SUPPORTING INFORMATION

Selective Isolation of Polycyclic Aromatic Hydrocarbons by Self-Assembly of a Tunable N→B Clathrate

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Materials and Methods

Chemicals such as phenylboronic acid (PBA), 2,3-dihydroxinaphthalene (DHN), 4,4'-bipyridine (BiPy), 1,2-di(4-pyridyl)ethylene (DPE), 1,2-di(4-pyridyl)ethane (DPEt), 4,4'-azopyridine (DPA), fluorene, naphthalene, phenanthrene, anthracene, pyrene, triphenylene, benzo(a)anthracene, perylene and solvents from commercial sources were used as received. Other compounds were synthesized according to the procedures described below. Mass spectra (FAB and CI) were taken on a JEOL MStation Mass-Spectrometer. The ^{1}H, ^{13}C and ^{11}B NMR spectra were obtained on a Varian Inova Spectrometer 400 MHz. Spectra were in ppm using TMS as reference for ^{1}H in DMSO-d_6 and $CDCl_3$, the residual solvent signal for ^{13}C and $BF_3{\cdot}OEt_2$ as an external standard for ^{11}B nuclei (δ = 19.3 ppm).

Thermogravimetric analyses (TGA) were obtained with a SDT Q600 TA Instrument. Approximately 3 mg of each solid sample was placed in an aluminum pan and analyzed in the temperature range of 50−400 °C with a heating rate of 10 °C/min and using a current of 100 mL/min of nitrogen as inert gas purge. Elemental analyses were obtained from Galbraith Laboratories Inc. (Knoxville, TN, USA).

Powder X-ray Diffraction (PXRD) analyses were carried out in the transmission mode on a BRUKER D8-ADVANCE diffractometer equipped with a LynxEye detector ($\lambda_{Cu-K\alpha1}$ = 1.5406 Å, monochromator: germanium). The equipment was operated at 40 kV and 40 mA, and data were collected at room temperature typically in the range of 2θ = 5−50° (step size 0.011°, step time 10 s). Single-crystal X-ray diffraction studies were performed on a Bruker-APEX diffractometer with a CCD area detector ($\alpha_{MoK\alpha}$ = 0.71073 Å, monochromator: graphite). Frames were collected at T =

293 K via ω/ϕ-rotation at 10 s per frame (SMART).[1] The measured intensities were reduced to F^2 and corrected for absorption with SADABS (SAINT-NT).[2] Corrections were made for Lorentz and polarization effects. Structure solution, refinement, and data output were carried out with the SHELXTL-NT program package.[3,4] Non-hydrogen atoms were refined anisotropically. C–H hydrogen atoms were placed in geometrically calculated positions using the riding model (C-H 0.93 Å, $U_{iso}(H) = 1.2U_{eq}$).

Synthesis of the Boronate Esters 1-5

Boronate Ester 1. An equimolar mixture of PBA (4.50 g, 37 mmol) and DHN (6.00 g, 37 mmol) in acetonitrile (150 mL) was heated under reflux for 60 minutes. The mixture was allowed to cool to room temperature and the pure product was obtained by filtration (7.2 g, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (dd, J = 6.4, 3.2 Hz, 2H), 7.53 (t, J = 7.4 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.66 (s, 2H), 7.87 (dd, J = 6.2, 3.3 Hz, 2H), 8.15 (d, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 108.6, 124.9, 127.8, 128.4, 130.6, 132.9, 135.4, 148.3. ^{11}B NMR (128.3 MHz, $CDCl_3$): δ 32.0. CI-HRMS calcd. for m/z = 247.0930 $[M+H]^+$, found m/z = 247.0922.

Boronate Ester 2. An equimolar mixture of PBA (1.1 g, 9.0 mmol) and catechol (1.0 g, 9.0 mmol) in acetonitrile (25 mL) was heated under reflux for 1 hour. The mixture was allowed to cool to room temperature and the solvent was removed under vacuum. The product was purified by recrystallization in chloroform (0.62 g, 35%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (dd, J = 5.8, 3.4 Hz, 2H), 7.35 (dd, J = 5.8, 3.4 Hz, 2H), 7.53 (t, J = 7.5 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 8.14 (d, J = 7.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 112.7, 122.9, 128.4, 132.5, 135.1, 148.6. ^{11}B NMR (128.3 MHz, $CDCl_3$): δ 32.0. CI-HRMS calcd. for m/z = 197.0774 $[M+H]^+$, found m/z = 197.0765.

Boronate Ester 3. An equimolar mixture of 2-naphthylboronic acid (0.7 g, 4.1 mmol) and catechol (0.45 g, 4.1 mmol) in acetonitrile (25 mL) was heated under reflux for 30 minutes. The mixture was allowed to cool to room temperature and the solvent was removed under vacuum. The product was purified by recrystallization in toluene (0.88 g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (dd, J = 3.3, 5.9 Hz, 2H), 7.39 (dd, J = 3.4, 5.8 Hz, 2H), 7.57 (td, J = 1.4, 6.9 Hz, 1H), 7.61 (td, J = 1.4, 6.9 Hz, 1H), 7.91 (da, J = 7.8 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.99 (da, J = 7.6 Hz, 1H), 8.12 (dd, J = 1.4, 8.2 Hz, 1H), 8.69 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 112.7, 122.9, 126.3, 127.7, 127.8, 128.0, 129.0, 130.0, 132.9, 135.5, 137.2, 148.6. ^{11}B NMR (128.3 MHz, $CDCl_3$): δ 32.4. CI-HRMS calcd. for m/z = 247.0930 $[M+H]^+$, found m/z = 247.0927.

Boronate Ester 4. An equimolar mixture of pentafluorophenylboronic acid (0.65 g, 3.1 mmol) and DHN (0.5 g, 3.1 mmol) in acetonitrile (10 mL) was heated under reflux for 30 minutes. The mixture was allowed to cool to room temperature and the pure product was obtained by filtration (0.42 g, 40%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.11 (s, 2H), 7.19 (dd, J = 6.1, 3.3 Hz, 2H), 7.62 (dd, J = 6.0, 3.3 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 103.9, 122.8, 126.4, 129.9, 136.7 (d, J = 248.0 Hz), 139.8 (d, J = 248.3 Hz), 147.6 (d, J = 240.2 Hz), 151.9. ^{11}B NMR (128.3 MHz, $CDCl_3$): δ 30.6. CI-HRMS calcd. for m/z = 337.0459 $[M+H]^+$, found m/z = 337.0456.

