homochiral coordination polymers with nanotublar channels for enantioselective sorption of chiral guest molecules

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General: ^{1}H-NMR spectra were recorded on JEOL JNM-GSX 400 spectrometer with tetramethylsilane (TMS) as the internal standard. IR spectra were recorded with a JASCO FT-IR 4100 spectrometer. Thermogravimetric analyses (TG) were performed on a Rigaku TG-8120 instrument. The solid-state CD spectra were recorded as KBr pellets on a JASCO J-820 circular dichromism system. Enantiomeric excesses were determined by high-performance liquid chromatography (HPLC) on Chiralpak AD-H column (Daisel).
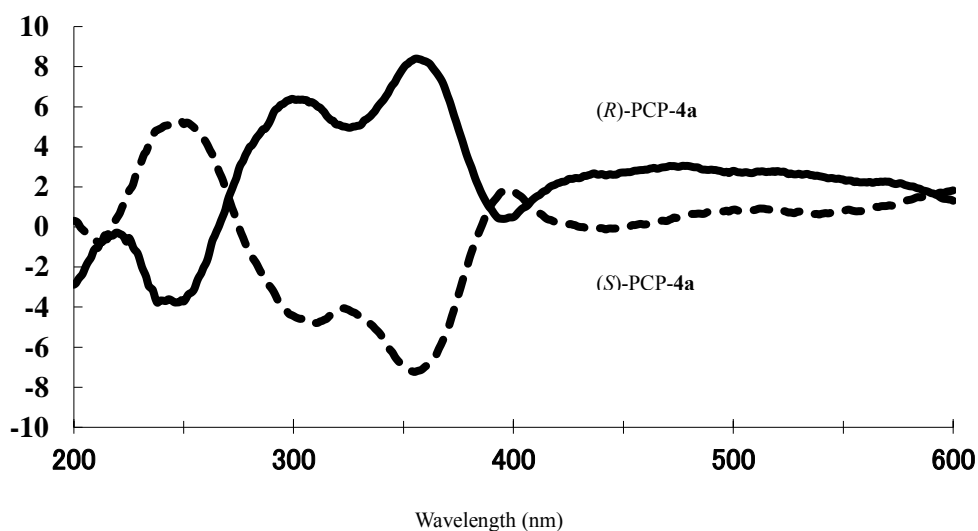

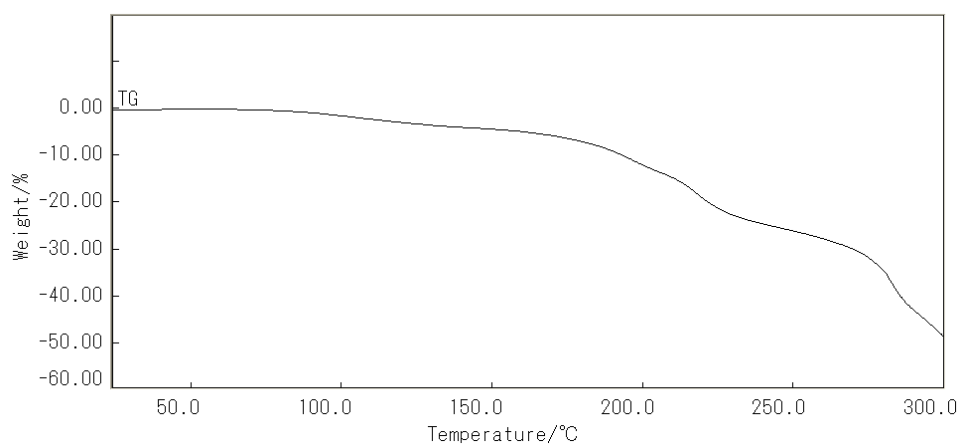Fig. S1 Solid CD spectra of (*R*)- and (*S*)-PCP-**4a** in KBr pellet.
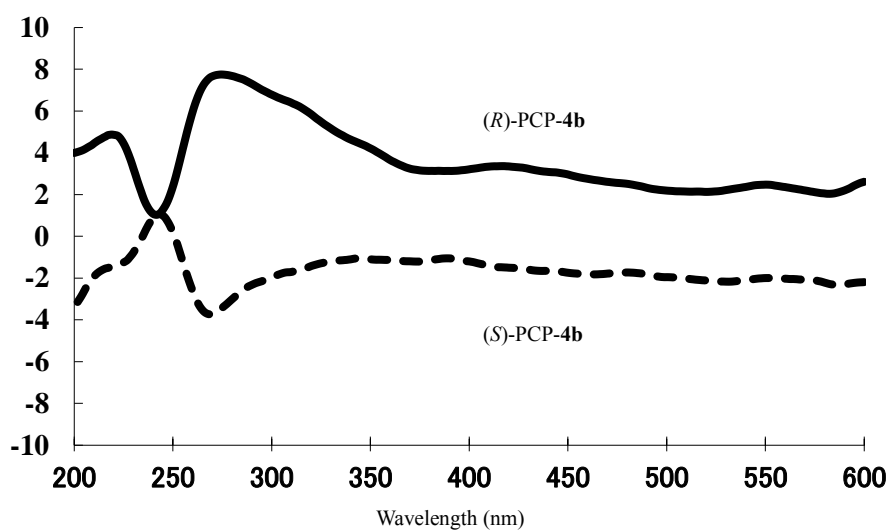
Fig. S2 TGA curves for (*R*)-PCP-**4a**.

