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Supporting Information for

Dynamic Polyimine Macrobicyclic Cryptands – Self-sorting with Component Selection

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1. Experimental

1.1. Materials and Methods

All chemicals and solvents were purchased from commercially available sources and were used without further purification. Aldehydes **B** and **H** were synthesised according to reported procedures^{1,2}. ¹H and ¹³C NMR spectra for the characterization of the products were recorded on a Bruker Ultrashield™ 300 + 300 Fourier-Transform spectrometer. ¹H NMR spectra for characterization of dynamic libraries of components were recorded in CDCl₃ on a Bruker 400 MHz spectrometer, using 1,4-dioxane as an internal standard. In ¹H NMR spectra chemical shift (δ) values are reported relative to TMS (δ = 0.00 ppm) and were measured in CDCl₃ stored over the anhydrous potassium carbonate (K₂CO₃). TOF-MS spectra were measured using chloroform solutions on a BRUKER Impact HD ESI-Q-TOF mass spectrometer. X-Ray diffraction data were obtained on a 4-circle Xcalibur EosS2 diffractometer (Agilent Technologies) equipped with a CCD detector.

1.2. Synthesis and isolation

1.2.1. A₃T₂ Cage

Synthesis of cage A₃T₂ Tren [N(CH₂CH₂NH₂)₃] (64.42 mg; 0.44 mmol) was dissolved in MeCN (1 mL), then isophthalic dialdehyde (88.52 mg; 0.66 mmol) in MeCN (14 mL) was added dropwise over 15 min. The resulting clear, colourless solution was stirred for 3 h at room temperature. The cloudy, greenish-yellow supernatant was filtered off from the yellow precipitate formed, which was washed on the filter with MeCN (10 mL), then dried under vacuum. Yield: 211 mg (75%). ¹H NMR (300 MHz, CDCl₃) δ 8.21, 8.19 (d, 6H, H₄), 7.59 (s, 6H, imine, H₃), 7.53 (t, 3H, H₅), 5.34 (s, 3H, H₆), 3.78-3.25 (dt, 12H, H₂), 2.98-2.67 (dt, 12H, H₁). Melting point = 419-423 K. TOF-MS: m/z = 587.3611 – calculated for C₃₆H₄₃N₈ (cage); found m/z = 587.3566 [M+H]⁺. Microanalysis: calculated (%) for C₃₆H₄₂N₈: C 73.69, H 7.21, N 19.10 %; found: C 73.58, H 7.32, N 19.16 %.

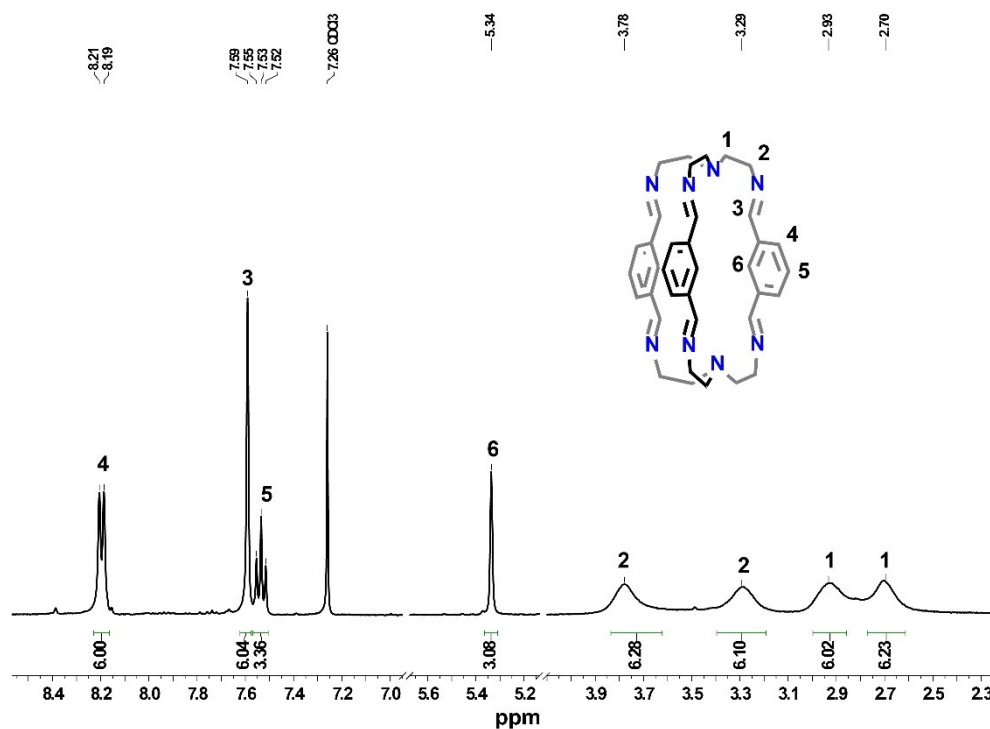


Figure S1. ¹H NMR spectra (300 MHz, CDCl₃) of synthesized and isolated A₃T₂ cage, recorded at RT.

1.2.2. B₃T₂ Cage

Synthesis of cage B₃T₂ To the solution of tren [N(CH₂CH₂NH₂)₃] (205,1 μL; 1,37 mmol) in 3 mL of MeCN was added dropwise to the solution of pyridine-2,6-dicarbaldehyde (277,67 mg; 2,05 mmol) in 12 mL of MeCN during 20 minutes. Before mixing both solutions were clear. After addition of first 5 portions (1 mL each), the reaction mixture became white-greenish suspension for a while. After 6th dose solution became white suspension permanently. The reaction mixture was left for stirring overnight. The yellow suspension was filtered off and dark yellow precipitate was washed with MeCN (10 mL) and dried in vacuum. The dark yellow precipitate was found as a desired cage (231.1 mg; 82% yield). ¹H NMR (300 MHz, CDCl₃) δ 8.12, 8.10 (d, 6H, H₄), 7.81 (t, 3H, H₅), 7.59 (s, 6H, imine, H₃), 3.59 (t, 12H, H₂), 2.88 (t, 12H, H₁). Melting point = 429-433 K. TOF-MS: m/z = 590.3468 – calculated for C₃₃H₄₀N₁₁ (cage); found m/z = 590.3471 [M+H]⁺. Microanalysis: calculated (%) for C₃₃H₃₉N₁₁: C 67.21, H 6.67, N 26.13; found: C 67.33, H 6.59, N 26.08 %.

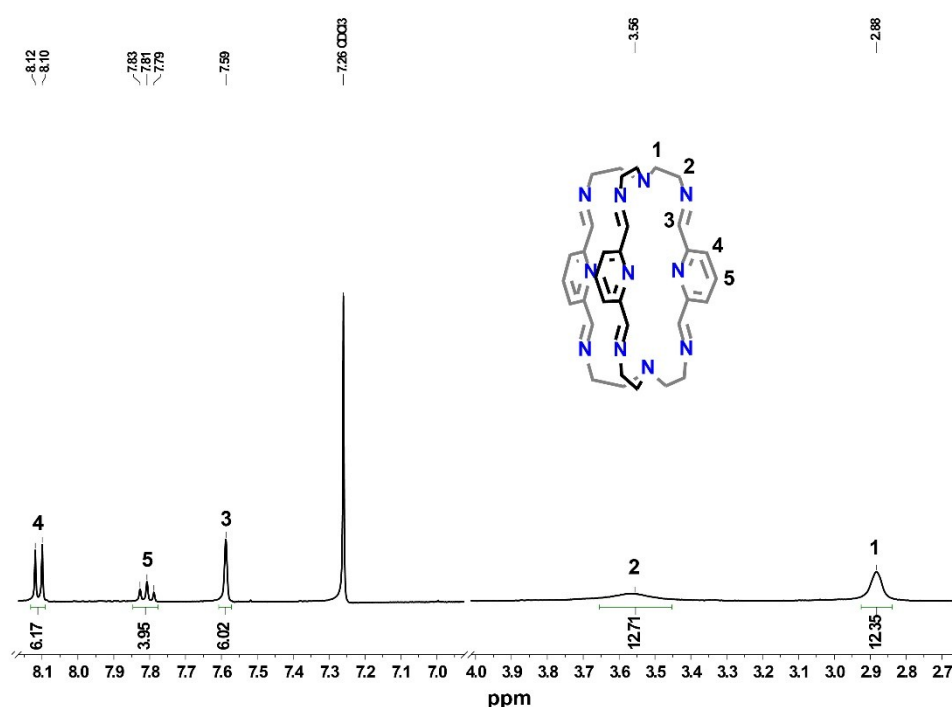


Figure S2. ¹H NMR spectra (300 MHz, CDCl₃) of synthesized and isolated B₃T₂ cage, recorded at RT.

1.2.3. C₃T₂ Cage

Synthesis of cage C₃T₂ The tren [N(CH₂CH₂NH₂)₃] (28.79 mg; 0.197 mmol) was dissolved in 1 mL of MeCN and then 2,5-furandicarbaldehyde (36.65 mg; 0.295 mmol) solution in 10 mL of MeCN was added dropwise during 15 minutes. A clear, yellow-brown solution was left for stirring overnight. The yellow-brownish suspension was filtered off and washed with MeCN (10 mL) and dried in vacuum. The light brown precipitate was found as a desired cage (94.27 mg; 73% yield). ¹H NMR (300 MHz, CDCl₃) δ 7.72 (s, 6H, imine, H₃), 7.08 (s, 6H, H₄), 3.52 (t, 12H, H₂), 2.76 (t, 12H, H₁). Melting point = 427-430 K. TOF-MS: m/z = 557.2989 – calculated for C₃₀H₃₇N₈O₃ (cage); found m/z = 557.3013 [M+H]⁺. Microanalysis: calculated (%) for C₃₀H₃₆N₈O₃: C 64.73, H 6.52, N 20.13; found: C 64.70, H 6.58, N 20.23 %.

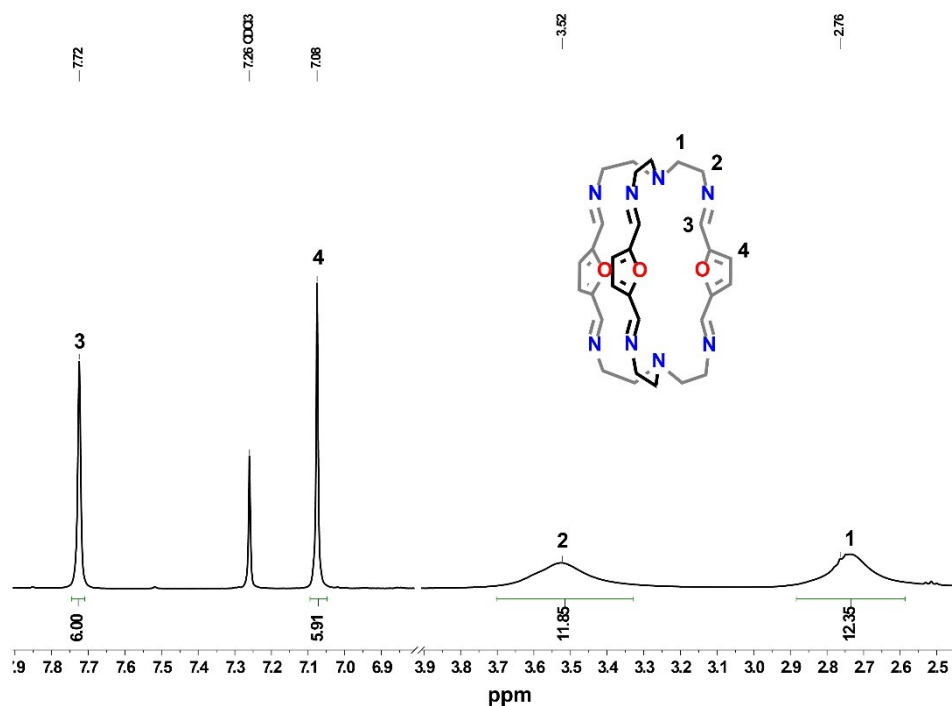


Figure S3. ¹H NMR spectra (300 MHz, CDCl₃) of synthesized and isolated C₃T₂ cage, recorded at RT.

