Supporting Information

Vapochromic Separation of Toluene and Pyridine Azeotropes by Adaptive Macrocycle Co-Crystals

Bin Li, Yun Wang, Yuan Wang, Yue Liu, Lu Wang, Zhi-Yuan Zhang and Chunju Li.**

Academy of Interdisciplinary Studies on Intelligent Molecules, Tianjin Key Laboratory of Structure and Performance for Functional Molecules, College of Chemistry, Tianjin Normal University, Tianjin 300387, P. R. China.

Corresponding author. E-mail: bli@tjnu.edu.cn; cjli@shu.edu.cn

Contents

1. Materials and methods

Toluene and pyridine were purchased from Adamas-beta Chemical Company without further purification. Per-ethylated pillar[5]arene (P5) and N,N'-bis(*n*-butyl)pyromellitic diimide (PDI) were prepared according to literature procedures.[S1,S2] ^{1}H NMR spectra were recorded using a Bruker Avance 400 MHz spectrometer. Single crystal X-ray diffraction data of Dioxane@P5-PDI was collected on a Bruker D8-Venture detector using Mo-Kα radiation (λ = 0.71073 Å), and Py@P5-PDI was collected on a Bruker APEX-II CCD detector using Ga-Kα radiation (λ = 1.34139 Å). The crystal structure was solved and refined against all F^2 values using the SHELX and Olex 2 suite of programs. [S3,S4] Diffuse reflectance spectra were recorded on a Shimadzu UV-3600i Plus spectrometer. Thermogravimetric Analysis (TGA) was recorded using a TA Instrument TA-Q500 and the samples were heated under nitrogen gas at a rate of 10 ºC /min. Powder X-ray diffraction (PXRD) data were measured with a powder X-ray diffractometer (D/max 2200vpc, Rigaku, Japan) using Cu Kα radiation (λ = 1.5046 Å) with a range 5–40 ºC. Head Space Gas Chromatographic (HS-GC) measurement was carried out using an Agilent 7890B instrument configured with an FID detector.

Sample preparation of P5-PDI*α*. P5 (3.0 g) was first of all mixed with PDI (0.75 g) in dioxane (30 mL) and dissolved by ultrasonic treatment. The solution was filtered with a 0.22-μm syringe filter. Then slow evaporation of the solvent within 5 days afforded orange co-crystals of Dioxane@P5-PDI. The resulting co-crystals were further activated under vacuum at 75 ºC for 12 h to obtain solvent-free crystalline materials of P5-PDIα.

Co-crystal growth of Py@P5-PDI. Co-crystals of Py@P5-PDI were grown by slow evaporation of a pyridine solution (1 mL) of P5 (20 mg) and PDI (6.0 mg) at room temperature. After a week, yellow co-crystals suitable for X-ray structural determination were obtained.

Vaporhromic experiments. An open 2 mL vial containing 10 mg of P5-PDIα was placed in a sealed 20 mL vial containing 1 mL of Py or Tol or Py/Tol mixture (*v*/*v* 50:50). P5-PDIα materials were exposed under saturated vapor pressure in the closed vessel at room temperature. Obvious naked-eye color changes could be observed over the time.

2. Characteristics of Dioxane@P5-PDI co-crystals

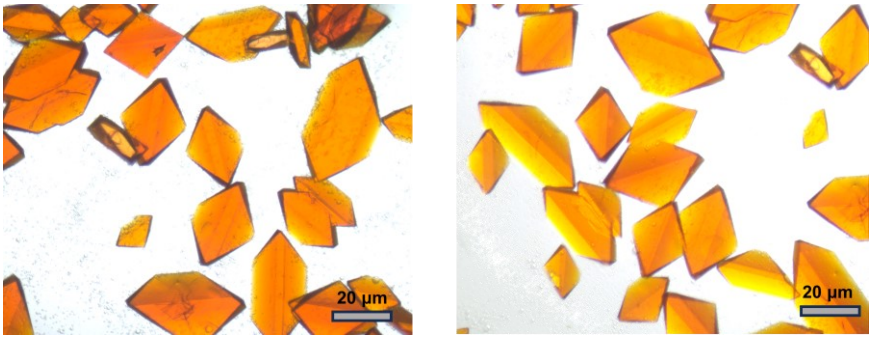

Figure S1. Photographs of the crystal growth of Dioxane@P5-PDI by slow evaporation of a solution of P5 and PDI in dioxane. Scale bar: 20 μm.

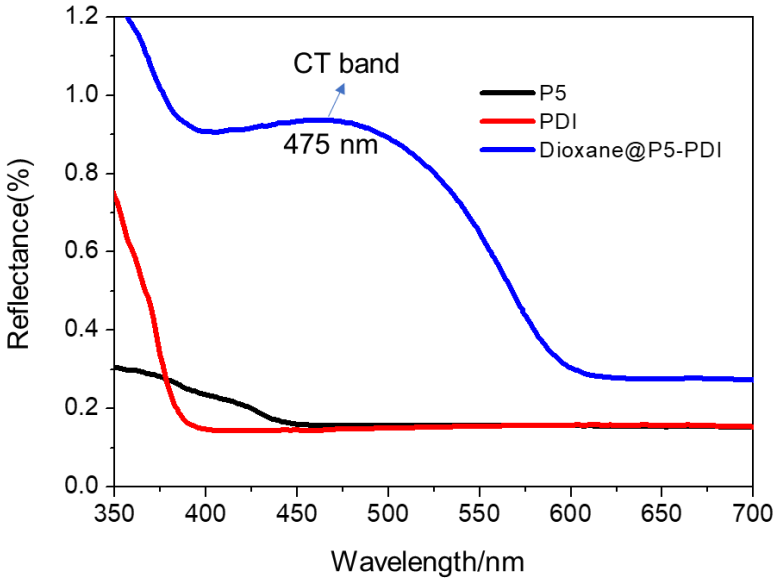

Figure S2. Diffuse reflectance spectra of individual P5 and PDI, and Dioxane@P5-PDI co-crystals. An obvious absorption at 475 nm was observed in Dioxane@P5-PDI, idicating the formation of CT complex between P5 and PDI.

Table S1. Crystal data and structure refinement for Dioxane@P5-PDI.

Formula	Dioxane@P5-PDI
Crystallization solvent	Dioxane
Formula	$C_{81}H_{106}N_2O_{18}$
Formula weight	1395.67
Temperature / K	100
Crystal system	Monoclinic
Space group	$P2_1/c$
a / Å	12.3241(18)
b / Å	33.684(6)
c / Å	20.229(3)
α / °	90
β / °	96.013(4)
γ / °	90
Volume / Å3	8351(2)
Z	4
ρ_{calc} g/cm^3	1.11
μ / mm^{-1}	0.078
Crystal size / mm^3	0.14 × 0.12 × 0.09
Radiation	Mo-Kα (λ = 0.71073 Å)
F(000)	3000.0
2Θ range for data collection /°	3.898 to 55.022
Index ranges	-14 ≤ h ≤ 15, -43 ≤ k ≤ 43, -26 ≤ l ≤ 26
Reflections collected	105718
R_{int}	0.0911
Goodness-of-fit on F^2	1.013
Final R_1 indexes [I>= 2σ(I)]	0.0616
Final R_1 indexes [all data]	0.1246
Final wR(F_2) indexes [all data]	0.1750
Largest diff. peak/hole / eÅ^{-3}	0.30/-0.34
CCDC number	**2340989**

