Electronic Supplementary Material (ESI) for Chemical Communications.

Control by one drop of solvent: selective preparation of guest release/trap-triggered interconvertible molecular crystals

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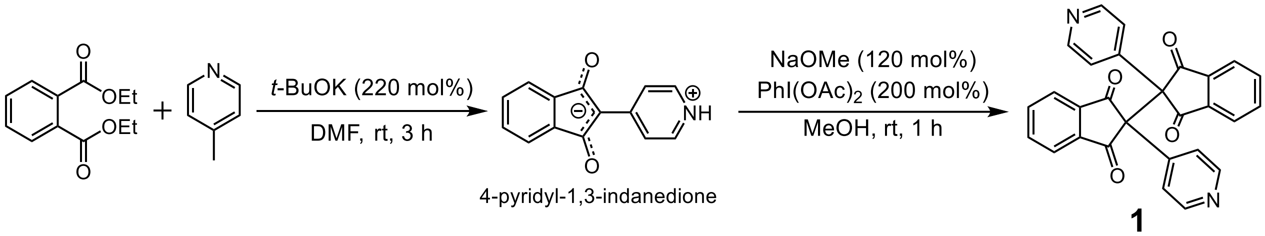
Table of Contents

1. General experimental information

All experiments with moisture- and air-sensitive compounds were performed in anhydrous solvents under argon atmosphere in flame-dried glassware. All reagents were purchased from commercial sources and used without further purification unless otherwise noted. TGA was recorded on a SHIMADZU TGA-50. Melting points were determined on Standford Research Systems MPA 100 and were uncorrected. Infrared (IR) spectra were recorded on a JASCO FT IR-4100 spectrometer using dispersed KBr pellets. ^{1}H and ^{13}C NMR spectra at 23 °C were measured on a JEOL REASONANCE JNM-ECZ400S spectrometer at 400 and 100 MHz, respectively. $CDCl_3$ was used as a solvent and the residual solvent peaks were used as an internal standard (^{1}H NMR: $CDCl_3$ 7.26 ppm; ^{13}C NMR: $CDCl_3$ 77.00 ppm). DMSO-*d*^{6} was used as a solvent and the residual solvent peaks were used as an internal standard (^{1}H NMR: DMSO-*d*^{6} 2.50 ppm; ^{13}C NMR: DMSO-*d*^{6} 39.51 ppm). Powder X-ray diffraction (PXRD) data were collected on a Rigaku Ultima-IV using graphite-monochromatized Cu-Kα radiation (λ = 1.54187 Å). Gas sorption experiments were performed on a Microtrac BEL BELSORP-miniII. TLC analysis was performed using Merck silica gel 60 F_{254}, and the preparative TLC (PTLC) purification was conducted using Wakogel B-5F PTLC plates. Silica gel chromatography was performed on Kanto Silicagel 60N (Spherical, Neutral) using a Yamazen preparative medium pressure liquid chromatography system. Elemental analyses (C, H, N) were measured on a J-Science Micro corder JM10 at the Analysis Center in Osaka University.

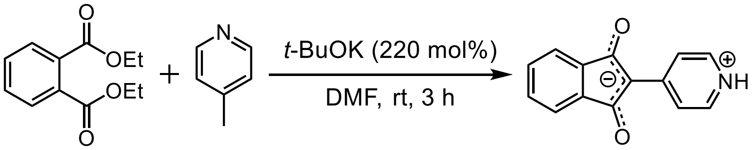
2. Synthesis



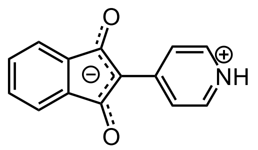
1

Scheme S1 Synthetic procedure for **1**.

1) Condensation Reaction



To a solution of potassium *t*-butoxide (6.17 g, 55.0 mmol) in dry DMF (50.0 mL) was added 4-methylpyridine (25.0 mmol). To this solution was slowly added diethylphthalate (4.95 mL, 25.0 mmol) in DMF (30.0 mL). After the stirring for 3 h at rt, the solution was evaporated to dryness under reduced pressure. After partitioning between H_2O-Et_2O, the H_2O layer was acidified with HCl to produce orange solid. The solid was filtered and washed with water to afford 4-pyridyl-1,3-indanedione (4.27 g, 19.1 mmol, 77% yield) as orange crystals.

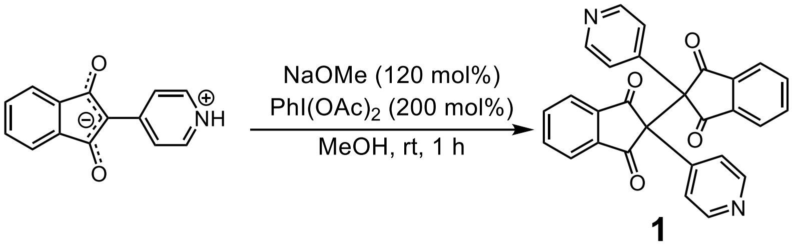


mp: 318 °C (dec); IR (KBr) 3445, 3239, 2960, 2920, 1616, 1562, 1508, 1418, 1360, 1182 cm^{-1}; ^{1}H NMR (400 MHz) (DMSO-*d*^{6}): *δ* (ppm) 13.23 (s, 1H), 8.73 (d, *J* = 6.4 Hz, 2H), 8.17 (d, *J* = 6.4 Hz, 2H), 7.50 (m, 4H); ^{13}C NMR (DMSO-*d*^{6}): *δ* (ppm) 190.04, 150.90, 139.71, 138.00, 131.96, 119.62, 114.84, 101.46; E.A. Calcd. for $C_{14}H_9NO_2(MeOH)_{0.4}(H_2O)_{0.3}$: C 71.63%, H 4.68%, N 5.80%, Found: C 71.75%, H 4.33%, N 5.92%.

Sample for elemental analysis was prepared by recrystallization from MeOH followed by the drying process at 40 °C in vacuum. As observed in Fig. S2, 4-pyridyl-1,3-indanedione appeared to form OH···O type hydrogen bond with solvent easily, which required further heating for the removal of solvent molecule. The pure sample data was available in the literature.[S1]

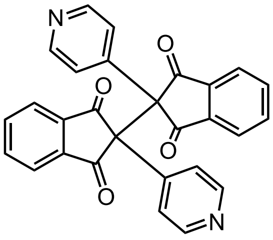
The single crystals of 4-pyridyl-1,3-indanedione suitable for X-ray crystallographic analysis were obtained by slow concentration from CH_2Cl_2 solution of it at room temperature for several days.

2) Dimerization Reaction



1

To the mixture of 4-pyridyl-1,3-indanedione (0.20 mmol) and Na (5.5 mg, 0.24 mmol) was added a dry MeOH (5.0 mL). After stirring for 10 min at rt, $PhI(OAc)_2$ (132.8 mg, 0.40 mmol) was added and the mixture was stirred for 1 h at rt. After evaporation of MeOH, 1 M $Na_2S_2O_3$ aq. was added, extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography (EtOAc:MeOH = 4:1) to afford **1** (42.6 mg, 0.096 mmol, 96%) as pale yellow solid.



mp: 255 °C (dec); IR (KBr) 3424, 3051, 1741, 1705, 1589, 1259, 796 cm^{-1}; ^{1}H NMR (400 MHz) ($CDCl_3$): *δ* (ppm) 8.54 (d, *J* = 6.2 Hz, 4H), 7.88 (m, 8H), 7.13 (d, *J* = 6.2 Hz, 4H); ^{13}C NMR ($CDCl_3$): *δ* (ppm) 196.01, 149.36, 140.86, 138.95, 136.53, 125.08, 124.21, 62.94; E.A. Calcd. for $C_{28}H_{14}N_2O_4$: C 75.67%, H 3.63%, N 6.30%, Found: C 75.27%, H 3.71%, N 6.28%.

Single Crystal Preparation of $\mathbf{1}_{close}$ and $\mathbf{1}_{open}$

The single crystals of $\mathbf{1}_{close}$ suitable for X-ray crystallographic analysis were obtained by vapor diffusion using CH_2Cl_2 solution with EtOH as the poor solvent at room temperature for 1 day.