1.2.4. D₃T₂ Cage

Synthesis of cage D₃T₂ The tren [N(CH₂CH₂NH₂)₃] (56.03 mg; 0.383 mmol) was dissolved in 1 mL of MeCN and then terephthal dialdehyde (77.07 mg; 0.575 mmol) in 10 mL of MeCN was added dropwise during 15 minutes. The resulting clear, colourless solution was left for stirring in 3h in room temperature. Then cloudy, white-cream solution was filtered off and creamy / light yellow precipitate was washed using MeCN (15 mL) and dried in vacuum. The precipitate was found as desired cage compound (262.99 mg; 78% yield). ¹H NMR (300 MHz, CDCl₃) δ 8.17 (s, 6H, imine, H₃), 7.17 (s, 12H, H₄), 3.77 (t, 12H, H₂), 2.77 (t, 12H, H₁). Melting point = 418-422 K. TOF-MS: m/z = 587.3611 – calculated for C₃₆H₄₃N₈ (cage); found m/z = 587.3548 [M+H]⁺. Microanalysis: calculated (%) for C₃₆H₄₂N₈: C 73.69, H 7.21, N 19.10; found: C 73.58, H 7.30, N 19.12 %.

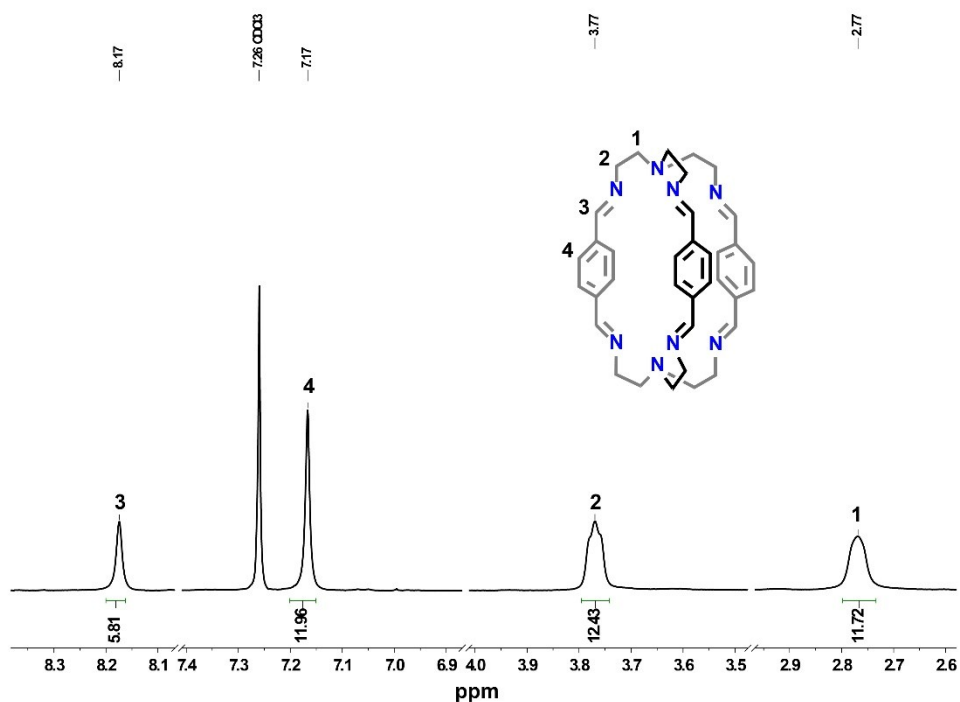


Figure S4. ¹H NMR spectra (300 MHz, CDCl₃) of synthesized and isolated D₃T₂ cage, recorded at RT.

1.2.5. E₃T₂ Cage

Synthesis of cage E₃T₂ The tren [N(CH₂CH₂NH₂)₃] (41.61 mg; 0.284 mmol) was dissolved in 1 mL of MeCN and then 4-(4-formylphenoxy)-benzaldehyde (96.54 mg; 0.427 mmol) dissolved in 10 mL of MeCN was added dropwise during 15 minutes. The clear, colourless solution was left for stirring overnight. Then the yellowish precipitate was filtered off and washed with MeCN (15 mL) and dried in vacuum. The yellowish precipitate was found as a desired compound (298.31 mg; 81% yield). ¹H NMR (300 MHz, CDCl₃) δ 7.68 (s, 6H, imine, H₃), 7.12-7.10 (d, 12H, H₄), 7.03-7.01 (d, 12H, H₅), 3.57 (t, 12H, H₂), 2.83 (t, 12H, H₁). Melting point = 422-426 K. TOF-MS: m/z = 863.4397 – calculated for C₅₄H₅₅N₈O₃ (cage); found m/z = 863.4438 [M+H]⁺. Microanalysis: calculated (%) for C₅₄H₅₄N₈O₃: C 75.15, H 6.31, N 12.98; found: C 75.21, H 6.37, N 12.94 %.

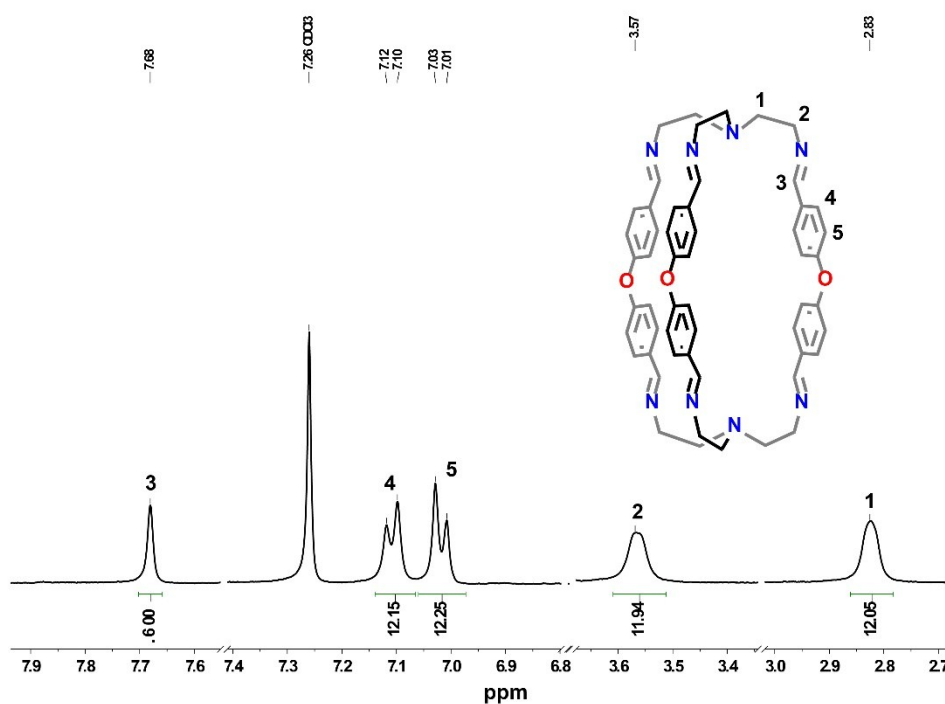


Figure S5. ¹H NMR spectra (300 MHz, CDCl₃) of synthesized and isolated E₃T₂ cage, recorded at RT.

1.2.6. F₃T₂ Cage

Synthesis of cage F₃T₂ The tren [N(CH₂CH₂NH₂)₃] (42.28 mg; 0.289 mmol) was dissolved in 1 mL of MeCN and then 4,4'-biphenyldicarboxaldehyde (91.17 mg; 0.434 mmol) dissolved in 10 mL of MeCN was added dropwise during 15 minutes. The clear, colorless solution was left for stirring overnight. Then the yellow precipitate was filtered off and washed with MeCN (10 mL) and dried in vacuum. The yellow precipitate was found as a desired compound (198 mg; 77.9% yield). ¹H NMR (300 MHz, CDCl₃) δ 8.28 (s, 6H, imine, H₃), 7.25-7.22 (d, 12H, H₅), 7.11-7.09 (d, 12H, H₄), 3.82 (t, 12H, H₂), 2.81 (t, 12H, H₂). Melting point = 414-419 K. TOF-MS: m/z = 815.0820 – calculated for C₅₄H₅₄N₈ (cage); found m/z = 815.4471. Microanalysis: calculated (%) for C₅₄H₅₄N₈: C 79.57, H 6.68, N 13.75; found: C 79.63, H 6.74, N 13.63 %.

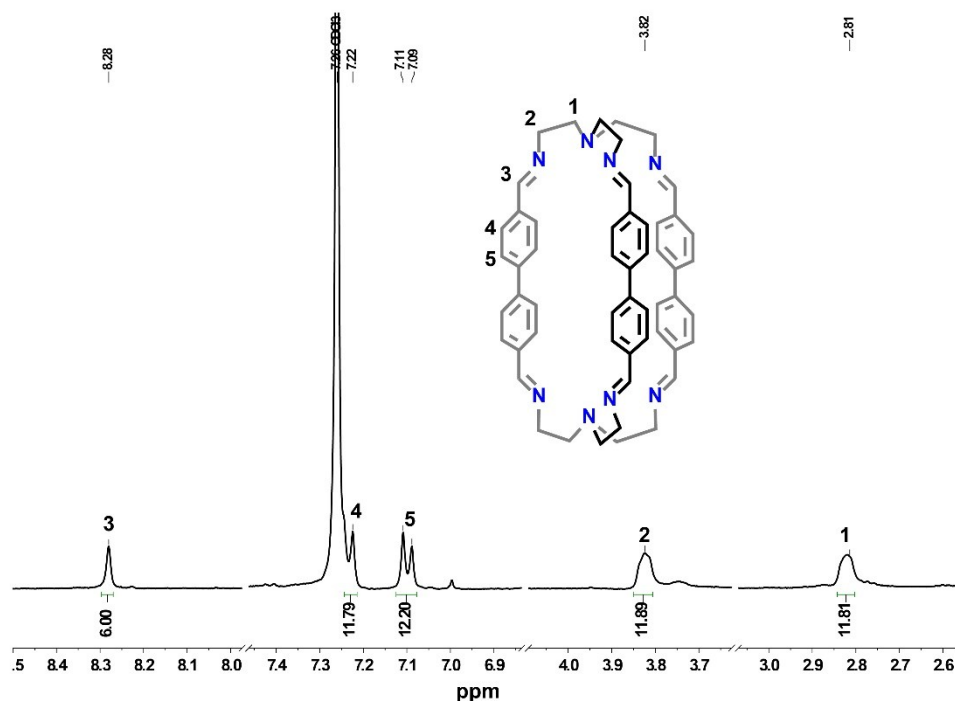


Figure S6. ¹H NMR spectra (300 MHz, CDCl₃) of synthesized and isolated F₃T₂ cage, recorded at RT. A trace amount of intermediate products, most likely open chain species (visible as broad peaks adjacent to that assigned as 1 and 2) was also observed in solution.

1.2.7. G₃T₂ Cage

Synthesis of cage G₃T₂ The tren [N(CH₂CH₂NH₂)₃] (65.73 mg; 0.449 mmol) was dissolved in 1 mL of MeCN and then 2,5-thiophenedicarboxaldehyde (94.49 mg; 0.674 mmol) dissolved in 10 mL of MeCN was added dropwise during 15 minutes. The clear, colorless solution was left for stirring overnight. Then brownish precipitate was filtered off and washed with MeCN (15 mL) and dried in vacuum. The brownish precipitate was found as a desired compound (112,21 mg; 84.5% yield). ¹H NMR (300 MHz, CDCl₃) δ 8.03 (s, 6H, imine, H₃), 7.42 (s, 6H, H₄), 3.64 (t, 12H, H₂), 2.72 (t, 12H, H₁). Melting point = 425-428 K. TOF-MS: m/z = 604.2225 – calculated for C₃₀H₃₆N₈S₃ (cage); found m/z = 604.2259. Microanalysis: calculated (%) for C₃₀H₃₆N₈S₃: C 59.57, H 6.00, N 18.53; found: C 59.62, H 6.07, N 18.56 %.