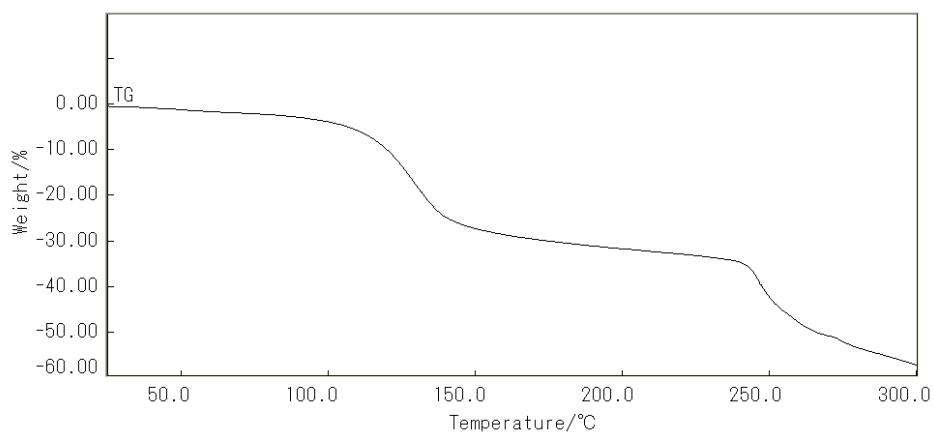Fig. S3 Solid CD spectra of (*R*)- and (*S*)-PCP-**4b** in KBr pellet.

Fig. S4 TGA curves for (*R*)-PCP-**4b**.

General sorption procedure: A racemic β-lactam (0.5 mmol) was dissolved in CH$_2$Cl$_2$ (5 mL), and the (*R*)-PCP (50 mg) was added in the solution. After stirring the mixture for 24 h at room temperature, the crystalline adsorbent was collected by filtration. The solid was extracted with MeOH (5 mL) for 1 h to retrieve the adsorbed β-lactam, and then the solvent was removed in *vacuo*. Enantiomeric excess (ee) of the remaining β-lactam was determined by HPLC on Chiralpak AD-H column (Daisel).
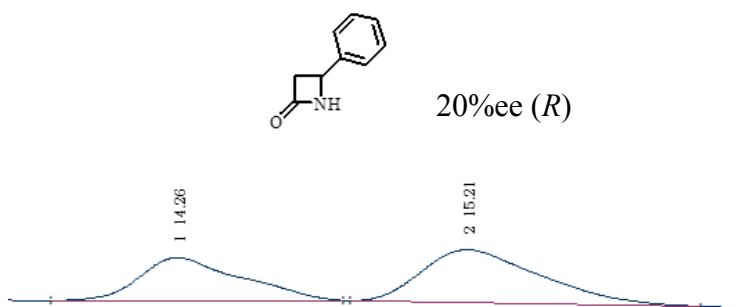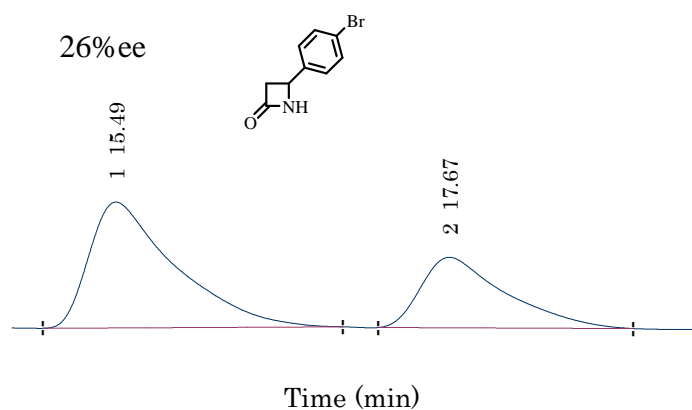
20%ee (*R*)

