Electronic Supplementary Material (ESI) for Analyst.

Supporting Information

Crystalline sponge X-ray analysis coupled with supercritical fluid chromatography: a novel analytical platform for the rapid separation, isolation, and characterization of analytes

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Experimental Procedures

Materials

MeOH (HPLC grade), isopropanol (IPA) (HPLC grade), MeCN (HPLC grade), methyl *t*-butyl ether (MTBE) (HPLC grade), nitrobenzene (special grade), zinc chloride, $ZnCl_2$, (special grade), copper(I) bromide, CuBr, (99.9%), cobalt(II) nitrate hexahydrate, $Co(NO_3)_2{\cdot}6H_2O$, (special grade) and *rac*-terpinen-4-ol were purchased from FUJIFILM Wako pure chemicals Ltd. 2,4,6-Tris(4-pyridyl)-1,3,5-triazine (tpt), *R*-mandelic acid (*R*-man), *S*-mandelic acid (*S*-man), 4,4'-bipyridine (bpy), *rac*-*trans*-stilben oxide, 1-acetylnaphtalene, 2-acetylnaphtalene, *rac*-hydrobenzoin, and *meso*-hydrobenzoin were purchased from TCI Co., Ltd. (*R*,*R*)-*Trans*-stilbene oxide was purchased from Toronto Research Chemicals. Benzene-1,3,5-triyl triisonicotinate (btt) was prepared according to a previous report.[S1] CO_2 (>99.995%) was purchased from TOMOE SHOKAI Co., Ltd. A screw-top 1.2 mL microvial (cat. no. 11090620) and a screw cap with a septum seal (cat. no. 53951-09FB) were purchased from Osaka Chemical Co., Ltd. A syringe needle (cat. no. NN-2425R) was purchased from TERUMO Corporation.

Preparation of MOF crystals

The crystalline sponge (CS) $[(ZnCl_2)_3(tpt)_2]_n$ (**1**) was prepared according to the reported procedure[S2] and stored in *n*-hexane before using. The CS $[CuBr{\cdot}(btt)]_n$ (**2**) was prepared according to the reported procedure[S1] and stored in chloroform before using. The CS $[Co_2(R\text{-man})_2(bpy)_3](NO_3)_2$ (**3*R***) and $[Co_2(S\text{-man})_2(bpy)_3](NO_3)_2$ (**3*S***) were prepared according to the reported procedure[S3] and stored in *n*-hexane before using.

Instruments

Supercritical fluid chromatography (SFC) was performed using a Shimadzu Nexera UC system (Shimadzu Corporation) equipped with a system controller, CBM-40, a CO_2 pump, LC-30 ADSF, a modifier solvent pump, LC-40D XR, a makeup solvent pump, LC-40D XR, autosampler, SIL-40CXR, column compartment, CTO-40C, a photodiode array detector, SPD-40M, a backpressure regulator, SFC-30A, and a faction collector, FRC-40SF.

Single crystal X-ray diffraction (XRD) data were collected on a Synergy-R (Rigaku Oxford Diffraction) diffractometer equipped with a micro-focus Cu Kα radiation source (λ = 1.5418 Å), a hybrid pixel array detector (HPAD), and a low temperature system using a cold nitrogen stream (100 K). Collected data were integrated, corrected, and scaled by the program CrysAlisPro. Empirical and numerical absorption corrections were applied in this process.

SFC-CSXRD analysis of *rac*-*trans*-stilben oxide (*rac*-**4**)

The CS (**1**) was transferred in a screw-top 1.2 mL microvial with *n*-hexane and the solvent was replaced by MTBE (50 μL). Then, the vial was set at the FRC-40SF. Two μL of *rac*-**4** (10 mg/mL in MeOH) was injected into the SFC system and each enantiomer was separated and collected into the vial containing **1**. After excess solvent was evaporated to about 50 μL at 50 °C, the vial was capped, pierced with a needle, and allowed to stand at 50 °C for 1 day to slowly evaporate the solvent. Then, the CS was mounted on an X-ray diffractometer for the diffraction study. The SFC conditions were as follows.

Column: CHIRALPAK IC-3 100 × 3.0 mm id, 3 μm (DAICEL Co., Ltd.)
Column temperature: 25 °C
Mobile phase: CO_2/MTBE = 90/10 (v/v)
Mobile phase flow rate: 3.0 mL/min
Back pressure: 10 MPa
Detector: UV 250 nm
Make-up solvent: MTBE
Make-up solvent flow rate: 5 mL/min

SFC-CSXRD analysis of regioisomers of acetylnaphtalenes (**5a** and **5b**)

The CS (**2**) was transferred in a screw-top 1.2 mL microvial with chloroform and the solvent was replaced by MeOH (50 μL). Then, the vial was set at the FRC-40SF. Five μL of a mixture solution of 1-acetylnaphtalene (**5a**) and 2-acetylnaphtalene (**5b**) (each 20 mg/mL in MeOH) was injected into the SFC system and each regioisomer was separated and collected into the vial containing **2**. After excess solvent was evaporated to about 20 μL at 50 °C, the vial was capped and allowed to stand at 50 °C for 4 days. Then, the CS was mounted on an X-ray diffractometer for the diffraction study. The SFC conditions were as follows.

Column: CHIRALPAK AD-H 250 × 4.6 mm id, 5 μm (DAICEL Co., Ltd.)
Column temperature: 35 °C
Mobile phase: CO_2/MeOH = 95/5 (v/v)
Mobile phase flow rate: 3.0 mL/min
Back pressure: 10 MPa
Detector: UV 330 nm
Make-up solvent: MeOH
Make-up solvent flow rate: 3 mL/min

SFC-CSXRD analysis of stereoisomers of hydrobenzoin (*rac*-**6** and *meso*-**6**)

The CS (**3*R*** or **3*S***) was transferred in a screw-top 1.2 mL microvial with *n*-hexane and the solvent was replaced by MeCN (50 μL). Then, the vial was set at the FRC-40SF. Ten μL of a mixture solution of *rac*-hydrobenzoin (*rac*-**6**, 20 mg/mL) and *meso*-hydrobenzoin

(*meso*-**6**, 10 mg/mL) in MeOH was injected into the SFC system and each stereoisomer was separated and collected into the vial containing **3*R*** or **3*S***. After excess solvent was evaporated to about 20 μL at 50 °C, the vial was capped and allowed to stand at 50 °C for 3 days. Then, the CS was mounted on an X-ray diffractometer for the diffraction study. The SFC conditions were as follows.

Column: CHIRALPAK IG 250 × 4.6 mm id, 5 μm (DAICEL Co., Ltd.)
Column temperature: 35 °C
Mobile phase: CO_2/MeCN = 40/60 (v/v)
Mobile phase flow rate: 4.0 mL/min
Back pressure: 10 MPa
Detector: UV 270 nm
Make-up solvent: MeCN
Make-up solvent flow rate: 0.3 mL/min

SFC-CSXRD analysis of *rac*-terpinen-4ol (*rac*-**7**)

The CS (**3*R*** or **3*S***) was transferred in a screw-top 1.2 mL microvial with *n*-hexane and the solvent was replaced by IPA (50 μL). Then, the vial was set at the FRC-40SF. Twenty μL of *rac*-terpinen-4ol (*rac*-**7**) (20 mg/mL in MeOH) was injected into the SFC system and each enantiomer was separated and collected into the vial containing **3*R*** or **3*S***. After excess solvent was evaporated to about 50 μL under a gentle N_2 stream, the vial was capped and allowed to stand at 50 °C for 3 days. Then, the CS was mounted on an X-ray diffractometer for the diffraction study. The SFC conditions were as follows.

Column: CHIRALPAK IG 250 × 4.6 mm id, 5 μm (DAICEL Co., Ltd.)
Column temperature: 35 °C
Mobile phase: CO_2/IPA = 95/5 (v/v)
Mobile phase flow rate: 3.0 mL/min
Back pressure: 10 MPa
Detector: UV 205 nm
Make-up solvent: IPA
Make-up solvent flow rate: 2.0 mL/min

Crystal structure analysis

All crystal structures were solved using SHELXT ver. 2018/2[S4] and refined using SHELXL ver. 2018/3[S5] programs. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were grown using the proper HFIX command and refined isotropically using the riding model. Populations of the guests and solvents in the crystal were estimated from the least-square refinement of a guest/solvent disorder model under the constraint that the sum of them should equal 100%.[S6] Otherwise, the populations of the guest and solvent molecules were estimated so that the values of their isotropic thermal parameters would be reasonable (U_{iso} = 0.125–0.200). A minimum number of restraints was applied for the guest compounds. Solvent MTBE, MeOH, MeCN, and IPA molecules in the pores were found in the difference electron density map and refined using the restraints (DFIX, DANG, SIMU, and ISOR). These molecules are expected to be severely disordered as a consequence of their high thermal motion and have an averaged structure of various geometries and orientations. This is a reason why some solvent molecules are distorted and energetically-unfavorable.