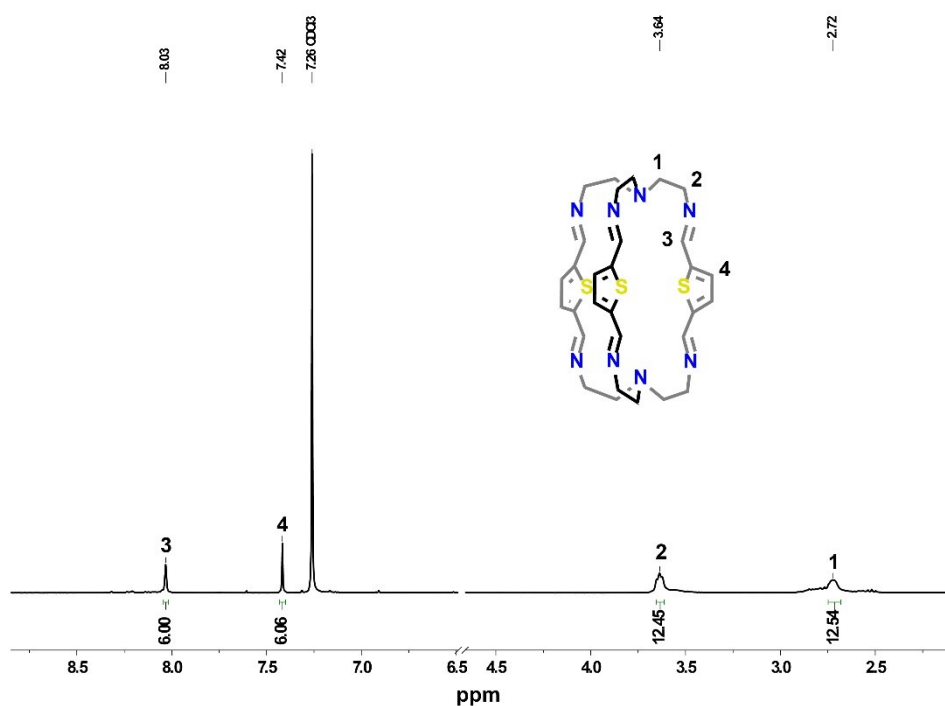


Figure S7. ¹H NMR spectra (300 MHz, CDCl₃) of synthesized and isolated G₃T₂ cage, recorded at RT. A trace amount of intermediate products, most likely open chain species (visible as broad peaks adjacent to that assigned as 1 and 2) was also observed in solution.

1.2.8. H₃T₂ Cage

Synthesis of cage H₃T₂ A solution of dialdehyde - 4,4'-(((oxybis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl))bis(oxy)dibenzaldehyde (43,7 mg; 0,108 mmol) in MeCN (12 mL) was added dropwise to a solution of tren [N(CH₂CH₂NH₂)₃] (10,8 µL; 0,072 mmol) in MeCN (3 mL) over a period of 20 minutes. After full addition, there was no changes observed. The reaction mixture was left for stirring overnight. After 2 h the resulting mixture began to be cloudy. The greenish solution with with/creamy precipitate was filtered off giving creamy powder of the cage which was washed with MeCN (10 mL) and dried in vacuo (55.91 mg; 375 yield). ¹H NMR (300 MHz, CDCl₃) δ 7.96 (s, 6H, imine, H₃), 7.30-7.28 (d, 12H, H₄), 6.77-6.75 (d, 12H, H₅), 4.10 (t, 12H, H₆), 3.89 (t, 12H, H₇), 3.73-3.71 (m, 24H, H₈, H₉), 3.62-3.56 (m, 12H, H₂), 2.85-2.80 (m, 12H, H₁). Melting point = 396-399 K. TOF-MS: m/z = 1390.7464 – calculated for C₇₈H₁₀₂N₈O₁₅ (cage); found m/z = 1390.7458. Microanalysis: calculated (%) for C₇₈H₁₀₂N₈O₁₅: C 67.32, H 7.39, N 8.05; found: C 67.41, H 7.52, N 7.98 %.

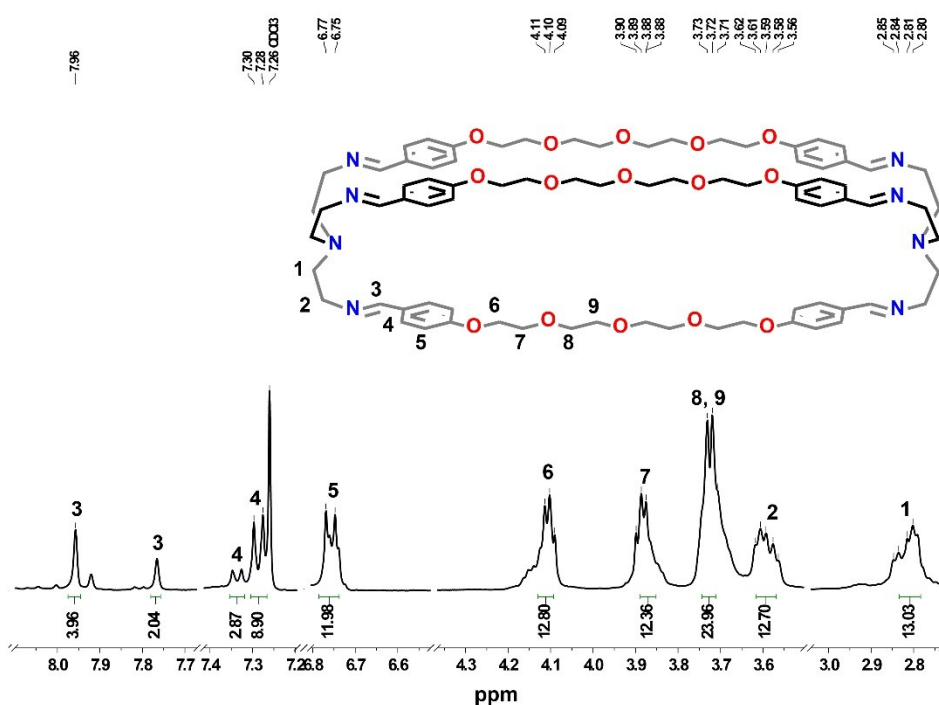


Figure S8. ¹H NMR spectra (300 MHz, CDCl₃) of synthesized and isolated H₃T₂ cage, recorded at RT. A trace amounts of intermediate products, most likely open chain species (visible as broad peaks adjacent to that assigned as 1 and 2) was also observed in solution.

1.3. Self-sorting experiments

1.3.1. Self-sorting experiment 3A + 3B + 2T

In a NMR tube, isophthalaldehyde (**A**) (4.08 mg; 0.0304 mmol) and pyridine-2,6-dicarbaldehyde (**B**) (4.18 mg; 0.0304 mmol) were dissolved in 250 μ L of deuterated chloroform (CDCl_3). Then a deuterated chloroform solution (300 μ L) containing tris(2-aminoethyl)amine (**T**) (2.97 mg; 0.0203 mmol) was added in two portions. The resulting solution mixture was stirred at room temperature for 24h, then in 318.15 K for another 24h and then again for 24h in RT. The clear solution of the library was checked by ^1H NMR spectroscopy (CDCl_3) just after mixing the components and after each 24h of stirring (RT/318.15 K/RT).

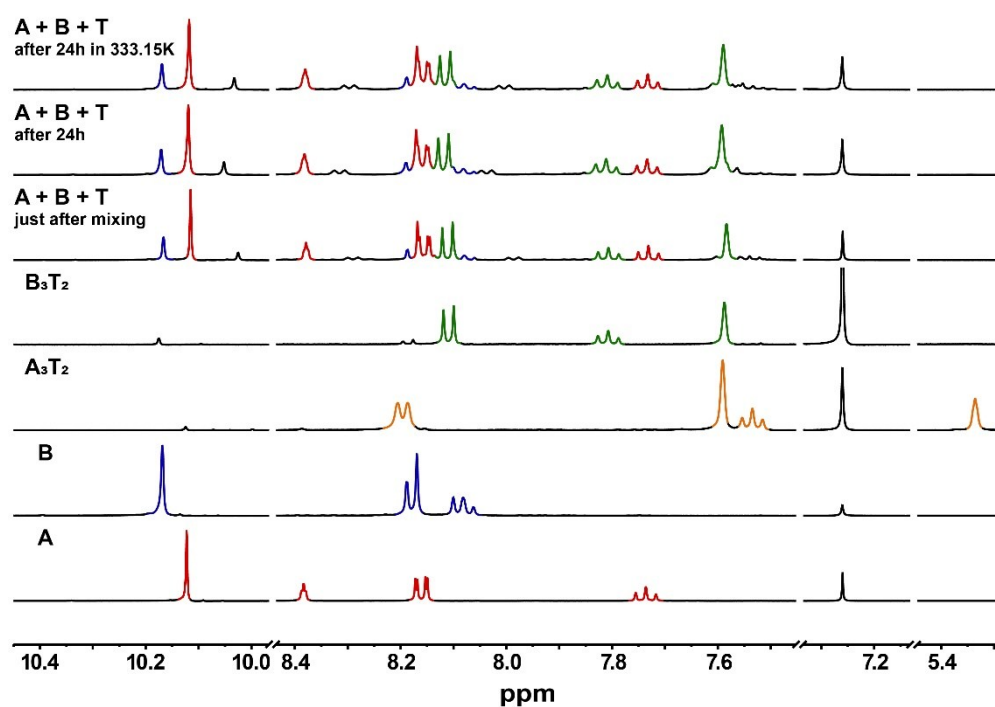


Figure S9. Comparison of ^1H NMR (400 MHz) spectra for self-sorting experiment **3A + 3B + 2T** depending on the time. The spectra of components and pure, isolated cages are also shown for comparison. All NMR spectra were recorded in CDCl_3 at room temperature.

1.3.2. Self-sorting experiment 3A + 3C + 2T

In a NMR tube, isophthalic dicarbaldehyde (**A**) (5.06 mg; 0.0377 mmol) and furan-2,5-dicarbaldehyde (**C**) (4.68 mg; 0.0377 mmol) were dissolved in 250 μL of deuterated chloroform (CDCl_3). Then a deuterated chloroform solution (300 μL) containing tris(2-aminoethyl)amine (**T**) (3.67 mg; 0.0251 mmol) was added in two portions. The resulting solution mixture was stirred at room temperature for 24h, then in 318.15 K for another 24h and then again for 24h in RT. The clear solution of library was checked by ^1H NMR spectroscopy (CDCl_3) just after mixing the components and after each 24h of stirring (RT/318.15 K/RT).

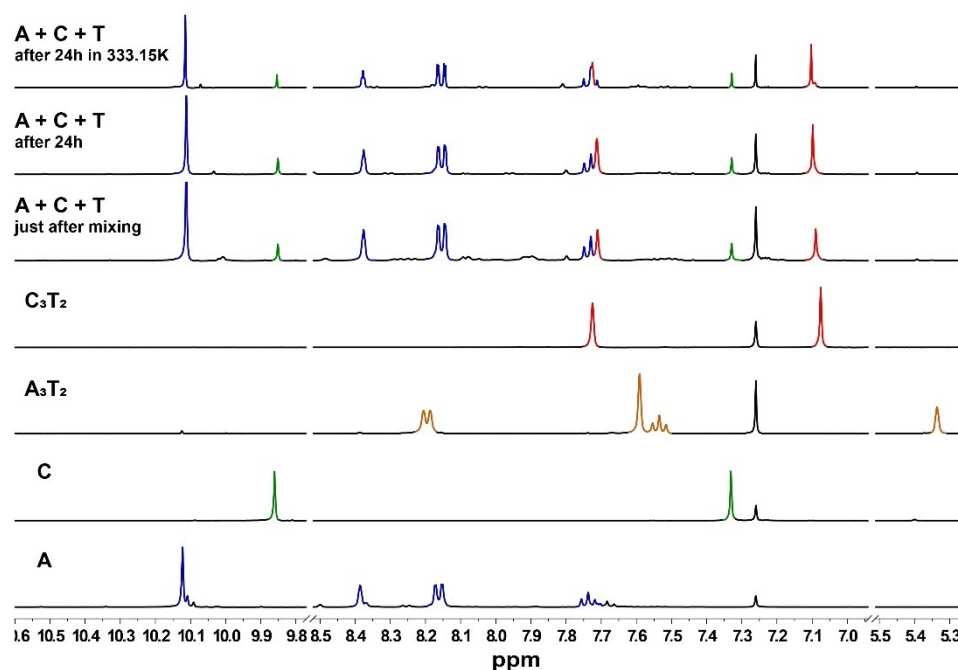


Figure S10. Comparison of ^1H NMR (400 MHz) spectra for self-sorting experiment **3A** + **3C** + **2T** depending on the time. The spectra of components and pure, isolated cages are also shown for comparison. All NMR spectra were recorded in CDCl_3 at room temperature.

1.3.3. Self-sorting experiment 3A + 3D + 2T

In a NMR tube, isophthalic dicarbaldehyde (**A**) (3.79 mg; 0.0283 mmol) and terephthalaldehyde (**D**) (3.79 mg; 0.0283 mmol) were dissolved in 250 μL of deuterated chloroform (CDCl_3). Then a deuterated chloroform solution (300 μL) containing tris(2-aminoethyl)amine (**T**) (2.75 mg; 0.0188 mmol) was added in two portions. The resulting solution mixture was stirred at room temperature for 24h, then in 318.15 K for another 24h and then again for 24h in RT. The clear solution of library was checked by ^1H NMR spectroscopy (CDCl_3) just after mixing the components and after each 24h of stirring (RT/318.15 K/RT).

