- Electronic Supplementary Information -

Adsorption and separation of poly-aromatic hydrocarbons by a hydrogen-bonded coordination polymer

Ryo Sekiya and Shin-ichi Nishikiori**

Department of Life Sciences, Graduate School of Arts and Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan

Department of Basic Sciences, Graduate School of Arts and Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan

csekiya@mail.ecc.u-tokyo.ac.jp

and

cnskor@mail.ecc.u-tokyo.ac.jp

Contents

Experimental Section

Supporting Figures

References

Experimental Section

Materials and Instrumentations

All chemicals and solvents were purchased from Kanto Chemical Co., Ltd., Wako Pure Chemical Co., Ltd., and Tokyo Kasei Kogyo Co., Ltd., and were used as received without further purification. ^{1}H NMR (500MHz) spectra were recorded on a JEOL α-500 spectrometer. Chemical shifts are quoted as parts per million (ppm) relative to tetramethylsilane ($CDCl_3$) and dimethylsulfoxide (DMSO-d_6). X-ray powder diffraction (XRD) patterns were collected on a Rigaku Multi-Flex X-ray diffractometer using graphite-monochromatized Cu Kα radiation (λ = 1.5418 Å) with a scanning rate of 0.020 ° sec^{-1} at room temperature.

X-ray Crystallography

X-ray crystallographic data of an inclusion compound of pyrene (**H$_{II}$**⊃(PY)) were collected on a Rigaku RAXIS-RAPID imaging plate area detector using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) at 103 K. The crystal structures were solved by direct method using the *SHELXS-97* program and refined by successive differential Fourier syntheses and full-matrix least-squares procedures using the *SHELXL-97* program.[1] Anisotropic thermal factors were applied to all non-hydrogen atoms.

Crystal data for H$_{II}$⊃(PY): M_r = 1044.4, green block crystal, crystal dimensions 0.32 × 0.18 × 0.09 mm^3, *Triclinic*, space group $P\bar{1}$ (#2), Z = 2, F(000) = 1067.8, $2\theta_{max}$ = 55.8 ° were a = 11.1430(6), b = 14.1170(8), c = 14.3720(8) Å, α = 98.177(1), β = 97.785(1), γ = 107.030(1) °, and V = 2101.89(10) Å^3. A total of 12860 reflections were collected of which 9093 reflections were independent (R_{int} = 0.018). The structure was refined to final R_1 = 0.039 for 7541 data [$I > 2\sigma(I)$] with 602 parameters, $wR2$ = 0.090 for all data, GOF = 1.038, and residual electron density max/min = 0.592/−0.334 eÅ^{-3}. CCDC 867556.

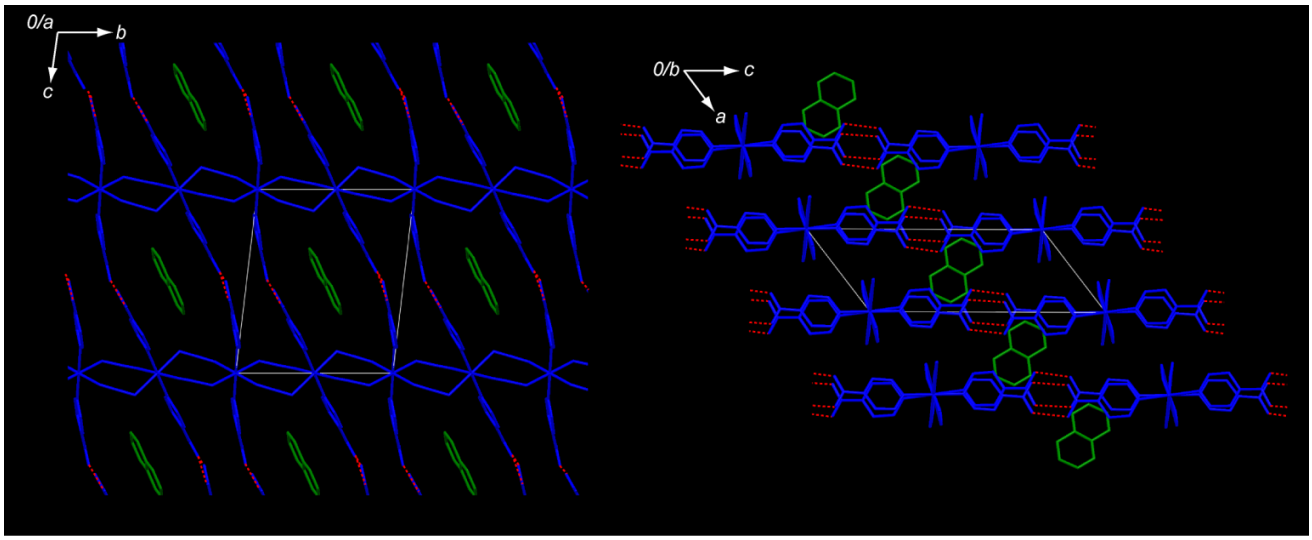

Fig. S1. X-ray crystal structure of $\mathbf{H_c}\supset$(NA) viewed along the *a* axis (left) and the *b* axis (right).[2] Colour scheme: blue (hydrogen-bonded CPs), green (NA). Red dotted lines denote hydrogen bonds between the carboxyl functional groups of the isoH ligands.