Boronate Ester 5. A mixture of PBA (0.5 g, 4.1 mmol) and 1,4,6,7-tetrabromo-2,3-naphthalenediol[5] (1 g , 2.1 mmol) in toluene (50 mL) was heated under reflux using a Dean-Stark apparatus for 2 h. The mixture was allowed to cool to room temperature and the pure product was obtained by filtration (0.87 g, 74%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.28 (m, 3H), 7.50 (d, J = 7.2 Hz, 2H), 8.17 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 95.0, 119.8, 127.4, 127.7, 128.0, 129.1, 131.4, 151.7. ^{11}B NMR (128.3 MHz, $CDCl_3$): δ 33.3. CI-HRMS calcd. for m/z = 558.7351 $[M+H]^+$, found m/z = 558.7358.

Synthesis of the N-B adducts A1-A3

Adduct A1.
Method 1. 0.180 g of DPE (1 mmol) were added to 30 mL of a solution of **1** (0.500 g, 2 mmol) in chloroform. The mixture was stirred for one hour; afterwards the resulting precipitate was collected by filtration to afford 0.604 g of the product (91%).
Method 2. 0.244 g of PBA (2 mmol), 0.320 g of DHN (2 mmol) and 0.182 g of DPE (1 mmol) were added to 15 mL of acetone. The resulting mixture was stirred and heated under reflux for 1 hour. The mixture was allowed to cool to room temperature and the pure product was obtained by filtration to afford 0.461 g (69 %) of the product. XRPD, 2Theta/°: 10.6, 12.6, 13.1, 14.1, 14.5, 15.7, 17.3, 17.6, 18.1, 18.2, 18.7, 19.7, 21.2, 21.6, 22.2, 22.4, 23.0, 23.4, 24.9, 25.5, 26.3, 26.6, 27.7, 29.6, 30.0, 30.5, 33.2. The molar composition evaluated by HPLC-UV, calcd.: PBA, 40%; DHN, 40%; DPE, 20%; found: PBA, 37.1%; DHN, 40.8%; DPE, 22.1%. Anal. calcd. for $C_{44}H_{32}N_2O_4B_2$: H, 4.78; N, 4.15. Found: H, 4.84; N, 4.19. m.p. (^{o}C): 245-246. Other data are shown in Figure S1 (^{1}H NMR) and Figure S2 (TGA).

Adduct A2 (or DHN@A2). 37 mg of DPEt (0.2 mmol) were added to a 4 mL of a solution of **1** (100 mg, 0.4 mmol) in chloroform. The mixture was stirred for one hour; whereupon the resulting precipitate was collected by filtration to afford 35 mg of the product (26%). Adduct **A2** was isolated as an inclusion complex with DHN as suggested by ^{1}H NMR (Figure S7a), PXRD (Figure S7b), elemental analysis and the relative composition by HPLC. XRPD, 2Theta/°: 7.6, 12.2, 13.1, 14.7, 15.2, 15.3, 15.4, 15.8, 17.4, 18.5, 19.0, 19.6, 20.2, 20.6, 21.7, 22.0, 23.0, 23.8, 24.1, 24.3, 24.7, 25.0, 25.4, 26.1, 26.3, 27.0, 28.3, 30.4, 30.9. The molar composition evaluated by HPLC-UV, DHN@A2 calcd.: PBA, 33.3%; DHN, 50%; DPEt, 16.7%; found: PBA, 30.0%; DHN, 52.3%; DPEt, 17.6%. Anal. calcd. for $C_{44}H_{34}N_2O_4B_2 \cdot C_{10}H_8O_2$: H, 5.06; N, 3.35. Found: H, 5.26; N, 3.56.

Adduct A3. 37 mg of DPA (0.2 mmol) were added to 4 mL of a solution of **1** (100 mg, 0.4 mmol) in chloroform. The mixture was stirred for one hour; whereupon the resulting precipitate was collected by filtration to afford 45 mg of the product (33%). XRPD, 2Theta/°: 10.4, 12.5, 13.4, 14.1, 14.5, 15.7, 17.3, 18.2, 18.6, 18.9, 19.8, 21.6, 21.8, 22.0, 23.2, 23.8, 25.2, 25.9, 26.1, 27.1, 28.0, 30.5. The molar composition evaluated by HPLC-UV, calcd.: PBA, 40%; DHN, 40%; DPE, 20%; found: PBA, 35.2%; DHN, 41.1%; DPE, 23.6%. Anal. calcd. for $C_{42}H_{30}N_4O_4B_2$: H, 4.47; N, 8.28. Found: H, 4.56; N, 8.33. m.p. (^{o}C): 200-201.

Screening Experiments in the presence of PAHs

PAH@A1:
74 mg of DPE (0.4 mmol) were added to 12 mL of a solution of **1** (200 mg, 0.8 mmol) and the corresponding PAH (0.4 mmol) in chloroform. The mixture was stirred for one hour; whereupon the resulting precipitate was collected by filtration. The PAHs employed were fluorene, naphthalene, phenanthrene, anthracene, pyrene, triphenylene, benzo(a)anthracene and perylene.

NAP@A1. (266 mg, 82%). PXRD, 2Theta/°: 7.6, 12.2, 13.0, 13.2, 15.2, 15.8, 17.6, 18.3, 18.9, 20.5, 21.6, 22.1, 23.6, 23.9, 24.6, 25.0, 25.4, 25.9, 26.2, 26.6, 26.8, 27.5, 28.2, 30.2, 30.7. The molar composition evaluated by HPLC-UV, calcd.: PBA, 33.3%; DHN, 33.3%; DPE, 16.7%; naphthalene, 16.7%; found: PBA, 29.8%; DHN, 34.9%; DPE, 17.8%; naphthalene, 17.5%. m.p. (^{o}C): 243-244.

FLR@A1. (257 mg, 77%). PXRD, 2Theta/°: 7.5, 12.2, 13.0, 13.2, 15.1, 15.7, 17.5, 18.1, 18.9, 19.6, 20.3, 20.4, 21.5, 21.7, 23.1, 23.8, 24.5, 24.8, 25.4, 25.7, 26.2, 26.5, 27.4, 28.1, 30.5. The molar composition evaluated by HPLC-UV, calcd.: PBA, 33.3%; DHN, 33.3%; DPE, 16.7%; fluorene, 16.7%; found: PBA, 30.8%; DHN, 36.8%; DPE, 18.4%; fluorene, 14.0%. m.p. (^{o}C): 237-238.

PHE@A1. (245 mg, 72%). XRPD, 2Theta/°: 7.4, 12.1, 12.8, 13.3, 14.9, 15.1, 15.7, 17.4, 17.7, 18.7, 19.6, 20.1, 21.4, 22.5, 23.5, 24.8, 25.1, 25.8, 26.7, 27.6, 28.8, 31.9. The molar composition evaluated by HPLC-UV, calcd.: PBA, 33.3%; DHN, 33.3%; DPE, 16.7%; phenantrene, 16.7%; found: PBA, 29.8%; DHN, 34.6%; DPE, 17.7%; phenantrene, 17.8%. m.p. (^{o}C): 248-249.