HPLC condition : CHIRALPAK AD-H, n-Hexane/IPA=95/5, F.R.=1.0 ml/min, UV=254 nm

40%ee

HPLC condition : CHIRALPAK AD-H, n-Hexane/IPA=95/5, F.R.=1.0 ml/min, UV=254nm

3

29%ee

1 14.89

2 15.86

HPLC condition : CHIRALPAK AD-H, n-Hexane/IPA=95/5, F.R.=1.0 ml/min, UV=254 nm

26%ee

1 15.49

2 17.67

Time (min)
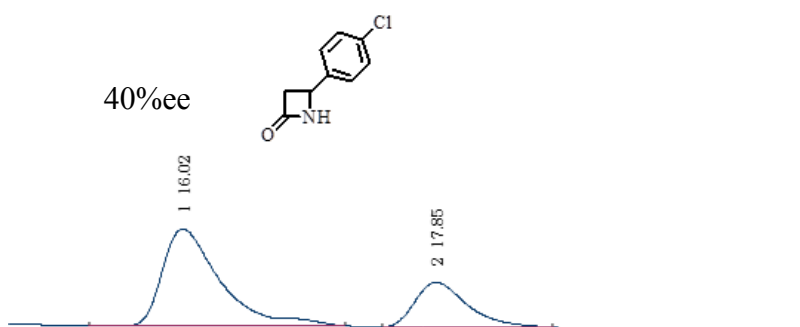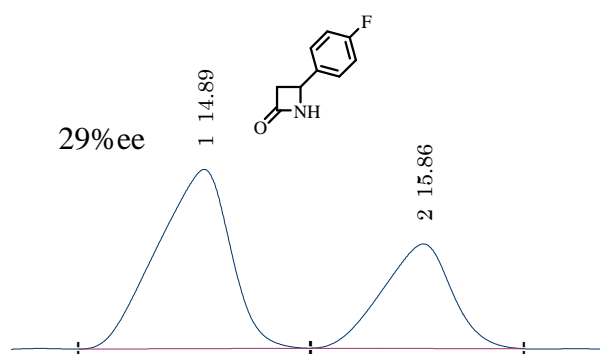
HPLC condition : CHIRALPAK AD-H, n-Hexane/IPA=95/5, F.R.=1.0 ml/min, UV=254 nm

X-ray diffraction: X-ray experiments were performed on a Rigaku RAXIS RAPID imaging plate area detector diffractometer [graphite-monochromated Mo Kα radiation (λ = 0.71073 Å); ω scans] for (*R*)-PCP-4**a**, a Rigaku Saturn724+ CCD area detector diffractometer mounted on a 1/4 χ goniometer for (*R*)-PCP-4**b** with a Rigaku low-temperature equipment. Data was collected at -150 °C for (*R*)-PCP-4**a** and -173 °C for (*R*)-PCP-4**b**, respectively. The crystal structures were solved by direct methods (SIR97[3]) and refined by full-matrix least-squares methods (SHELXL97[4]). All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using the riding model. All calculations were performed by using the crystallographic

software package CrystalStructure[5] and Yadokari-XG 2009[6]. The crystal structure parameters for (R)-PCP-4**a** and (R)-PCP-4**b** are listed in Table S1. Crystallographic data (excluding structure factors) for the structures described in this paper have been deposited with the Cambridge Crystallographic Data Centre (supplementary publication nos. CCDC 954513-954514). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Table S1 crystal structure parameters for (R)-PCP-4**a** and (R)-PCP-4**b**