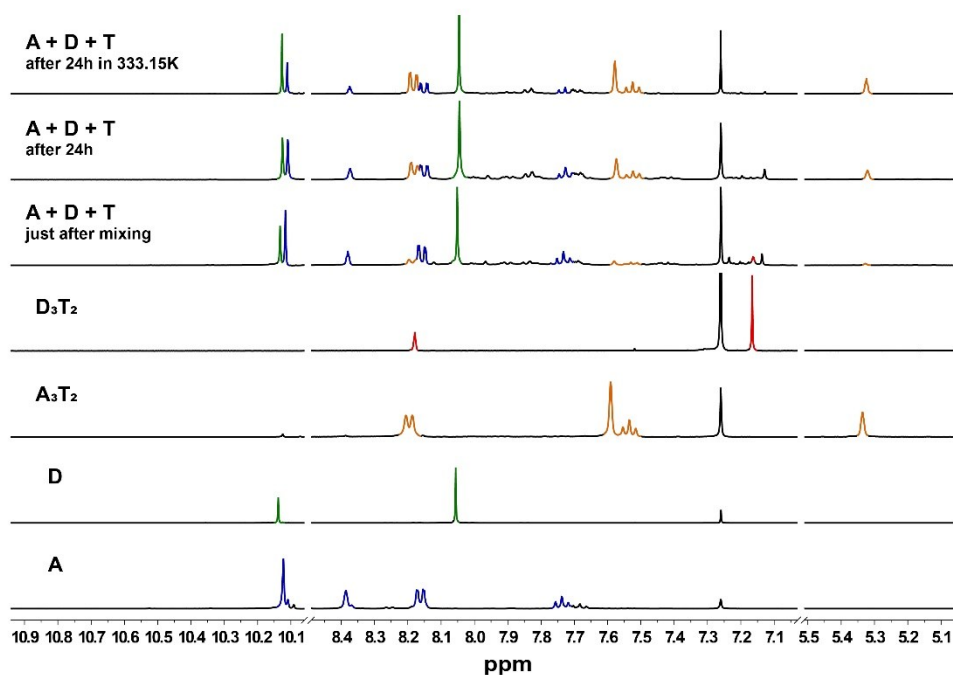


Figure S11. Comparison of ^1H NMR (400 MHz) spectra for self-sorting experiment **3A + 3D + 2T** depending on the time. The spectra of components and pure, isolated cages are also shown for comparison. All NMR spectra were recorded in CDCl_3 at room temperature.

1.3.4. Self-sorting experiment 3A + 3E + 2T

In a NMR tube, isophthalic dialdehyde (**A**) (3.57 mg; 0.0266 mmol) and 4-(4-formylphenoxy)benzaldehyde (**E**) (6.02 mg; 0.0266 mmol) were dissolved in 250 μL of deuterated chloroform (CDCl_3). Then a deuterated chloroform solution (300 μL) containing tris(2-aminoethyl)amine (**T**) (2.59 mg; 0.0177 mmol) was added in two portions. The resulting solution mixture was stirred at room temperature for 24h, then in 318.15 K for another 24h and then again for 24h in RT. The clear solution of library was checked by ^1H NMR spectroscopy (CDCl_3) just after mixing the components and after each 24h of stirring (RT/318.15 K/RT).

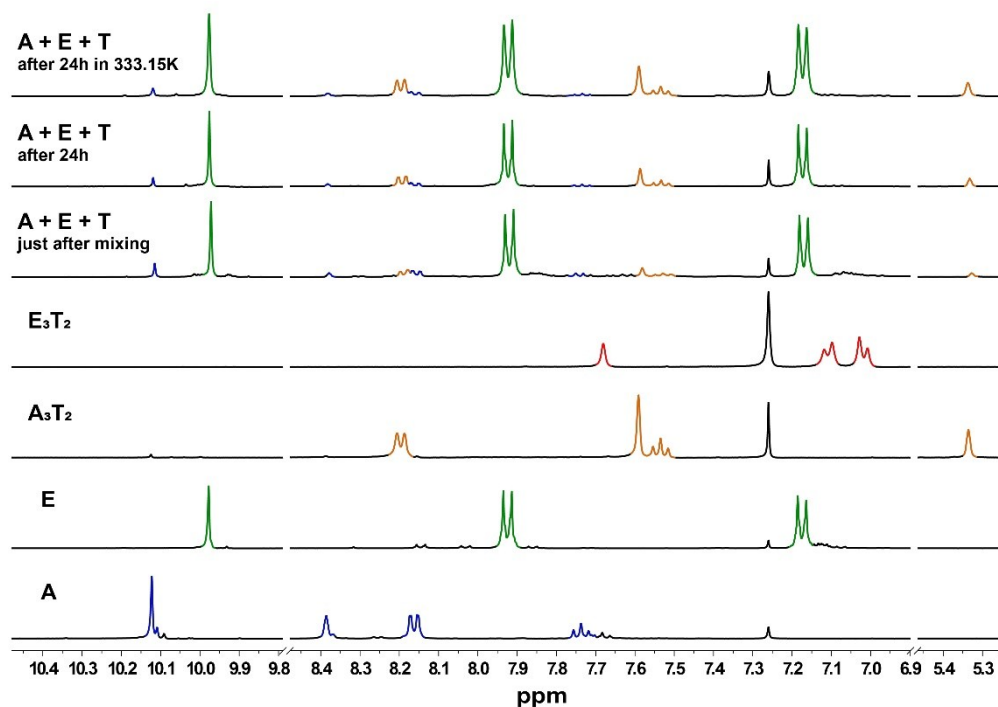


Figure S12. Comparison of ^1H NMR (400 MHz) spectra for self-sorting experiment **3A + 3E + 2T** depending on the time. The spectra of components and pure, isolated cages are also shown for comparison. All NMR spectra were recorded in CDCl_3 at room temperature.

1.3.5. Self-sorting experiment 3A + 3H + 2T

In a NMR tube, isophthalic dialdehyde (**A**) (0.86 mg; 0.0064 mmol) and 4,4'-((((oxybis(ethane-2,1-diy))bis(oxy))bis(ethane-2,1-diy))bis(oxy))dibenzaldehyde (**H**) (2.58 mg; 0.0064 mmol) were dissolved in 250 μL of deuterated chloroform (CDCl_3). Then a deuterated chloroform solution (300 μL) containing tris(2-aminoethyl)amine (**T**) (0.62 mg; 0.0043 mmol) was added in two portions. The resulting solution mixture was stirred at room temperature for 24h, then in 318.15 K for another 24h and then again for 24h at RT. The clear solution of library was checked by ^1H NMR spectroscopy (CDCl_3) just after mixing the components and after each 24h of stirring (RT/318.15 K/RT).

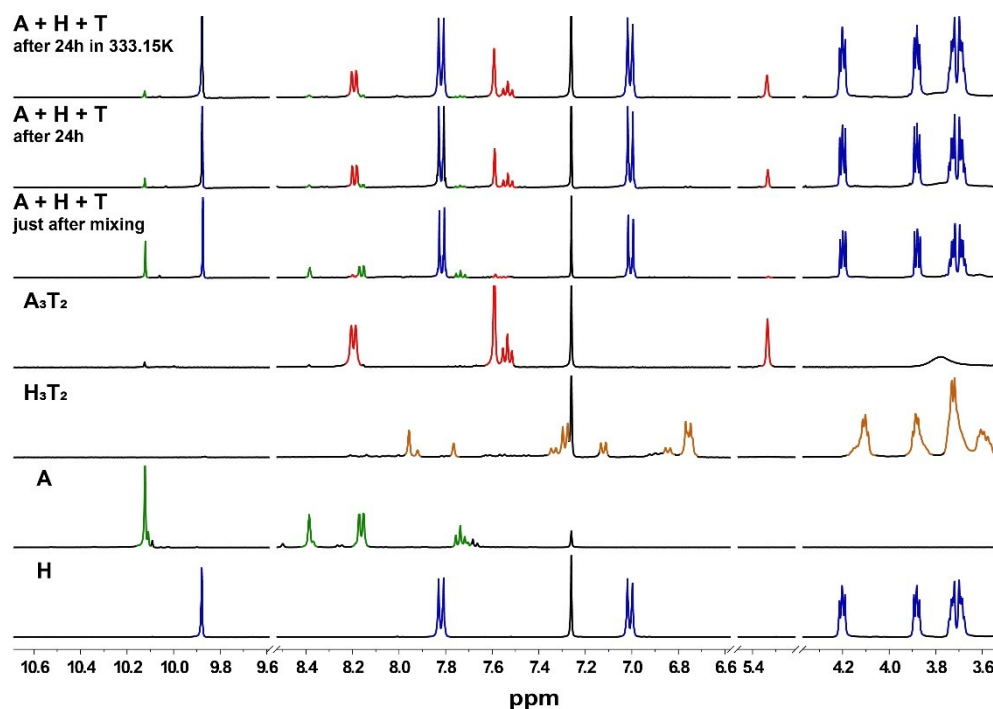


Figure S13. Comparison of ^1H NMR (400 MHz) spectra for self-sorting experiment **3A + 3H + 2T** depending on the time. The spectra of components and pure, isolated cages are also shown for comparison. All NMR spectra were recorded in CDCl_3 at room temperature.

1.3.6. Self-sorting experiment 3B + 3C + 2T

In a NMR tube, pyridine-2,6-dicarbaldehyde (**B**) (3.21 mg; 0.0238 mmol) and furan-2,5-dicarbaldehyde (**C**) (2.96 mg; 0.0238 mmol) were dissolved in 250 μL of deuterated chloroform (CDCl_3). Then a deuterated chloroform solution (300 μL) containing tris(2-aminoethyl)amine (**T**) (2.32 mg; 0.0159 mmol) was added in two portions. The resulting solution mixture was stirred at room temperature for 24h, then in 318.15 K for another 24h and then again for 24h in RT. The clear solution of library was checked by ^1H NMR spectroscopy (CDCl_3) just after mixing the components and after each 24h of stirring (RT/318.15 K/RT).

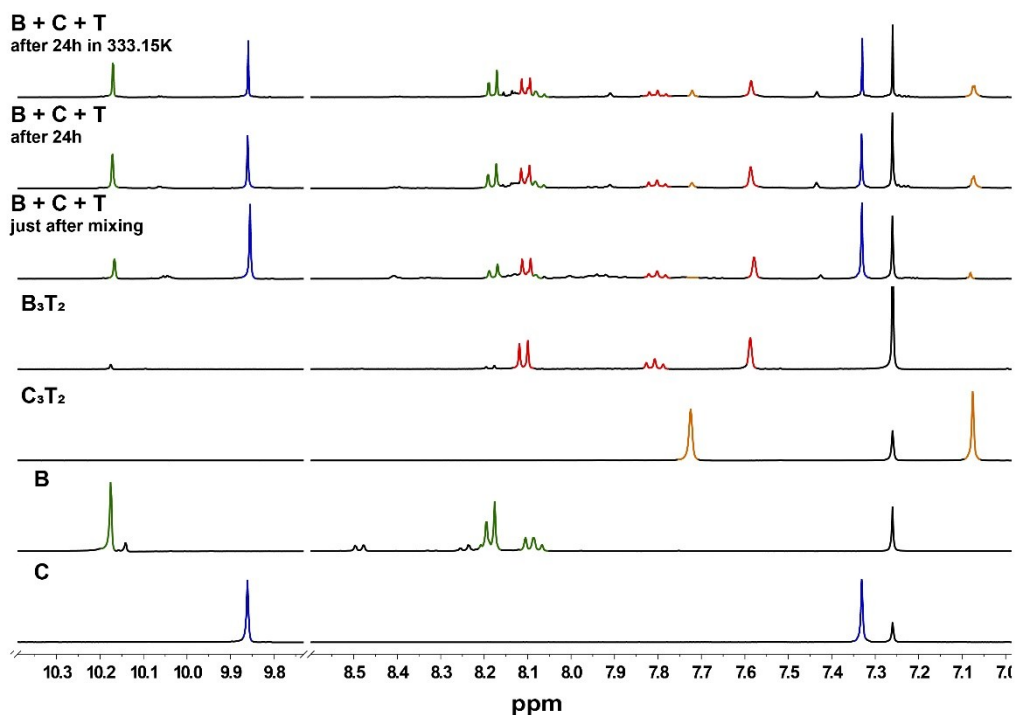


Figure S14. Comparison of ^1H NMR (400 MHz) spectra for self-sorting experiment **3B** + **3C** + **2T** depending on the time. The spectra of components and pure, isolated cages are also shown for comparison. All NMR spectra were recorded in CDCl_3 at room temperature.