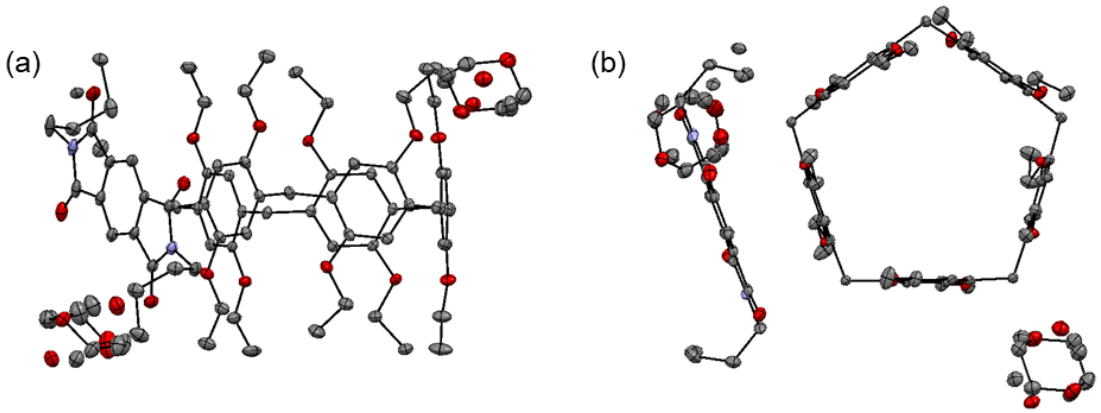

Figure S3. ORTEP drawing of Dioxane@P5-PDI with one P5, one PDI and two dioxane in the asymmetric unit from plane view (a) and side-on view (b). The thermal ellipsoids are displayed at a 30% probability. Hydrogen atoms have been omitted for clarity.

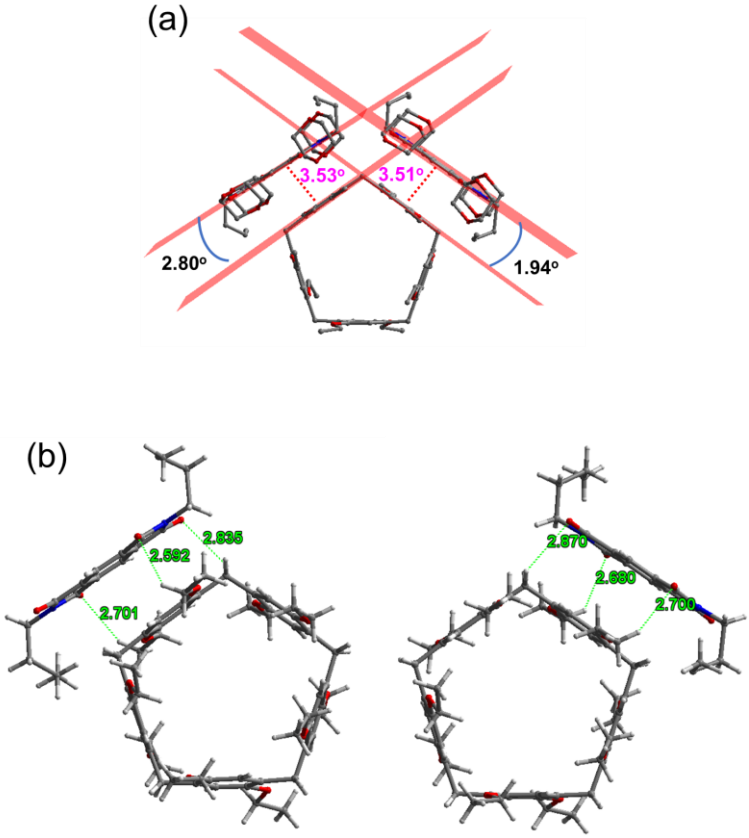

Figure S4. (a) The centroid–centroid distances [3.51 and 3.53 Å] and the dihedral angles [1.94° and 2.80°] of face-to-face π···π interactions between adjacent P5 and PDI in the crystal structure of Dioxane@P5-PDI. (b) The C–H···O interactions [2.59–2.87 Å] between P5 and PDI.

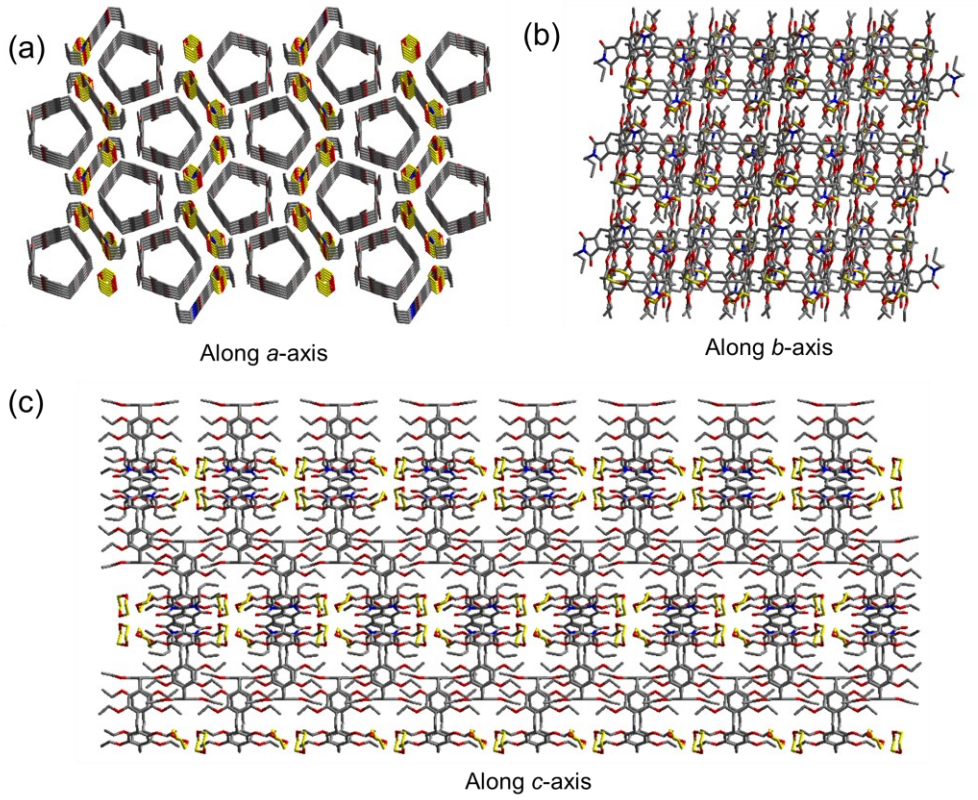

Figure S5. The packing modes of Dioxane@P5-PDI along the crystallographic *a*, *b*, and *c*-axis, respectively.