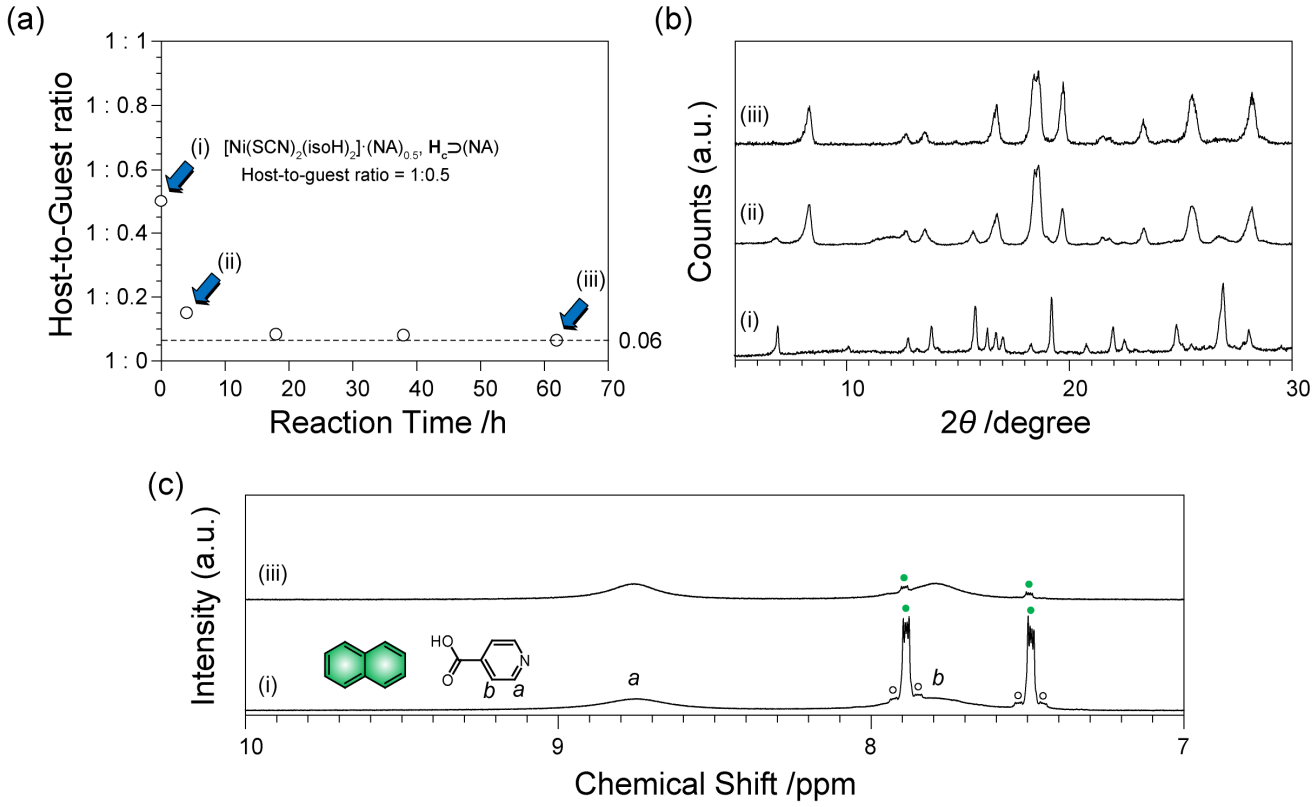

Fig. S2. (a) Time course experiment of the thermal treatment of $\mathbf{H_c}\supset$(NA) at 140 °C in vacuo. (○) denotes the host-to-guest ratio determined by ^{1}H NMR spectroscopy. (Host = $[Ni(SCN)_2(isoH)_2]$, Guest = NA) Reaction time: (i) 0, (ii) 4 and (iii) 62 h. (b) X-ray powder diffraction (XRD) patterns of (i), (ii) and (iii). (c) ^{1}H NMR spectra (500 MHz, DMSO-d_6, rt) of (i) and (iii). The signals of the isoH ligand are broadened due to coordination of the isoH ligand to the paramagnetic Ni^{2+} center. (○) denotes spinning side band.

Previously, we reported the TG analysis of $\mathbf{H_c}\supset$(NA).[2] $\mathbf{H_c}\supset$(NA) showed an initial weight loss of 11% at 150 °C, corresponding to release of NA from the channels (13%, calculated). This means that 15 % of NA remained inside of residual-host $\mathbf{H_{res}}$. This is in good agreement of the time course experiment. Fig. S2(a) shows that 12 – 13% of NA remained inside of $\mathbf{H_{res}}$. Most likely, this is due to the change of the crystal structure upon removal of NA (Fig. S2b (i) – (iii)), which physically obstructs removal of remaining NA.

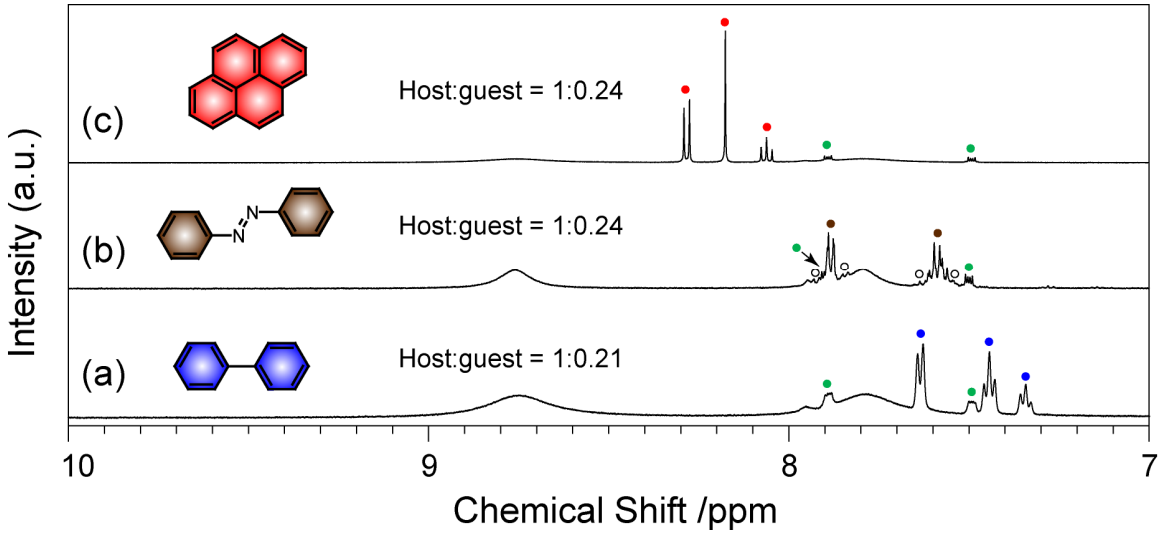

Fig. S3. ^{1}H NMR spectra (500 MHz, DMSO-d_6, rt) of (a) $\mathbf{H}_{res}$⊃(BI), (b) $\mathbf{H}_{res}$⊃(AZ) and (c) $\mathbf{H}_{res}$⊃(PY). The host-to-guest ratios were determined by the relative signal intensities of remaining NA and the guest. (○) denotes spinning side band.