ANT@A1. (280 mg, 82%). XRPD, 2Theta/°: 7.5, 12.3, 13.0, 15.0, 15.3, 15.9, 17.9, 18.9, 19.9, 20.1, 20.4, 21.3, 22.5, 23.4, 24.6, 25.1, 25.3, 25.7, 26.2, 26.5, 27.7, 28.0, 31.1. The molar composition evaluated by HPLC-UV, calcd.: PBA, 33.3%; DHN, 33.3%; DPE, 16.7%; anthracene, 16.7%; found: PBA, 29.6%; DHN, 36.2%; DPE, 17.6%; anthracene, 16.5%. Anal. calcd. for $C_{58}H_{42}N_2O_4B_2$: H, 4.97; N, 3.29. Found: H, 4.94; N, 3.41. m.p. (^{o}C): 238-239.

Method 2. Solutions containing 32 mg of DHN (0.2 mmol in 1 mL 5% methanol in chloroform, v/v), 18 mg of DPE (0.1 mmol in 1 mL $CHCl_3$), 18 mg of anthracene (0.1 mmol in 2 mL $CHCl_3$) and 24 mg of PBA (0.2 mmol in 1 mL $CHCl_3$) were added to a flask in the mentioned order and the mixture was stirred for one hour. A solid precipitated that was collected by filtration to afford 41 mg (48%) of the title product with identical PXRD.

PYR@A1. (319 mg, 91%). XRPD, 2Theta/°: 7.2, 7.5, 12.4, 12.7, 12.8, 14.4, 15.0, 15.1, 15.2, 15.9, 16.2, 16.5, 16.6, 17.4, 18.1, 18.5, 18.8, 19.3, 19.5, 20.2, 20.5, 21.8, 23.0, 24.3, 25.0, 25.4, 26.0. The molar composition evaluated by HPLC-Uv, calcd.: PBA, 33.3%; DHN, 33.3%; DPE, 16.7%; pyrene, 16.7%; found: PBA, 29.8%; DHN, 35.3%; DPE, 17.6%; pyrene, 17.2%. m.p. (^{o}C): 259-260.

PAH@A2:
37 mg of DPEt (0.2 mmol) were added to 4 mL of a solution of **1** (100 mg, 0.4 mmol) and the corresponding PAH (0.2 mmol) in chloroform. The mixture was stirred for one hour; whereupon the

resulting precipitate was collected by filtration. The PAHs employed were fluorene, naphthalene, phenanthrene, anthracene, pyrene, triphenylene, benzo(a)anthracene and perylene.

PHE@A2. (137 mg, 81%). PXRD, 2Theta/°: 7.5, 13.0, 3.1, 14.9, 15.6, 17.3, 17.8, 18.9, 20.0, 20.3, 21.4, 22.5, 23.5, 24.5, 24.9, 25.3, 25.6, 26.1, 26.2, 26.5, 27.8. The molar composition evaluated by HPLC-UV, calcd.: PBA, 33.3%; DHN, 33.3%; DPE, 16.7%; phenanthrene, 16.7%; found: PBA, 30.0%; DHN, 35.2%; DPE, 17.6%; phenanthrene, 17.3%. m.p. (^{o}C): 227-228.

ANT@A2. (122 mg, 73%). PXRD, 2Theta/°: 7.6, 12.4, 12.9, 13.1, 15.2, 15.5, 15.8, 17.3, 18.0, 19.2, 19.8, 20.6, 21.3, 22.6, 23.4, 24.2, 24.7, 24.9, 25.3, 25.5, 26.1, 26.4, 27.5, 28.2, 31.0. The molar composition evaluated by HPLC-UV, calcd: PBA, 33.3%; DHN, 33.3%; DPE, 16.7%; anthracene, 16.7%; found: PBA, 29.5%; DHN, 35.7%; DPE, 17.3%; anthracene, 17.5%. m.p. (^{o}C): 220-221.

PYR@A2. (153 mg, 89%). PXRD, 2Theta/°: 7.3, 12.6, 13.3, 14.6, 15.0, 15.1, 15.6, 15.8, 17.2, 17.4, 17.9, 18.3, 19.5, 19.8, 19.9, 21.2, 22.1, 23.3, 24.2, 24.7, 24.9, 25.1, 25.3, 25.7, 25.9, 26.3, 27.5, 30.5, 32.6. The molar composition evaluated by HPLC-UV, calcd.: PBA, 33.3%; DHN, 33.3%; DPE, 16.7%; pyrene, 16.7%; found: PBA, 30.0%; DHN, 35.2%; DPE, 17.7%; pyrene, 17.1%. m.p. (^{o}C): 238-239.

PAH@A3.
74 mg of DPA (0.4 mmol) were added to 8 mL of a solution of **1** (200 mg, 0.8 mmol) and the corresponding PAH (0.4 mmol) in chloroform. The mixture was stirred for one hour; whereupon the resulting precipitate was collected by filtration. The PAHs employed were fluorene, naphthalene, phenanthrene, anthracene, pyrene, thriphenylene, benzo(a)anthracene and perylene.

PYR@A3. was obtained (312 mg, 93%). PXRD, 2Theta/°: 7.2, 7.9, 11.3, 11.8, 12.9, 14.3, 16.0, 16.4, 16.7, 17.2, 18.3, 19.3, 20.3, 21.6, 21.8, 23.6, 24.3, 24.6, 25.1, 25.9, 26.0, 26.2, 27.1, 27.5, 28.9. The molar composition evaluated by HPLC-UV, calcd.: PBA, 33.3%; DHN, 33.3%; DPE, 16.7%; pyrene, 16.7%; found: PBA, 30.6%; DHN, 35.2%; DPE, 17.4%; pyrene, 16.8%. m.p. (^{o}C): 234-235.

(acetone)$_2$@A1. 244 mg of PBA (2 mmol), 320 mg of DHN (2 mmol) and 182 mg of DPE (1 mmol) were added to 15 mL of acetone. The resulting mixture was stirred on an ice bath at 6°C for one hour. The pure product was obtained by filtration to afford 712 mg (90%) of product. PXRD, 2Theta/°: 8.5, 11.8, 13.6, 14.4, 16.1, 16.7, 17.7, 19.9, 20.1, 20.3, 21.1, 21.2, 21.3, 22.0, 23.7, 24.4, 25.1, 28.1, 28.3, 31.9. The molar composition evaluated by HPLC-UV, calcd.: PBA, 28.6%; DHN, 28.6%; DPE, 14.3%; acetone, 28.6%; found: PBA, 26.6%; DHN, 27.1%; DPE, 15.6%; acetone 30.7%. See Figure S2 for TGA.
toluene@A1. 74 mg of DPE (0.4 mmol) were added to 5 mL of a solution of **1** (200 mg, 0.8 mmol) in toluene. The mixture was stirred for one hour; whereupon the resulting precipitate was collected by filtration to afford 290 mg of the product (95 %).
Method 2. 244 mg of PBA (2 mmol), 320 mg of DHN (2 mmol) and 182 mg of DPE (1 mmol) were added to 15 mL of toluene. The resulting mixture was stirred and heated under reflux for 1 hour. The mixture was allowed to cool to room temperature and the pure product was obtained by