1.3.7. Self-sorting experiment 3B + 3D + 2T

In a NMR tube, pyridine-2,6-dicarbaldehyde (**B**) (3.50 mg; 0.0259 mmol) and terephthalaldehyde (**D**) (3.47 mg; 0.0259 mmol) were dissolved in 250 μL of deuterated chloroform (CDCl_3). Then a deuterated chloroform solution (300 μL) containing tris(2-aminoethyl)amine (**T**) (2.52 mg; 0.0173 mmol) was added in two portions. The resulting solution mixture was stirred at room temperature for 24h, then in 318.15 K for another 24h and then again for 24h in RT. The clear solution of library was checked by ^1H NMR spectroscopy (CDCl_3) just after mixing the components and after each 24h of stirring (RT/318.15 K/RT).

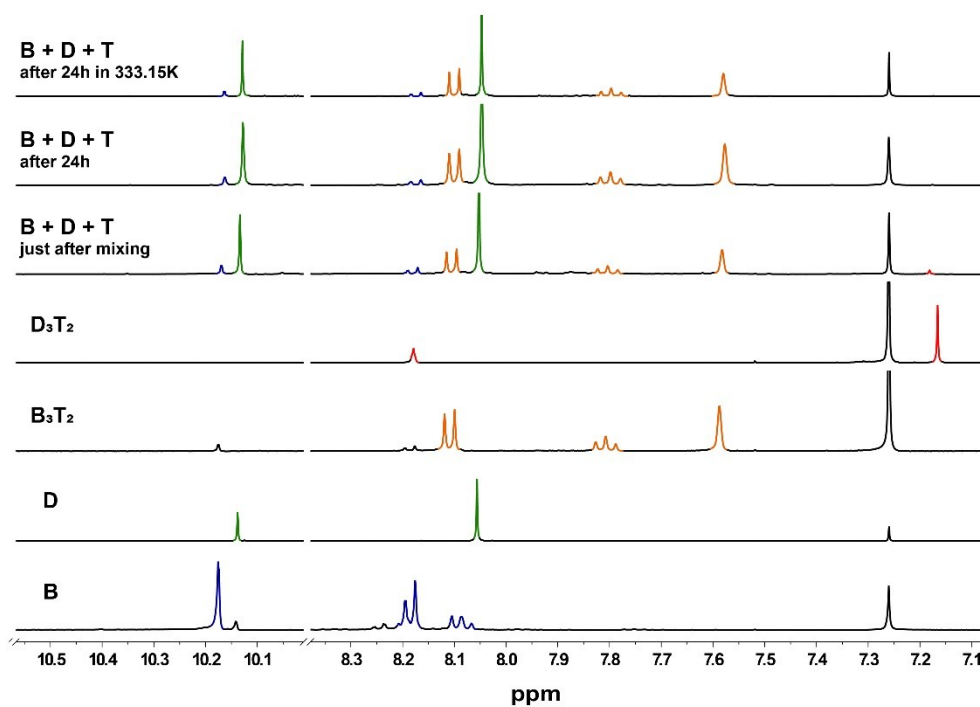


Figure S15. Comparison of ^1H NMR (400 MHz) spectra for self-sorting experiment **3B + 3D + 2T** depending on the time. The spectra of components and pure, isolated cages are also shown for comparison. All NMR spectra were recorded in CDCl_3 at room temperature.

1.3.8. Self-sorting experiment 3B + 3E + 2T

In a NMR tube, pyridine-2,6-dicarbaldehyde (**B**) (2.80 mg; 0.0207 mmol) and 4-(4-formylphenoxy)benzaldehyde (**E**) (4.68 mg; 0.0207 mmol) were dissolved in 250 μL of deuterated chloroform (CDCl_3). Then a deuterated chloroform solution (300 μL) containing tris(2-aminoethyl)amine (**T**) (2.02 mg; 0.0138 mmol) was added in two portions. The resulting solution mixture was stirred at room temperature for 24h, then in 318.15 K for another 24h and then again for 24h in RT. The clear solution of library was checked by ^1H NMR spectroscopy (CDCl_3) just after mixing the components and after each 24h of stirring (RT/318.15 K/RT).

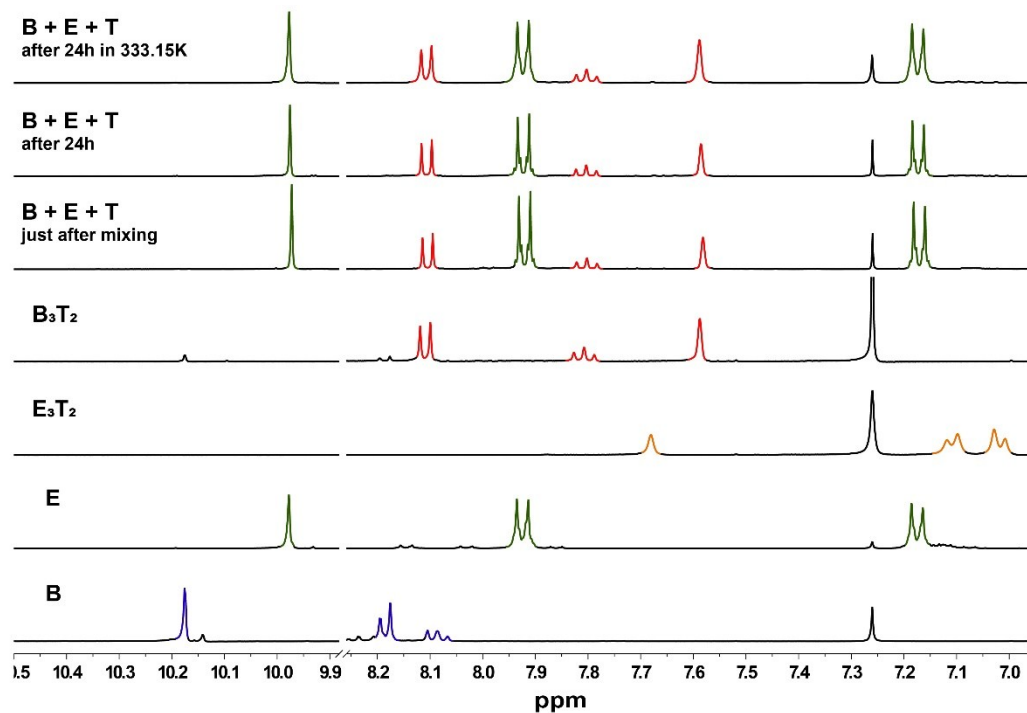


Figure S16. Comparison of ^1H NMR (400 MHz) spectra for self-sorting experiment **3B + 3E + 2T** depending on the time. The spectra of components and pure, isolated cages are also shown for comparison. All NMR spectra were recorded in CDCl_3 at room temperature.

1.3.9. Self-sorting experiment **3B** + **3H** + **2T**

In a NMR tube, pyridine-2,6-dicarbaldehyde (**B**) (1.21 mg; 0.0089 mmol) and 4,4'-((((oxybis(ethane-2,1-diy))bis(oxy))bis(ethane-2,1-diy))bis(oxy))dibenzaldehyde (**H**) (3.62 mg; 0.0089 mmol) were dissolved in 250 μL of deuterated chloroform (CDCl_3). Then a deuterated chloroform solution (300 μL) containing tris(2-aminoethyl)amine (**T**) (0.88 mg; 0.0059 mmol) was added in two portions. The resulting solution mixture was stirred at room temperature for 24h, then in 318.15 K for another 24h and then again for 24h in RT. The clear solution of library was checked by ^1H NMR spectroscopy (CDCl_3) just after mixing the components and after each 24h of stirring (RT/318.15 K/RT).

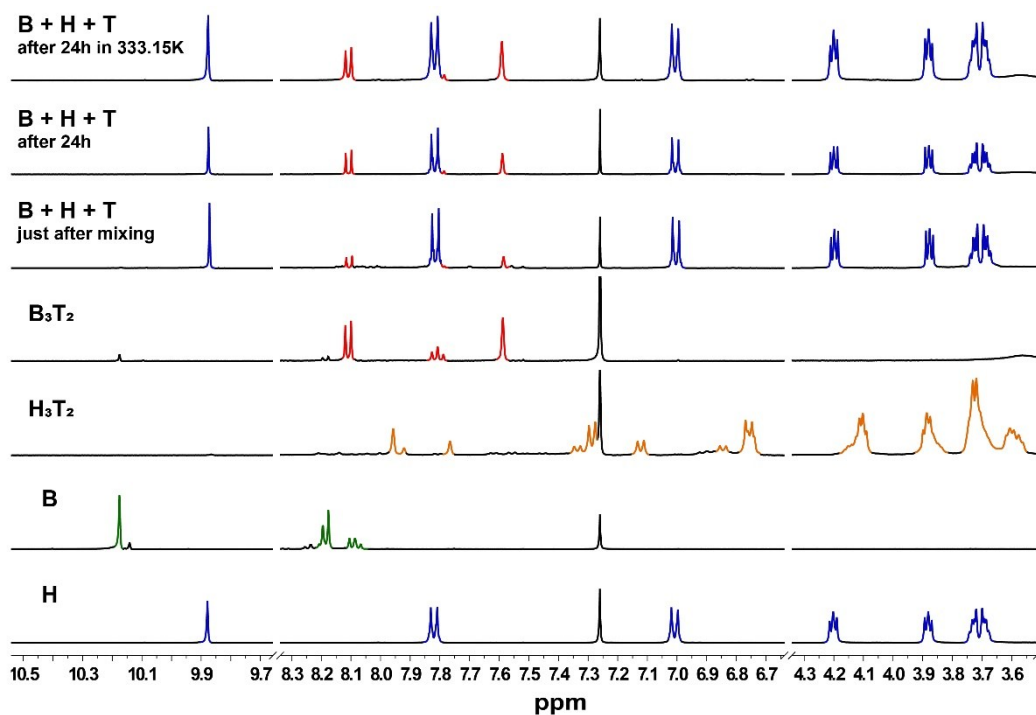


Figure S17. Comparison of ^1H NMR (400 MHz) spectra for self-sorting experiment **3B** + **3H** + **2T** depending on the time. The spectra of components and pure, isolated cages are also shown for comparison. All NMR spectra were recorded in CDCl_3 at room temperature.

1.3.10. Self-sorting experiment 3C + 3D + 2T

In a NMR tube, furan-2,5-dicarbaldehyde (**C**) (3.16 mg; 0.0255 mmol) and terephthalaldehyde (**D**) (3.42 mg; 0.0255 mmol) were dissolved in 250 μL of deuterated chloroform (CDCl_3). Then a deuterated chloroform solution (300 μL) containing tris(2-aminoethyl)amine (**T**) (2.49 mg; 0.0171 mmol) was added in two portions. The resulting solution mixture was stirred at room temperature for 24h, then in 318.15 K for another 24h and then again for 24h in RT. The clear solution of library was checked by ^1H NMR spectroscopy (CDCl_3) just after mixing the components and after each 24h of stirring (RT/318.15 K/RT).

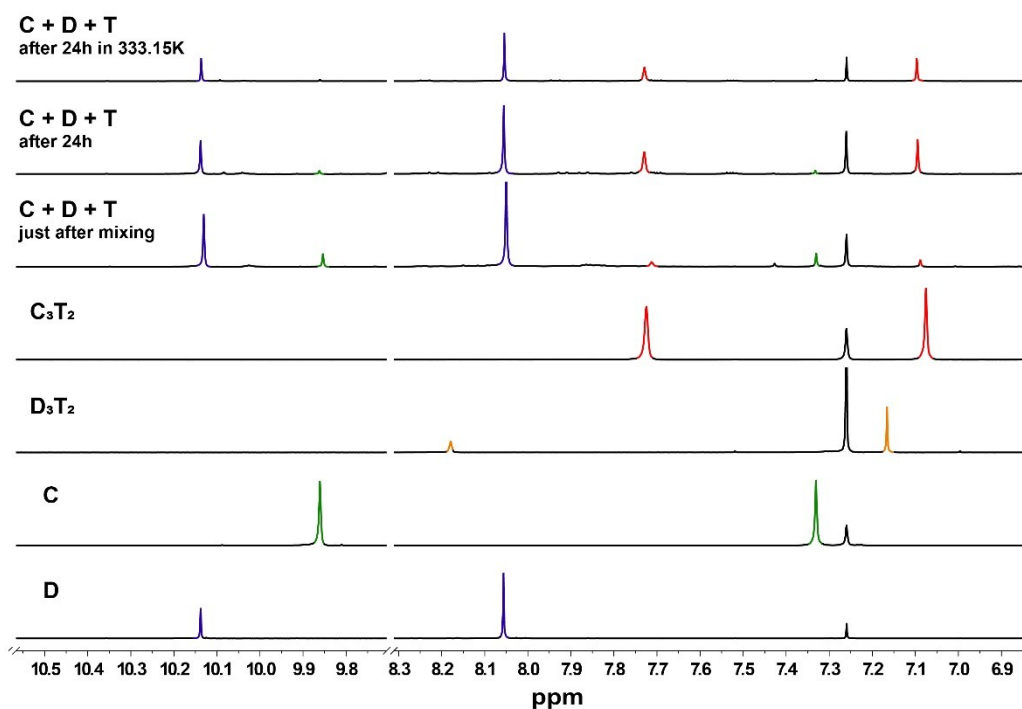


Figure S18. Comparison of ^1H NMR (400 MHz) spectra for self-sorting experiment **3C + 3D + 2T** depending on the time. The spectra of components and pure, isolated cages are also shown for comparison. All NMR spectra were recorded in CDCl_3 at room temperature.