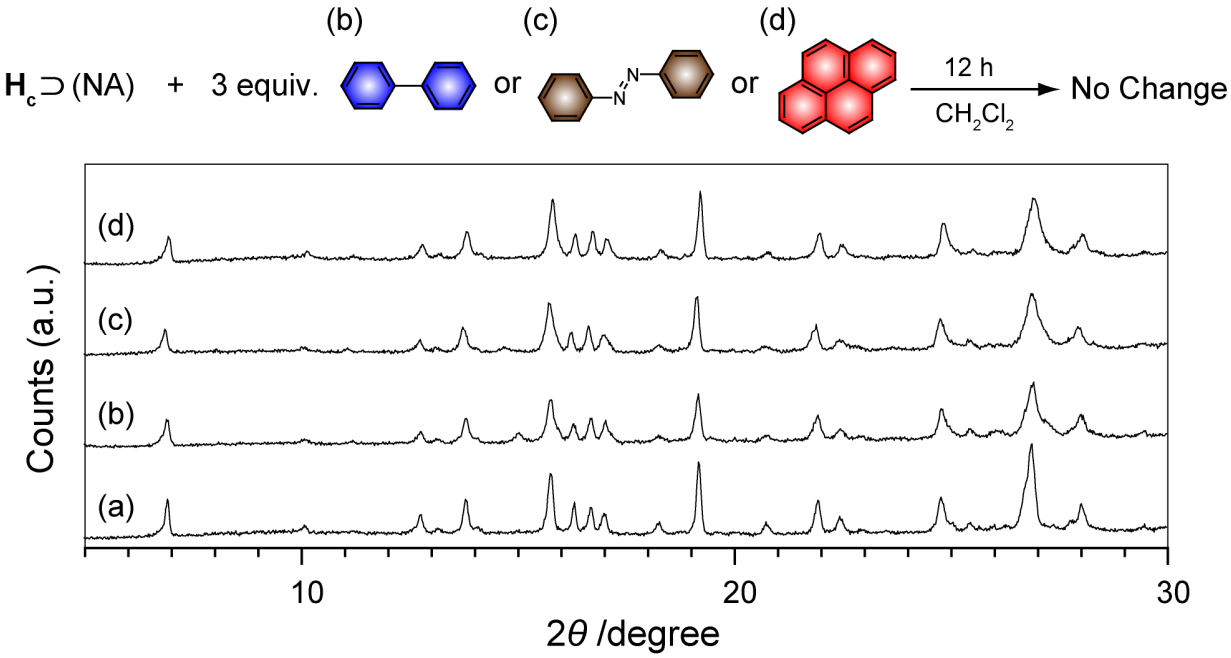

Fig. S4. (a) Observed XRD pattern of $\mathbf{H}_c$⊃(NA). (b), (c) and (d) observed XRD patterns of the samples prepared by immersing $\mathbf{H}_c$⊃(NA) in CH_2Cl_2 solutions containing three equiv. (b) BI, (c) AZ or (d) PY at rt for 12 h.

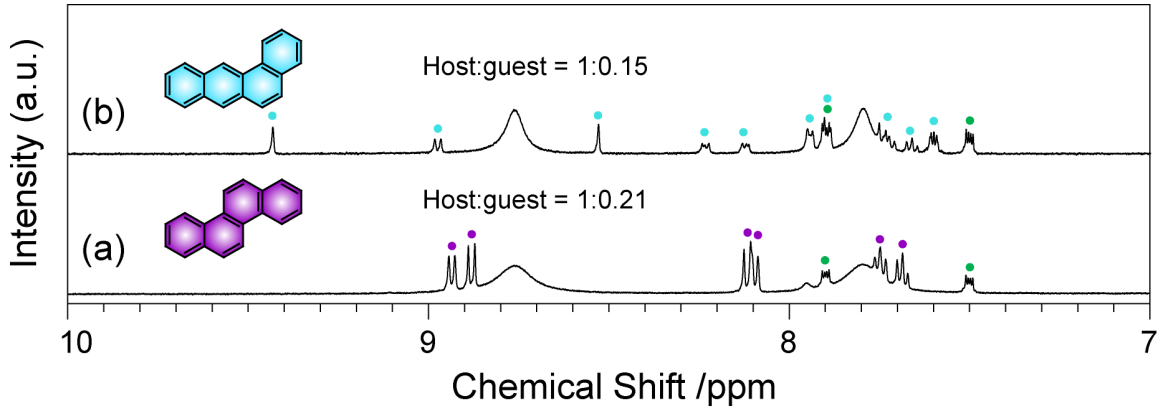

Fig. S5. ^{1}H NMR spectra (500 MHz, DMSO-d_6, rt) of (a) $\mathbf{H}_{res}$⊃(CH) and (b) $\mathbf{H}_{res}$⊃(BE). The host-to-guest ratios were determined by the relative signal intensities of remaining NA and the guest.

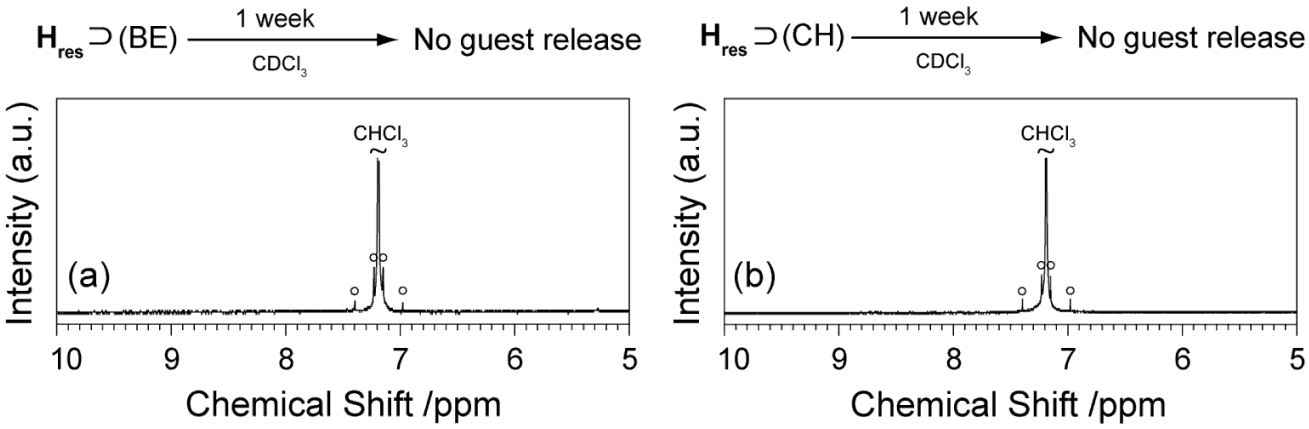

Fig. S6. ^{1}H NMR spectra (500 MHz, $CDCl_3$, rt) of the $CDCl_3$ solutions after filtration of (a) $\mathbf{H}_{res}$⊃(BE) and (b) $\mathbf{H}_{res}$⊃(CH). $\mathbf{H}_{res}$⊃(BE) and (b) $\mathbf{H}_{res}$⊃(CH) were immersed in the $CDCl_3$ solutions at rt for a week. (○) denotes spinning side band.