filtration to afford 725 mg (95 %) of the product. PXRD, 2Theta/°: 11.0, 12.2, 12.6, 14.2, 15.3, 16.6, 16.9, 18.5, 18.9, 19.6, 20.4, 20.6, 20.7, 22.2, 22.7, 23.0, 23.9, 24.2, 24.6, 25.0, 25.4, 25.8, 26.1, 26.3, 26.6, 27.6, 28.3, 28.6, 29.6, 30.4, 30.9, 33.5, 39.6, 39.9, 41.2. The molar composition evaluated by HPLC-UV, calcd.: PBA, 33.3%; DHN, 33.3%; DPE, 16.7%; toluene, 16.7%; found: PBA, 31.9%; DHN, 31.5%; DPE, 18.6%; toluene 18.0%. See Figure S2 for TGA.

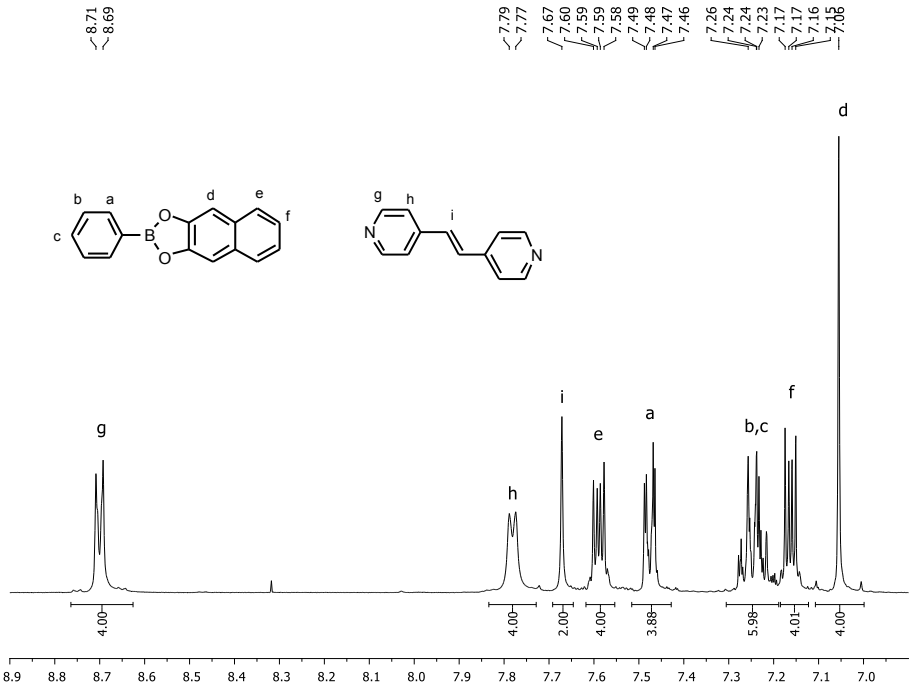


Figure S1. ^{1}H NMR spectrum of **A1** in DMSO-d_6.

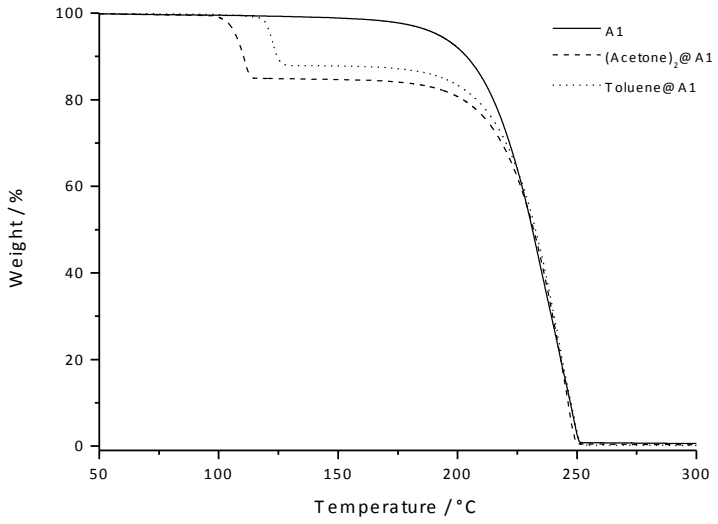


Figure S2. Thermogravimetric analysis for **A1**, (acetone)$_2$@A1 (weight loss 14.7%, corresponding to two acetone molecules) and toluene@A1(weight loss 12.1%, corresponding to one toluene molecule).

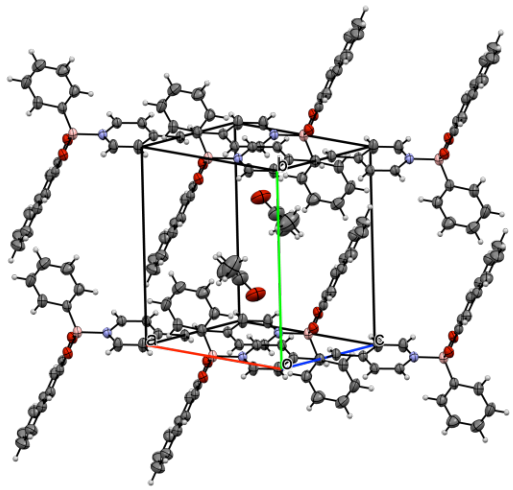


Figure S3. Asymmetric unit cell of (acetone)$_2$@A1.

Table S1. The relative composition of PAH, PBA, DHN and DPE was measured by HPLC and is indicated as % mol. The PAHs and the adduct components were obtained from independent experiments that quantified the hydrophobic (PHAs) and the hydrophilic (PBA, DHN, DPE) fraction.[a] See Figures S6a and S6b for the HPLC traces.