Results

Crystallographic data for **4a**⊂**1**

Crystal size: 249 × 205 × 107 μm^3, refined formula: $C_{100.10}H_{74.40}Cl_{12}N_{24}O_{2.20}Zn_6$, formula weight (*Mr*) = 2466.28, colorless block, crystal system: Monoclinic, space group *C*2, *Z* = 4, 30066 unique reflections merged from recorded 142344 ones (2.667° < θ < 75.174°) were used for structural analysis (R_{int} = 0.0212). Lattice parameters, *R*-factor on $F^2 > 2\sigma(F^2)$, weighted *R*-factor, goodness-of-fit, and Flack parameter (calculated from 12338 Parsons' quotients) are follows: *a* = 33.96777(12) Å, *b* = 14.44849(4) Å, *c* = 31.66428(14) Å, β = 102.7113(4)°, *V* = 15159.41(10) Å^3, *R* = 0.0703, *wR* = 0.2169, *S* = 1.083, χ = 0.020(4). Calculated density is 1.081. Linear absorption coefficient (μ) is 3.338. Residual electron density (max/min) is 0.94/−0.57 eÅ^{-3}. CCDC number 2062638.

The ORTEP diagram of the asymmetric unit of **4a**⊂**1** is shown in Figure S1. Four molecules of **4a** (guests A, B, C and D) were found in the asymmetric unit. The guests B and C are partially overlapped and their occupancies are estimated as 51.6(8)% and 48.4(8)%, respectively, by least square refinement, whereas the occupancies of guests A and D are estimated as 50% and 40%, respectively, so that their isotropic thermal parameters would have reasonable values (U_{iso} = 0.125–0.200), which was fixed in the refinement. Some restraints should be applied in the refinement of a disordered model. Two chemically equivalent benzene rings of guest A are related using the SAME command. Other restraints used for the refinement are summarized in Figure S2.

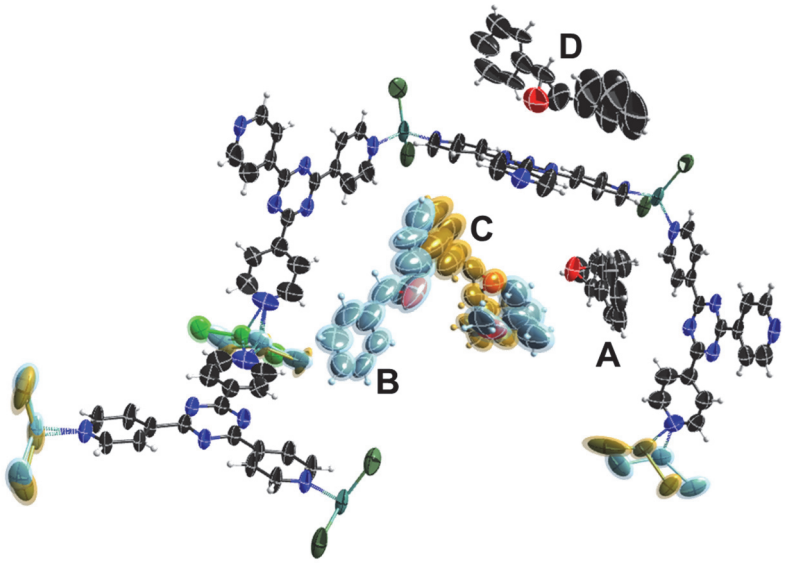

Figure S1. ORTEP diagram with 50% probability in the asymmetric unit of **4a**⊂**1**. Enclosed atoms by the PART command in SHELXL were represented using the difference color code.

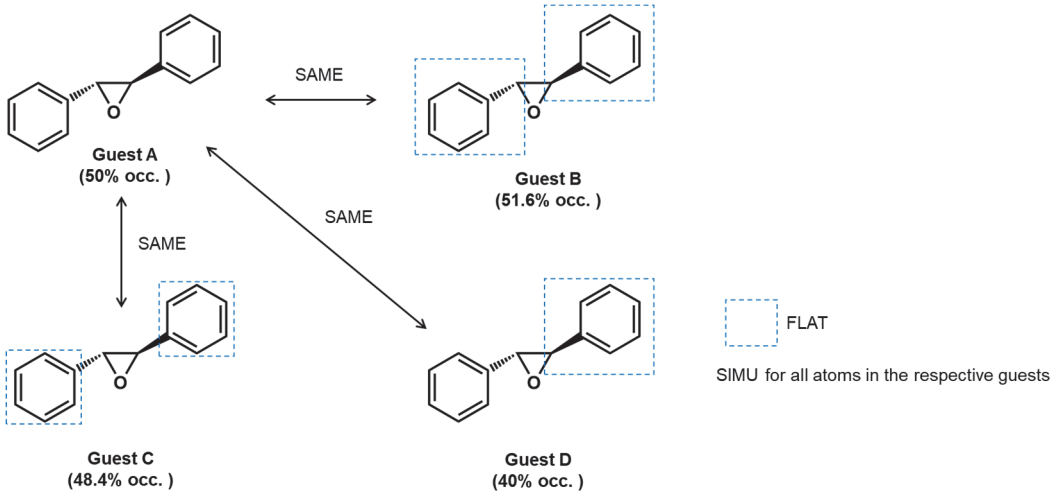

Figure S2. Restraints applied in the refinement.

Crystallographic data for **4b**⊂**1**

Crystal size: 250 × 85 × 61 μm^3, refined formula: $C_{100.10}H_{74.40}Cl_{12}N_{24}O_{2.20}Zn_6$, formula weight (*Mr*) = 2466.28, colorless block, crystal system: Monoclinic, space group *C*2, *Z* = 4, 30342 unique reflections merged from recorded 143710 ones (2.668° < θ < 75.154°) were used for structural analysis (R_{int} = 0.0320). Lattice parameters, *R*-factor on $F^2 > 2\sigma(F^2)$, weighted *R*-factor, goodness-of-fit, and Flack parameter (calculated from 11212 Parsons' quotients) are follows: *a* = 33.9894(2) Å, *b* = 14.44550(10) Å, *c* = 31.8985(2) Å, β = 103.0040(10)°, *V* = 15260.30(18) Å^3, *R* = 0.0791, *wR* = 0.2446, *S* = 1.062, χ = 0.024(6). Calculated density is 1.073. Linear absorption coefficient (μ) is 3.315. Residual electron density (max/min) is 1.09/−0.58 eÅ^{-3}. CCDC number 2062639.

The ORTEP diagram of the asymmetric unit of **4b**⊂**1** is shown in Figure S3. Four molecules of **4b** (guests A, B, C and D) were found in the asymmetric unit. The guests B and C are partially overlapped and their occupancies are estimated as 56.1(10)% and 43.9(10)%, respectively, by least square refinement, whereas the occupancies of guests A and D are estimated as 50% and 40%, respectively, so that their isotropic thermal parameters would have reasonable values (U_{iso} = 0.125–0.200), which was fixed in the refinement. Some restraints should be applied in the refinement of a disordered model. Two chemically equivalent benzene rings of guest A are related using the SAME command. Other restraints used for the refinement are summarized in Figure S4.

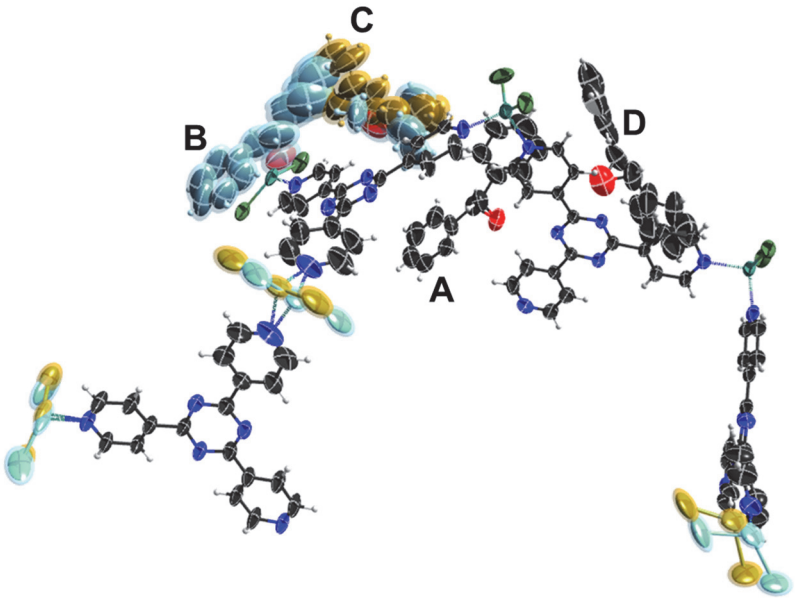

Figure S3. ORTEP diagram with 50% probability in the asymmetric unit of **4b**⊂**1**. Enclosed atoms by the PART command in SHELXL were represented using the difference color code.