The single crystals of $\mathbf{1}_{open}$ suitable for X-ray crystallographic analysis were obtained by vapor diffusion of **1** (1 mg, 2.2 *μ*mol) in CH_2Cl_2 (0.3 mL) including hexane (100 *μ*L, 0.76 mmol) with EtOH as the poor solvent at room temperature for 1 day. The same method using other solvents (pentane, decane, cyclohexane, toluene, *t*-BuOH, $(CH_2Cl)_2$, benzene) instead of hexane also gave the corresponding solvent-incorporated $\mathbf{1}_{\mathrm{open}}$ crystals.

Preparation of crystalline powder samples

Crystalline powder samples of $\mathbf{1}_{\mathrm{open}}$ and $\mathbf{1}_{\mathrm{close}}$ were prepared by re-precipitation by dropping of **1** (10 mg)/CH_2Cl_2 (3 mL) to hexane or other trigger solvents (20 mL) (for $\mathbf{1}_{\mathrm{open}}$) or by heating of $\mathbf{1}_{\mathrm{open}}$ powder at 170 °C for 1 h (for $\mathbf{1}_{\mathrm{close}}$). The precipitate was collected and dried under reduced pressure at ambient temperature. The obtained powder crystals were applied to each measurement after confirmation of their structures by PXRD analysis.

Guest selectivity experiments

Crystal samples for guest selectivity experiment were prepared by vapor diffusion of **1** (4.4 mg, 0.01 mmol) in CH_2Cl_2 (1 mL) including each guest (1.0 mmol)/EtOH at room temperature for 1 day. The trapped amount of the guest solvents were analyzed by ^{1}H NMR after the removal of the residual surface solvent under the reduced pressure at ambient temperature for 2 h.

3. Single crystal X-ray analysis

The diffraction data for $\mathbf{1}_{\text{close}}$ (with EtOH) and $\mathbf{1}_{\text{open}}$ (with hexane) were recorded on a DECTRIS PILATUS3 X CdTM 1M Detector System (λ = 0.43158 Å) at 100 K at SPring-8 BL02B1. The diffraction images were processed by using RIGAKU RAPID AUTO.[S2]

The diffraction data for $\mathbf{1}_{\text{close}}$ (with CH_3CN), $\mathbf{1}_{\text{open}}$ (with pentane, cyclohexane, dihloroethane, benzene) were recorded on an ADSC Q210 CCD area detector with a synchrotron radiation (λ =0.70000 Å) at 2D beamline in Pohang Accelerator Laboratory (PAL). The diffraction images were processed by using HKL3000.[S3]

The diffraction data for $\mathbf{1}_{\text{close}}$ (with cyclohexanol, EtOAc), $\mathbf{1}_{\text{open}}$ (with *t*-BuOH, CH_2Cl_2, toluene, decane) were recorded on a XtaLAB Synergy with a Mo-target (λ = 0.71073 Å for $\mathbf{1}_{\text{close}}$s and $\mathbf{1}_{\text{open}}$) equipped with a Rigaku HyPix-6000HE as the detector at 150 K in house. The diffraction images were processed by using CrysAlisPro.[S4]

The diffraction data for 4-pyridyl-1,3-indanedione was collected on a Rigaku FR-E Superbright rotating-anode X-ray source with a Mo-target (λ = 0.71073 Å) equipped with a Rigaku RAXIS VII imaging plate as the detector at 150 K in house. The diffraction images were processed by using RIGAKU RAPID AUTO.[S2]

The structures were solved by a direct method (XS[S5]) and a dual space method (SHELXT-2015, 2018/2[S6]), and refined by full-matrix least squares calculations on F^2 (SHELXL-2018/3)[S7] using the Olex2 [S8] program package.

$\mathbf{1}_{\text{close}}$: $C_{28}H_{16}N_2O_4$, tetragonal, space group $I4_1/a$ (No. 88), a = 15.926(2) Å, b = 15.926(2) Å, c = 15.916(3) Å, V = 4037(1) Å^3, ρ_{calcd} = 1.462 g/cm^3, Z = 8, 2244 unique reflections out of 2318 with $I>2\sigma(I)$, 154 parameters, 1.809°<θ<27.439°, R_1= 0.0378, wR_2= 0.0983, GOF = 1.081.

$\mathbf{1}_{\text{close}}$ (with CH_3CN): $C_{28}H_{16}N_2O_4$, tetragonal, space group $I4_1/a$ (No. 88), a = 15.926(2) Å, b = 15.926(2) Å, c = 15.926(3) Å, V = 4039(2) Å^3, ρ_{calcd} = 1.462 g/cm^3, Z = 8, 2718 unique reflections out of 2942 with $I>2\sigma(I)$, 154 parameters, 1.781°<θ<29.499°, R_1= 0.0452, wR_2= 0.1234, GOF = 1.088.

$\mathbf{1}_{\text{close}}$ (with cyclohexanol): $C_{28}H_{16}N_2O_4$, tetragonal, space group $I4_1/a$ (No. 88), a = 15.9394(7) Å, b = 15.9394(7) Å, c = 15.9489(7) Å, V = 4052.0(4) Å^3, ρ_{calcd} = 1.457 g/cm^3, Z = 8, 2362 unique reflections out of 2668 with $I>2\sigma(I)$, 154 parameters, 2.5510°<θ<31.0060°, R_1= 0.0385, wR_2= 0.0972, GOF = 1.035.

$\mathbf{1}_{\text{close}}$ (with EtOAc): $C_{28}H_{16}N_2O_4$, tetragonal, space group $I4_1/a$ (No. 88), a = 15.9380(8) Å, b = 15.9380(8) Å, c = 15.9529(7) Å, V = 4052.4(4) Å^3, ρ_{calcd} = 1.457 g/cm^3, Z = 8, 2402 unique reflections out of 2957 with $I>2\sigma(I)$, 154 parameters, 2.556°<θ<30.735°, R_1= 0.0363, wR_2= 0.0941, GOF = 1.065.

$\mathbf{1}_{\text{open}}$ (with hexane): $C_{15.75}H_{12.10}NO_2$, monoclinic, space group $C2/c$ (No. 15), a = 15.450(3) Å, b = 17.951(4) Å, c = 8.532(2) Å, β = 97.51(3)°, V = 2345.8(8) Å^3, ρ_{calcd} = 1.401 g/cm^3, Z = 8, 2294 unique reflections out of 2692 with $I>2\sigma(I)$, 178 parameters, 1.061°<θ<16.275°, R_1= 0.0779, wR_2= 0.2447, GOF = 1.117.

$\mathbf{1}_{\text{open}}$ (with cyclohexane): $C_{14.93}H_{9.9}NO_2$, monoclinic, space group $C2/c$ (No. 15), a = 15.564(3) Å, b = 18.062(4) Å, c = 8.508(2) Å, β = 96.99(3)°, V = 2373.9(8) Å^3, ρ_{calcd} = 1.317 g/cm^3, Z = 8, 3080 unique reflections out of 3404 with $I>2\sigma(I)$, 193 parameters, $2.795° < \theta < 29.527°$ R_1= 0.0741, wR_2= 0.2160, GOF = 1.079.

1$_{\text{open}}$ (with pentane): $C_{15.50}H_{11}NO_2$, monoclinic, space group *C*2/*c* (No. 15), *a* = 15.487(3) Å, *b* = 17.983(4) Å, *c* = 8.517(2) Å, β = 97.19(3)°, *V* = 2353.4(8) Å^3, ρ_{calcd} = 1.373 g/cm^3, *Z* = 8, 3059 unique reflections out of 3342 with $I>2\sigma(I)$, 174 parameters, $2.231° < \theta < 29.524°$ R_1= 0.0521, wR_2= 0.1576, GOF = 1.073.

1$_{\text{open}}$ (with decane): $C_{15.50}H_{11.30}NO_2$, monoclinic, space group *C*2/*c* (No. 15), *a* = 15.4960(3) Å, *b* = 17.8919(3) Å, *c* = 8.5454(2) Å, β = 97.664(2)°, *V* = 2348.07(8) Å^3, ρ_{calcd} = 1.378 g/cm^3, *Z* = 8, 3007 unique reflections out of 3290 with $I>2\sigma(I)$, 168 parameters, $2.277° < \theta < 30.983°$ R_1= 0.0426, wR_2= 0.1180, GOF = 1.076.