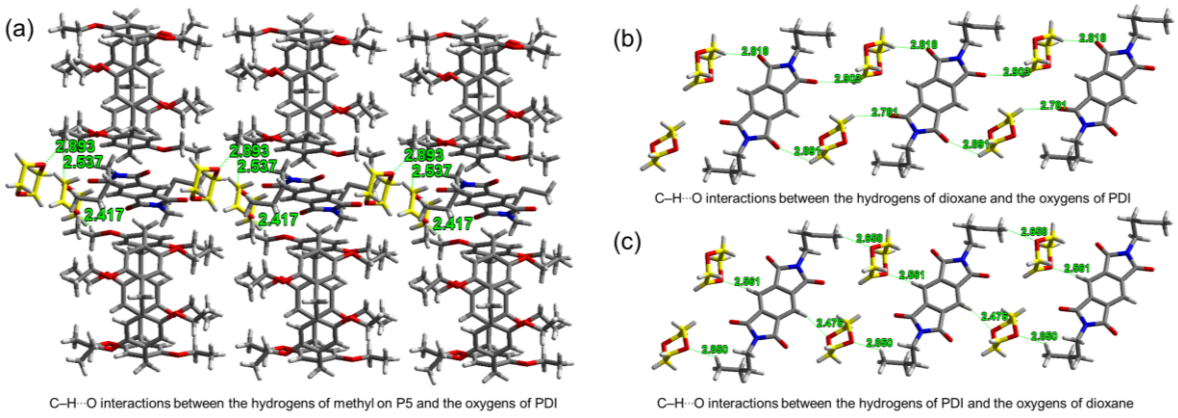

Figure S6. (a) The C–H···O interactions [2.42–2.89 Å] between the oxygens of dioxane and hydrogens of methyl on P5 in Dioxane@P5-PDI. (b) The C–H···O interactions [2.78–2.90 Å] between the hydrogens of dioxane and the oxygens of PDI in Dioxane@P5-PDI. (c) The C–H···O interactions [2.48–2.85 Å] between the oxygens of dioxane and the hydrogens of PDI.

3. Characterization of P5-PDI*α* materials

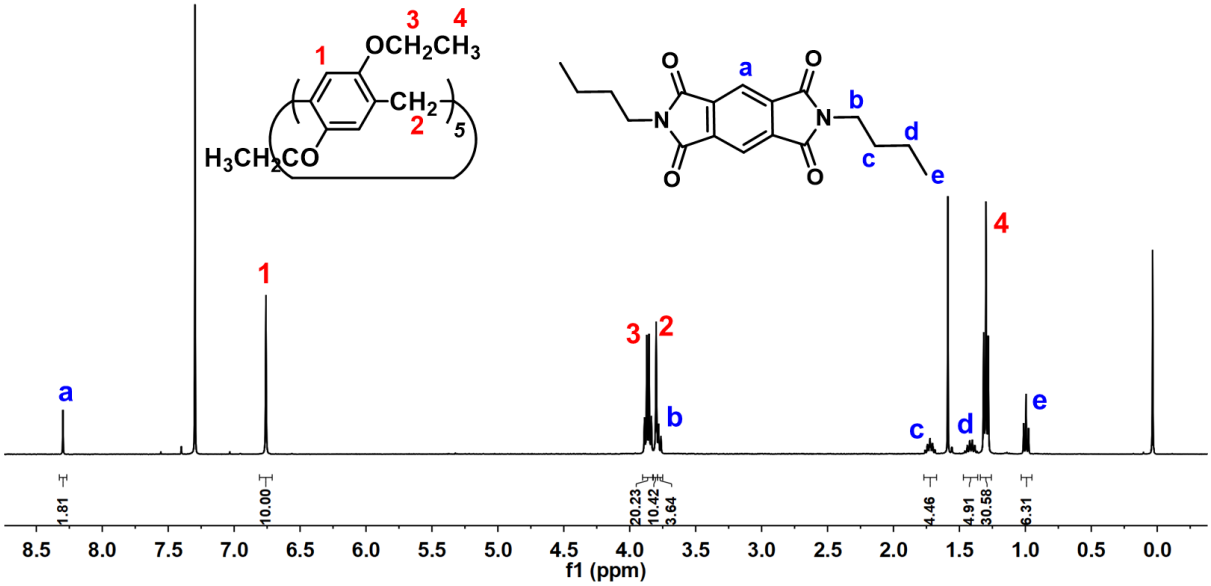

Figure S7. ^{1}H NMR spectrum (400 MHz, 298K, $CDCl_3$) of P5-PDI*α*, showing a 1:1 stoichiometric ratio of P5 and PDI without any dioxane peaks.

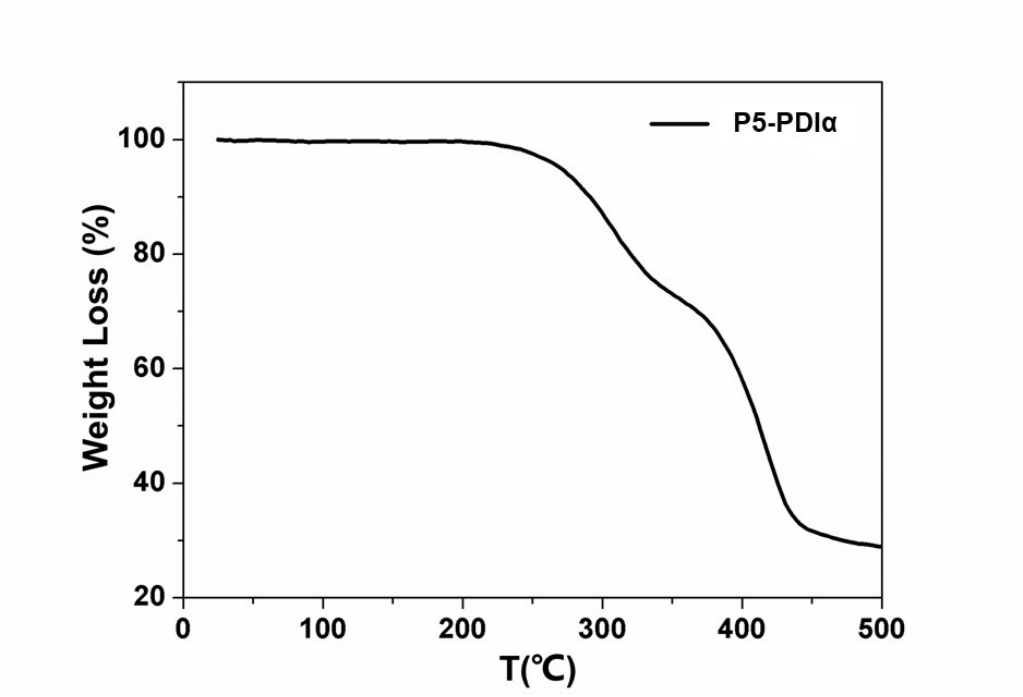

Figure S8. TGA curve of P5-PDI*α* recorded under a nitrogen atmosphere. Almost no weight loss occurs below 200 °C, supporting its high stability and the complete removal of solvents through activation.

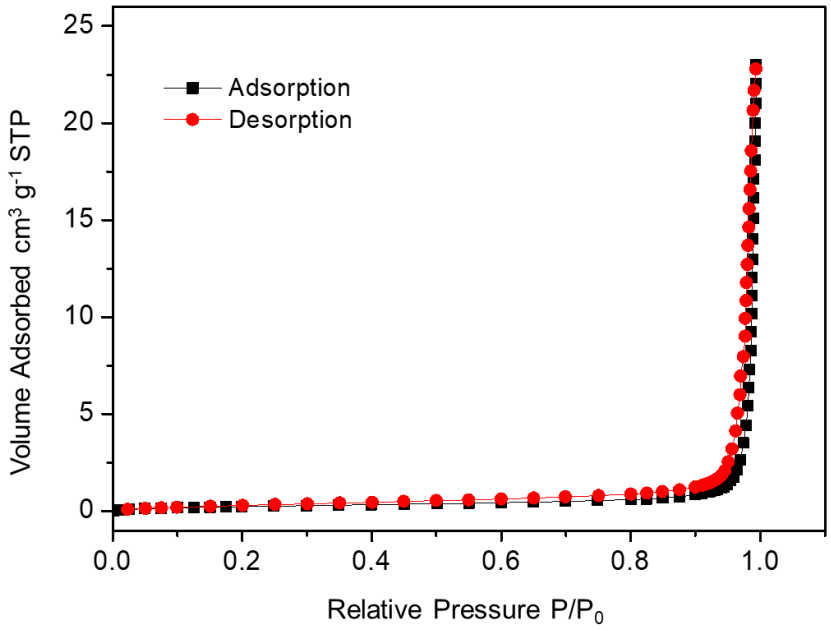

Figure S9. N_2 adsorption/desorption isotherm of P5-PDI*α*.