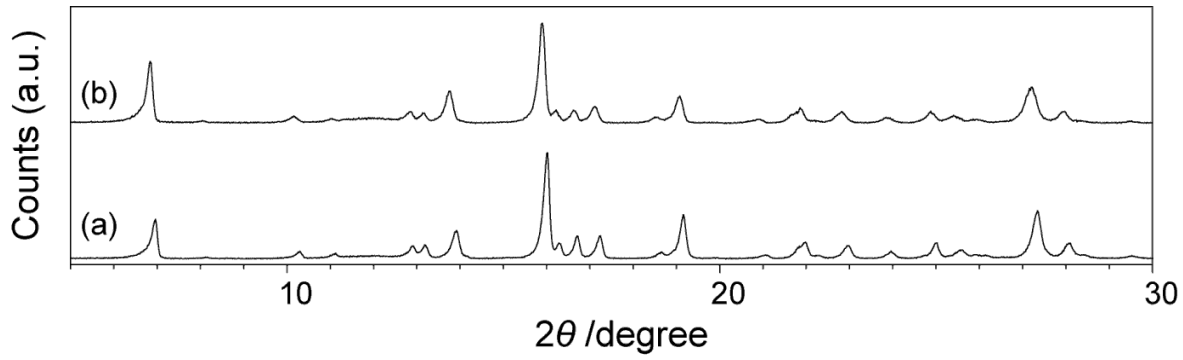

Fig. S7. Observed XRD patterns of (a) $\mathbf{H_c}\supset$(BI) and (b) $\mathbf{H_{res}}\supset$(BI).

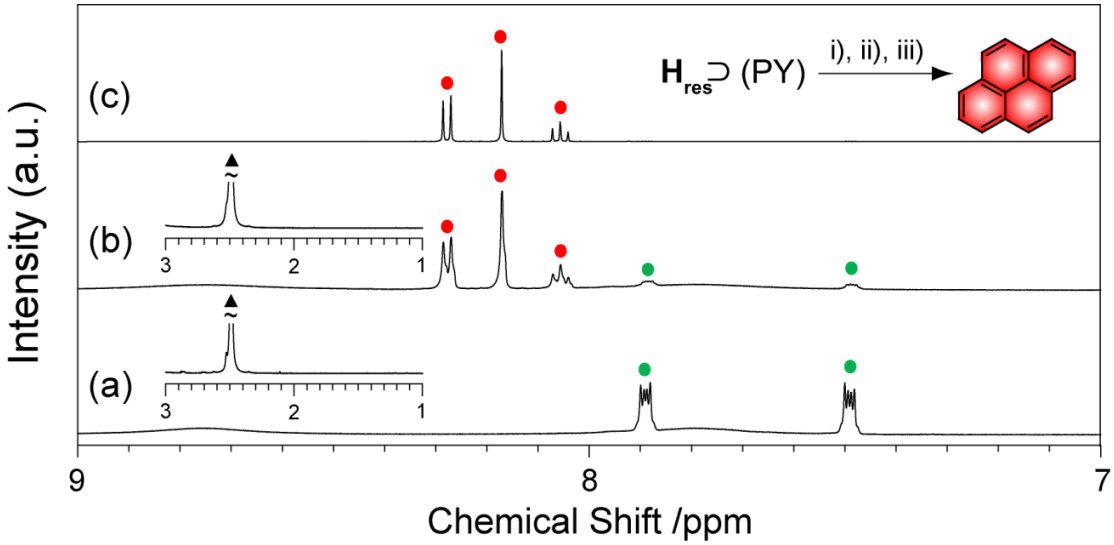

Fig. S8. ^{1}H NMR spectra (500 MHz, DMSO-d_6, rt) of (a) $\mathbf{H_c}\supset$(NA), (b) $\mathbf{H_{res}}\supset$(PY) and (c) isolated PY. Reaction conditions: i) 1 mol L^{-1} of HCl (3 mL), ii) extraction of the adsorbed guests with CH_2Cl_2 (3 mL × 3) and iii) removal of co-existing NA under reduced pressure. Green and red circles denote NA and PY, respectively. (▲) denotes DMSO.

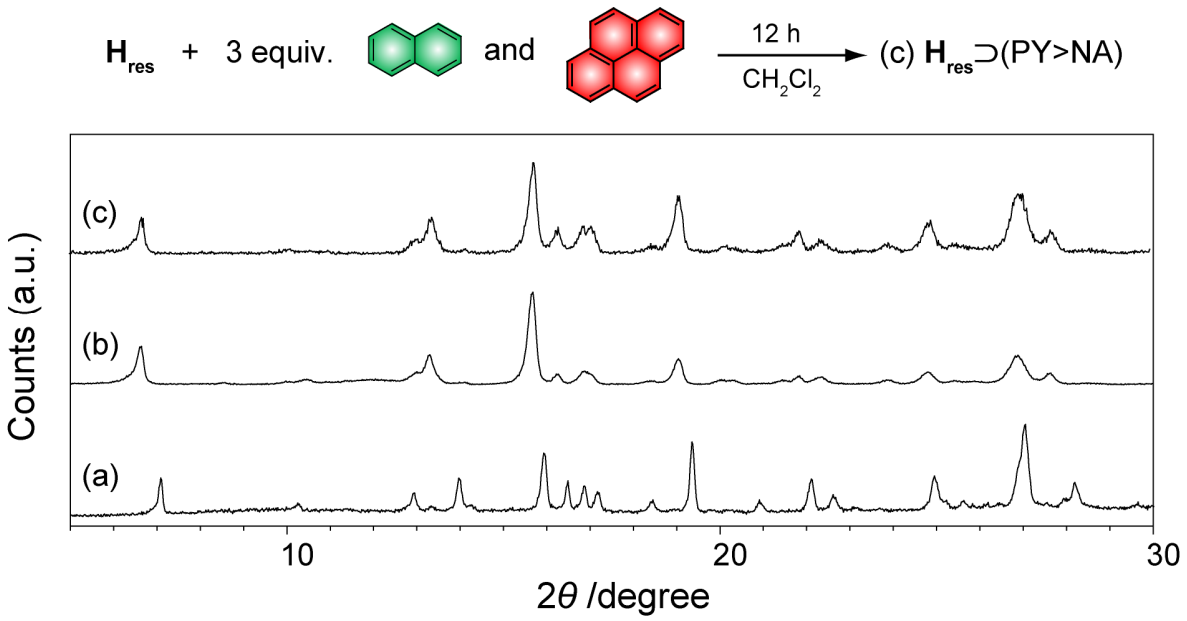

Fig. S9. Observed XRD patterns of (a) $\mathbf{H}_{res}\supset$(NA), (b) $\mathbf{H}_{res}\supset$(PY) and (c) $\mathbf{H}_{res}\supset$(PY>NA).