1$_{\text{open}}$ (with toluene): $C_{16.25}H_{10.62}NO_2$, monoclinic, space group *C*2/*c* (No. 15), *a* = 15.4912(5) Å, *b* = 18.1068(5) Å, *c* = 8.5193(3) Å, β = 97.128(3)°, *V* = 2371.2(1) Å^3, ρ_{calcd} = 1.411 g/cm^3, *Z* = 8, 2745 unique reflections out of 3155 with $I>2\sigma(I)$, 190 parameters, $2.250° < \theta < 30.792°$ R_1= 0.0418, wR_2= 0.1124, GOF = 1.069.

1$_{\text{open}}$ (with benzene): $C_{15.25}H_{9.25}NO_2$, monoclinic, space group *C*2/*c* (No. 15), *a* = 15.512(3) Å, *b* = 17.987(4) Å, *c* = 8.514(2) Å, β = 97.05(3)°, *V* = 2357.8(8) Å^3, ρ_{calcd} = 1.344 g/cm^3, *Z* = 8, 3003 unique reflections out of 3389 with $I>2\sigma(I)$, 174 parameters, $2.796° < \theta < 29.514°$ R_1= 0.0705, wR_2= 0.2061, GOF = 1.120.

1$_{\text{open}}$ (with CH_2Cl_2): $C_{14.36}H_{8.72}Cl_{0.73}NO_2$, monoclinic, space group *C*2/*c* (No. 15), *a* = 15.4081(6) Å, *b* = 18.0628(8) Å, *c* = 8.5341(4) Å, β = 97.705(4)°, *V* = 2353.7(2) Å^3, ρ_{calcd} = 1.429 g/cm^3 , *Z* = 8, 2641 unique reflections out of 3023 with $I>2\sigma(I)$, 182 parameters, $2.656° < \theta < 30.945°$, R_1= 0.0479, wR_2= 0.1332, GOF = 1.079.

1$_{\text{open}}$ (with dichloroethane): $C_{14.46}H_{8.90}Cl_{0.46}NO_2$, monoclinic, space group *C*2/*c* (No. 15), *a* = 15.442(3) Å, *b* = 18.010(4) Å, *c* = 8.515(2) Å, β = 97.36(3)°, *V* = 2348.6(8) Å^3 , ρ_{calcd} = 1.387 g/cm^3 , *Z* = 8, 3044 unique reflections out of 3417 with $I>2\sigma(I)$, 167 parameters, $2.227° < \theta < 29.528°$, R_1= 0.0617, wR_2= 0.1915, GOF = 1.092.

1$_{\text{open}}$ (with *t*-BuOH): $C_{15}H_8NO_{2.50}$, monoclinic, space group *C*2/*c* (No. 15), *a* = 15.5901(3) Å, *b* = 18.1053(4) Å, *c* = 8.5158(2) Å, β = 97.025(2)°, *V* = 2385.65(9) Å^3 , ρ_{calcd} = 1.314 g/cm^3 , *Z* = 8, 2943 unique reflections out of 3302 with $I>2\sigma(I)$, 176 parameters, $2.2530° < \theta < 31.0820°$, R_1= 0.0551, wR_2= 0.1661, GOF = 1.122.

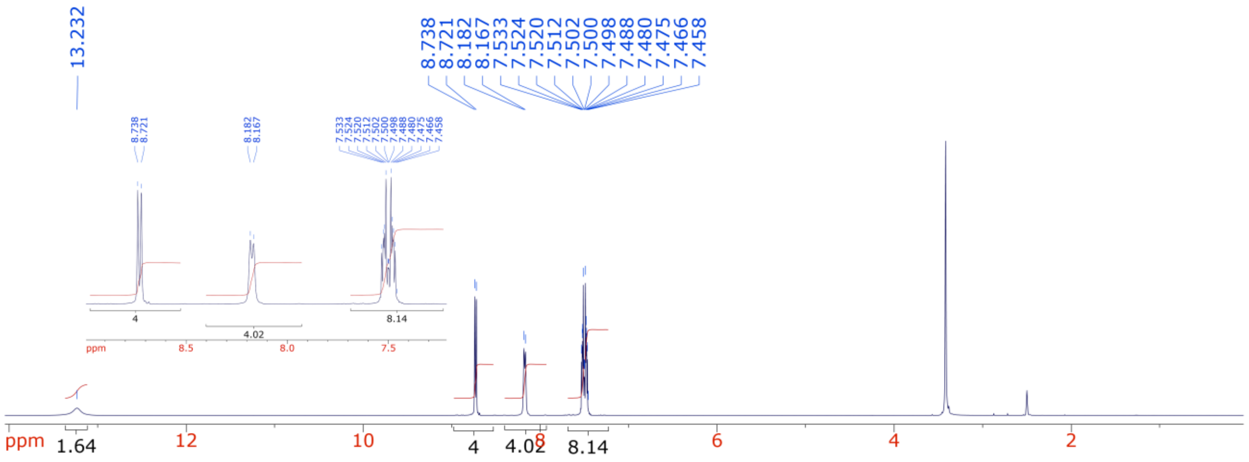
2 (4-pyridyl-1,3-indanedione): $C_{14}H_{10}NO_3$, monoclinic, space group *C*2/*m* (No. 12), *a* = 11.0304(7) Å, *b* = 11.8210(5) Å, *c* = 9.3939(5) Å, β = 115.468(2)°, *V* = 1105.9(1) Å^3, ρ_{calcd} = 1.443 g/cm^3, *Z* = 4, 1043 unique reflections out of 1332 with $I>2\sigma(I)$, 90 parameters, $3.45° < \theta < 27.46°$ R_1= 0.0401, wR_2= 0.1001, GOF = 1.107.

CCDC 1887664 (**1**$_{\text{open}}$ (with CH_2Cl_2)), 1887665 (**1**$_{\text{open}}$ (with benzene)), 1887666 (**1**$_{\text{open}}$ (with dichloroethane)), 1887667 (**1**$_{\text{close}}$ (with EtOAc)), 1887668 (**1**$_{\text{close}}$ (with cyclohexanol)), 1887669 (**1**$_{\text{open}}$ (with cyclohexane)), 1887670 (**1**$_{\text{close}}$), 1887671 (**1**$_{\text{close}}$ (with CH_3CN)), 1887672 (**1**$_{\text{close}}$ (with toluene)), 1887673 (**1**$_{\text{open}}$ (with hexane)), 1887674 (**1**$_{\text{open}}$ (with *t*-BuOH)), 1887675 (**1**$_{\text{open}}$ (with pentane)) 1887676 (4-pyridyl-

1,3-indanedione) and 1997278 (**1**$_{\text{open}}$ (with decane)) contain the crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (https://www.ccdc.cam.ac.uk/).