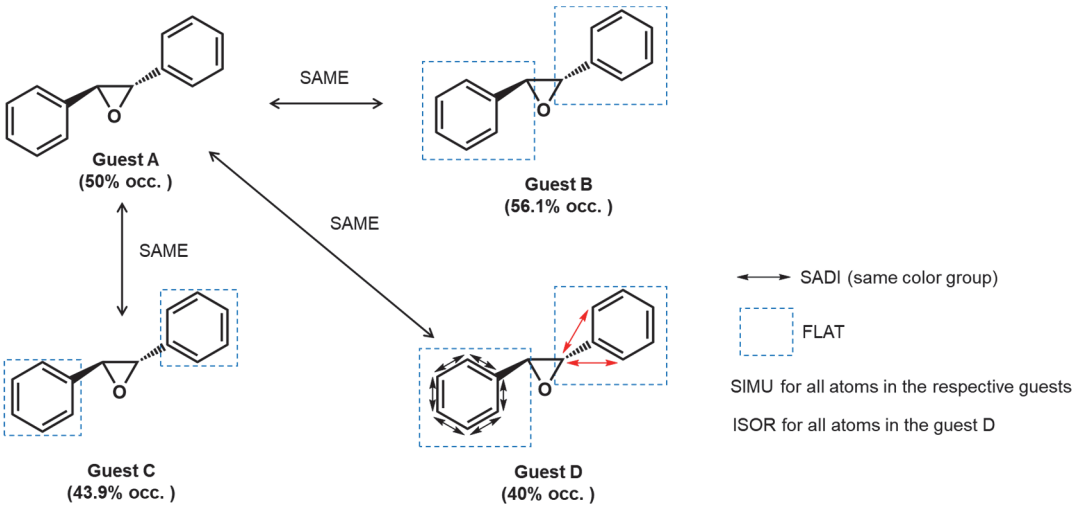

Figure S4. Restraints applied in the refinement.

Crystallographic data for **5a**⊂**2**

Crystal size: 589 × 252 × 161 μm^3, refined formula: $C_{69.86}H_{48.51}Br_2Cu_2N_6O_{14.22}$, formula weight (*Mr*) = 1486.41, red block, crystal system: Monoclinic, space group $P2_1/c$, Z = 4, 19834 unique reflections merged from recorded 56167 ones (2.887° < θ < 75.207°) were used for structural analysis (R_{int} = 0.058). Lattice parameters, *R*-factor on $F^2 > 2\sigma(F^2)$, weighted *R*-factor, and goodness-of-fit are follows: a = 31.9635(7) Å, b = 7.78000(10) Å, c = 30.6494(6) Å, β = 115.897(3)°, V = 6856.4(3) Å^3, R = 0.0631, wR = 0.1926, S = 1.121. Calculated density is 1.440. Linear absorption coefficient (μ) is 2.696. Residual electron density (max/min) is 0.91/−1.00 eÅ^{-3}. CCDC number 2062640.

The ORTEP diagram of the asymmetric unit of **5a**⊂**2** is shown in Figure S5. Four molecules of **5a** (guests A, B, C and D) were found in the asymmetric unit. The guests A and B are partially overlapped and disordered with each other. Furthermore, the guest B is located close to an inversion center and is partially overlapped on the symmetrically generated one. The occupancies of guests A and B are estimated as 76.3(4)% and 23.7(4)%, respectively, by least square refinement. The guests C and D and solvent methanol molecules are partially overlapped and disordered with one another. The occupancies of the guests C and D are estimated as 37.2(7)% and 41.4(6)%, respectively, by least square refinement. Some restraints should be applied in the refinement of a disordered model. The restraints used for the refinement are summarized in Figure S6. The assignment of O and C atoms in the acetyl group is based on differences in observed electron density and bond length (Fig. S7).

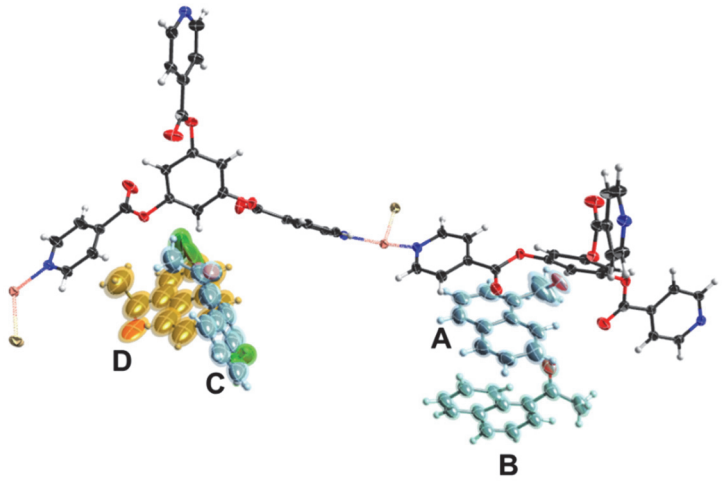

Figure S5. ORTEP diagram with 50% probability in the asymmetric unit of **5a**⊂**2**. Enclosed atoms by the PART command in SHELXL were represented using the difference color code.

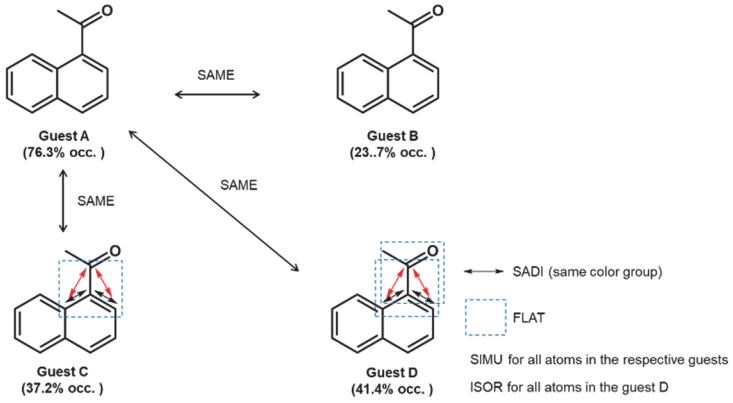

Figure S6. Restraints applied in the refinement.

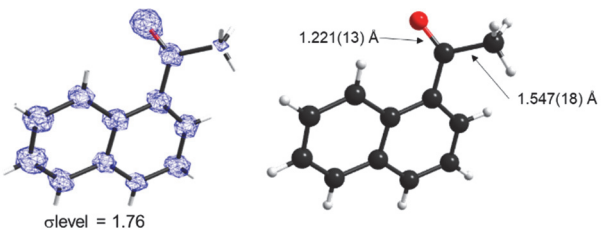

Figure S7. F_o map (σlevel = 1.76) and bond length in guest A.

Crystallographic data for **5b**⊂**2**

Crystal size: 461 × 243 × 128 μm^3, refined formula: $C_{36}H_{25}BrCuN_3O_7$, formula weight (*Mr*) = 755.04, red block, crystal system: Monoclinic, space group *I*2/*a*, *Z* = 8, 6571 unique reflections merged from recorded 21846 ones (3.307° < θ < 75.161°) were used for structural analysis (R_{int} = 0.0301). Lattice parameters, *R*-factor on $F^2 > 2\sigma(F^2)$, weighted *R*-factor, and goodness-of-fit are follows: *a* = 30.0915(10) Å, *b* = 7.71070(10) Å, *c* = 32.6089(11) Å, β = 117.332(4)°, *V* = 6721.5(4) Å^3, *R* = 0.0845, *wR* = 0.2394, *S* = 1.123. Calculated density is 1.492. Linear absorption coefficient (μ) is 2.758. Residual electron density (max/min) is 1.01/−0.67 eÅ^{-3}. CCDC number 2062641.