Figure S10. Color changes of P5-PDI*α* after adsorption of dioxane and Dioxane@P5-PDI after desorption of dioxane.

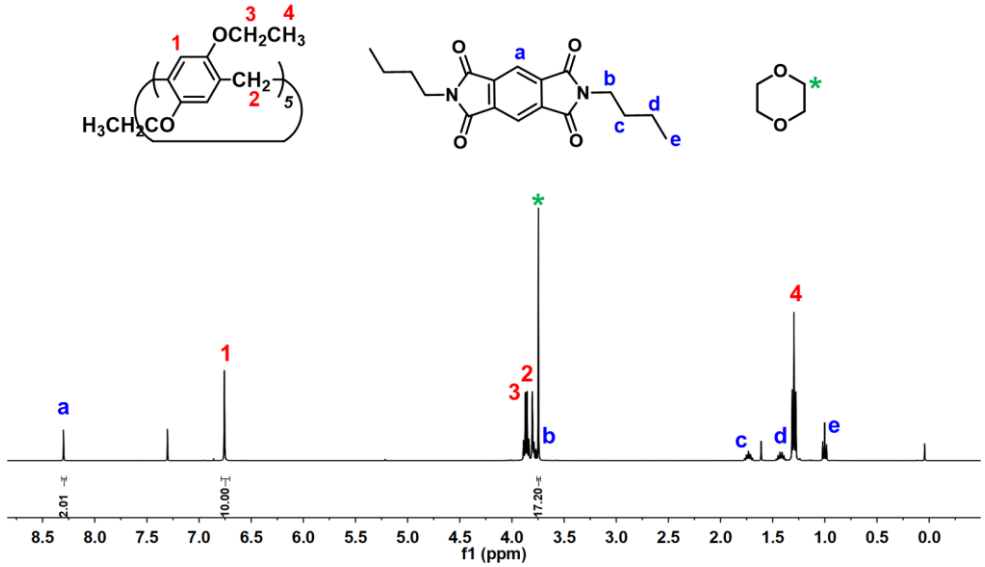

Figure S11. ^{1}H NMR spectrum (400MHz, 298K, $CDCl_3$) of P5-PDI*α* after adsorption of dioxane.

4. Single-component solid-vapor sorption experiments

For single-component Py or Tol adsorption experiment, an open 3 mL vial containing 5.0 mg of P5-PDIα adsorbent was placed in a sealed 20 mL vial containing 1 mL of Py or Tol. Uptake amount in the P5-PDIα crystals was monitored over time by ^{1}H NMR spectra by completely dissolving the crystals in $CDCl_3$. Desorption experiments after uptake saturation were carried out by TGA analysis. The purity of Py was measured by GC. Before measurements, the crystals were heated at 30 °C to remove the surface-physically adsorbed vapor molecules.

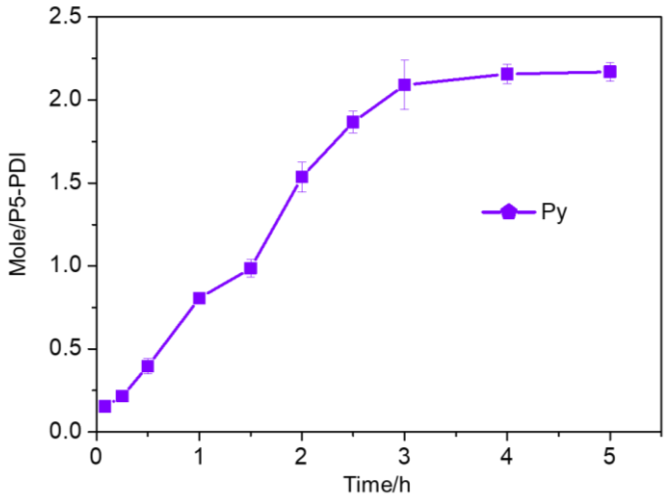

Figure S12. Time-dependent solid–vapor sorption plots of P5-PDIα for single-component Py vapor.

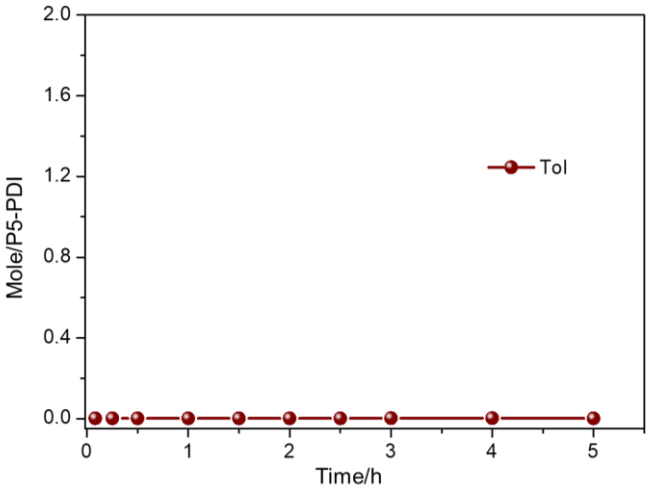

Figure S13. Time-dependent solid−vapor sorption plots of P5-PDIα for single-component Tol vapor. Absolutely no Tol was adsorbed.

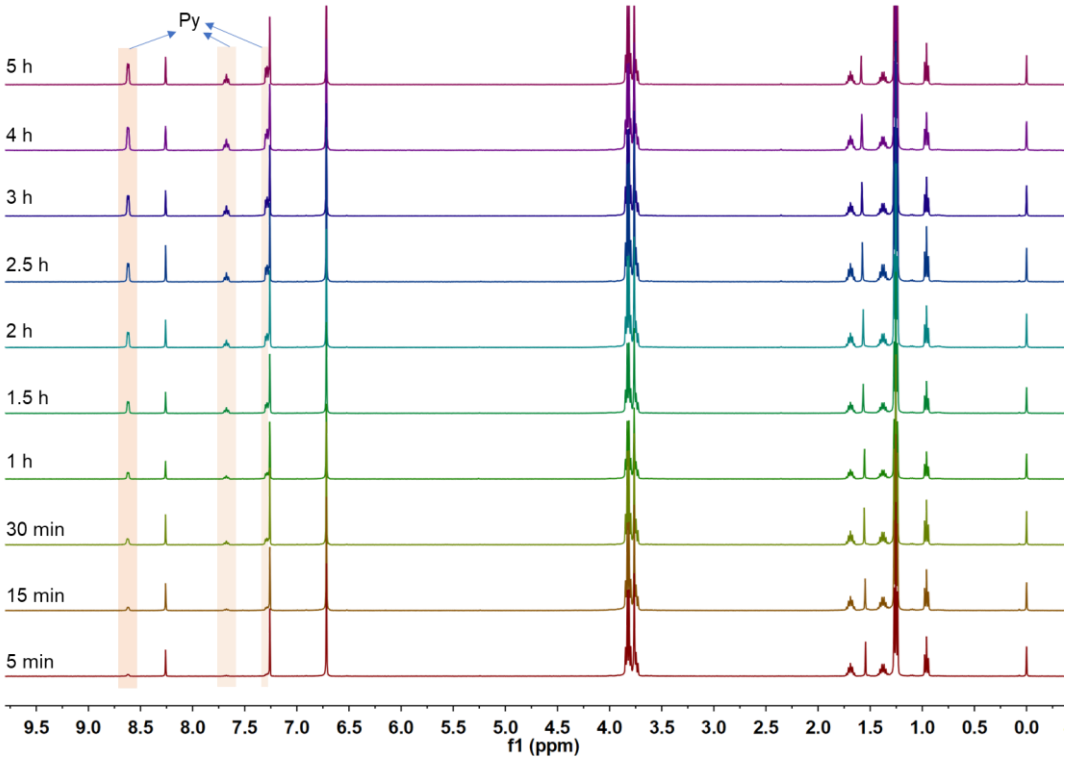

Figure S14. Time-dependent ^{1}H NMR spectra (400 MHz, 298K, $CDCl_3$) of P5-PDIα after uptake of Py vapor. The relative uptake of Py by P5-PDIα is plotted in Figure S12.