4. Supporting figures and table

^{1}H NMR



^{13}C NMR

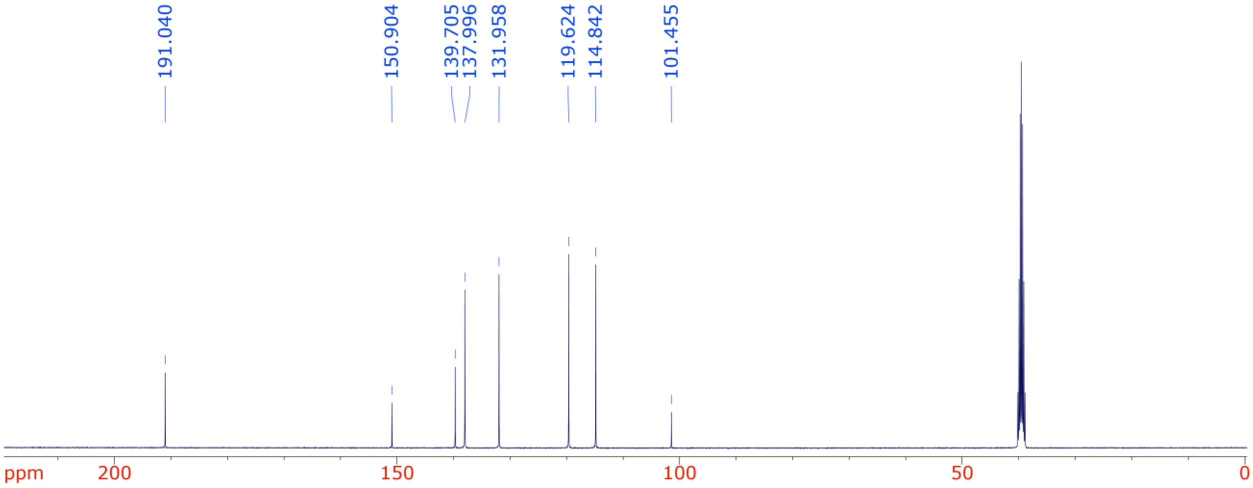
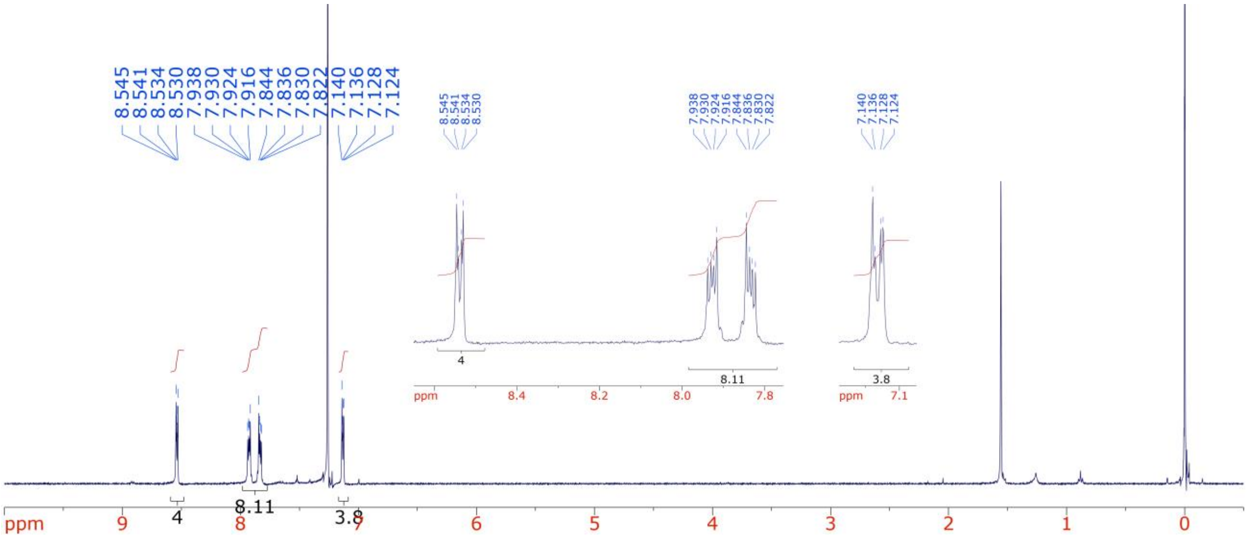


Fig. S1.

^{1}H NMR and ^{13}C NMR spectra of 4-pyridyl-1,3-indanedione measured in DMSO-*d*^{6}.

^{1}H NMR



^{13}C NMR

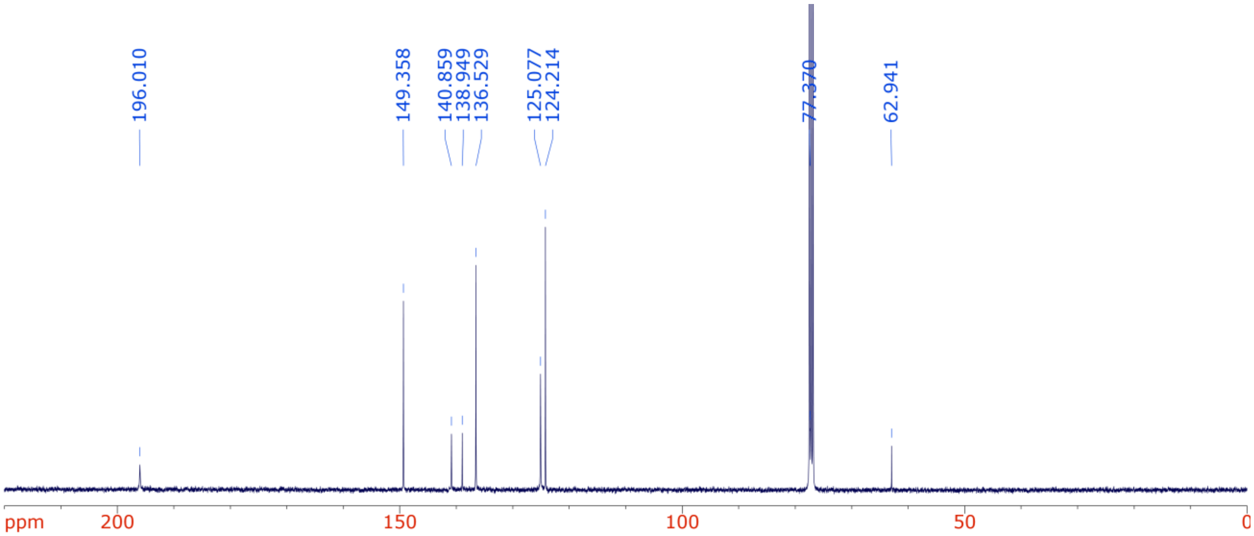


Fig. S2.

^{1}H NMR and ^{13}C NMR spectra of **1** measured in $CDCl_3$.

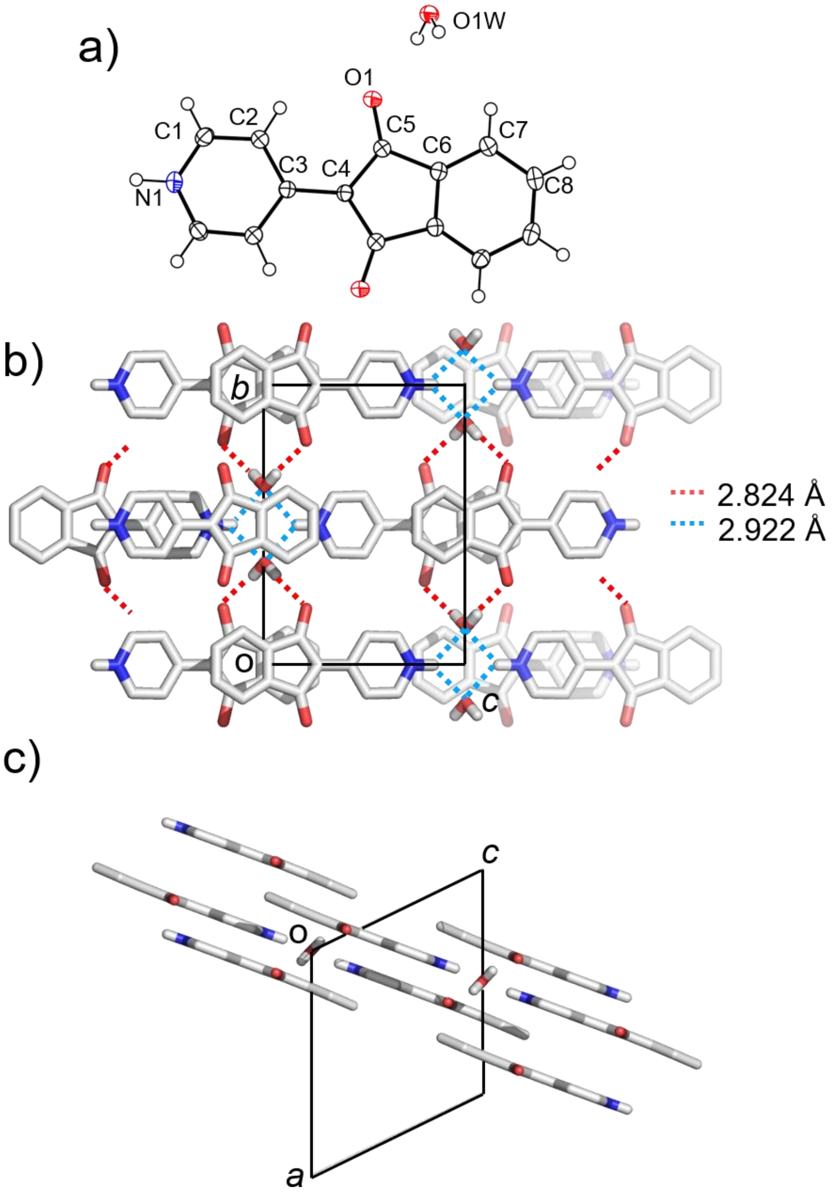


Fig. S3.