The ORTEP diagram of the asymmetric unit of **5b**⊂**2** is shown in Figure S8. One of the isonicotyl moieties in the host-framework shows two orientations, and the SAME and EADP commands were used in the refinement of a disordered model. Two molecules of **5b** (guests A and B) were found in the asymmetric unit. The guests A and B are partially overlapped and disordered with each other. The occupancies of guests A and B are estimated as 56.0(8)% and 44.0(8)%, respectively, by least square refinement. Some restraints and constraints should be applied in the refinement of a disordered guest model. The restraints and constraints in the guest molecules used for the refinement are summarized in Figure S9. The assignment of O and C atoms in the acetyl group is based on differences in observed electron density and bond length (Fig. S10).

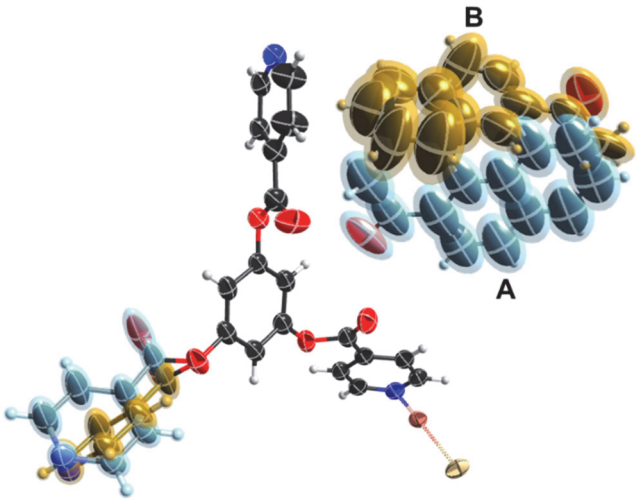

Figure S8. ORTEP diagram with 50% probability in the asymmetric unit of **5b**⊂**2**. Enclosed atoms by the PART command in SHELXL were represented using the difference color code.

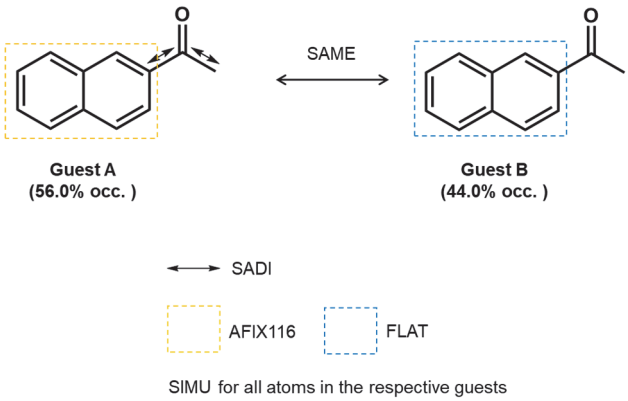

Figure S9. Restraints and constraints applied in the refinement.

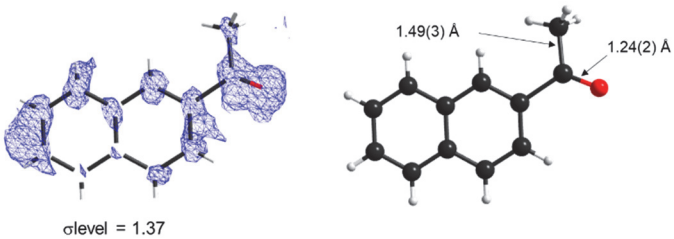

Figure S10. F_o map (σlevel = 1.37) and bond length in guest A.

Crystallographic data for **6a**⊂**3*R***

Crystal size: 196 × 119 × 98 μm^3, refined formula: $C_{62}H_{55}Co_2N_9O_{14.35}$, formula weight (*Mr*) = 1273.61, red block, crystal system: Monoclinic, space group $P2_1$, Z = 2, 11579 unique reflections merged from recorded 56328 ones (3.527° < θ < 74.853°) were used for structural analysis (R_{int} = 0.0393). Lattice parameters, *R*-factor on $F^2 > 2\sigma(F^2)$, weighted *R*-factor, goodness-of-fit, and Flack parameter (calculated from 4701 Parsons' quotients) are follows: a = 10.19140(10) Å, b = 25.0599(4) Å, c = 11.42750(10) Å, β = 91.9200(10)°, V = 2916.89(6) Å^3, R = 0.0857, wR = 0.2214, S = 1.163, χ = 0.066(3). Calculated density is 1.450. Linear absorption coefficient (μ) is 5.096. Residual electron density (max/min) is 1.61/−1.05 eÅ^{-3}. CCDC number 2062642.

The ORTEP diagram of the asymmetric unit of **6a**⊂**3*R*** is shown in Figure S11. One molecule of **6a** (guest A) was found in the asymmetric unit with 100% occupancy. Some restraints should be applied in the refinement. Two chemically equivalent benzene rings of guest A are related using the SAME command. The SIMU command was used for the whole molecule of guest A. The chemical structure of **6a** is shown in Figure S12.

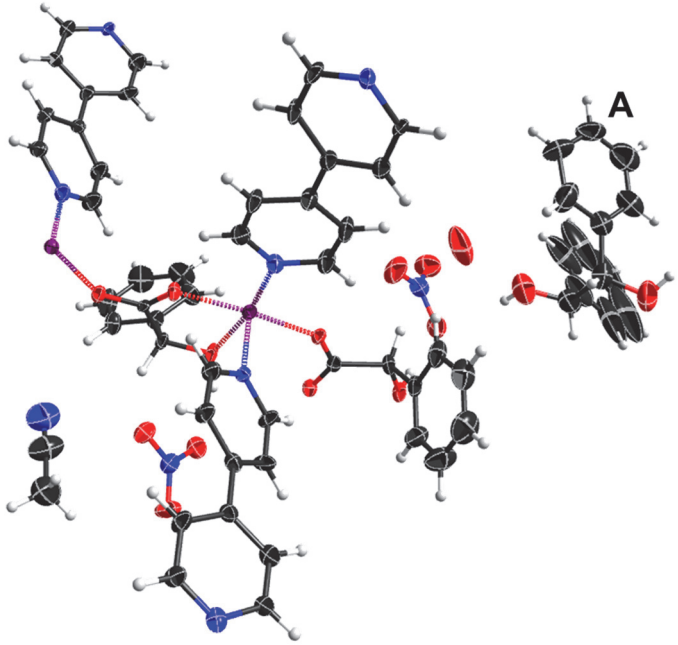

Figure S11. ORTEP diagram with 50% probability in the asymmetric unit of **6a**⊂**3*R***.

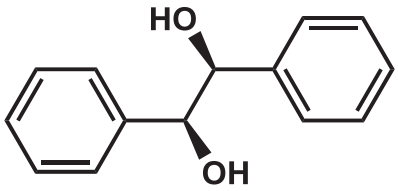

Figure S12. Chemical structure of **6a**.

Crystallographic data for **6b**⊂**3*R***

Crystal size: 163 × 160 × 131 μm^3, refined formula: $C_{62}H_{55}Co_2N_9O_{14.60}$, formula weight (*Mr*) = 1277.61, red block, crystal system: Monoclinic, space group $P2_1$, Z = 2, 11624 unique reflections merged from recorded 56441 ones (3.546° < θ < 74.871°) were used for structural analysis (R_{int} = 0.0292). Lattice parameters, *R*-factor on $F^2 > 2\sigma(F^2)$, weighted *R*-factor, goodness-of-fit, and Flack parameter (calculated from 4842 Parsons' quotients) are follows: a = 10.20900(10) Å, b = 24.9298(3) Å, c = 11.44310(10) Å, β = 92.1620(10)°, V = 2910.29(5) Å^3, R = 0.0642, wR = 0.1738, S = 1.165, χ = 0.016(3). Calculated density is 1.458. Linear absorption coefficient (μ) is 5.113. Residual electron density (max/min) is 1.00/−0.76 eÅ^{-3}. CCDC number 2062643.

The ORTEP diagram of the asymmetric unit of **6b**⊂**3*R*** is shown in Figure S13. One of two NO_3^- anions was split into three positionally disordered models along with one water molecule. One molecule of **6b** (guest A) was found in the asymmetric unit with 100% occupancy. The guest A was refined without any restraints. The chemical structure of **6b** is shown in Figure S14.