1.3.11. Self-sorting experiment 3C + 3E + 2T

In a NMR tube, furan-2,5-dicarbaldehyde (**C**) (3.80 mg; 0.0306 mmol) and 4-(4-formylphenoxy)benzaldehyde (**E**) (6.92 mg; 0.0306 mmol) were dissolved in 250 μL of deuterated chloroform (CDCl_3). Then a deuterated chloroform solution (300 μL) containing tris(2-aminoethyl)amine (**T**) (2.98 mg; 0.0204 mmol) was added in two portions. The resulting solution mixture was stirred at room temperature for 24h, then in 318.15 K for another 24h and then again for 24h in RT. The clear solution of library was checked by ^1H NMR spectroscopy (CDCl_3) just after mixing the components and after each 24h of stirring (RT/318.15 K/RT).

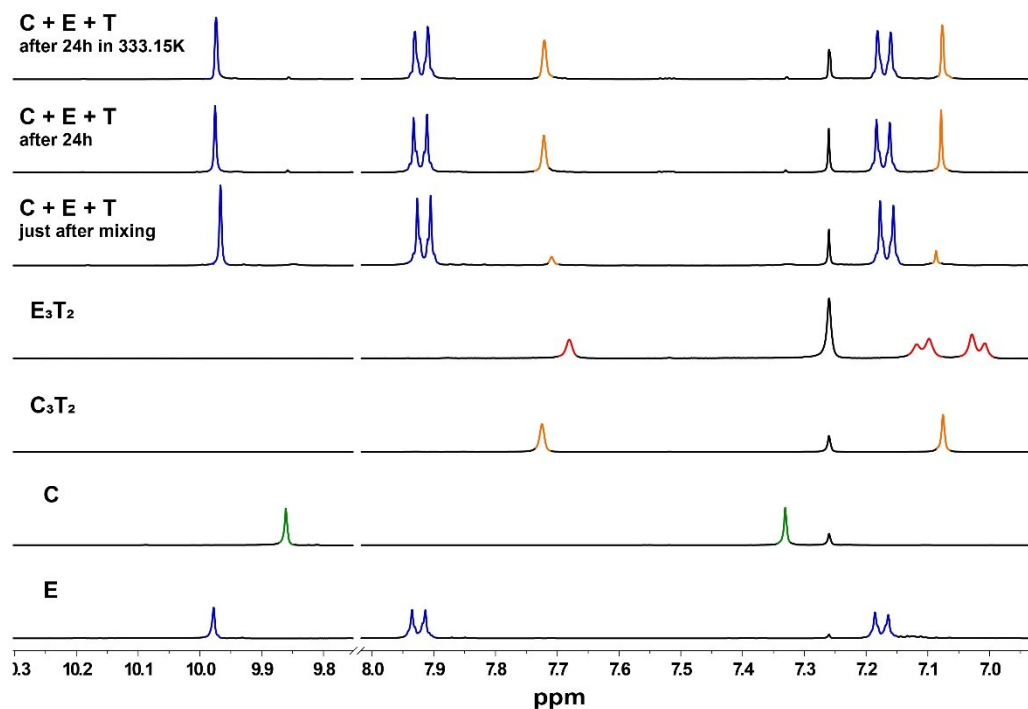


Figure S19. Comparison of ^1H NMR (400 MHz) spectra for self-sorting experiment **3C + 3E + 2T** depending on the time. The spectra of components and pure, isolated cages are also shown for comparison. All NMR spectra were recorded in CDCl_3 at room temperature.

1.3.12. Self-sorting experiment 3C + 3H + 2T

In a NMR tube, furan-2,5-dicarbaldehyde (**C**) (2.51 mg; 0.0202 mmol) and 4,4'-((((oxybis(ethane-2,1-diy))bis(oxy))bis(ethane-2,1-diy))bis(oxy))dibenzaldehyde (**H**) (8.17 mg; 0.0202 mmol) were dissolved in 250 μL of deuterated chloroform (CDCl_3). Then a deuterated chloroform solution (300 μL) containing tris(2-aminoethyl)amine (**T**) (1.97 mg; 0.0135 mmol) was added in two portions. The resulting solution mixture was stirred at room temperature for 24h, then in 318.15 K for another 24h and then again for 24h in RT. The clear solution of library was checked by ^1H NMR spectroscopy (CDCl_3) just after mixing the components and after each 24h of stirring (RT/318.15 K/RT).

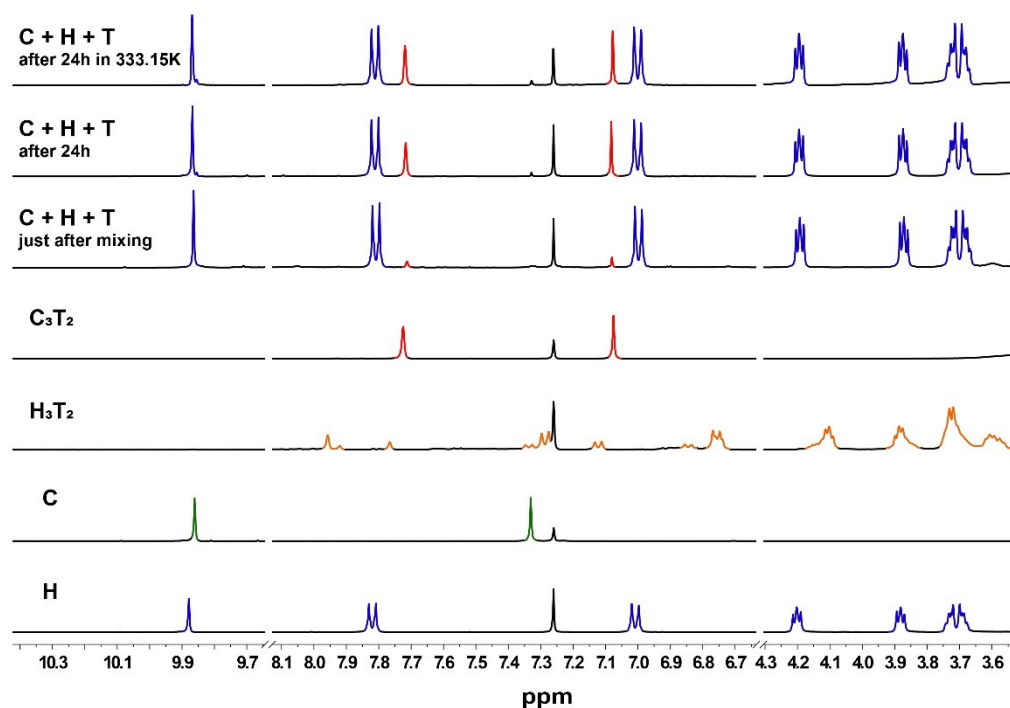


Figure S20. Comparison of ^1H NMR (400 MHz) spectra for self-sorting experiment **3C + 3H + 2T** depending on the time. The spectra of components and pure, isolated cages are also shown for comparison. All NMR spectra were recorded in CDCl_3 at room temperature.

1.3.13. Self-sorting experiment 3D + 3E + 2T

In a NMR tube, terephthalaldehyde (**D**) (1.91 mg; 0.0143 mmol) and 4-(4-formylphenoxy)benzaldehyde (**E**) (3.23 mg; 0.0143 mmol) were dissolved in 250 μL of deuterated chloroform (CDCl_3). Then a deuterated chloroform solution (300 μL) containing tris(2-aminoethyl)amine (**T**) (1.39 mg; 0.0095 mmol) was added in two portions. The resulting solution mixture was stirred at room temperature for 24h, then in 318.15 K for another 24h and then again for 24h in RT. The clear solution of library was checked by ^1H NMR spectroscopy (CDCl_3) just after mixing the components and after each 24h of stirring (RT/318.15 K/RT).

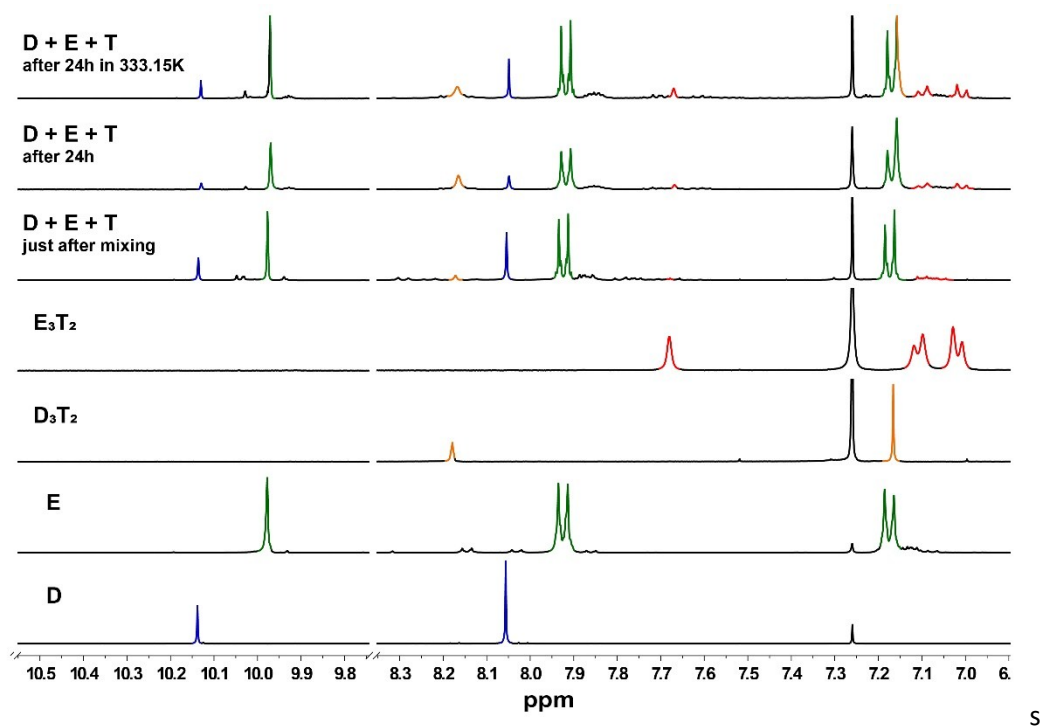


Figure S21. Comparison of ^1H NMR (400 MHz) spectra for self-sorting experiment **3D + 3E + 2T** depending on the time. The spectra of components and pure, isolated cages are also shown for comparison. All NMR spectra were recorded in CDCl_3 at room temperature.

1.3.14. Self-sorting experiment 3D + 3H + 2T

In a NMR tube, terephthalaldehyde (**D**) (0.95 mg; 0.0071 mmol) and 4,4'-(((oxybis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl))bis(oxy)dibenzaldehyde (**H**) (2.85 mg; 0.0071 mmol) were dissolved in 250 μL of deuterated chloroform (CDCl_3). Then a deuterated chloroform solution (300 μL) containing tris(2-aminoethyl)amine (**T**) (0.69 mg; 0.0047 mmol) was added in two portions. The resulting solution mixture was stirred at room temperature for 24h, then in 318.15 K for another 24h and then again for 24h in RT. The clear solution of library was checked by ^1H NMR spectroscopy (CDCl_3) just after mixing the components and after each 24h of stirring (RT/318.15 K/RT).