Crystal structure of 4-pyridyl-1,3-indanedione. a) Displacement ellipsoid plot at 50% probability. b) Packing structure viewed from the *a* axis. Red-dotted line: OH···O type hydrogen bonds (2.824 Å). Blue-dotted line: NH···O type hydrogen bonds (2.922 Å). c) Packing structure viewed from the *b* axis. Gray, C; blue, N; red, O. Hydrogen atoms which are not contributing to the formation of hydrogen bonds are omitted for clarity in figure b) and c).

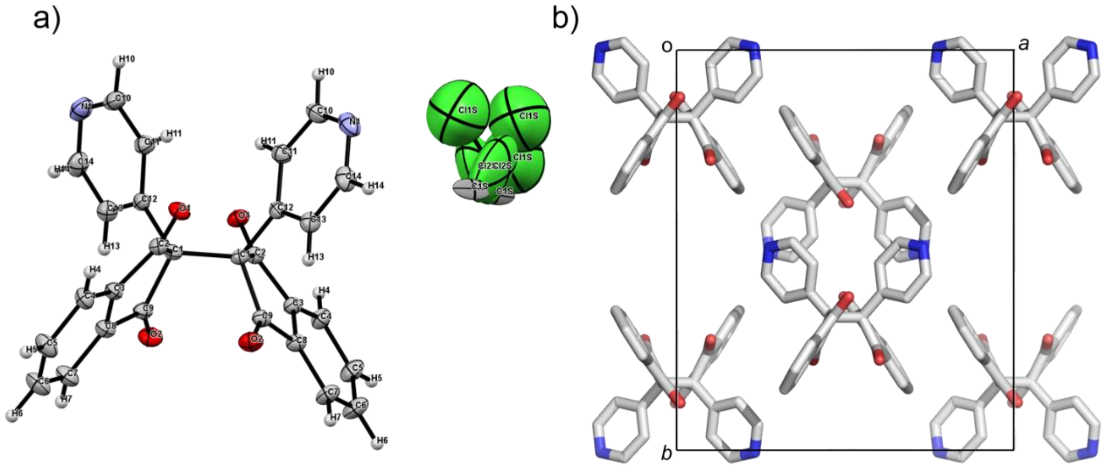


Fig. S4.

Crystal structure of $\mathbf{1}_{\text{open}}$ obtained by slow diffusion from CH_2Cl_2. a) Displacement ellipsoid plot of $\mathbf{1}_{\text{open}}$ at 50% probability. b) Porous structure viewed from the *c* axis. Solvent molecules are omitted for clarity.

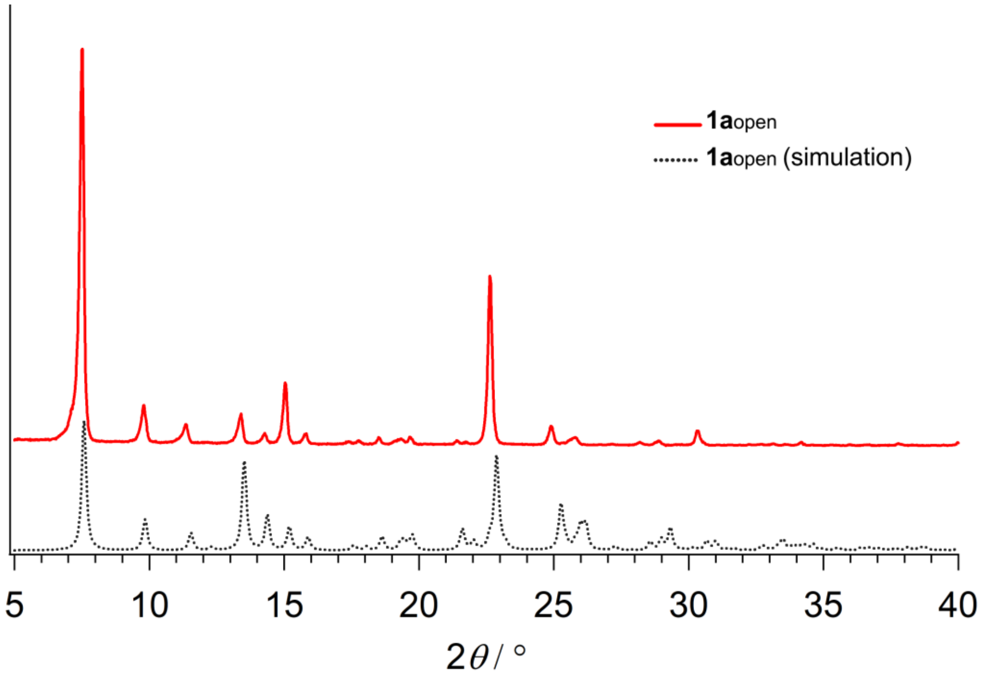


Fig. S5.

PXRD pattern of the crystalline powder of **1**$_{open}$.obtained by the addition of an excess amount of hexane in the saturated CH_2Cl_2 solution of **1**. Simulation pattern is generated from the single crystalline data measured at 100 K.

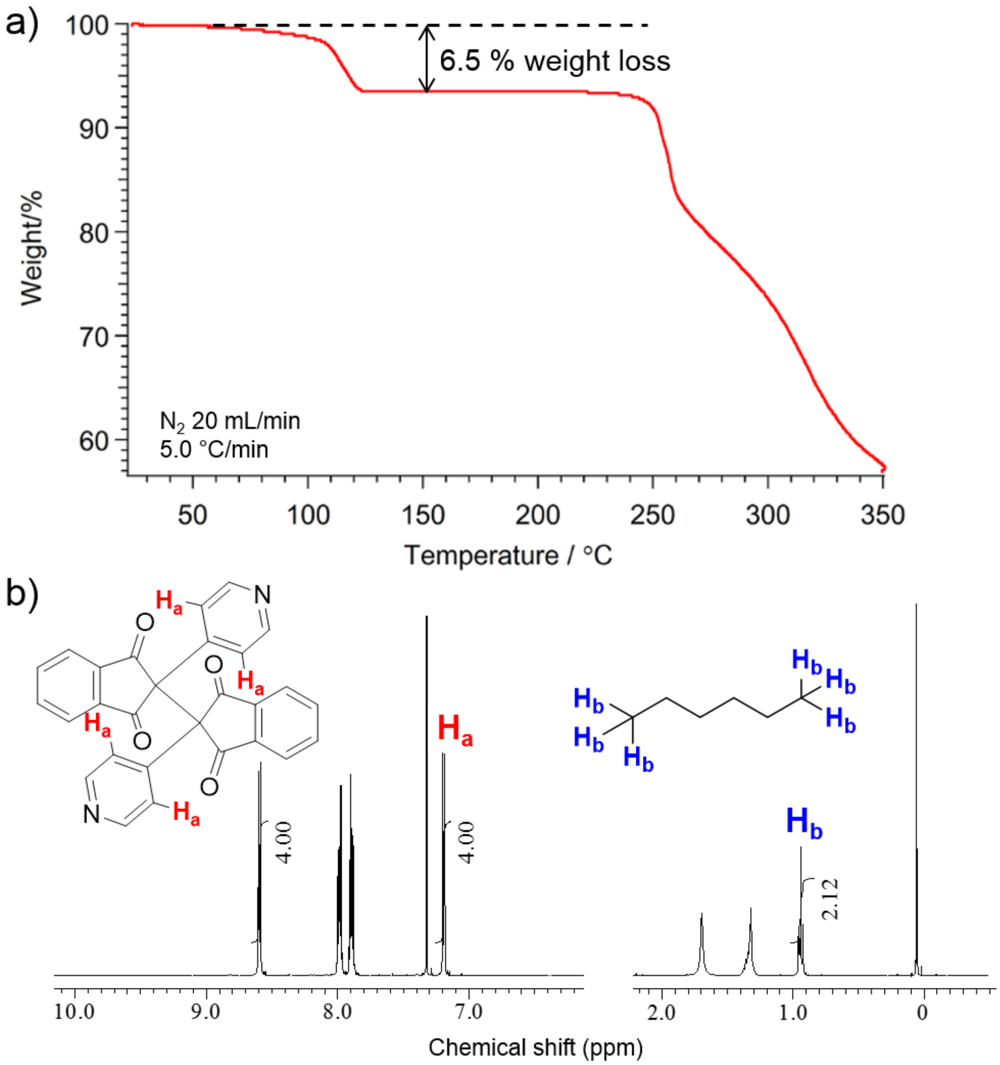


Fig. S6.