Compound	(R)-PCP-4**a**	(R)-PCP-4**b**
Chemical formula	$C_{38}H_{40}CuN_4O_{10}$	$C_{40.50}H_{35.50}CuN_{3.50}O_7$
Formula Mass	776.28	746.76
Crystal system	Trigonal	Orthorhombic
$a/\text{Å}$	8.89960(10)	22.934(4)
$b/\text{Å}$	8.89960(10)	30.885(5)
$c/\text{Å}$	39.5773(11)	10.5055(18)
$\alpha/°$	90.00	90.00
$\beta/°$	90.00	90.00
$\gamma/°$	120.00	90.00
Unit cell volume/Å^3	2714.68(11)	7441(2)
Temperature/K	123(2)	100(2)
Space group	$P3_221$	$C222_1$
No. of formula units per unit cell, Z	3	8
Absorption coefficient, μ/mm^{-1}	0.668	0.641
No. of reflections measured	26777	30654
No. of independent reflections	4148	8488
R_{int}	0.0561	0.0435
Final R_1 values ($I > 2\sigma(I)$)	0.0524	0.0535
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1377	0.1495
Final R_1 values (all data)	0.0558	0.0587
Final $wR(F^2)$ values (all data)	0.1453	0.1539
Goodness of fit on F^2	1.124	1.110
Flack parameter	0.03(2)	0.028(15)

Table S2 Selected bond lengths, angles and torsion angles for (*R*)-PCP-4**a** and (*R*)-PCP-4**b**.

atom	length (Å)	atom	angle (°)
Cu1—O3	1.9287(19)	N1—Cu1—N1	170.21(16)
Cu1—N1	1.436(2)	O3—Cu1—O3	172.35(15)
		O3—Cu1—O5	86.18(8)
		N1—Cu1—O5	94.89(8)
		C2—C1—C1^{i}—C2^{i}	-107.6(2)
Cu1—O2	1.9577(17)	N1—Cu1—O2	86.74(6)
Cu1—N2	2.040(2)	N2—Cu1—N2^{ii}	157.71(13)
Cu1—N1	2.334(3)	N1—Cu1—N2	101.15(7)
Cu2—O5	1.9711(17)	O2—Cu1—O2^{ii}	173.47(11)
Cu2—N3	2.250(3)	O5—Cu2—O5^{iii}	174.72(10)
Cu2—N4	2.033(2)	N4—Cu2—N4^{iii}	162.86(12)
		O5—Cu2—N4	91.14(8)
		N3—Cu2—N4	98.57(6)
		N3—Cu2—O5	87.36(5)
		C2—C1—C11—C12	-94.51(5)