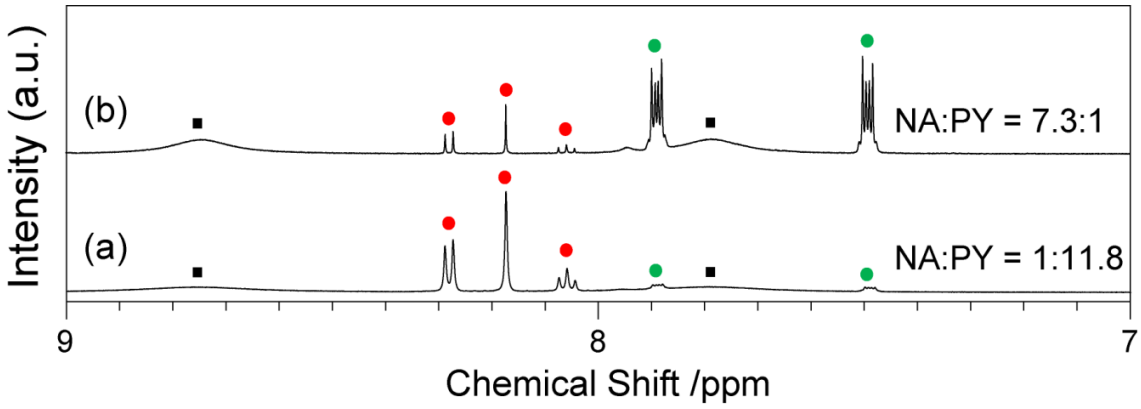

Fig. S10. ^{1}H NMR spectra (500 MHz, DMSO-d_6, rt) of (a) $\mathbf{H}_{res}\supset$(PY>NA) and (b) $\mathbf{H}_{res}\supset$(NA>PY). Green and red circles denote NA and PY, respectively. (■) denotes the isoH ligand.

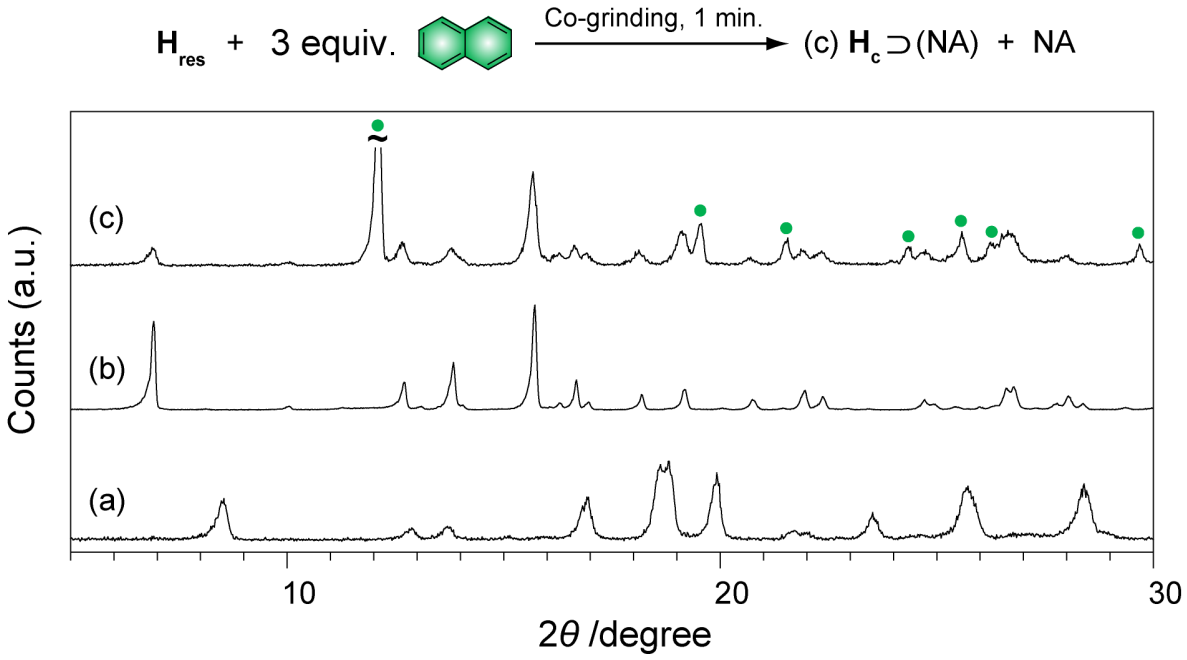

Fig. S11. Observed XRD patterns of (a) $\mathbf{H}_{res}$, (b) $\mathbf{H}_{c}\supset$(NA) and (c) the sample prepared by co-grinding of $\mathbf{H}_{res}$ and three equiv. NA for 1 min followed by standing at rt for 30 min. The green circles denote the diffraction peaks of NA.