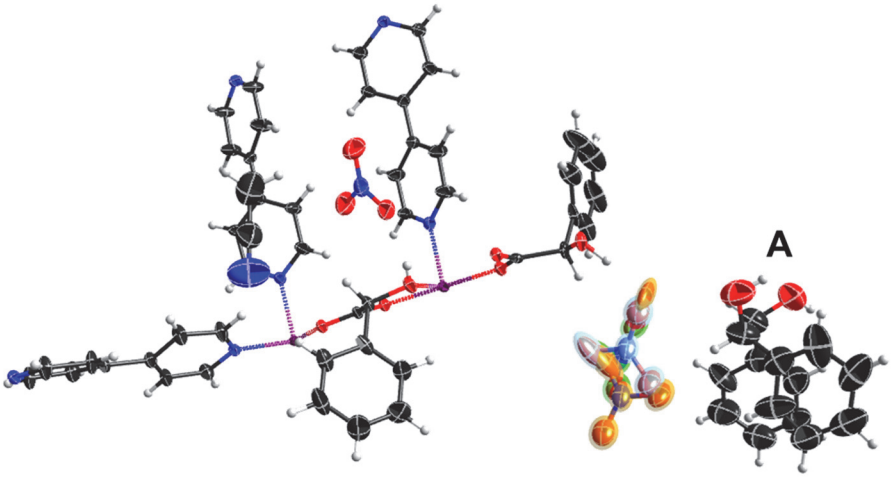

Figure S13. ORTEP diagram with 50% probability in the asymmetric unit of **6b**⊂**3*R***. Enclosed atoms by the PART command in SHELXL were represented using the difference color code.

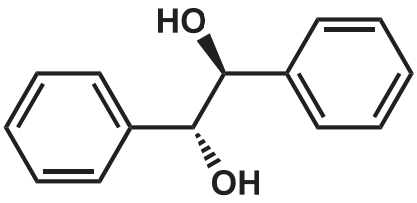

Figure S14. Chemical structure of **6b**.

Crystallographic data for **6c**⊂**3*R***

Crystal size: 0.161 × 0.097 × 0.068 μm^3, refined formula: $C_{62}H_{55}Co_2N_9O_{14.23}$, formula weight (*Mr*) = 1271.75, red block, crystal system: Monoclinic, space group $P2_1$, Z = 2, 11510 unique reflections merged from recorded 55438 ones (3.534° < θ < 74.825°) were used for structural analysis (R_{int} = 0.0437). Lattice parameters, R-factor on $F^2 > 2\sigma(F^2)$, weighted R-factor, goodness-of-fit, and Flack parameter (calculated from 4641 Parsons' quotients) are follows: a = 10.19700(10) Å, b = 25.0123(3) Å, c = 11.43370(10) Å, β = 91.6080(10)°, V = 2915.02(5) Å^3, R = 0.0681, wR = 0.1821, S = 1.136, χ = 0.011(2). Calculated density is 1.449. Linear absorption coefficient (μ) is 5.097. Residual electron density (max/min) is 2.09/−0.48 eÅ^{-3}. CCDC number 2062644.

The ORTEP diagram of the asymmetric unit of **6c**⊂**3*R*** is shown in Figure S15. One of two NO_3^- anions was split into two positionally disordered models along with one water molecule. Two positionally disordered molecules of **6c** (guests A and B) were found in the asymmetric unit. The occupancies of guests A and B are estimated as 53.4(11)% and 46.6(11)%, respectively, by least square refinement. Some restraints should be applied in the refinement of a disordered model. Two chemically equivalent benzene rings of guest A are related using the SAME command. Other restraints in the guest molecules used for the refinement are summarized in Figure S16.

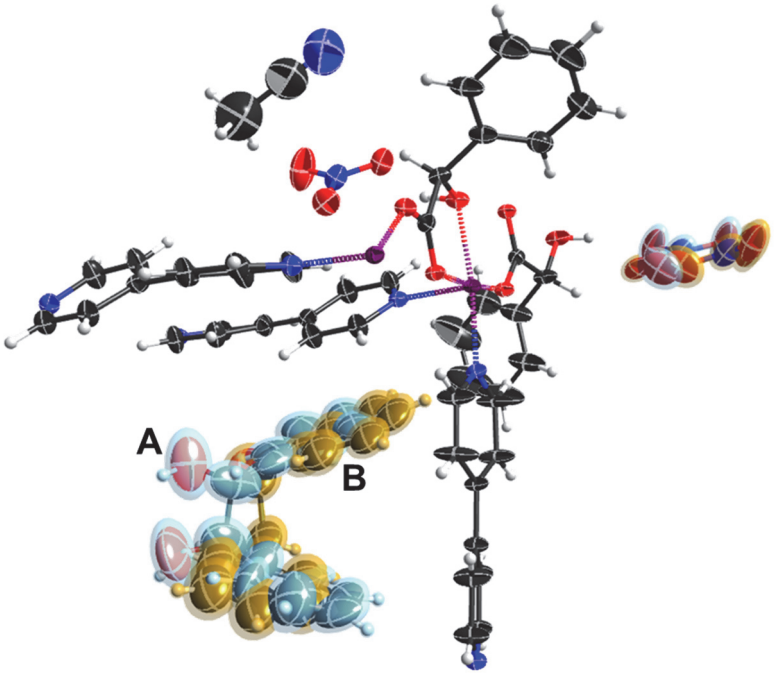

Figure S15. ORTEP diagram with 50% probability in the asymmetric unit of **6c**⊂**3*R***. Enclosed atoms by the PART command in SHELXL were represented using the difference color code.

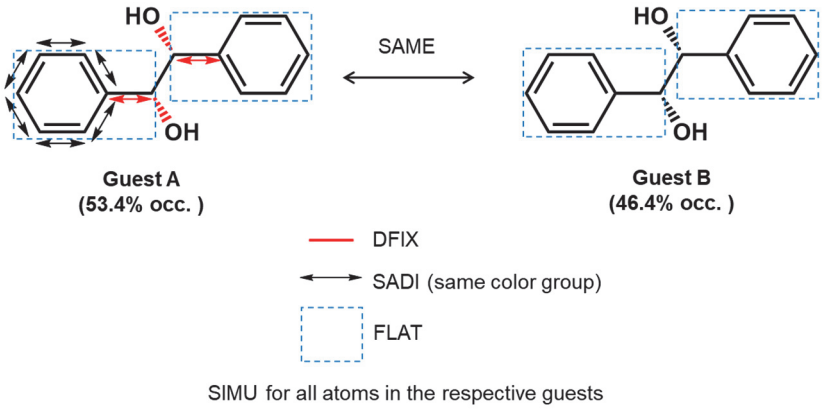

Figure S16. Restraints applied in the refinement.

Crystallographic data for **6a**⊂**3*S***

Crystal size: 0.135 × 0.071 × 0.056 μm^3, refined formula: $C_{60.70}H_{53.05}Co_2N_{8.35}O_{14.87}$, formula weight (*Mr*) = 1255.28, red block, crystal system: Monoclinic, space group $P2_1$, Z = 2, 11415 unique reflections merged from recorded 55500 ones (3.556° < θ < 75.039°) were used for structural analysis (R_{int} = 0.0421). Lattice parameters, R-factor on $F^2 > 2\sigma(F^2)$, weighted R-factor, goodness-of-fit, and Flack parameter (calculated from 4736 Parsons' quotients) are follows: a = 10.19210(10) Å, b = 24.8616(3) Å, c = 11.44350(10) Å, β = 91.1810(10)°, V = 2899.07(5) Å^3, R = 0.0693, wR = 0.1880, S = 1.168, χ = 0.014(2). Calculated density is 1.438. Linear absorption coefficient (μ) is 5.123. Residual electron density (max/min) is 2.16/−0.53 eÅ^{-3}. CCDC number 2062645.

The ORTEP diagram of the asymmetric unit of **6a**⊂**3*S*** is shown in Figure S17. One of two NO_3^- anions was split into two positionally disordered models along with one water molecule. Two positionally disordered molecules of **6a** (guests A and B) were found in the asymmetric unit. The occupancies of guests A and B are estimated as 65.7(12)% and 34.3(12)%, respectively, by least square refinement. Some restraints should be applied in the refinement of a disordered model. Two chemically equivalent benzene rings of guest A are related using the SAME command. Other restraints in the guest molecules used for the refinement are summarized in Figure S18.