Symmetry code (i) (2 - *x*, 1 - *x* + *y*, 2/3 - *z*) ii (- *x*, *y*, 1/2 - *z*), iii (1 - *x*, *y*, 1/2 - *z*)
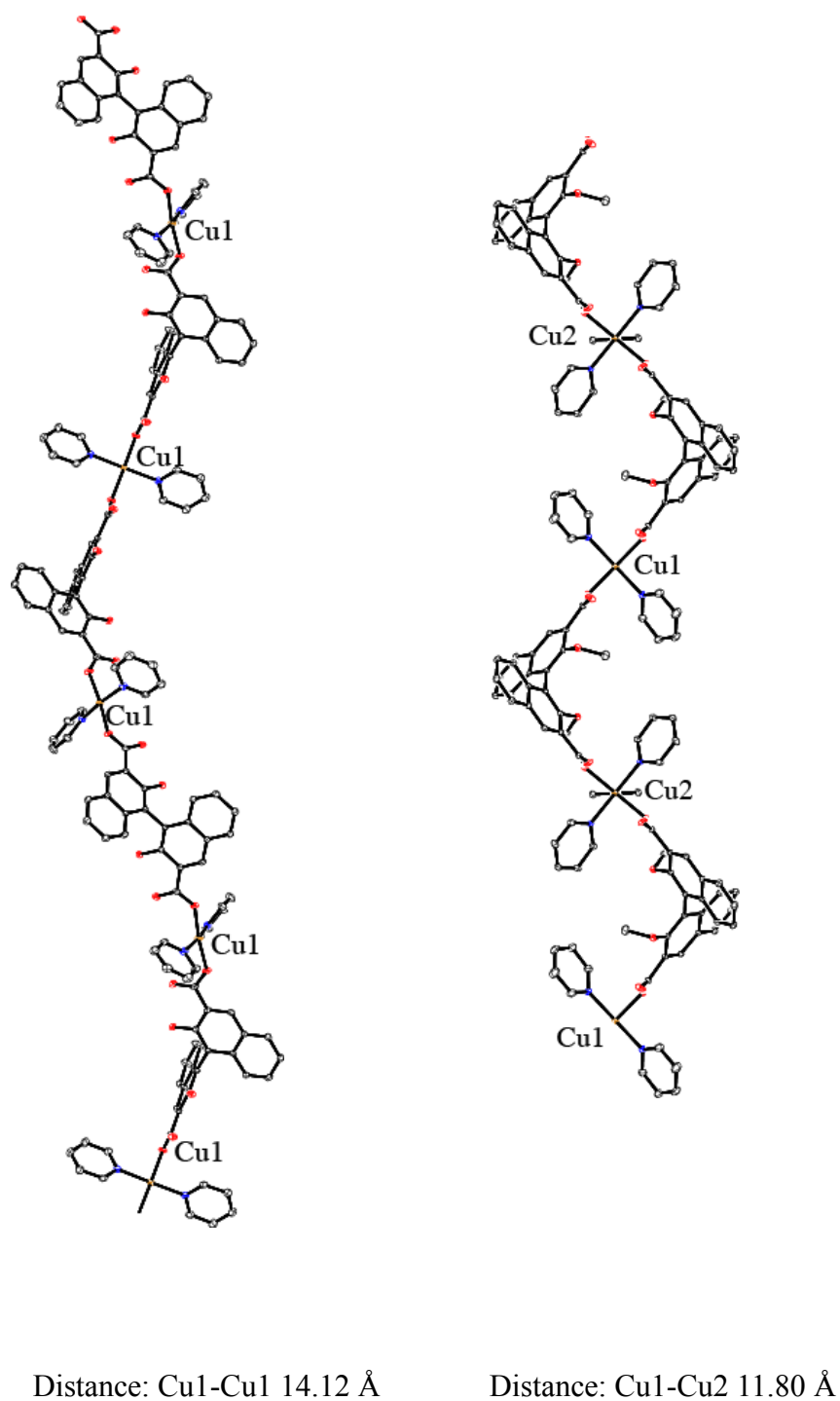
Distance: Cu1-Cu1 14.12 Å   Distance: Cu1-Cu2 11.80 Å

Fig. S5 The chain structures in (*R*)-PCP-4**a** (left, helix,) and (*R*)-PCP-4**b** (right, zigzag). The hydrogen atoms and guest molecules of H_2O and DMF are omitted for clarity.
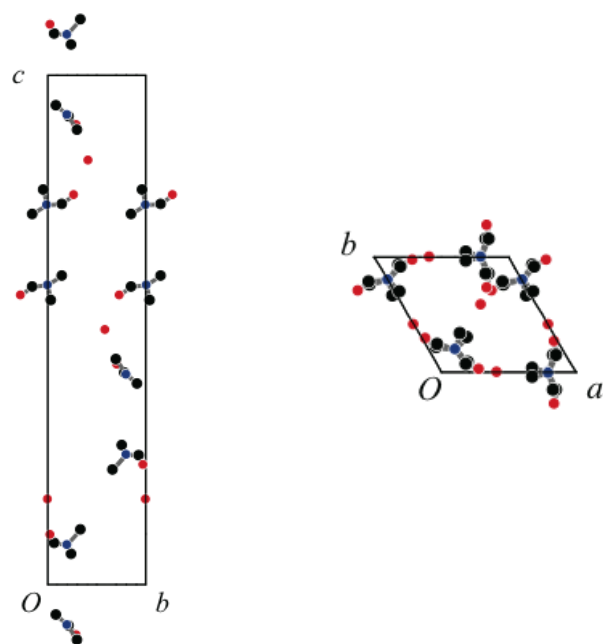
Figure S6. Arrangement of DMF and H$_2$O molecules in the channel of (R)-PCP-4**a** viewed down the a-axis (left) and the c-axis (right).
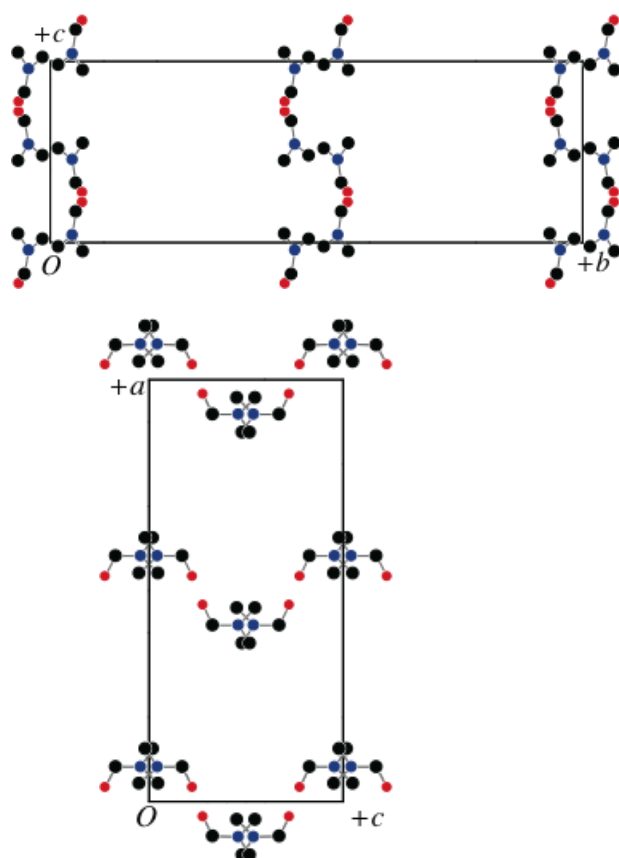
Figure S7. Helical arrangement of DMF molecules in the channel of (R)-PCP-4**b** viewed down the a-axis (top) and the b-axis.