Hexane encapsulation in $\mathbf{1}_{\text{open}}$. a) TGA of the crystalline powder of $\mathbf{1}_{\text{open}}$. b) ^{1}H NMR spectra of the corresponding crystalline powder $\mathbf{1}_{\text{open}}$ in $CDCl_3$.

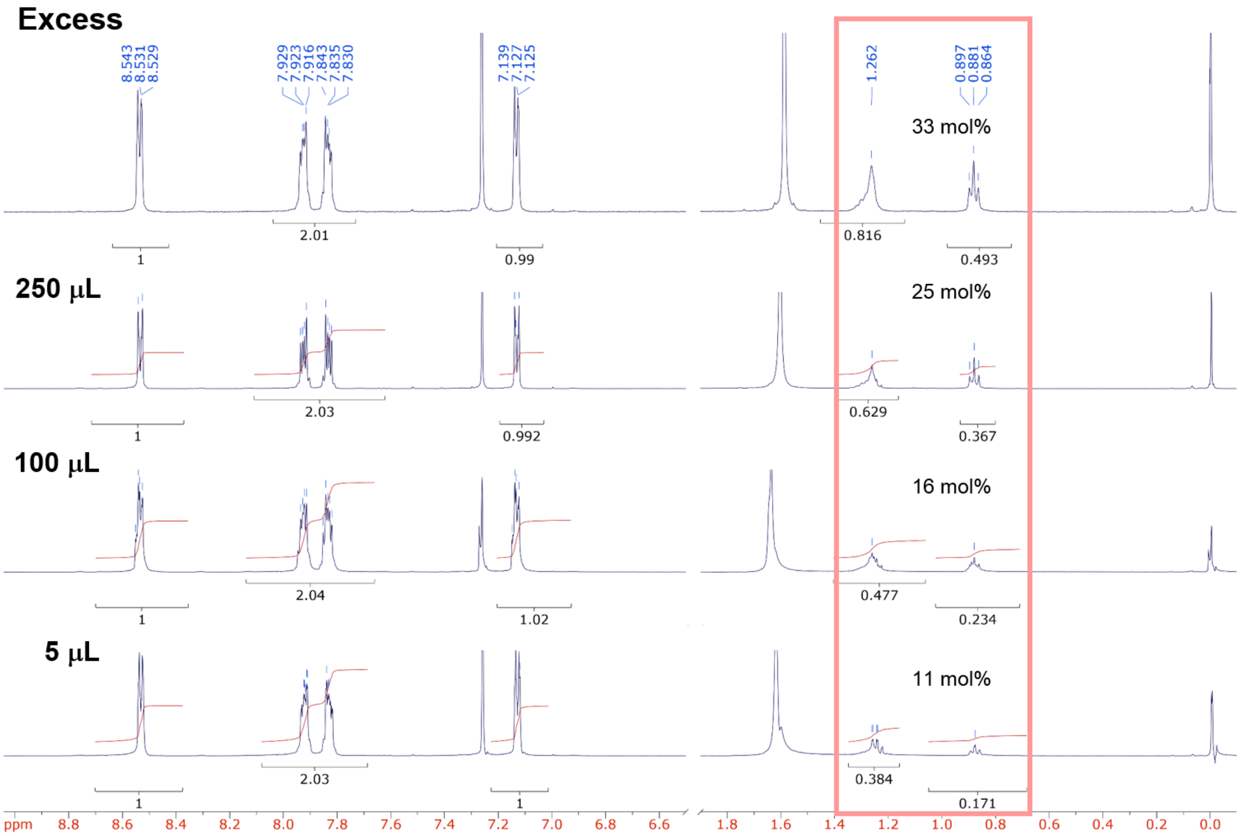


Fig. S7.

^{1}H NMR spectra of single crystals of $\mathbf{1}_{\text{open}}$ prepared by vapor diffusion of **1** (1.0 mg, 2.2 μmol) in CH_2Cl_2 (0.3 mL) including hexane (5 μL~excess) with EtOH as the poor solvent at room temperature for 1 day. All the single crystals were dried at 40 °C under reduced pressure for 1 day before the measurement.

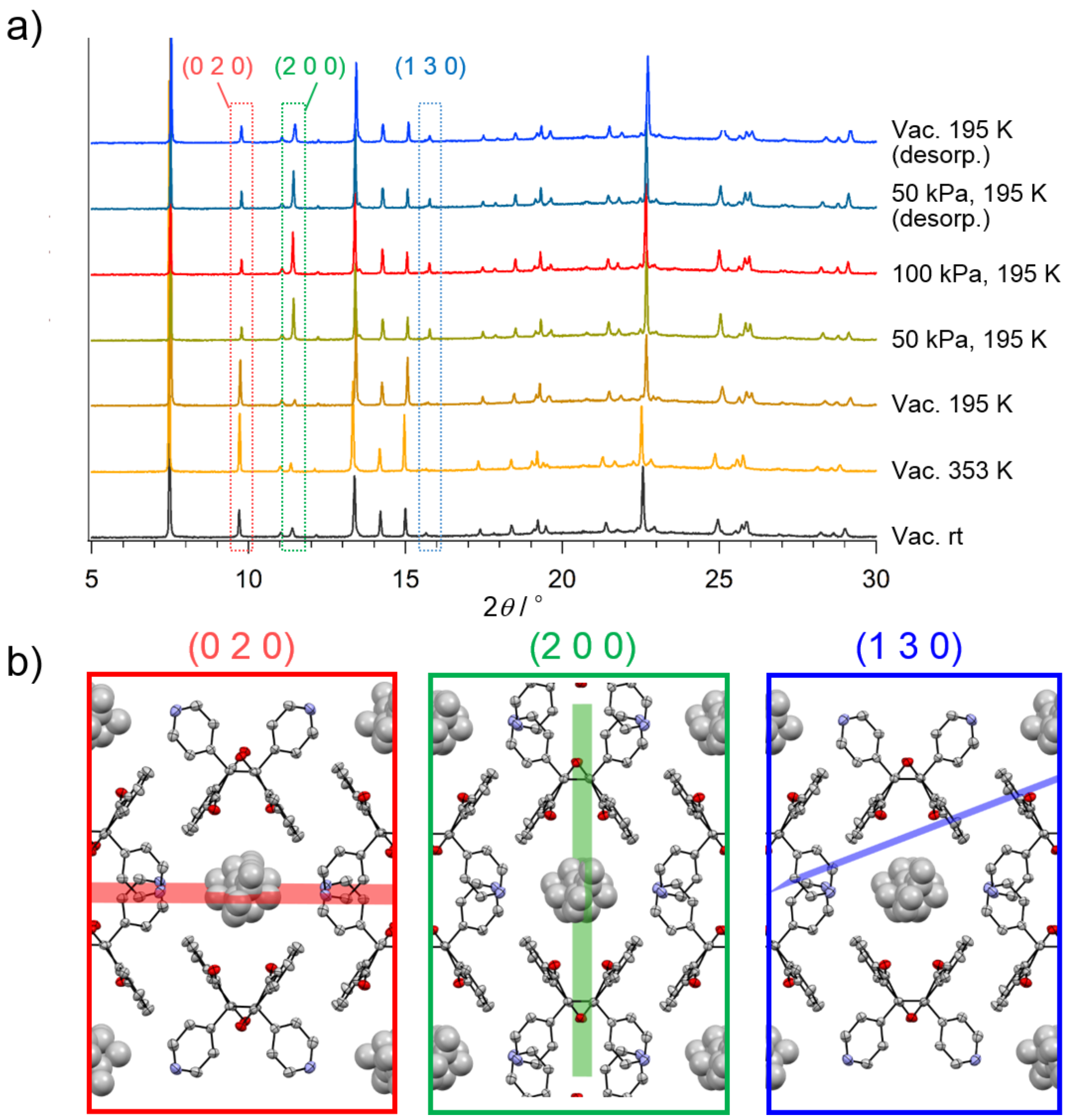


Fig. S8.