	Observed Ratio (normalized to PAH)			
Solid	PAH	PBA	DHN	Diamine
PAHs@Adduct (1:1) % Calcd.	16.7	33.3	33.3	16.7
NAP@A1	17.5 (1.05)	29.8 (1.78)	34.9 (2.09)	17.8 (1.07)
FLR@A1	14.0 (0.84)	30.8 (1.84)	36.8 (2.20)	18.4 (1.10)
PHE@A1	17.8 (1.07)	29.8 (1.78)	34.6 (2.07)	17.7 (1.06)
ANT@A1	16.5 (0.99)	29.6 (1.77)	36.2 (2.17)	17.6 (1.05)
PYR@A1	16.5 (0.99)	29.8 (1.78)	35.8 (2.14)	17.9 (1.07)
PHE@A2	17.3 (1.04)	30.0 (1.80)	35.2 (2.11)	17.5 (1.05)
ANT@A2	17.5 (1.05)	29.5 (1.77)	35.7 (2.14)	17.3 (1.04)
PYR@A2	17.1 (1.02)	30.0 (1.80)	35.2 (2.11)	17.7 (1.06)
PYR@A3	16.8 (1.01)	30.6 (1.83)	35.2 (2.11)	17.4 (1.04)

[a] HPLC Analysis: For the identification and quantitation of PBA, DHN, diamine and PAHs, two different methods were developed on a 3.5μm Zorbax Eclipse XDB-C18 column (3mm x 100 mm) and a Hitachi LaChrom Ultra HPLC system coupled to an UV diode-array detector and an autosampler. The column was maintained at 40°C. The detection wavelength was chosen at 210 and 260 nm. The flow rate was kept constant at 0.5 mL/min and a 10 μL of sample injection volume. The following gradient was used for the hydrophilic fraction (PBA, DHN and diamine): 15 minutes of a mixture water:acetonitrile 80:20 (v/v), then a 17 min ramp to reach 100% of acetonitrile, this solvent being further maintained for 20 min. The hydrophobic fraction (i.e., PAHs) was analyzed with the following gradient: starting from a mixture of water-methanol (50:50, v/v) and acetonitrile in a ratio 75:25 (v/v), a 15 min ramp was run until reaching 60:40 (v/v).

Samples for analysis were prepared by dissolving 4 mg of the corresponding solid PAH@AX (X=1-3) into 5 mL of methanol in volumetric flasks. Calibration curves were obtained separately for each of the components PBA, DHN, diamine and PAHs. The amount measured for each of the components in μg/mL was converted into percent mol present in the original solid. Values showed in the parenthesis correspond to the quotient ratio experimental/calculated.

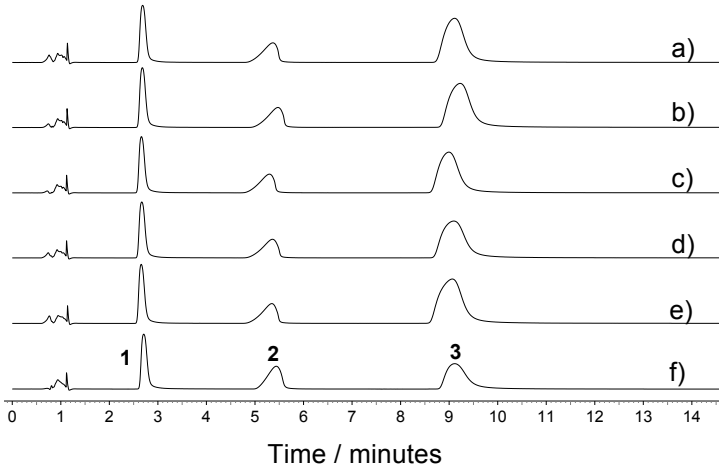


Figure S4a. HPLC traces for the hydrophilic fraction of (from top to bottom): a) PYR@A1; b) ANT@A1; c) PHE@A1; d) FLR@A1; e) NAP@A1; f) standard solution in MeOH containing: PBA (1), DPE (2) and DHN (3).

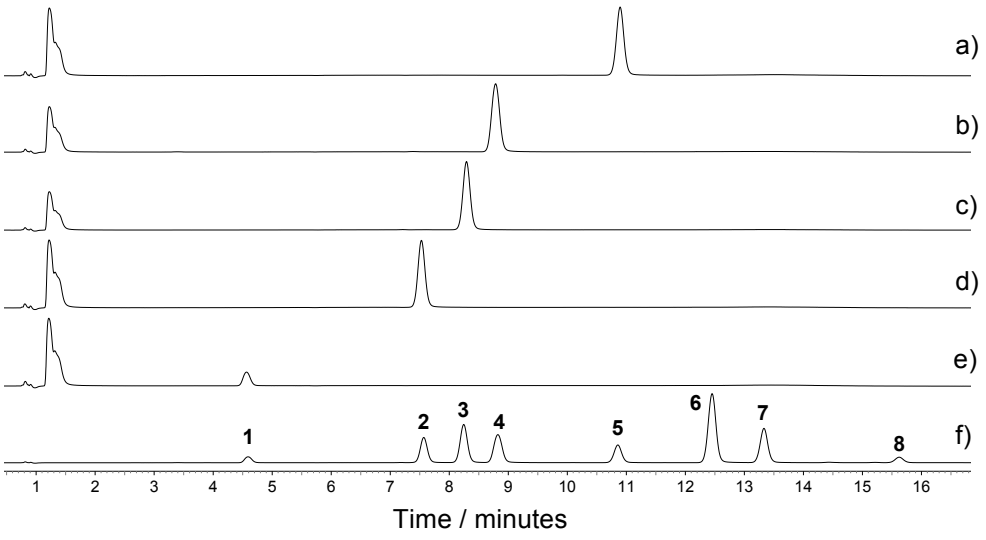
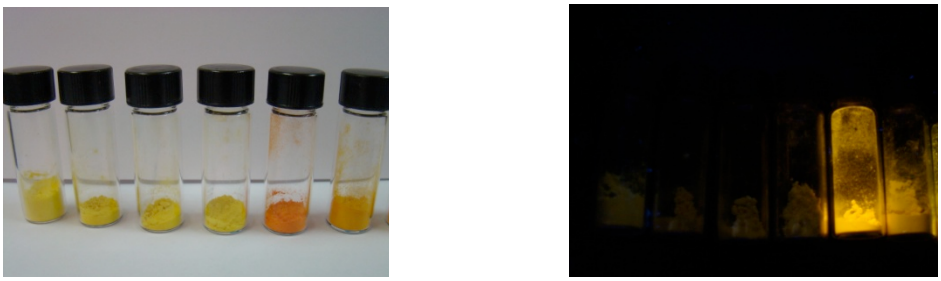
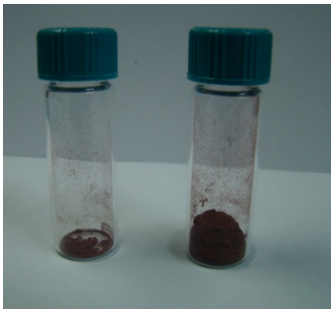


Figure S4b. HPLC traces for the hydrophobic fraction of (from top to bottom): a) PYR@A1; b) ANT@A1; c) PHE@A1; d) FLR@A1; e) NAP@A1; f) Standard solution in MeOH containing: NAP (1), FLR (2), PHE (3), ANT (4), PYR (5), TRP (6), BaA (7) and PER (8).



S5a. Solids under ambient light (left) and UV light (right): **A1**, NAP@A1, FLR@A1, PHE@A1, ANT@A1, PYR@A1.