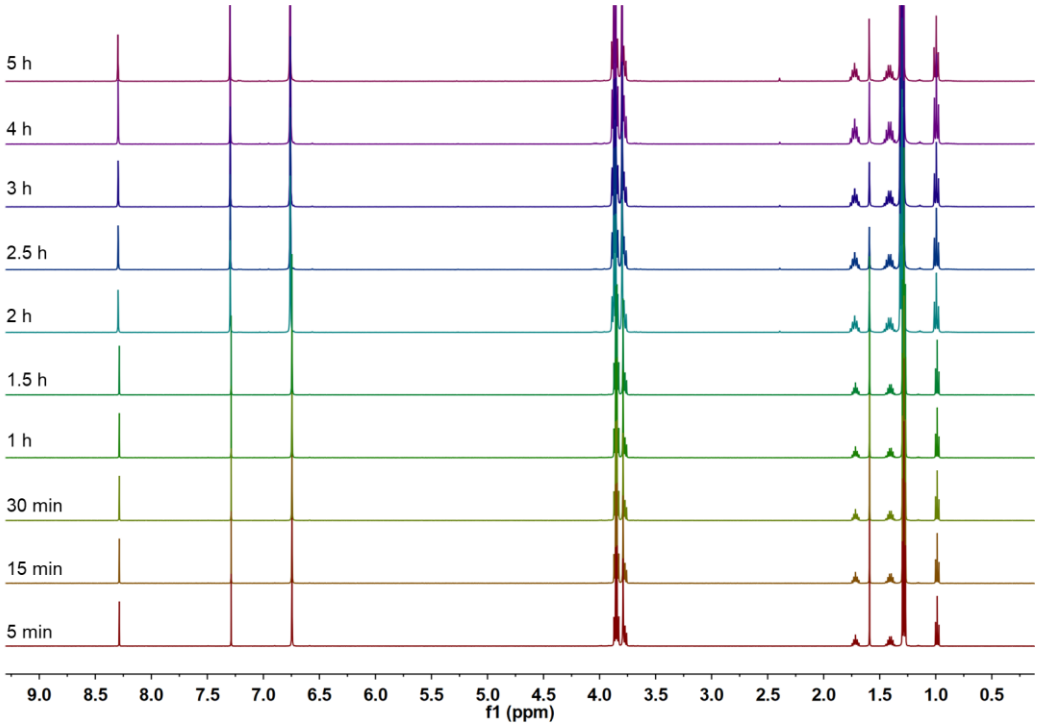

Figure S15. Time-dependent ^{1}H NMR spectra (400 MHz, 298K, $CDCl_3$) of P5-PDIα after uptake of Tol vapor. The relative uptake of Tol by P5-PDIα is plotted in Figure S13. Absolutely no Tol was adsorbed.

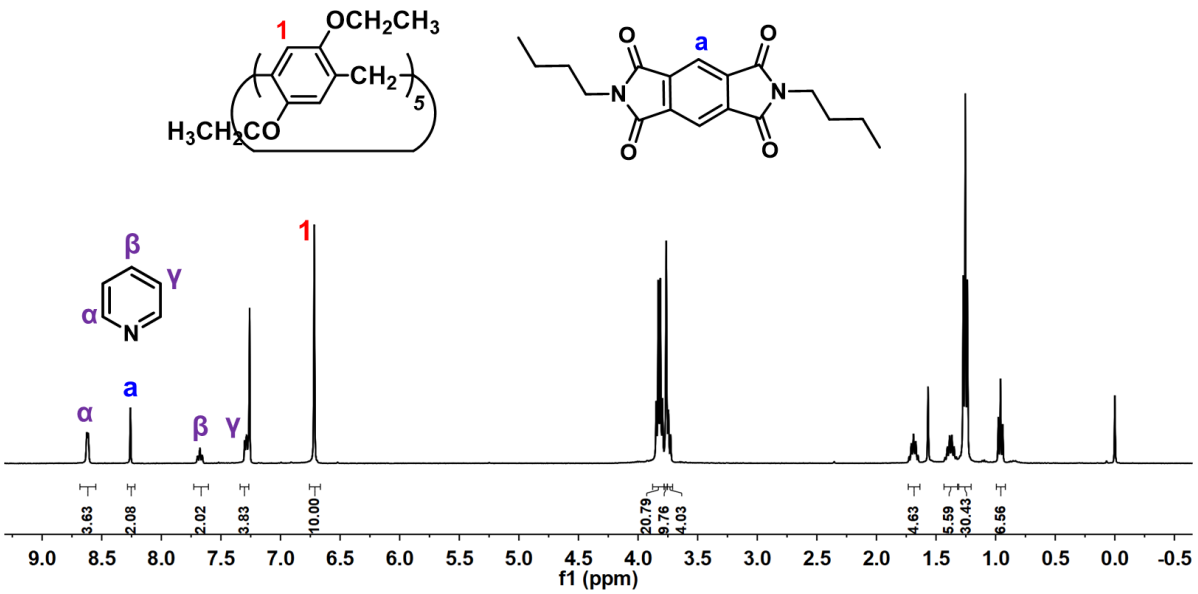

Figure S16. ^{1}H NMR spectrum (400MHz, 298K, $CDCl_3$) of P5-PDI*α* after adsorption of Py for 5 h.