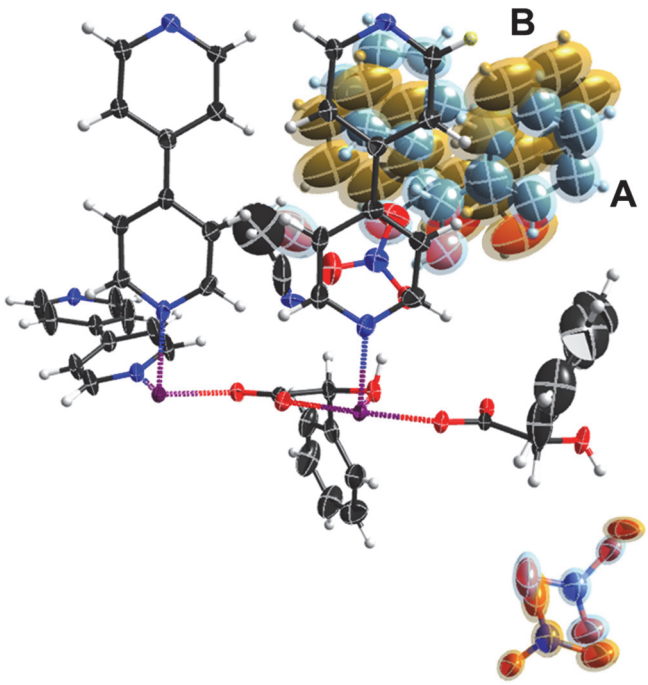

Figure S17. ORTEP diagram with 50% probability in the asymmetric unit of **6a**⊂**3*S***. Enclosed atoms by the PART command in SHELXL were represented using the difference color code.

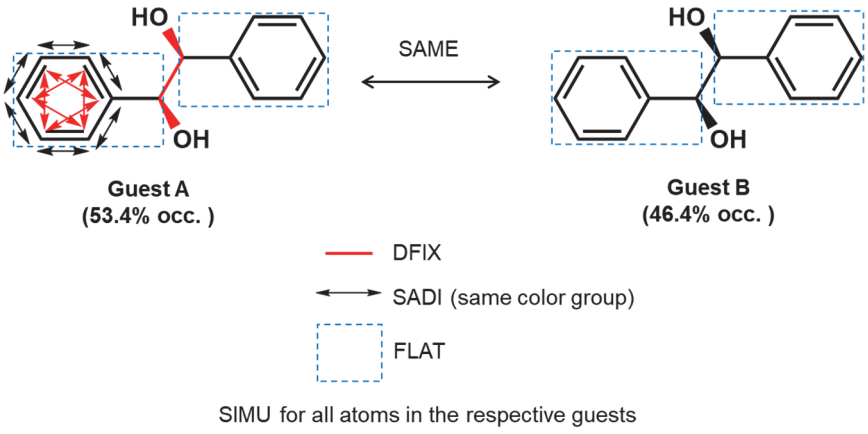

Figure S18. Restraints applied in the refinement.

Crystallographic data for **6b**⊂**3*S***

Crystal size: 0.275 × 0.143 × 0.132 μm^3, refined formula: $C_{62}H_{55}Co_2N_9O_{14.49}$, formula weight (*Mr*) = 1275.86, red block, crystal system: Monoclinic, space group $P2_1$, Z = 2, 11460 unique reflections merged from recorded 55214 ones (3.548° < θ < 74.551°) were used for structural analysis (R_{int} = 0.0347). Lattice parameters, R-factor on $F^2 > 2\sigma(F^2)$, weighted R-factor, goodness-of-fit, and Flack parameter (calculated from 4509 Parsons' quotients) are follows: a = 10.20100(10) Å, b = 24.9173(4) Å, c = 11.43790(10) Å, β = 91.9910(10)°, V = 2905.55(6) Å^3, R = 0.0746, wR = 0.2025, S = 1.162, χ = 0.019(4). Calculated density is 1.458. Linear absorption coefficient (μ) is 5.119. Residual electron density (max/min) is 1.42/−0.59 eÅ^{-3}. CCDC number 2062646.

The ORTEP diagram of the asymmetric unit of **6b**⊂**3*S*** is shown in Figure S19. One of two NO_3^- anions was split into three positionally disordered models along with one water molecule. One molecule of **6b** (guest A) was found in the asymmetric unit with 100% occupancy. Some restraints should be applied in the refinement. The restraints used for the refinement are summarized in Figure S20.

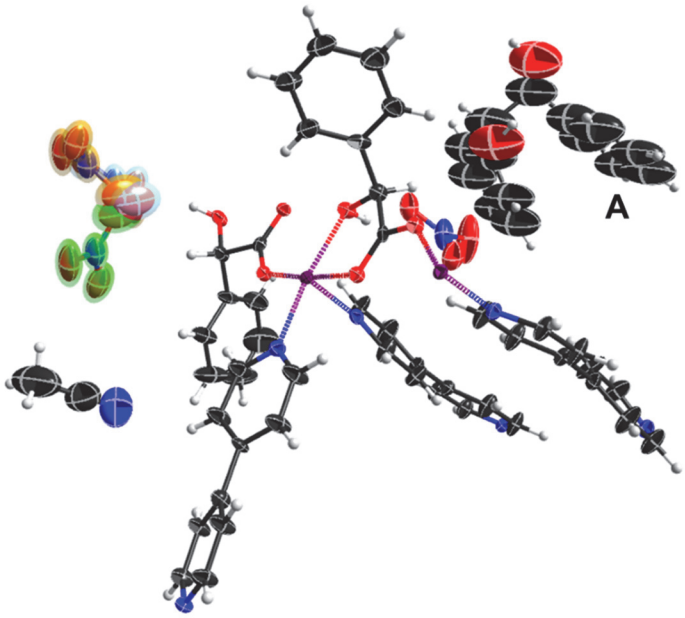

Figure S19. ORTEP diagram with 50% probability in the asymmetric unit of **6b**⊂**3*S***. Enclosed atoms by the PART command in SHELXL were represented using the difference color code.

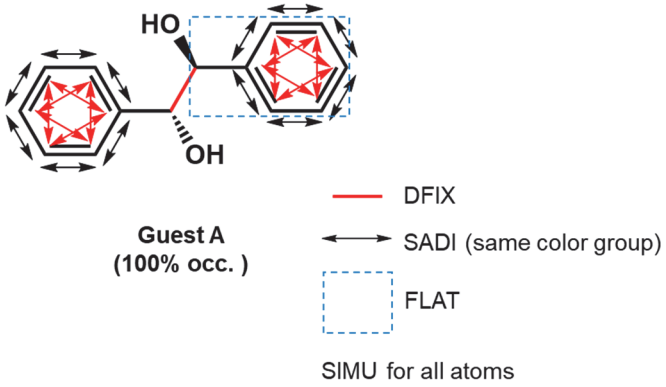

Figure S20. Restraints applied in the refinement.

Crystallographic data for **6c**⊂**3*S***

Crystal size: 0.207 × 0.091 × 0.055 μm^3, refined formula: $C_{63.30}H_{56.95}Co_2N_{9.65}O_{14.66}$, formula weight (*Mr*) = 1305.19, red block, crystal system: Monoclinic, space group $P2_1$, Z = 2, 11486 unique reflections merged from recorded 55926 ones (3.529° < θ < 74.614°) were used for structural analysis (R_{int} = 0.0378). Lattice parameters, R-factor on $F^2 > 2\sigma(F^2)$, weighted R-factor, goodness-of-fit, and Flack parameter (calculated from 4698 Parsons' quotients) are follows: a = 10.20960(10) Å, b = 25.0473(2) Å, c = 11.43730(10) Å, β = 91.8980(10)°, V = 2923.17(4) Å^3, R = 0.0568, wR = 0.1463, S = 1.206, χ = 0.019(2). Calculated density is 1.483. Linear absorption coefficient (μ) is 5.108. Residual electron density (max/min) is 0.54/−0.61 eÅ^{-3}. CCDC number 2062647.

The ORTEP diagram of the asymmetric unit of **6c**⊂**3*S*** is shown in Figure S21. One of two NO_3^- anions was split into two positionally disordered models along with one water molecule. One molecule of **6c** (guest A) was found in the asymmetric unit with 100% occupancy. Some restraints should be applied in the refinement. Two chemically equivalent benzene rings of guest A are related using the SAME command. The SIMU command was used for the whole molecule of guest A. The chemical structure of **6c** is shown in Figure S22.