Experimental for Powder X-ray Diffraction (PXRD)

X-ray powder diffraction measurements were recorded on a Rigaku RINT2100 diffractometer equipped with a Cu X-ray source operating at 40kV and 40mA and a secondary graphite monochromator allowing to select the Kα radiation of Cu (λ = 1.5418 Å). A scanning range of 2θ values from 2° to 60° at a scan rate of 1°/min was applied and the intensity of diffracted X-rays being collected at intervals of 0.02°.
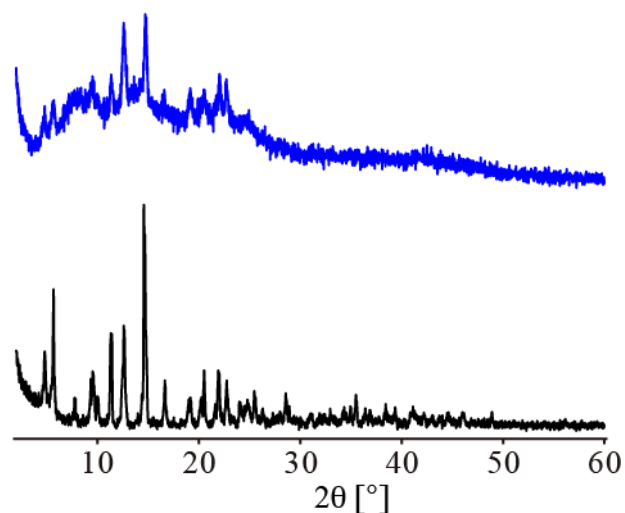
(a)
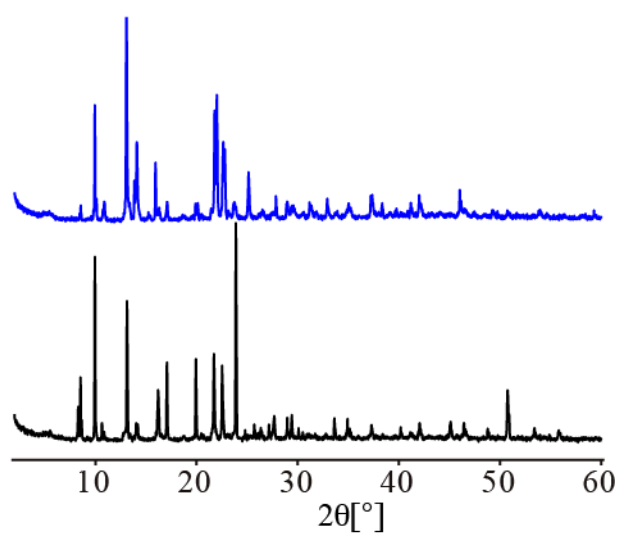
(b)

Figure S8. Powder XRD patterns of (a) (*R*)-PCP-**4a** and (b) (*R*)-PCP-**4b**. Black and blue lines show the samples as synthesized and after sorption experiments, respectively.