S5b.Solids under ambient light (left) and UV light (right): **A2** (or DHN@A2), PHE@A2, ANT@A2, PYR@A2.



S5c. Solids under ambient light: **A3**, and PYR@A3.

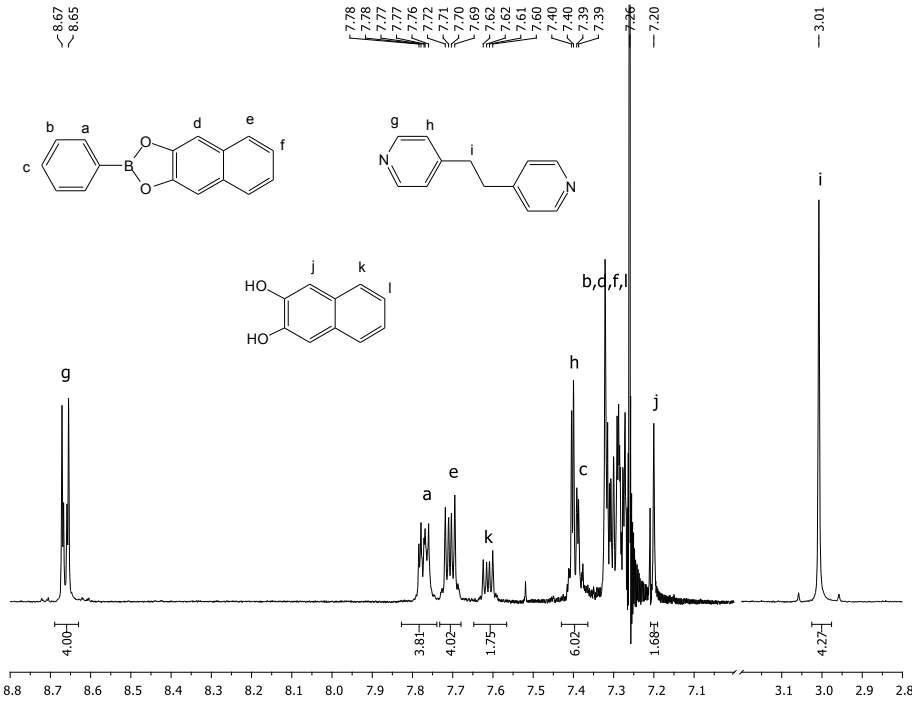


Figure S7a. ^{1}H NMR spectra of adduct **A2** (or DHN@A2) in $CDCl_3$.

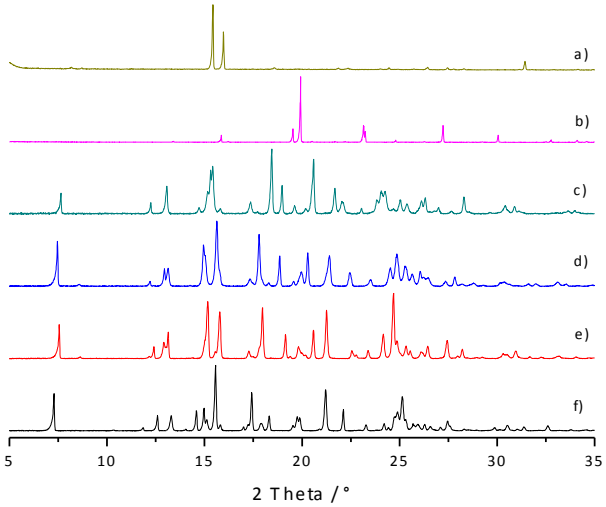


Figure S7b. PXRD patterns of the solids obtained from the mixture of **1**, DPEt and a single PAH (from top to bottom): a) **1**; b) DPEt; c) **A2** (or DHN@A2); d) PHE@A2; e) ANT@A2; f) PYR@A2.

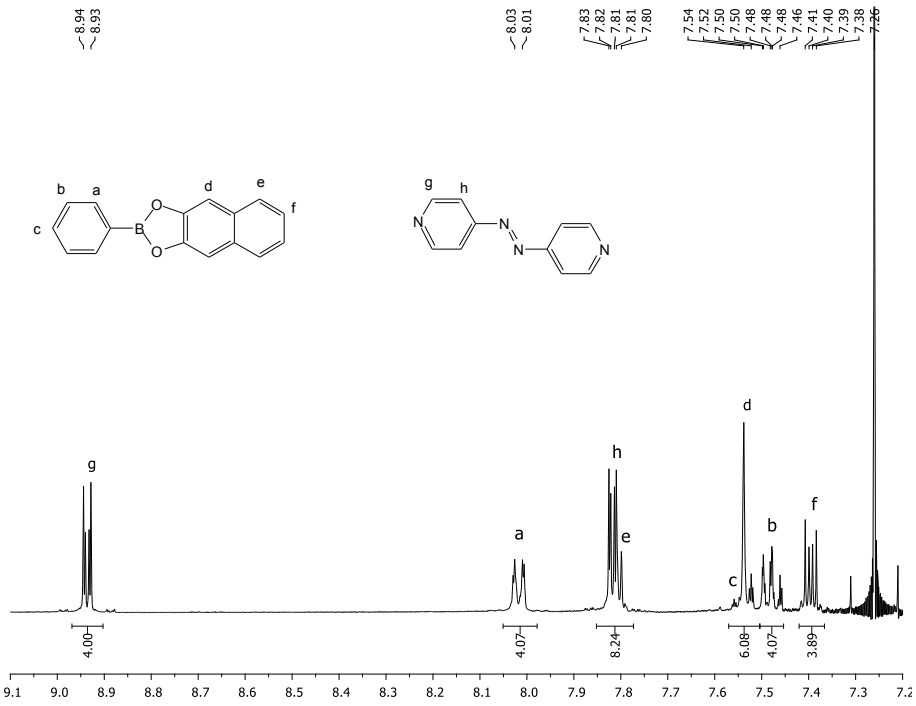


Figure S8a. ^{1}H NMR spectrum of **A3** in $CDCl_3$.

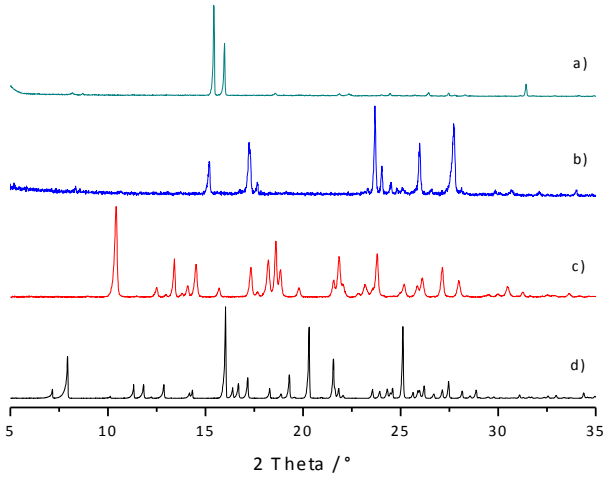


Figure S8b. PXRD patterns of the solids obtained from the mixture of **1**, DPA and a single PAH (from top to bottom): a) **1**; b) DPA; c) **A3**; d) PYR@A3.