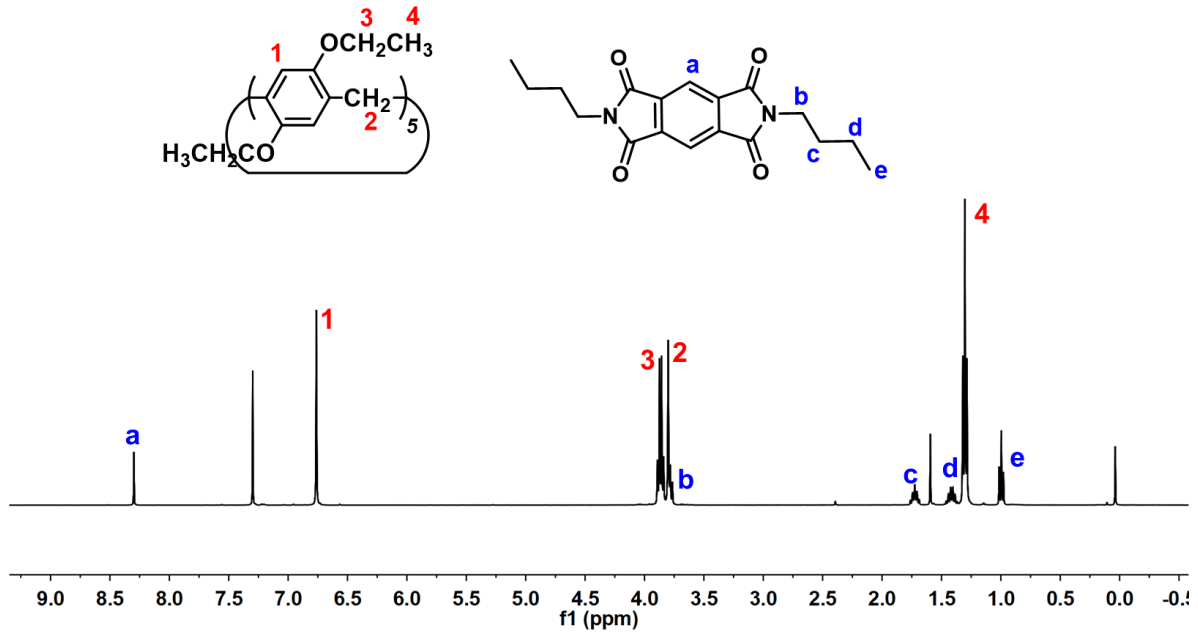

Figure S17. ^{1}H NMR spectrum (400MHz, 298K, $CDCl_3$) of P5-PDI*α* after adsorption of Tol for 5 h. No Tol peaks were found.

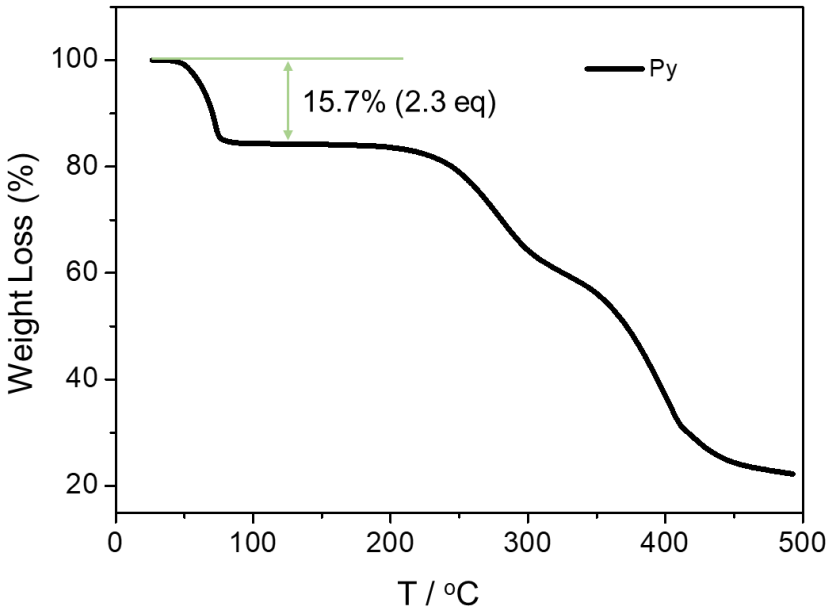

Figure S18. TGA profile of P5-PDI*α* after uptake of Py. About two Py molecules per P5-PDI were lost at 200 °C.

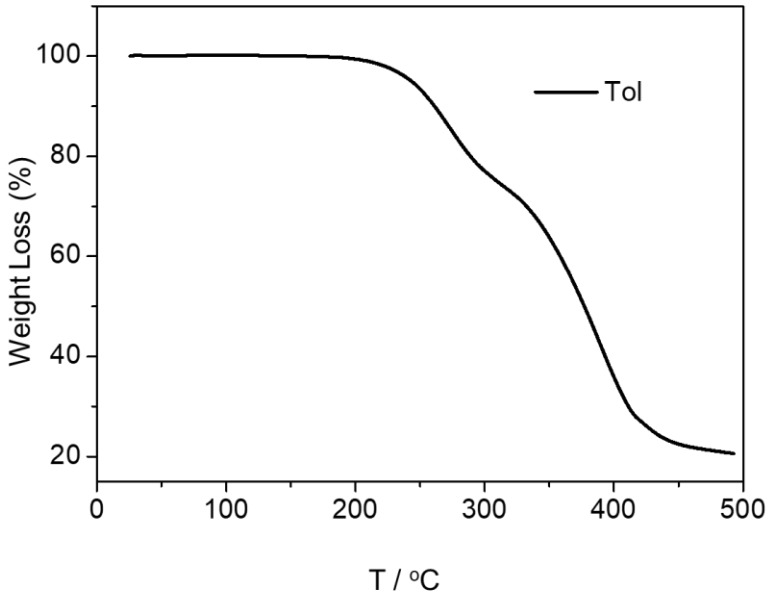

Figure S19. TGA profile of P5-PDI*α* after uptake of Tol. Almost no weight loss occurs below 200 °C, indicating no Tol is adsorbed.

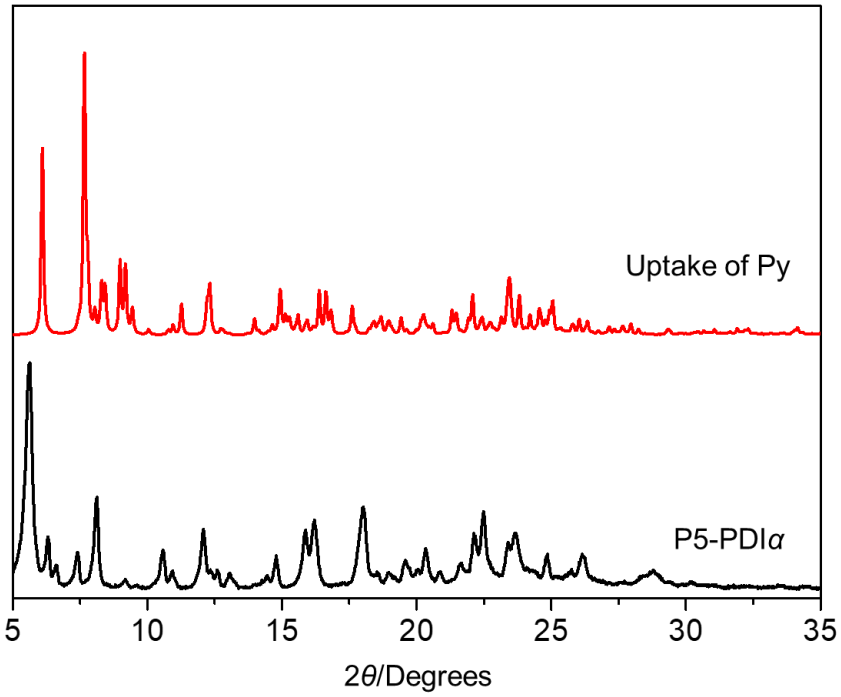

Figure S20. PXRD patterns of P5-PDIα before and after capture of Py.