PXRD pattern change during CO_2 vapour trapping in $\mathbf{1}_{\mathrm{open}}$ (guest: hexane) measured at BL02B2 in SPring-8 (2017B1325). The measurement was started from the vacuuming process from at rt, then heated up to 353 K, and finally cooled down to 195 K. The resulting PXRD pattern after cool down process (third from the bottom) shows that the initial open form was retained after vacuuming process, indicating that still the guest solvent existed in the pore. Then CO_2 vapour was introduced and PXRD pattern was measured at 50 kPa and 100 Pa as sorption process. Further desorption process was also measured at 50 kPa and vacuum condition. Although the main structure did not show significant change during the experiment, drastic peak intensity changes at $2\theta = 9.8$, 11.4 and 15.8°, which corresponded to (0 2 0), (2 0 0) sand (1 3 0) planes were observed, indicating the further CO_2 trapping within the channel.

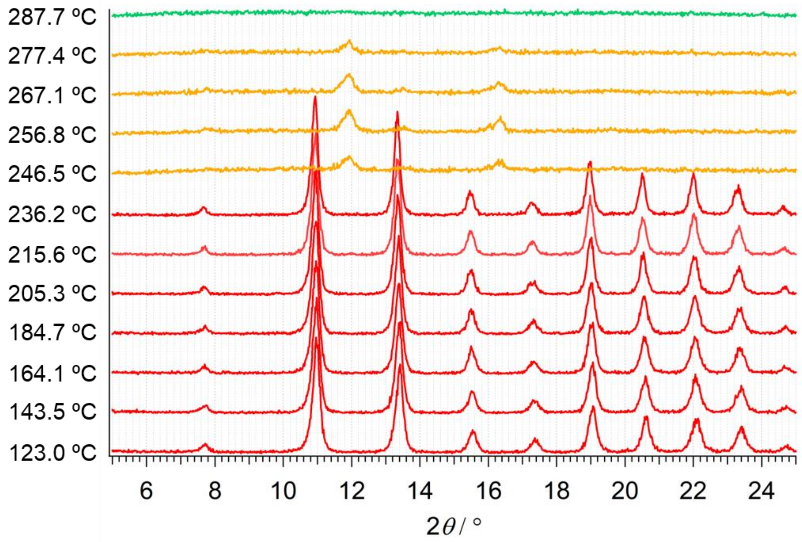


Fig. S9.

PXRD pattern of **1**$_{\text{open}}$ at more than 120 °C. The heating rate was 3 °C/min.

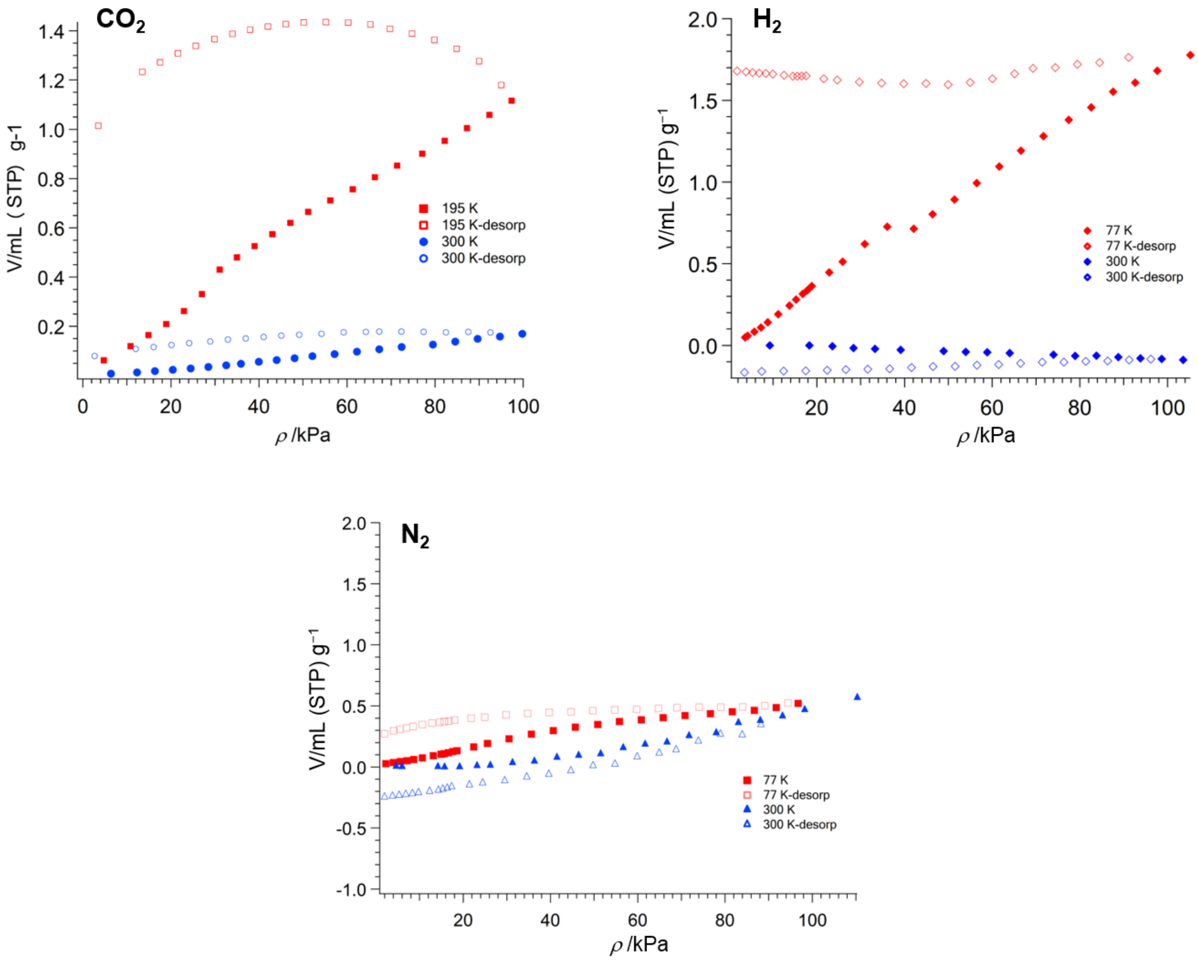


Fig. S10.

CO_2, H_2 and N_2 adsorption isotherms of powder crystal of $\mathbf{1}_{close}$.

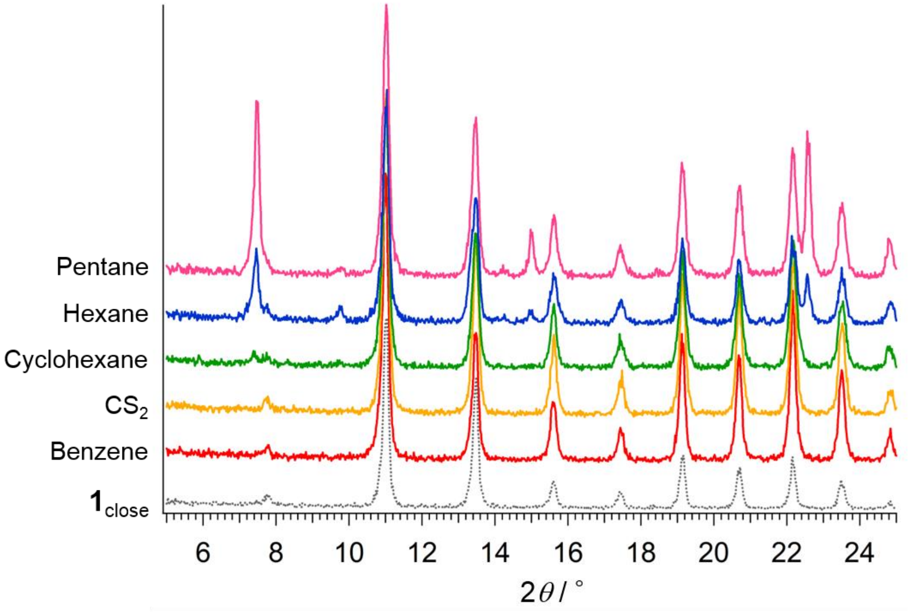


Fig. S11.