Extraction from a solution containing all eight PAHs: 37 mg of the corresponding diamine (DPE, DPEt or DPA; 0.2 mmol) were added to 6 mL of a solution containing the boronate ester **1** (100 mg, 0.4 mmol) and 0.2 mmol of ech fluorene, naphthalene, phenanthrene, anthracene, pyrene, triphenylene, benzo(a)anthracene and perylene in chloroform. The mixture was stirred for one hour; whereupon the resulting precipitate was collected by filtration to afford 8PAHs@A1 (136 mg), 8PAHs@A2 (146 mg) and 8PAHs@A3 (107 mg), respectively. See Figure S9 for PXRD data of each solid.

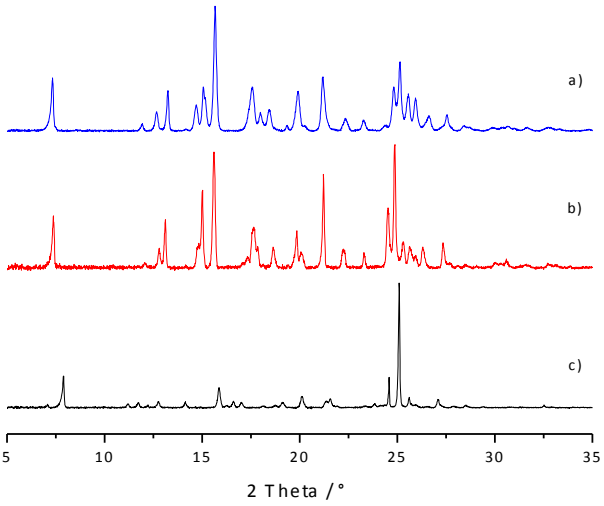


Figure S9. PXRD patterns of the solids obtained from the mixture of **1**, the diamine (DPE or DPEt or DPA) and a solution containing all eight PHAs (from top to bottom): a) 8PAHs@A1; b) 8PAHs@A2; c) 8PAHs@A3.

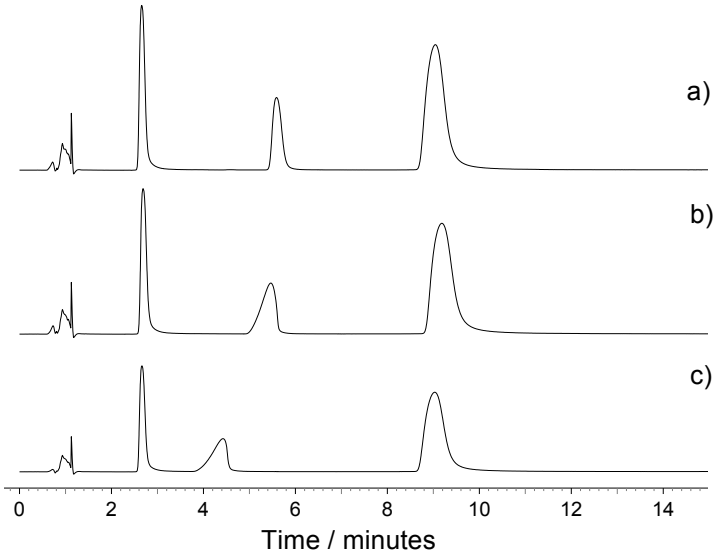


Figure S10a. HPLC traces of the hydrophilic fraction for solids obtained from the mixture of **1**, the diamine (DPE or DPEt or DPA) and a solution containing all eight PHAs (from top to bottom): a) 8PAHs@A3; b) 8PAHs@A1; c) 8PAHs@A2.

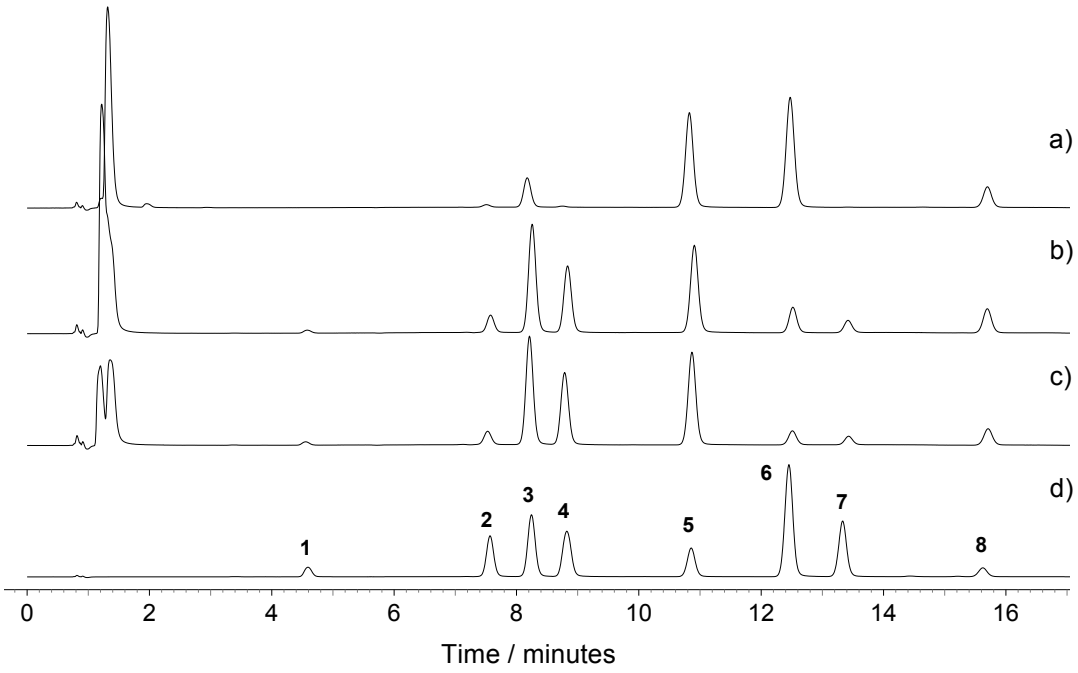


Figure S10b. HPLC traces of the hydrophobic fraction for solids obtained from the mixture of **1**, the diamine (DPE or DPEt or DPA) and a solution containing all eight PAHs (from top to bottom): a) 8PAHs@A3; b) 8PAHs@A1; c) 8PAHs@A2; d) standard solution containing: NAP (1), FLR (2), PHE (3), ANT (4), PYR (5), TRP (6), BaA (7) and PER (8).