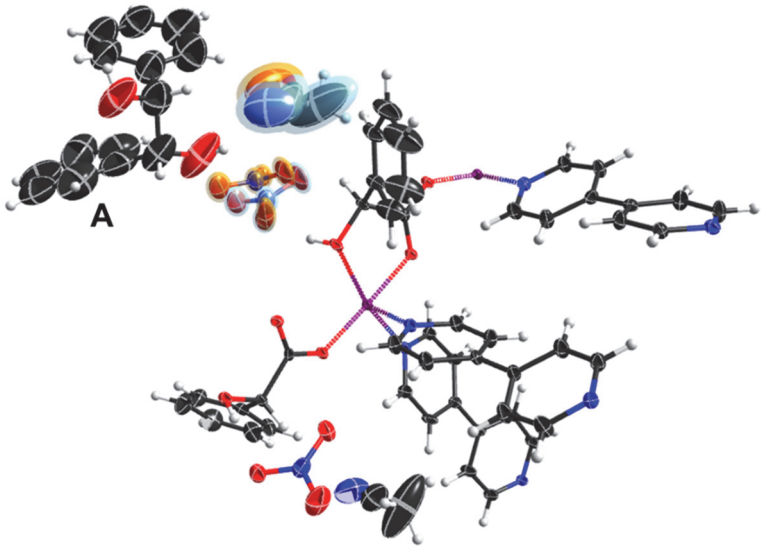

Figure S21. ORTEP diagram with 50% probability in the asymmetric unit of **6c**⊂**3*S***. Enclosed atoms by the PART command in SHELXL were represented using the difference color code.

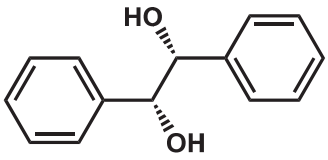

Figure S22. Chemical structure of **6c**.

Crystallographic data for **7a**⊂**3*R***

Crystal size: 0.247 × 0.124 × 0.102 μm^3, refined formula: $C_{57.80}H_{60.80}Co_2N_8O_{14.19}$, formula weight (*Mr*) = 1212.48, red block, crystal system: Monoclinic, space group $P2_1$, Z = 2, 11271 unique reflections merged from recorded 55046 ones (3.574° < θ < 74.851°) were used for structural analysis (R_{int} = 0.0385). Lattice parameters, R-factor on $F^2 > 2\sigma(F^2)$, weighted R-factor, goodness-of-fit, and Flack parameter (calculated from 4479 Parsons' quotients) are follows: a = 10.19040(10) Å, b = 24.7362(2) Å, c = 11.42990(10) Å, β = 91.7800(10)°, V = 2879.76(4) Å^3, R = 0.0501, wR = 0.1367, S = 1.075, χ = −0.007(2). Calculated density is 1.398. Linear absorption coefficient (μ) is 5.121. Residual electron density (max/min) is 0.80/−0.42 eÅ^{-3}. CCDC number 2062648.

The ORTEP diagram of the asymmetric unit of **7a**⊂**3*R*** is shown in Figure S23. One of two NO_3^- anions was split into two positionally disordered models along with one water molecule. Two positionally disordered molecules of **7a** (guests A and B) were found in the asymmetric unit. The occupancies of guests A and B were first estimated by least square refinement, and then fixed as 60% and 40%, respectively. Some restraints and constraints should be applied in the refinement of a disordered model. The restraints used for the refinement are summarized in Figure S24.

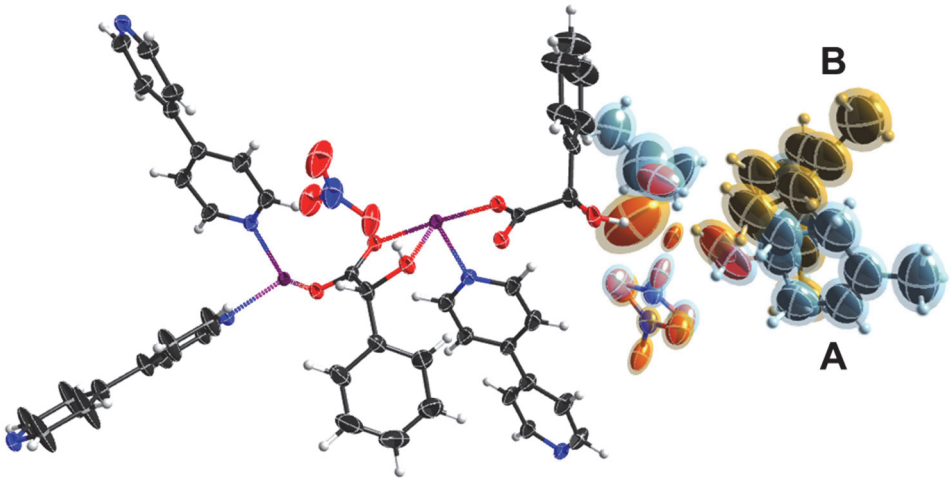

Figure S23. ORTEP diagram with 50% probability in the asymmetric unit of **7a**⊂**3*R***. Enclosed atoms by the PART command in SHELXL were represented using the difference color code.

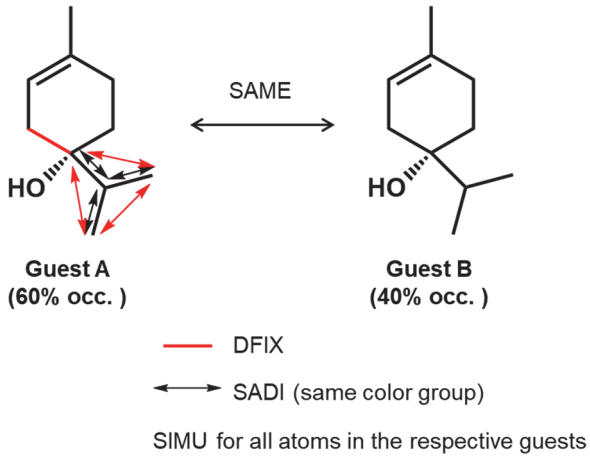

Figure S24. Restraints applied in the refinement.

Crystallographic data for **7b**⊂**3*R***

Crystal size: 0.204 × 0.176 × 0.117 μm^3, refined formula: $C_{59}H_{64}Co_2N_8O_{14.16}$, formula weight (*Mr*) = 1229.59, red block, crystal system: Monoclinic, space group $P2_1$, Z = 2, 11513 unique reflections merged from recorded 55539 ones (3.592° < θ < 74.972°) were used for structural analysis (R_{int} = 0.0431). Lattice parameters, R-factor on $F^2 > 2\sigma(F^2)$, weighted R-factor, goodness-of-fit, and Flack parameter (calculated from 4465 Parsons' quotients) are follows: a = 10.19880(10) Å, b = 24.6101(2) Å, c = 11.43370(10) Å, β = 92.7540(10)°, V = 2866.47(4) Å^3, R = 0.0530, wR = 0.1444, S = 1.070, χ = −0.005(3). Calculated density is 1.425. Linear absorption coefficient (μ) is 5.152. Residual electron density (max/min) is 0.56/−0.48 eÅ^{-3}. CCDC number 2062649.

The ORTEP diagram of the asymmetric unit of **7b**⊂**3*R*** is shown in Figure S25. One of two NO_3^- anions was split into two positionally disordered models along with one water molecule. One molecule of **7b** (guest A) was found in the asymmetric unit with 100% occupancy. One restraint should be applied in the refinement. The restraint used for the refinement is shown in Figure S26.

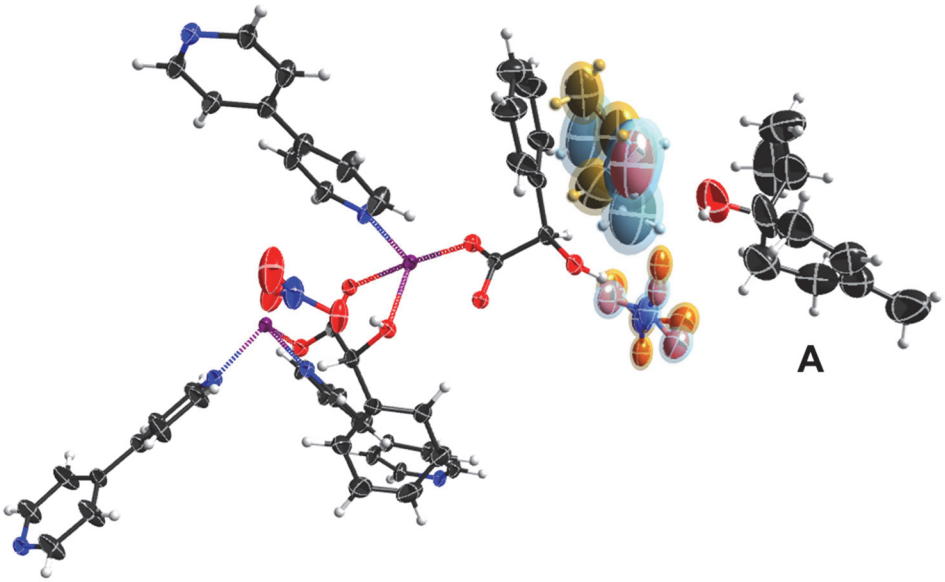

Figure S25. ORTEP diagram with 50% probability in the asymmetric unit of **7b**⊂**3*R***. Enclosed atoms by the PART command in SHELXL were represented using the difference color code.