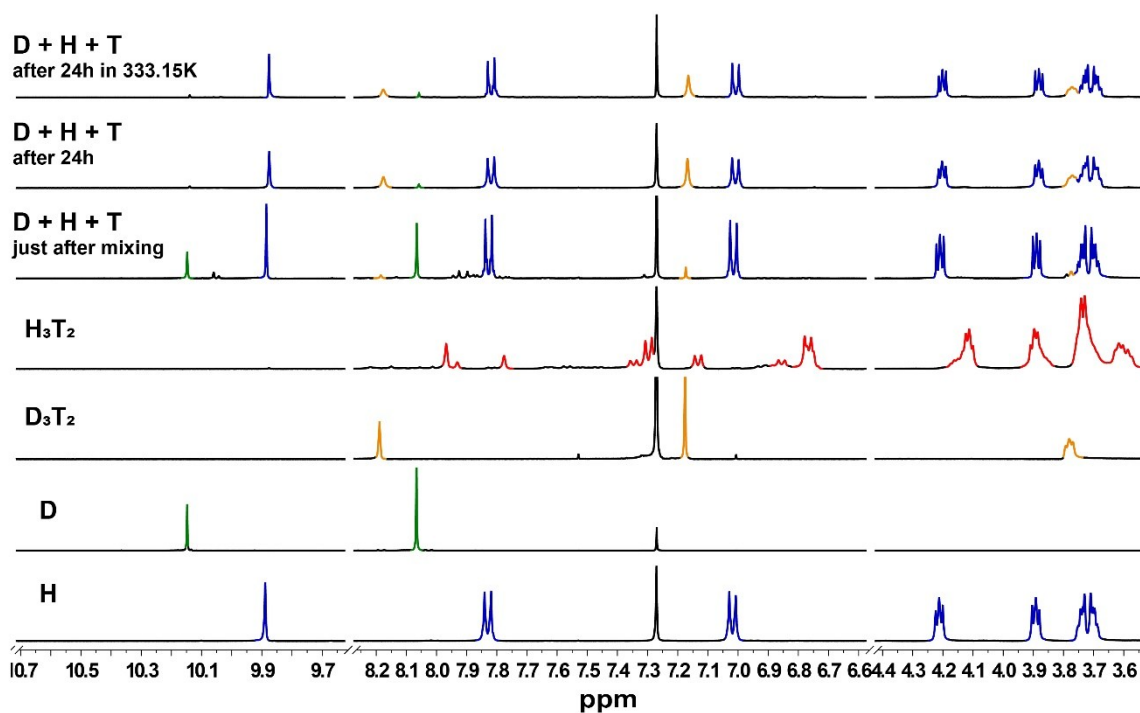


Figure S22. Comparison of ^1H NMR (400 MHz) spectra for self-sorting experiment **3D + 3H + 2T** depending on the time. The spectra of components and pure, isolated cages are also shown for comparison. All NMR spectra were recorded in CDCl_3 at room temperature.

1.3.15. Self-sorting experiment 3E + 3H + 2T

In a NMR tube, 4-(4-formylphenoxy)benzaldehyde (**E**) (1.35 mg; 0.0059 mmol) and 4,4'-((((oxybis(ethane-2,1-diy))bis(oxy))bis(ethane-2,1-diy))bis(oxy))dibenzaldehyde (**H**) (2.40 mg; 0.0059 mmol) were dissolved in 250 μL of deuterated chloroform (CDCl_3). Then a deuterated chloroform solution (300 μL) containing tris(2-aminoethyl)amine (**T**) (0.58 mg; 0.0039 mmol) was added in two portions. The resulting solution mixture was stirred at room temperature for 24h, then in 318.15 K for another 24h and then again for 24h in RT. The clear solution of library was checked by ^1H NMR spectroscopy (CDCl_3) just after mixing the components and after each 24h of stirring (RT/318.15 K/RT).

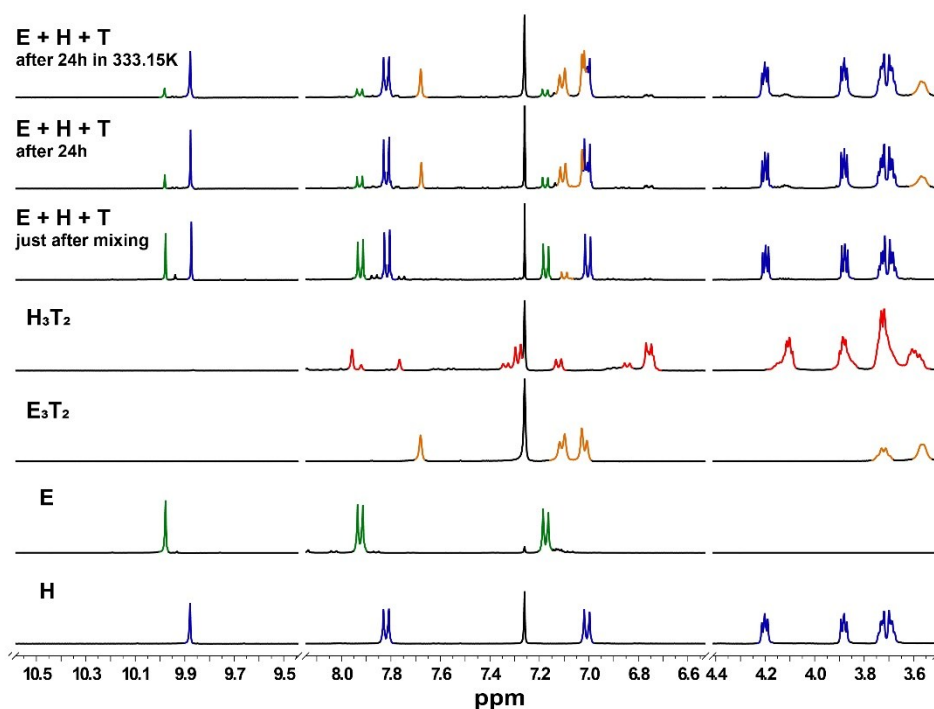


Figure S23. Comparison of ^1H NMR (400 MHz) spectra for self-sorting experiment **3E + 3H + 2T** depending on the time. The spectra of components and pure, isolated cages are also shown for comparison. All NMR spectra were recorded in CDCl_3 at room temperature.

1.4. Complex self-sorting experiments

1.4.1. Self-sorting experiment $3A + 3B + 3C + 3D + 3E + 3H + n2T$

In a NMR tube, isophthalic dialdehyde (**A**) (1.71 mg; 0.0127 mmol), pyridine-2,6-dicarbaldehyde (**B**) (1.72 mg; 0.0127 mmol), furan-2,5-dicarbaldehyde (**C**) (1.58 mg; 0.0127 mmol), terephthal aldehyde (**D**) (1.71 mg; 0.0127 mmol), 4-(4-formylphenoxy)benzaldehyde (**E**) (2.88 mg; 0.0127 mmol) and 4,4'-(((oxybis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl))bis(oxy)dibenzaldehyde (**H**) (5.12 mg; 0.0127 mmol) were dissolved in 450 μL of deuterated chloroform (CDCl_3). Then a titration was performed with deuterated chloroform stock solution containing tris(2-aminoethyl)amine (**T**) (1.24 mg; 0.0085 mmol). The resulting solution mixture was stirred at room temperature for 24h after addition of each portion. The clear solution of library was checked by ^1H NMR spectroscopy (CDCl_3) after mixing the components and after each 24h of stirring (RT/318.15 K/RT).

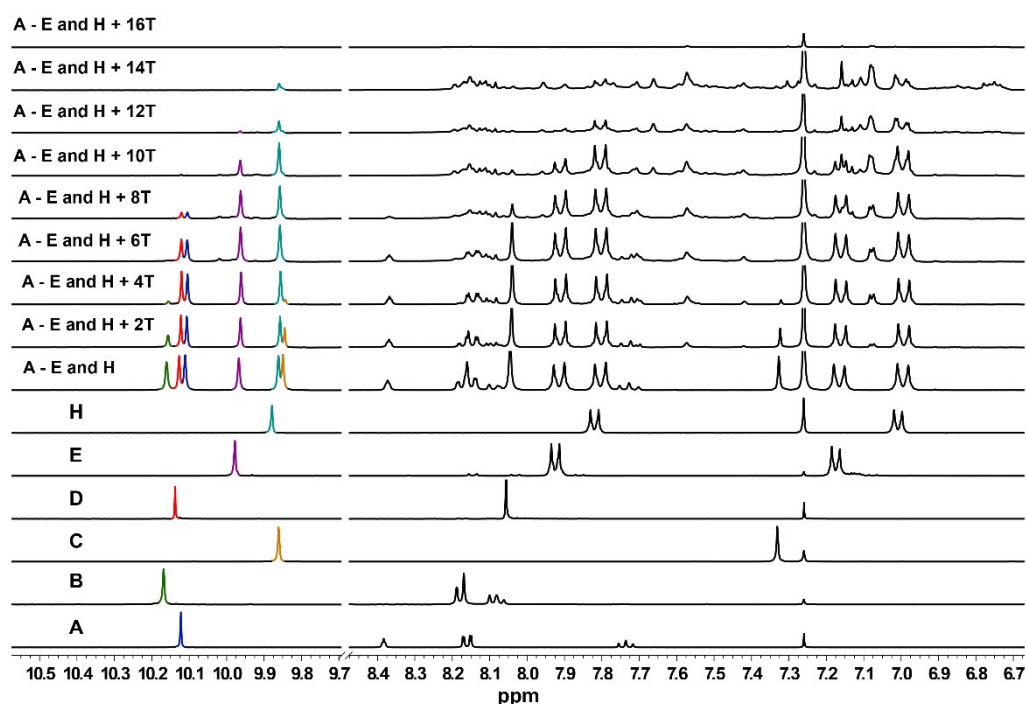


Figure S24. Comparison of ^1H NMR (400 MHz) spectra for self-sorting experiment involving titration of $3A + 3B + 3C + 3D + 3E + 3H$ with doses of $2T$. The spectra of components are also shown for comparison. All NMR spectra were recorded in CDCl_3 at room temperature.

1.4.2. Self-sorting experiment 3D + 3E + 3F + n2T

In a NMR tube, terephthal aldehyde (**D**) (2.99 mg; 0.0223 mmol), 4-(4-formylphenoxy)benzaldehyde (**E**) (5.04 mg; 0.0223 mmol) and 4,4'-biphenyldicarboxaldehyde (**F**) (4.68 mg; 0.0223 mmol) were dissolved in 450 μL of deuterated chloroform (CDCl_3). Then a titration was performed with deuterated chloroform stock solution containing tris(2-aminoethyl)amine (**T**) (2.17 mg; 0.0148 mmol). The resulting solution mixture was stirred at room temperature for 24h after addition of each portion. The clear solution of library was checked by ^1H NMR spectroscopy (CDCl_3) after mixing the components and after each 24h of stirring (RT/318.15 K/RT).

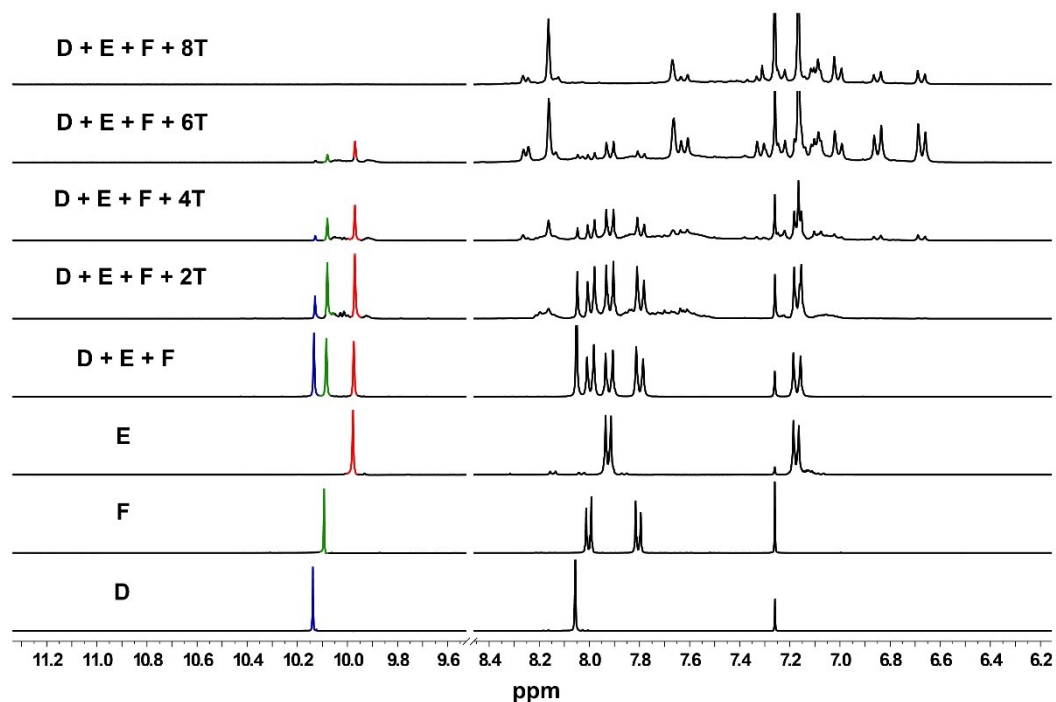


Figure S25. Comparison of ^1H NMR (400 MHz) spectra for self-sorting experiment involving titration of **3D** + **3E** + **3F** with doses of **2T**. The spectra of components are also shown for comparison. All NMR spectra were recorded in CDCl_3 at room temperature.