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Experimental for BET surface area

Nitrogen adsorption measurements were performed on a Germini VII 2390p Analyzer at 77K using the volumetric method. The specific surface area was obtained from N_2 adsorption isotherms and was calculated by Brunauer-Emmett-Teller (BET method). The BET surface area of (R)-PCP-**4a** and (R)-PCP-**4b** were 0.481 m^2/g and 1.29 m^2/g, respectively.
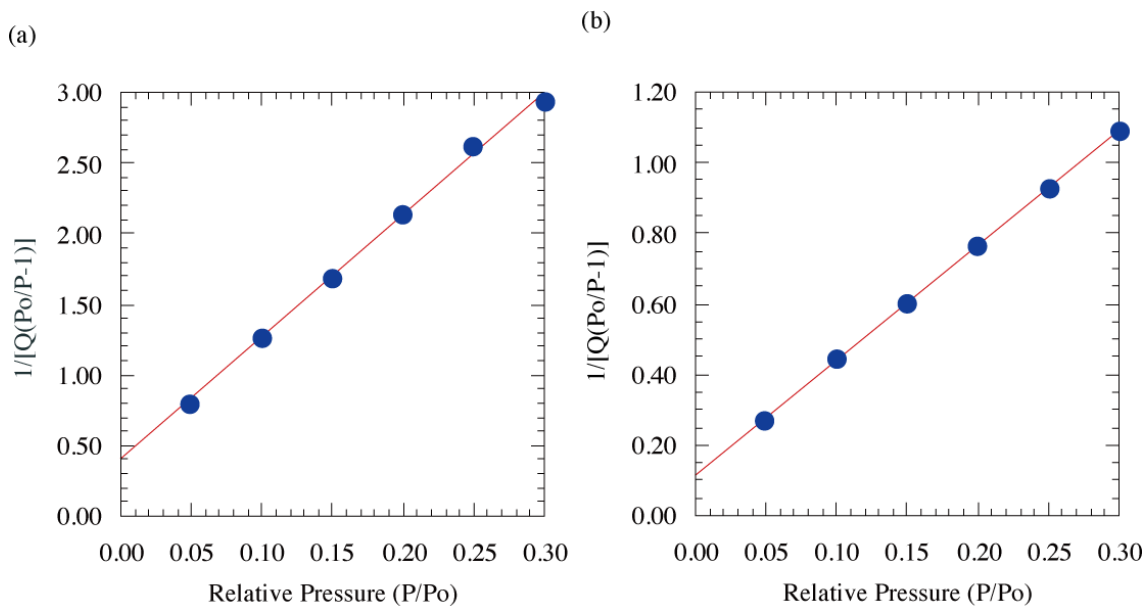
(a)

(b)

Figure S9. BET surface area plots of (a) (R)-PCP-**4a** and (R)-PCP-**4b**.

References

1. D.J. Cram, R.C. Hegeson, S.C. Peacock, L.J. Kaplan, L.A. Domeier, P. Moreau, K. Koga, J.M. Mayer, Y. Chao, M.G. Siegel, D.H. Hoffman, G. Dotsevi, Y. Sogah, *J. Org. Chem.*, **1978**, *43*, 1930-1946.

2. P.K. Baruah, R. Gonnade, P.R. Rajamohanan, H. Hofmann, G.J. Sanjayan, *J. Org. Chem.*, **2007**, *72*, 5077-5084.

3. A. Altomare, M. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.,* 1999, **32**, 115–119.

4. G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112–122.

5. CrystalStructure 3.8; Crystal Structure Analysis Package; Rigaku and Rigaku Americas (2000–2007): 9009 New Trails Dr., The Woodlands, TX 77381, USA.

6. C. Kabuto, S. Akine, T. Nemoto, E. Kwon, *J. Cryst. Soc. Jpn.,* 2009, **51**, 218-224.