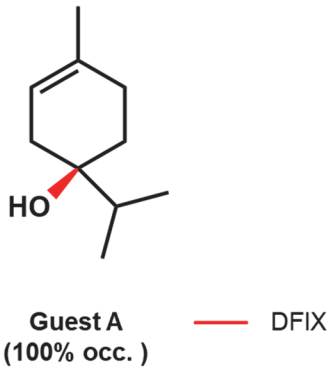

Figure S26. Restraint applied in the refinement.

Crystallographic data for **7a**⊂**3*S***

Crystal size: 0.324 × 0.244 × 0.201 μm^3, refined formula: $C_{59}H_{64}Co_2N_8O_{14.19}$, formula weight (*Mr*) = 1230.01, red block, crystal system: Monoclinic, space group $P2_1$, Z = 2, 23229 unique reflections merged from recorded 103594 ones (3.585° < θ < 82.310°) were used for structural analysis (R_{int} = 0.107). Lattice parameters, *R*-factor on $F^2 > 2\sigma(F^2)$, weighted *R*-factor, goodness-of-fit, and Flack parameter (calculated from 4079 Parsons' quotients) are follows: a = 10.1997(2) Å, b = 24.6572(6) Å, c = 11.4298(2) Å, β = 92.469(2)°, V = 2871.88(10) Å^3, R = 0.1188, wR = 0.3341, S = 1.038, χ = 0.027(22). Calculated density is 1.422. Linear absorption coefficient (μ) is 5.142. Residual electron density (max/min) is 1.88/−0.71 eÅ^{-3}. CCDC number 2062650.

The ORTEP diagram of the asymmetric unit of **7a**⊂**3*S*** is shown in Figure S27. One of two NO_3^- anions was split into two positionally disordered models along with one water molecule. One molecule of **7a** (guest A) was found in the asymmetric unit with 100% occupancy. The guest A was refined without any restraints. The chemical structure of **7a** is shown in Figure S28.

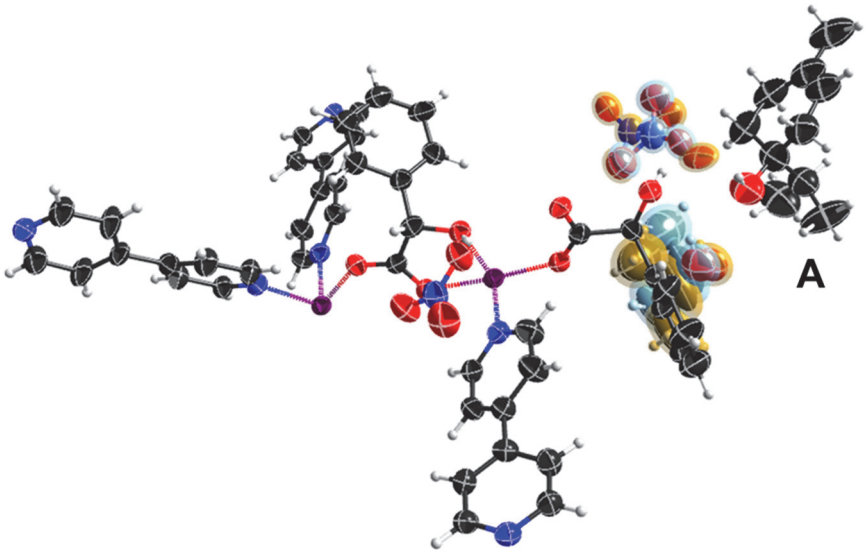

Figure S27. ORTEP diagram with 50% probability in the asymmetric unit of **7a**⊂**3*S***. Enclosed atoms by the PART command in SHELXL were represented using the difference color code.

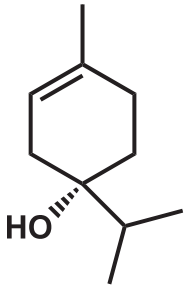

Figure S28. Chemical structure of **7a**.

Crystallographic data for **7b**⊂**3*S***

Crystal size: 0.240 × 0.149 × 0.112 μm^3, refined formula: $C_{58.03}H_{61.41}Co_2N_8O_{14.17}$, formula weight (*Mr*) = 1215.50, red block, crystal system: Monoclinic, space group $P2_1$, Z = 2, 11443 unique reflections merged from recorded 54653 ones (3.568° < θ < 75.090°) were used for structural analysis (R_{int} = 0.0512). Lattice parameters, R-factor on $F^2 > 2\sigma(F^2)$, weighted R-factor, goodness-of-fit, and Flack parameter (calculated from 4079 Parsons' quotients) are follows: a = 10.1785(2) Å, b = 24.7746(4) Å, c = 11.42570(10) Å, β = 91.4300(10)°, V = 2880.30(8) Å^3, R = 0.0589, wR = 0.1570, S = 1.062, χ = 0.006(4). Calculated density is 1.402. Linear absorption coefficient (μ) is 5.121. Residual electron density (max/min) is 0.76/−0.57 eÅ^{-3}. CCDC number 2062651.

The ORTEP diagram of the asymmetric unit of **7b**⊂**3*S*** is shown in Figure S29. One of two NO_3^- anions was split into two positionally disordered models along with one water molecule. Two positionally disordered molecules of **7b** (guests A and B) were found in the asymmetric unit. The occupancies of guests A and B were estimated as 67.9(10)% and 32.1(10)%, respectively, by least square refinement. Some restraints should be applied in the refinement of a disordered model. The restraints used for the refinement are summarized in Figure S30.

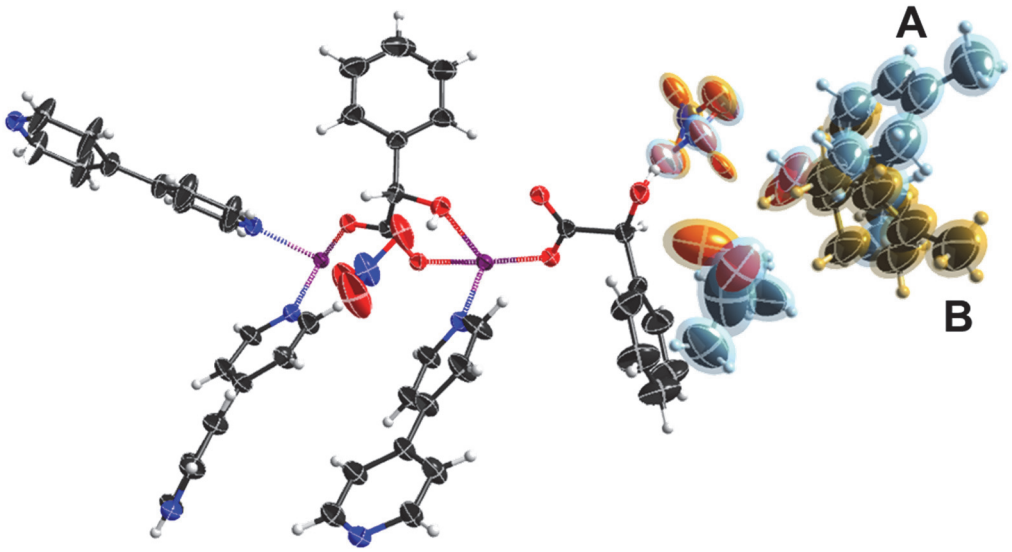

Figure S29. ORTEP diagram with 50% probability in the asymmetric unit of **7b**⊂**3*S***. Enclosed atoms by the PART command in SHELXL were represented using the difference color code.

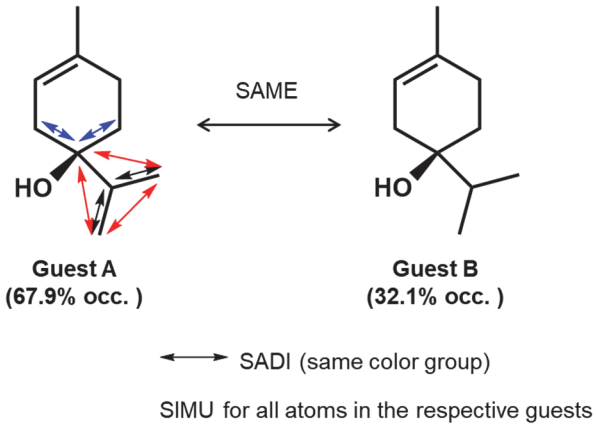

Figure S30. Restraints applied in the refinement.

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