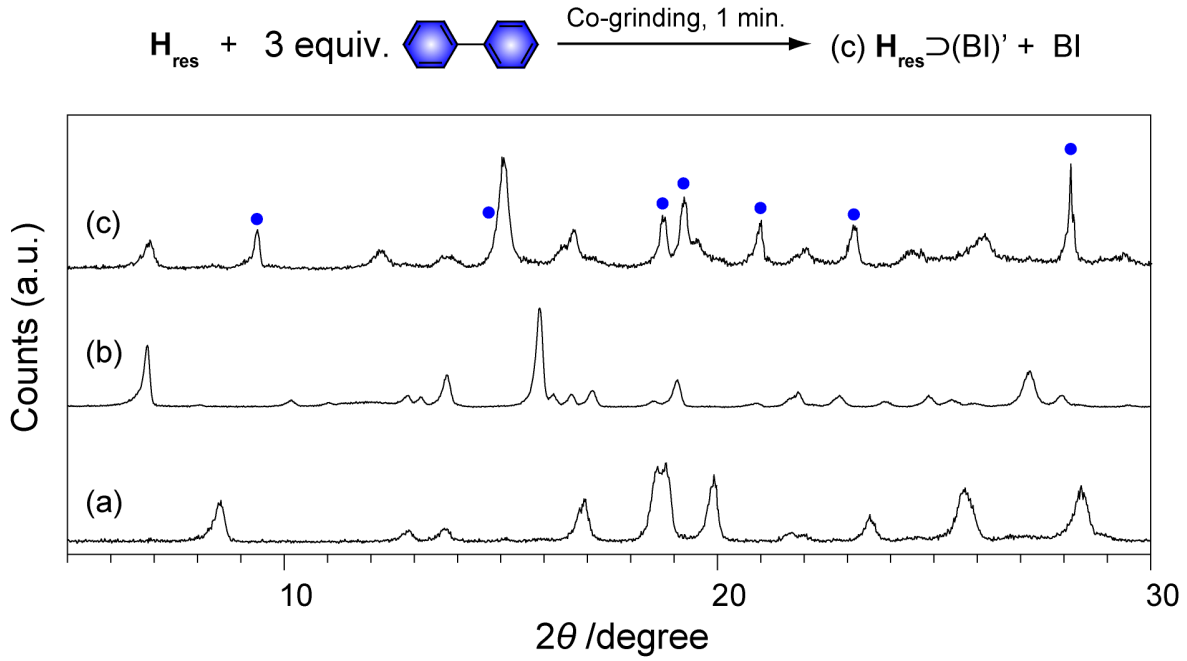

Fig. S12. Observed XRD patterns of (a) $\mathbf{H}_{res}$, (b) $\mathbf{H}_{res}\supset$(BI) and (c) the sample prepared by co-grinding of $\mathbf{H}_{res}$ (30 mg) and three equiv. BI for 1 min followed by standing at rt for 30 min. The blue circles denote the diffraction peaks of BI.

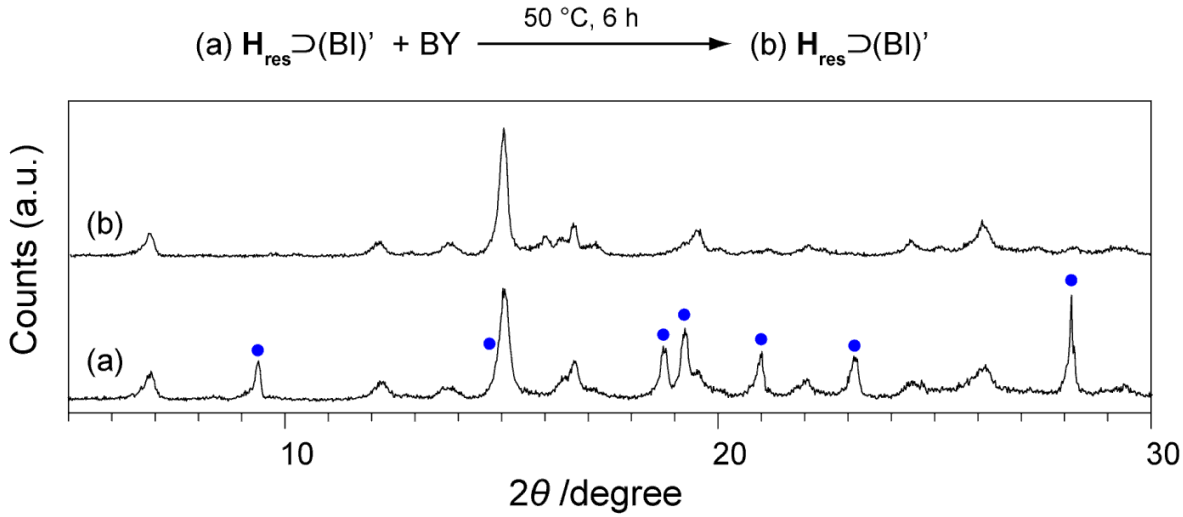

Fig. S13. Observed XRD patterns of (a) a mixture of $\mathbf{H}_{res}$⊃(BI)'+BI (see also Fig. S12c) and (b) $\mathbf{H}_{res}$⊃(BI)' that was obtained by thermal treatment of the mixture of $\mathbf{H}_{res}$⊃(BI)'+BI at 50 °C for 6 h. The blue circles denote the diffraction peaks of BI.