Table S2. Percent proportion of PAHs found for the solids 8PAHs@A1, 8PAHs@A2 and 8PAHs@A3.[a]

	8PAHs@A1	8PAHs@A2	8PAHs@A3
NAP	2.53 ± 0.01	2.81 ± 0.03	--
FLR	2.69 ± 0.01	2.0 ± 0.10	0.41 ± 0.02
PHE	11.6 ± 0.10	11.6 ± 0.20	4.9 ± 0.30
ANT	6.8 ± 0.10	7.5 ± 0.20	--
PYR	17.8 ± 0.20	18.8 ± 0.60	31.8 ± 1.5
TRP	0.542 ± 0.004	--	8.1 ± 0.30
BaA	1.092 ± 0.005	0.7 ± 0.01	--
PER	5.26 ± 0.04	3.6 ± 0.1	7.0 ± 0.10
Adduct	51.9 ± 0.7	52.9 ± 1.3	51.8 ± 3.7

[a] See Table S1 for HPLC experimental conditions.

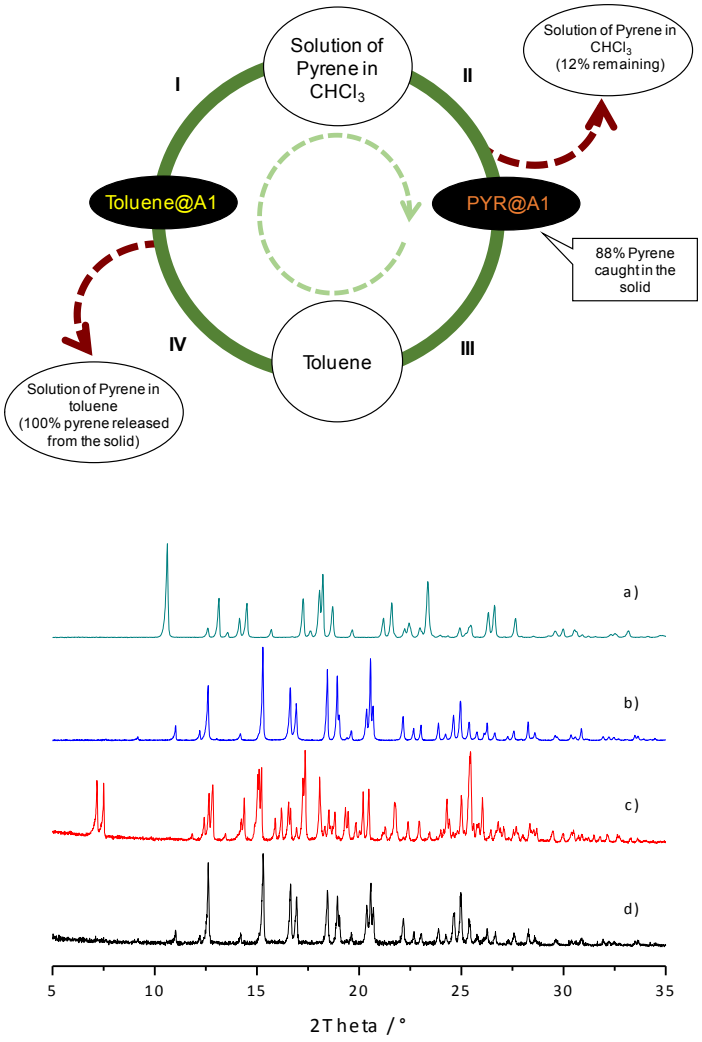


Figure S11. (Top) "Catch and Release" cycle of PYR with **A1**: I. 100 mg of toluene@A1 (0.130 mmol) were added to a pyrene solution in chloroform (2mL, 68 mM); II. The mixture was stirred for one hour and PYR@A1 was obtained by filtration (98 mg, 88%). The pyrene left in the filtrate was quantified by UV-vis spectroscopy indicating the presence of approximately 12% of the initial amount. III. 98 mg of PYR@A1 (obtained in II) were added to 3mL of toluene; IV. The mixture was stirred at 100°C for one hour and the remaining solid (toluene@A1) was obtained by filtration (68 mg, 79%). PYR was fully released back into the toluene solution according to Uv-vis quantification. For this experiment toluene solvate was preferred over the acetone solvate given its higher stability and facile conversion to PYR@A1 after exposure to the solution of pyrene in chloroform. Figure in the bottom: PXRD patterns of the solids: a) **A1**; b) toluene@A1 (initial stage of the cycle); c) PYR@A1 (obtained in stage II of the cycle); d) toluene@A1 (at the end of the cycle).

Table S3. Solubility data for the clathrates obtained from the screening experiments (see Table 1).

	Solubility (10^{-3} M)
NAP@A1	2.6 ± 0.08
FLR@A1	4.5 ± 0.13
PHE@A1	3.3 ± 0.11
ANT@A1	3.6 ± 0.11
PYR@A1	2.1 ± 0.07
PHE@A2	6.1 ± 0.12
ANT@A2	6.0 ± 0.05
PYR@A2	5.1 ± 0.07
PYR@A3	4.3 ± 0.08

Experimental procedure for the determination of the solubility: A saturated solution of the corresponding solid in chloroform was stirred at 25°C for 3 h, whereupon 2 mL samples were taken and filtered through a 0.45 μm pore disk. After dilution in a 1:25 ratio in methanol, the content of the corresponding PAH in the different solids was quantified by HPLC according to aforementioned methodology (Table S1). Preliminary experiments monitoring the concentration at 0.5, 1, 2, 4 and 8 h showed that saturation was reached within one hour.

Table S4. Crystallographic data for compounds (acetone)$_2$@A1 and ANT@A1.

Crystal data [a]	**(acetone)$_2$@A1**	**ANT@A1**
Formula	$C_{44}H_{32}B_2N_2O_4 \cdot (C_3H_6O)_2$	$C_{44}H_{32}B_2N_2O_4 \cdot (C_{14}H_{10})$
MW (g mol^{-1})	790.49	852.55
Space group	*P-1*	*P21/c*
a (Å)	9.0771(3)	7.3455(3)
b (Å)	10.8773(3)	20.4878(9)
c (Å)	11.3414(4)	14.8292(7)
α (°)	77.9240(10)	90
β (°)	81.0780(10)	103.6060(10)
γ (°)	76.8330(10)	90
V (Å^3)	1059.41(6)	2169.06(17)
Z	1	2

μ (mm^{-1})	0.080	0.081
ρ_{calcd} (g cm^{-3})	1.239	1.305
$R^{[b, c]}$	0.0446	0.0458
$R_w^{[d, e]}$	0.1231	0.1252
GOF	1.036	1.17

[a] $\lambda_{MoK\alpha}$ = 0.71073 Å. [b] $F_o > 2\sigma(F_o)$. [c] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [d] All data. [e] $R_w = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{½}$.

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