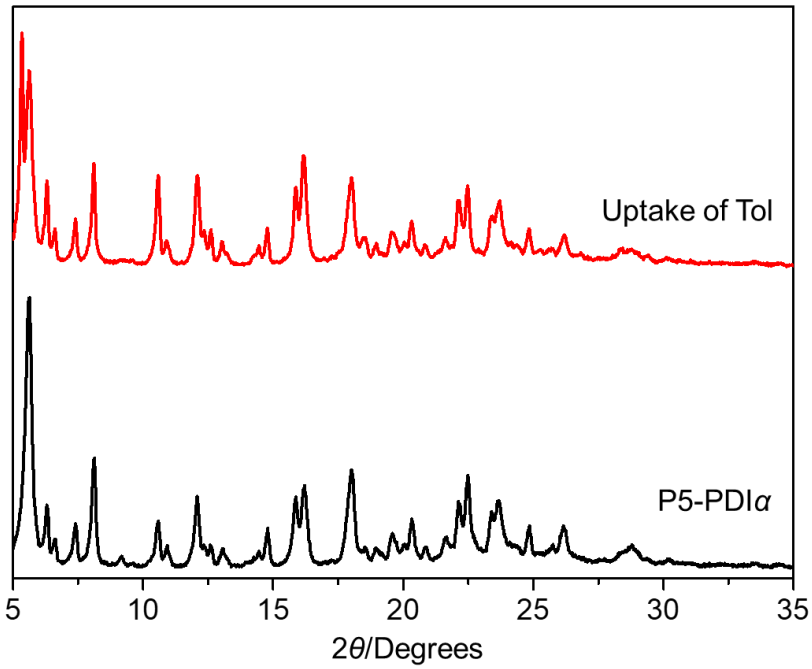

Figure S21. PXRD patterns of P5-PDIα before and after capture of Tol. No structural transformation was observed.

5. Crystal engineering of Py@P5-PDI co-crystals

Table S2. Crystal data and structure refinement for Py@P5-PDI.

Formula	Py@P5-PDI
Crystallization solvent	Pyridine
Formula	$C_{93}H_{110}N_6O_{14}$
Formula weight	1535.86
Temperature / K	193.00
Crystal system	Triclinic
Space group	*P*-1
a / Å	12.0800(5)
b / Å	12.4509(5)
c / Å	29.1324(11)
α / °	94.272(2)
β / °	92.465(2)
γ / °	106.740(2)
Volume / Å3	4174.8(3)
Z	2
ρ_{calc} g/cm^3	1.222
μ / mm^{-1}	0.419
Crystal size / mm^3	0.12 × 0.11 × 0.08
Radiation	Ga-*K*α (λ = 1.34139 Å)
F(000)	1476
2Θ range for data collection /°	6.476 to 105.956
Index ranges	-14<=h<=14, -14<=k<=14, -34<=l<=34
Reflections collected	54799
R_{int}	0.0482
Goodness-of-fit on F^2	1.179
Final R_1 indexes [I>= 2σ(I)]	0.0871
Final R_1 indexes [all data]	0.1358
Final wR(F_2) indexes [all data]	0.2856
Largest diff. peak/hole / eÅ^{-3}	0.77/-0.75
CCDC number	**2340990**

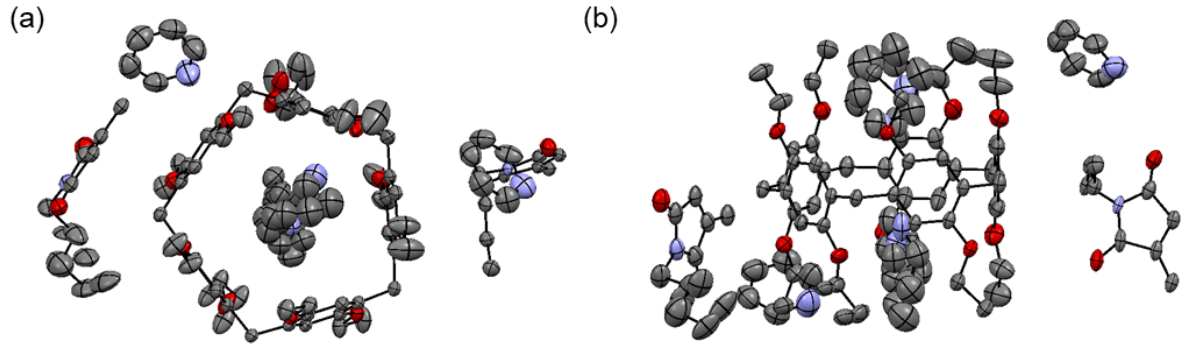

Figure S22. ORTEP drawing of Py@P5-PDI with one P5, one PDI (with occupancy factor of 0.5) and four Py in the asymmetric unit from plane view (a) and side-on view (b). The thermal ellipsoids are displayed at a 30% probability. Hydrogen atoms have been omitted for clarity.

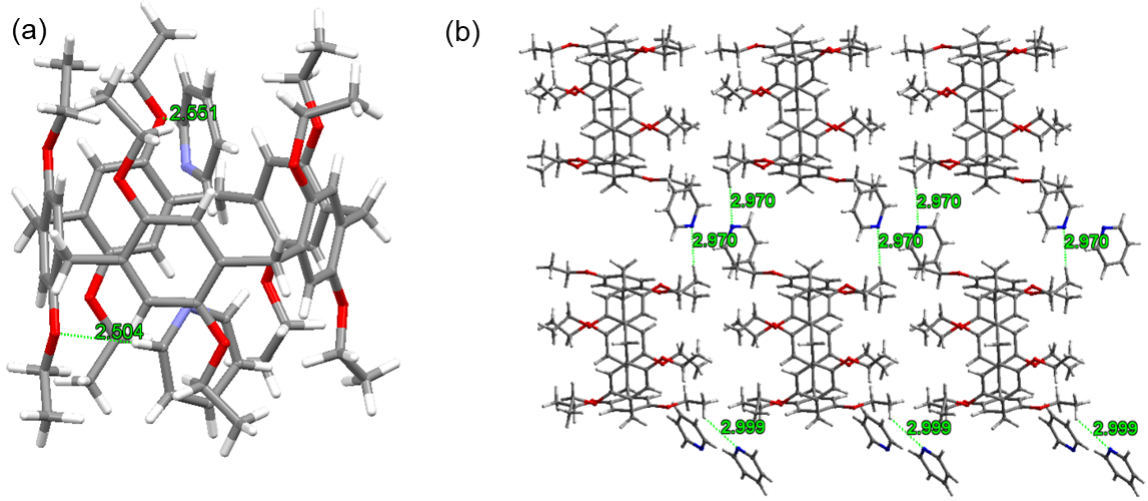

Figure S23 (a) C–H···O interactions [2.55 and 2.50 Å] between P5 and Py contained in P5 cavity. (b) C–H···N interactions [2.97 and 3.00 Å] between P5 and outside Py in the crystal struture of Py@P5-PDI. The PDI molecules are omitted for clarity.

6. Two-component solid-vapor sorption experiments

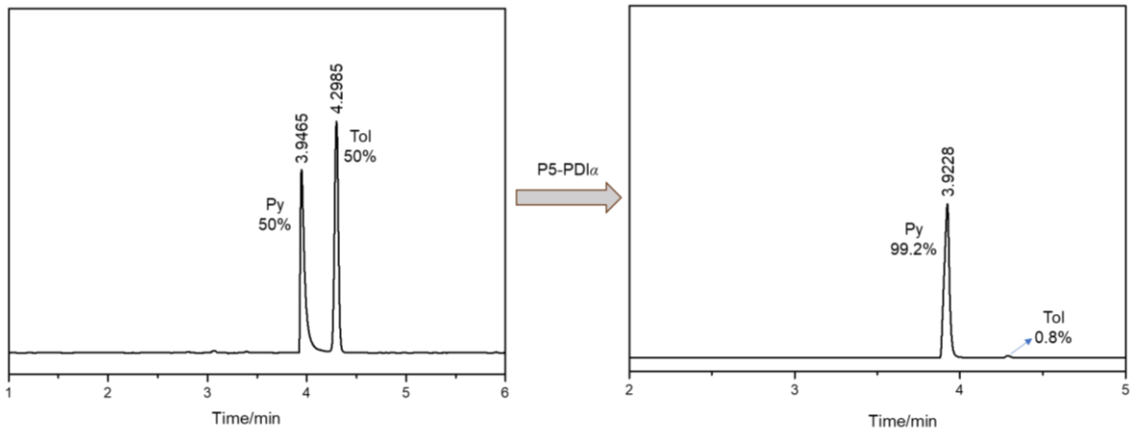

Figure S24. Relative Py and Tol uptake in P5-PDI*α* after saturation using GC.