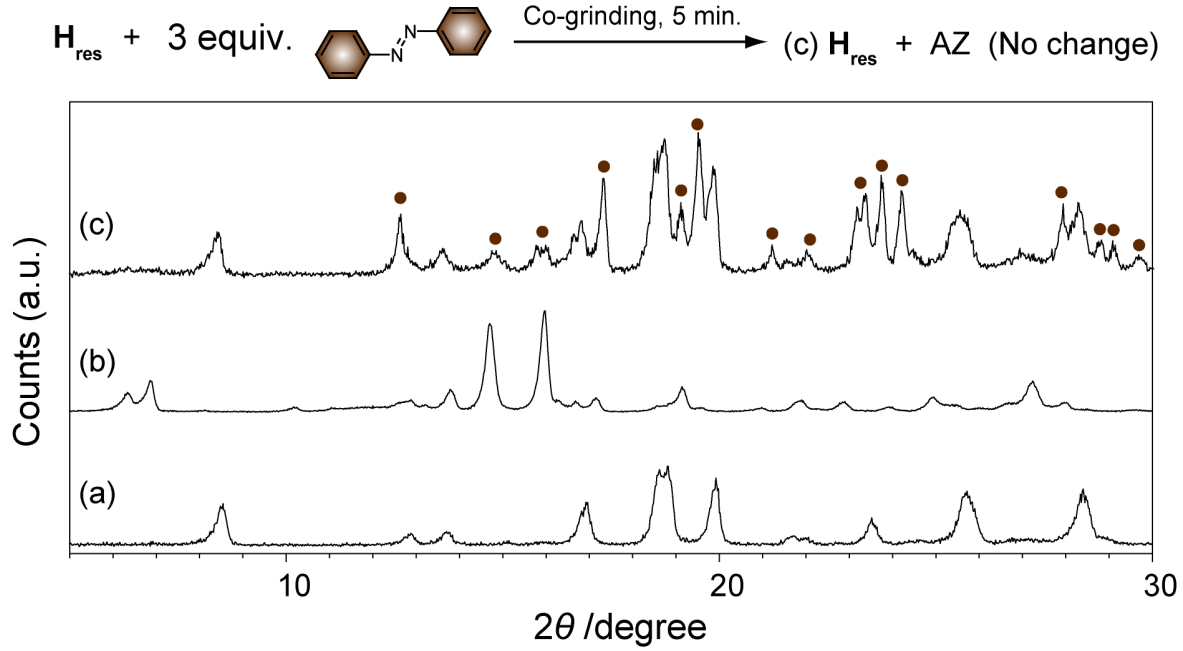

Fig. S14. Observed XRD patterns of (a) $\mathbf{H}_{res}$, (b) $\mathbf{H}_{res}$⊃(AZ) and (c) the sample prepared by co-grinding of $\mathbf{H}_{res}$ and three equiv of AZ for 5 min followed by standing at rt for 30 min. The brown circles denote the diffraction peaks of AZ.

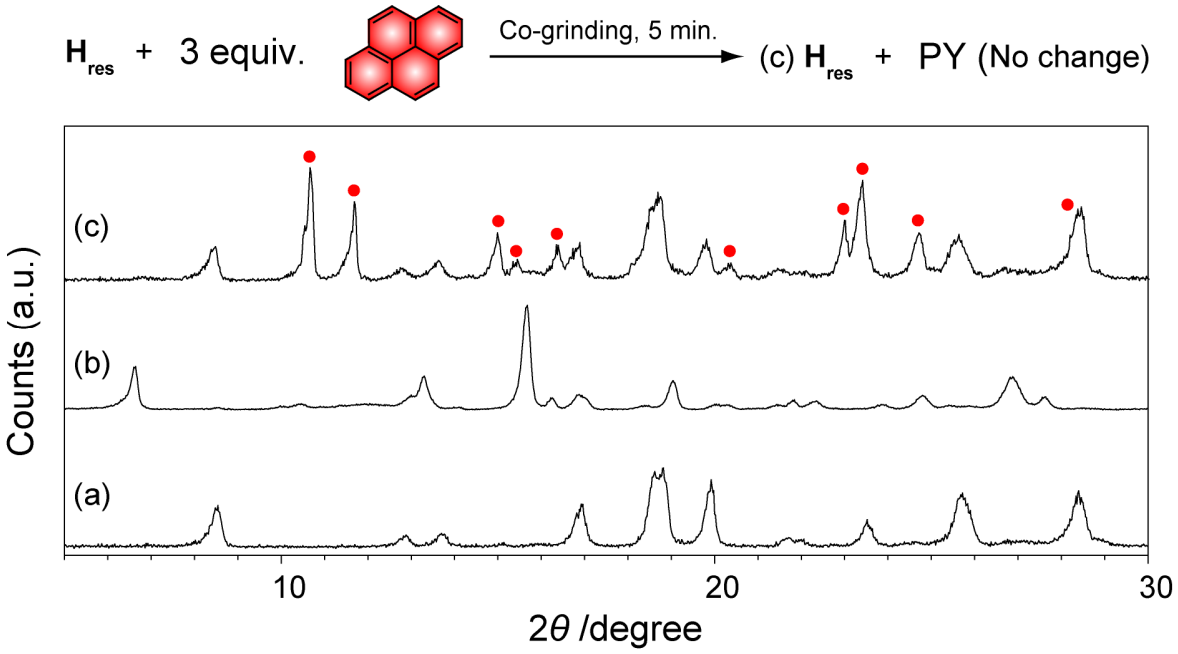

Fig. S15. Observed XRD patterns of (a) $\mathbf{H}_{res}$, (b) $\mathbf{H}_{res}\supset$(PY) and (c) the sample prepared by co-grinding of $\mathbf{H}_{res}$ and three equiv of PY for 5 min followed by standing at rt for 30 min. The red circles denote the diffraction peaks of PY.