PXRD patterns of powder crystals of $\mathbf{1}_{close}$ after soaking in benzene, CS_2, cyclohexane, hexane and pentane for 2 days at 60 °C.

Preferring **1**$_{\text{close}}$	$E_T(30)$ (kcal· mol^{-1})	Preferring **1**$_{\text{open}}$	$E_T(30)$ (kcal· mol^{-1})
EtOH	51.9	Cyclohexane	30.9
CH_3CN	45.6	Hexane	31.0
Cyclohexanol	47.2	Pentane	31.0
		Decane	31.0
EtOAc	38.1	Toluene	33.9
		Benzene	34.3
		CH_2Cl_2	40.7
		$(CH_2Cl)_2$	41.3
		t-BuOH	43.3

Table. S1

Solvent preferences for the crystal formation.

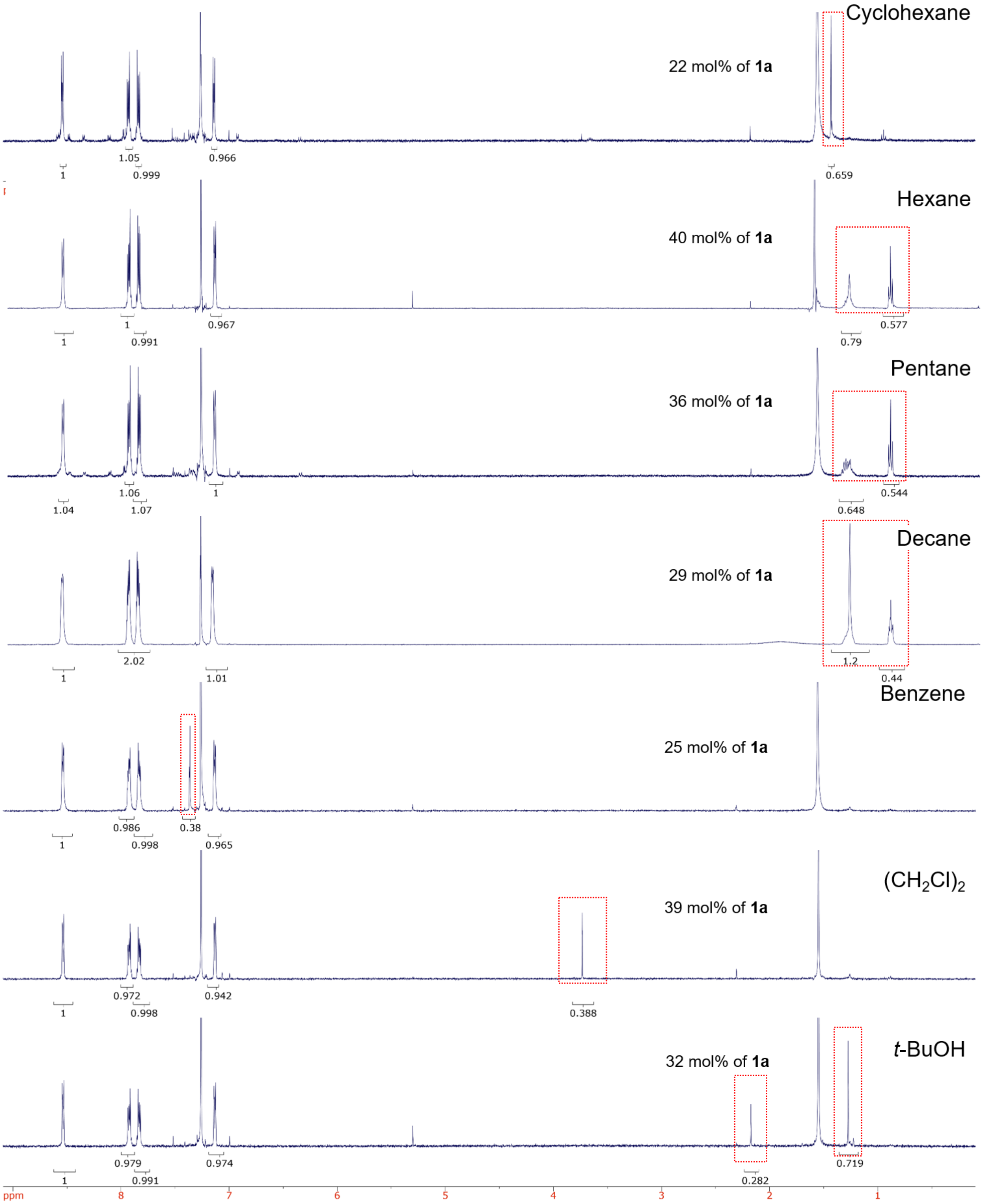


Fig. S12.

^{1}H NMR spectra of powder crystals of **1**$_{\mathrm{open}}$ prepared by using various kinds of trigger solvents. Corresponding trigger solvent peaks are enclosed by red dotted line.

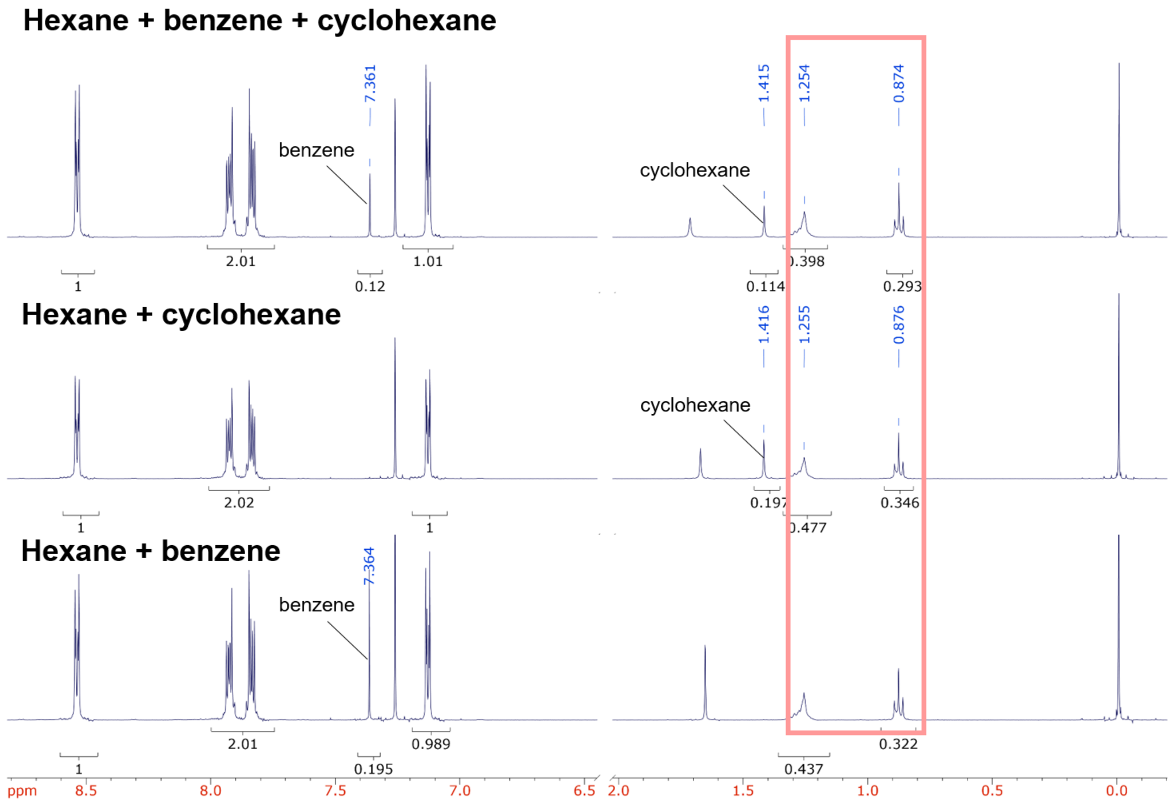


Fig. S13.

^{1}H NMR spectra of single crystals of $\mathbf{1}_{\mathrm{open}}$ prepared in the mixed solvent systems (Hexane + benzene. Hexane + cyclohexane and hexane + benezene + cyclohexane).

5. References

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