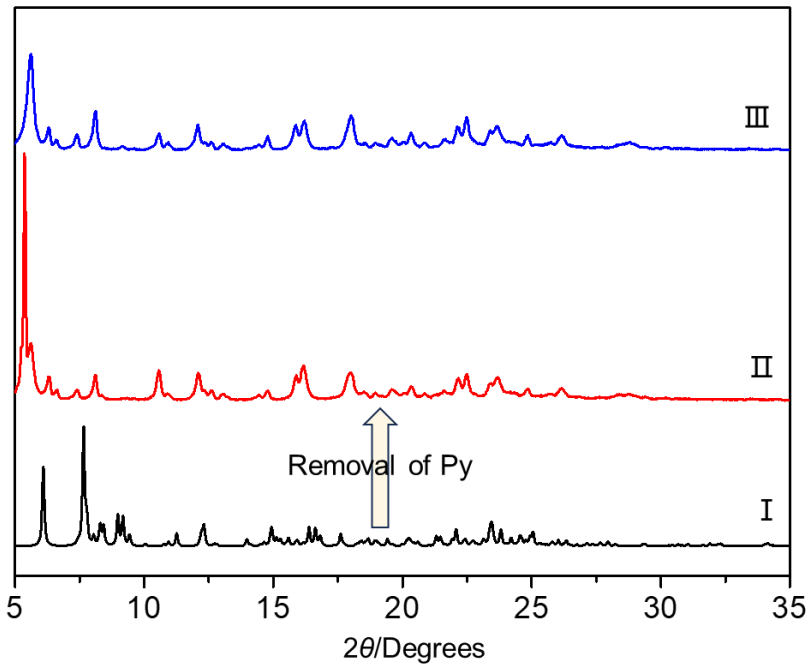

Figure S25. PXRD patterns of P5-PDI: (I) Py@P5-PDI; (II) after release of Py upon heating. (III) P5-PDI*α*. The results showed the structure of Py@P5-PDI transform back to the original structure of P5-PDI*α* after removing Py upon heating.

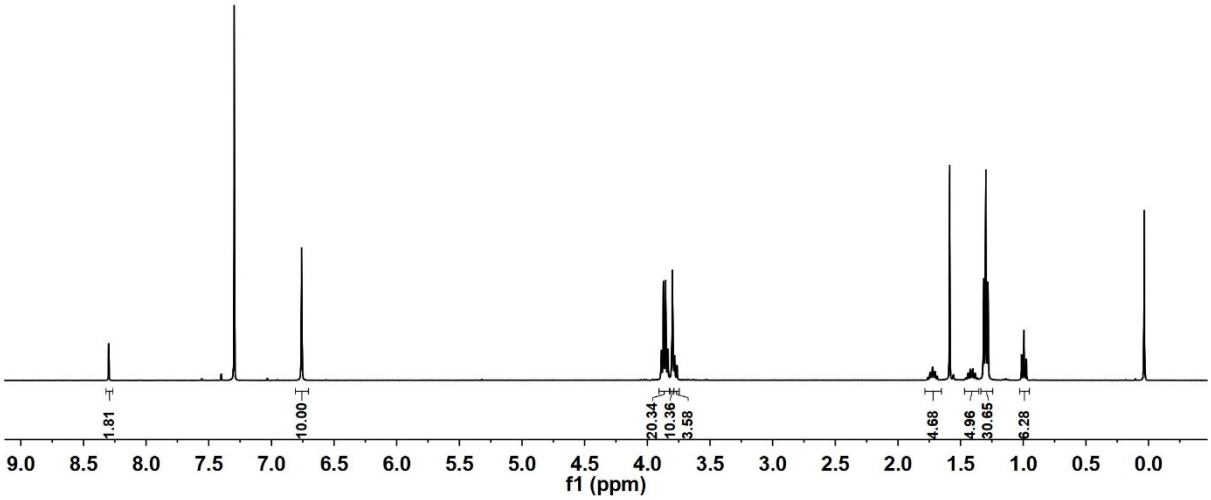

Figure S26. ^{1}H NMR spectrum (400MHz, 298K, $CDCl_3$) of Py@P5-PDI after desorption of Py by heating. No Py peaks were found.

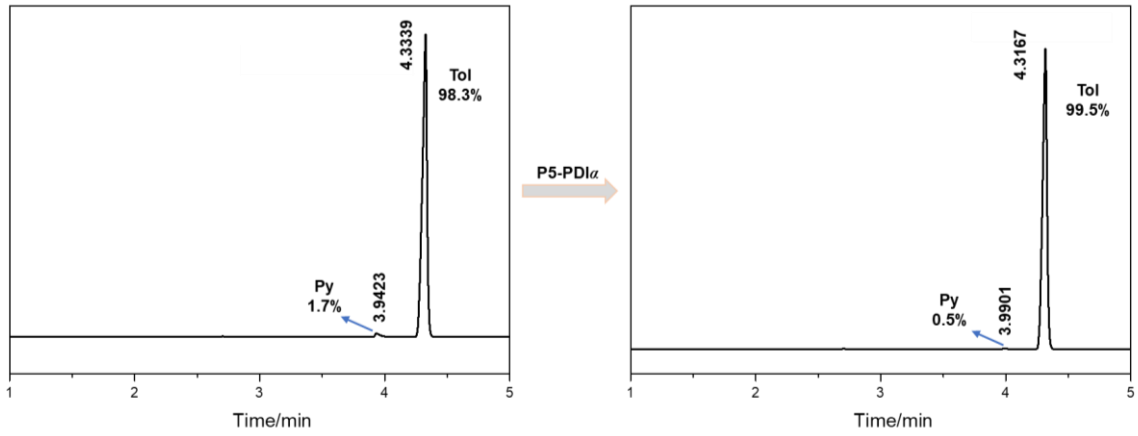

Figure S27. Relative Py and Tol uptake in P5-PDI*α* after adsorption of the Tol/Py mixtures (*v*:*v* = 98:2).

For the Tol purification experiment, an open 5.00 mL vial containing 50.00 mg of guest-free P5-PDI*α* adsorbent was placed in a sealed 20.00 mL vial containing 100 μL of Tol and Py mixtures. The mixture ratios were approximately 98:2. The purity of Tol before and after adsorption were measured by GC.

7. References

(S1) T. Ogoshi, S. Kanai, S. Fujinami, T.-a. Yamagishi and Y. Nakamoto, *para*-Bridged symmetrical pillar[5]arenes: their lewis acid catalyzed synthesis and host–guest property. *J. Am. Chem. Soc.* **2008**, *130*, 5022.

(S2) S. De and S. Ramakrishnan, Macromolecules **2009**, *42*, 8599.

(S3) G. M. Sheldrick, Crystal structure refinement with SHELXL. *Acta Crystallogr. C*. **2015**, *71*, 3.

(S4) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *OLEX2:* a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339.