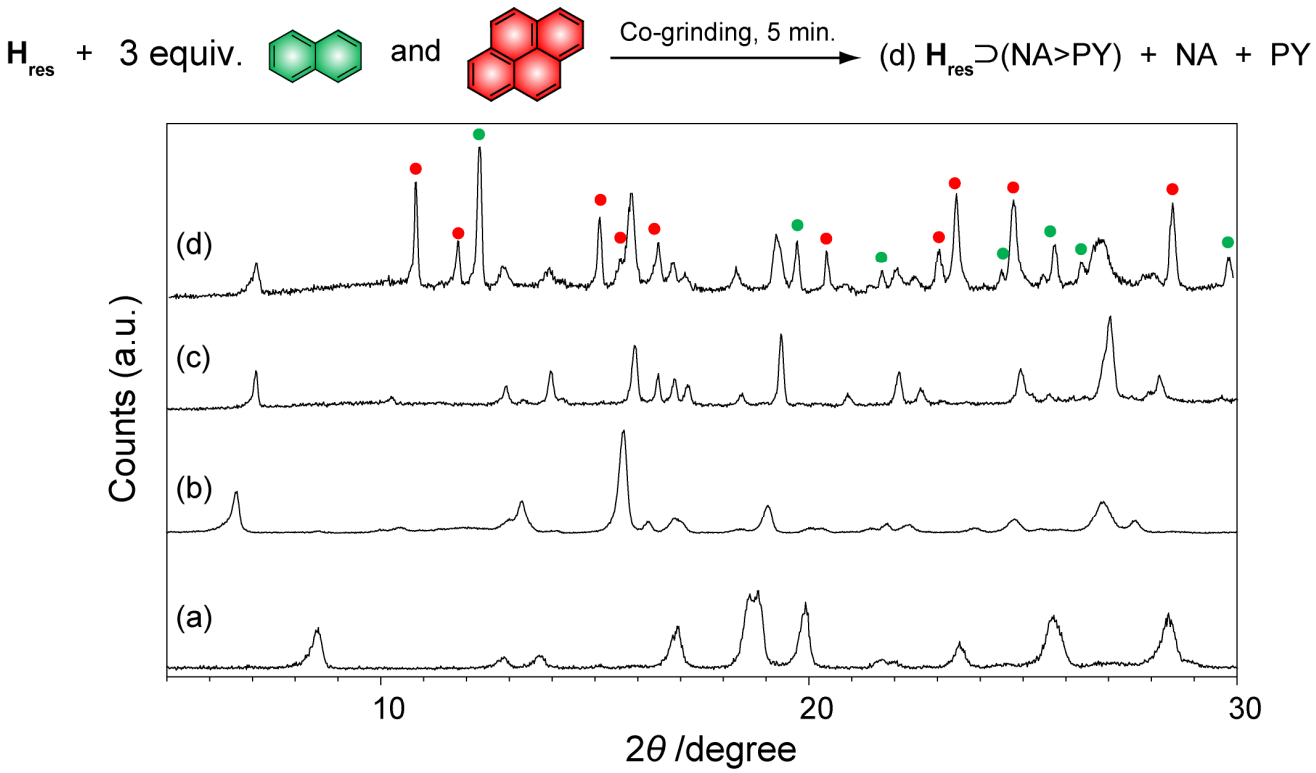

Fig. S16. Observed XRD patterns of (a) $\mathbf{H}_{res}$, (b) $\mathbf{H}_{res}\supset$(PY), (c) $\mathbf{H}_{c}\supset$(NA) and (d) the sample prepared by co-grinding of $\mathbf{H}_{res}$ with three equiv. NA and PY for 5 min followed by standing at rt for 30 min. The green and red circles denote the diffraction peaks of NA and PY, respectively.

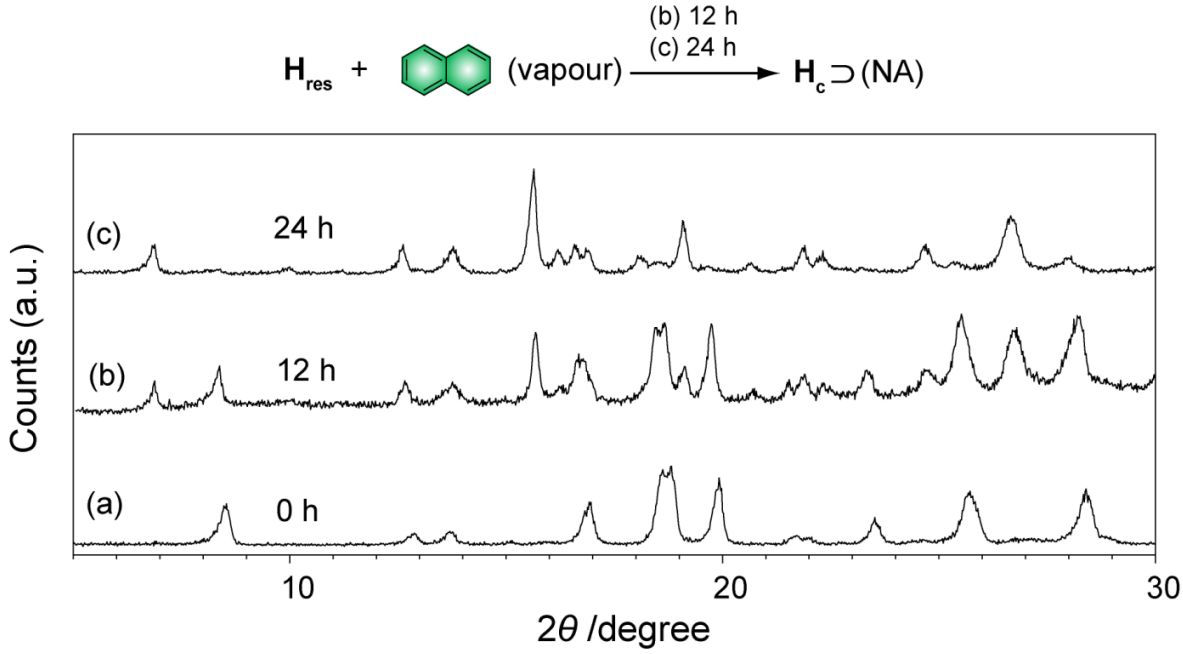

Fig. S17. Observed XRD patterns of the sample prepared by exposure of $\mathbf{H}_{res}$ to the saturated vapour of NA in a Petri dish at rt for (a) 0, (b) 12 and (c) 24 h.

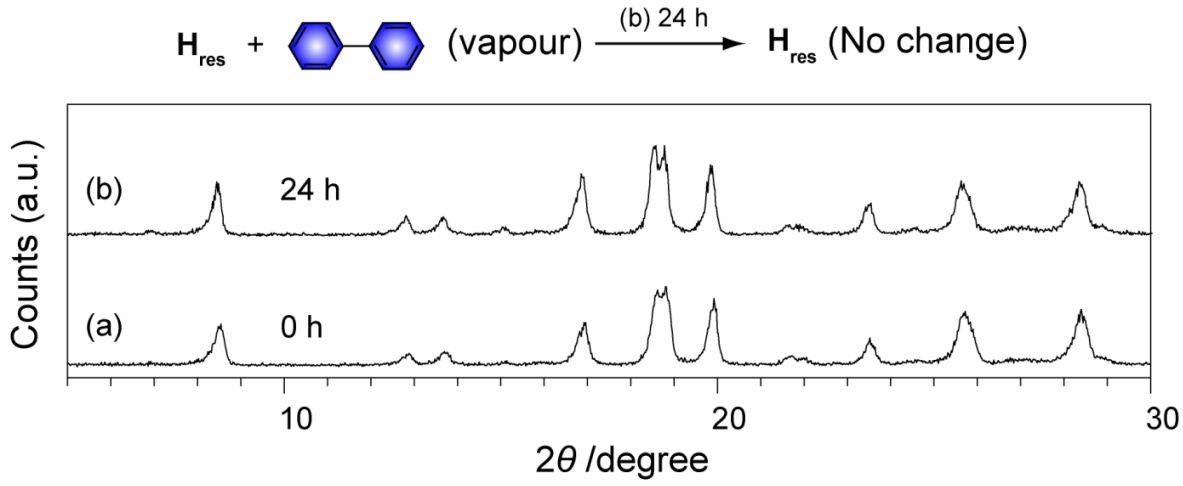

Fig. S18. Observed XRD patterns of the sample prepared by exposure of $\mathbf{H_{res}}$ to the saturated vapour of BI in a Petri dish at rt for (a) 0 and (b) 24 h.

References

References

(1) G. M. Sheldrick, *Acta Cryst*., *A*, 2008, **64**, 112.

(2) R. Sekiya, S. Nishikiori and K. Ogura, *J*. *Am*. *Chem*. *Soc*., 2004, **127**, 16587–16600.