1.4.3. Self-sorting experiment **3B** + **3C** + **3G** + **n2T**

In a NMR tube, pyridine-2,6-dicarbaldehyde (**B**) (5.54 mg; 0.041 mmol), furan-2,5-dicarbaldehyde (**C**) (5.09 mg; 0.041 mmol) and 2,5-thiophenedicarbaldehyde (**G**) (5.75 mg; 0.041 mmol) were dissolved in 450 μL of deuterated chloroform (CDCl_3). Then a titration was performed with deuterated chloroform stock solution containing tris(2-aminoethyl)amine (**T**) (4.00 mg; 0.0273 mmol). The resulting solution mixture was stirred at room temperature for 24h after addition of each portion. The clear solution of library was checked by ^1H NMR spectroscopy (CDCl_3) after mixing the components and after each 24h of stirring (RT/318.15 K/RT).

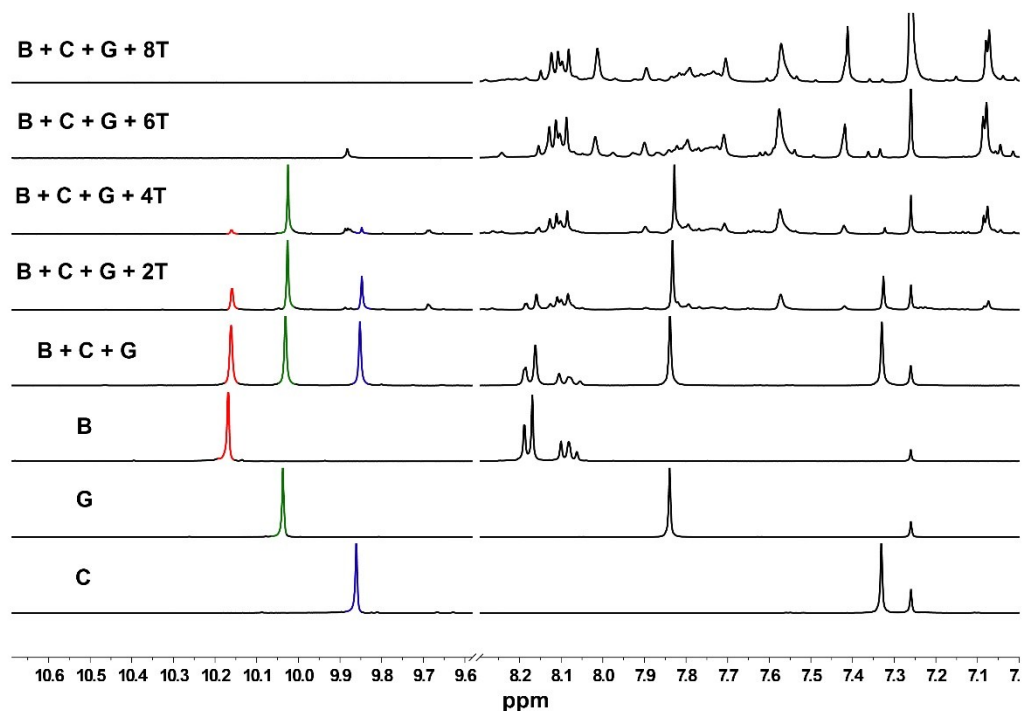


Figure S26. Comparison of ^1H NMR (400 MHz) spectra for self-sorting experiment involving titration of **3B** + **3C** + **3G** with doses of **2T**. The spectra of components are also shown for comparison. All NMR spectra were recorded in CDCl_3 at room temperature.

1.5. NMR spectra of an acid/base assisted equilibration

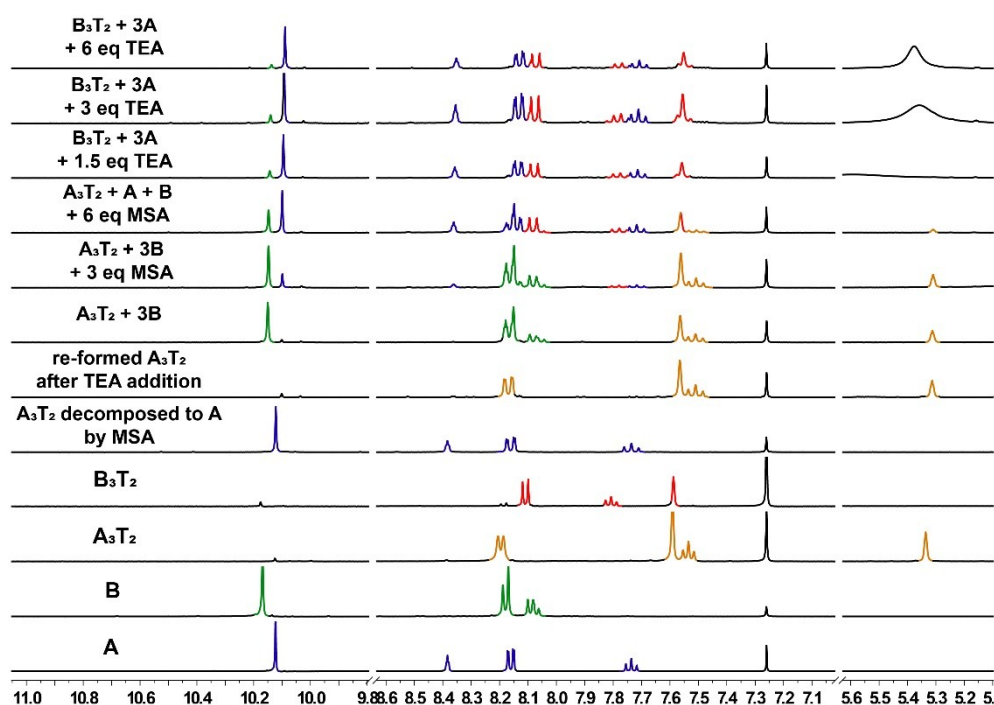


Figure S27. ¹H NMR (400 MHz) spectra of an acid/base (MSA/TEA) assisted equilibration experiment on $A_3T_2 + 3B \rightarrow 3A + B_3T_2$ system. Stacked with spectra of components A and B and isolated cages A_3T_2 and B_3T_2 . All NMR spectra were recorded at room temperature in $CDCl_3$

1.6. NMR spectra of an exchange experiment $A_3T_2 + 3B \rightarrow 3A + B_3T_2$

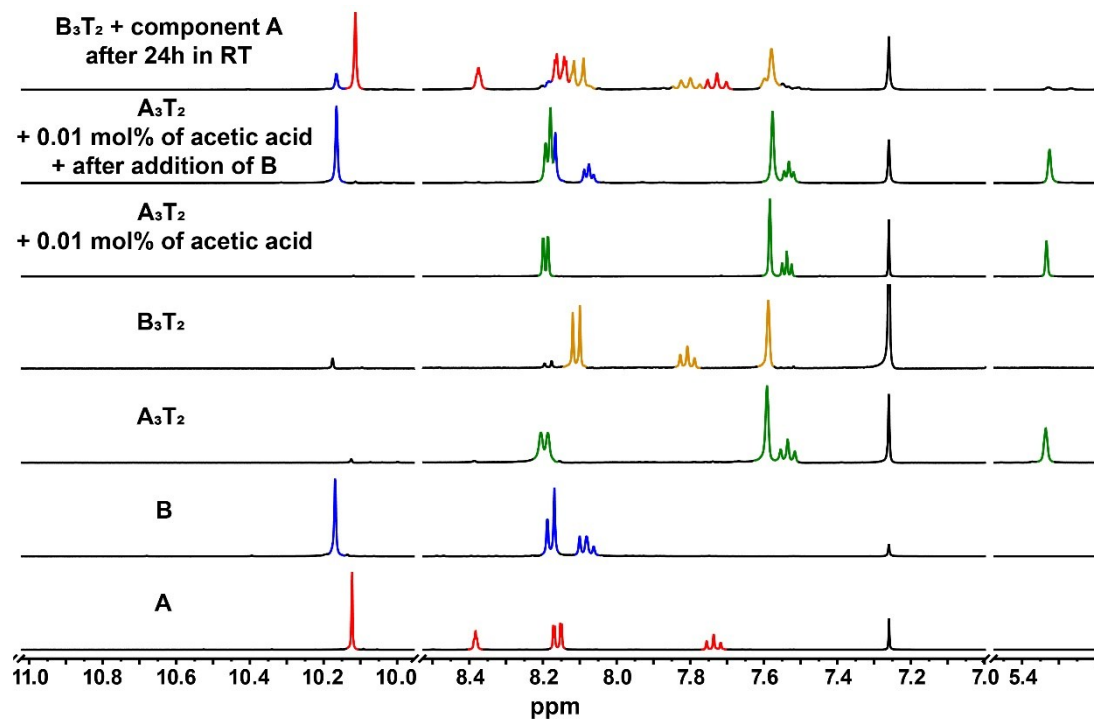


Figure S28. ¹H NMR (400 MHz) spectra of an exchange experiment $A_3T_2 + 3B \rightarrow 3A + B_3T_2$. Stacked with spectra of components A and B and isolated cages A_3T_2 and B_3T_2 . All NMR spectra were recorded at room temperature in $CDCl_3$

1.7. Schematic representation of a self-sorting experiment $3A + 3B + 2T$

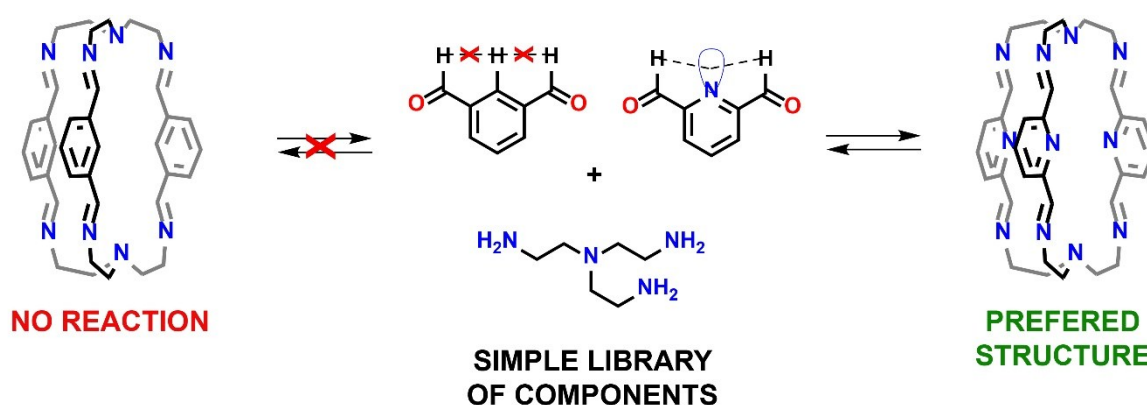


Figure S29. Schematic representation of a self-sorting experiment in a simple library composed of **3A** + **3B** + **2T**. Both dialdehydes (**A** and **B**) and their imines (**A₃T₂** and **B₃T₂**, respectively) contain a fully conjugated system of the aromatic ring and its substituents but only in **B** are attractive interactions possible between the two imine C-H bonds adjacent to the aromatic ring and the adjacent pyridine nitrogen atom of the another cage arm.³ A possible additional factor that works in favour of cage **B₃T₂** with respect to cage **A₃T₂** are intramolecular interactions that may occur between C-H bonds and the N lone pair. Both cages, however, are stabilized through intramolecular hydrogen bonding interactions between imine protons of one arm of the cage and imine nitrogen atom of another.³

2. Crystallography

Diffraction data were collected at room temperature using graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) with the ω -scan technique. For data reduction, UB-matrix determination and absorption correction CrysAlisPro software was used.

Using Olex2⁴, the structures were solved by direct methods using SHELXL⁵ and refined by full-matrix least-squares against F² utilizing SHELXL. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in idealized positions by molecular 3+3 geometry and refined as rigid groups. Uiso of hydrogen atoms were set as 1.2 (for C-carriers) and 1.5 (for O-carriers) times Ueq of the corresponding carrier atom. Crystal and refinement data are summarised in Table. The data have been deposited in the form of cifs with the Cambridge Crystallographic Data Centre (CCDC), deposition number CCDC 1853998 and 1853999. These can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

3. References

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