Supplementary Information for

Syntheses of Three-Dimensional Catenanes under Kinetic Control

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Section A. General Information

All commercially available reagents were used as received. Anhydrous MeCN, DMF, THF and CH$_2$Cl$_2$ were obtained using a solvent drying system. Analytical and preparative HPLC experiments were carried out using an Agilent 1260 Infinity system plus an Agilent C$_{18}$ 250 mm × 10 mm column. Both normal and reversed phase column chromatography were carried out using CombiFlash® Automation Systems. UV-Vis Absorption spectra were recorded in a conventional rectangular quartz cell (10 × 10 × 45 mm) on a UV-3600 Shimadzu spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance 500 and 600 MHz spectrometers, with working frequencies of 500 and 600 MHz for $^1$H, respectively, and 125 and 150 MHz for $^{13}$C nuclei, respectively. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents (CDCl$_3$: $\delta_H = 7.26$ and $\delta_C = 77.16$ ppm; CD$_3$OD: $\delta_H = 3.31$ and $\delta_C = 49.0$ ppm). Abbreviations are used in the description of NMR spectroscopic data as follows: chemical shift ($\delta$, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, td = triplet of doublets), coupling constant ($J$, Hz). High-resolution mass spectra (HRMS) were measured on an Agilent 6210 Time of Flight LC/MS system or on an Agilent 6545 LC/Q-TOF mass spectrometer. Single-crystal X-ray diffraction (SCXRD) data were collected on a XtaLAB Synergy R, DW system, HyPix diffractometer.
Section B. Synthetic Protocols

1. Synthesis of 2,4,6-tris-[4-(4-pyridylmethyl)phenyl]-1,3,5-triazine / TPPT

**Figure S1. Synthesis of TPPT**

**TPPT:** The synthesis of **TPPT** was conducted according to a reported procedure\textsuperscript{S1} with slight modifications\textsuperscript{S2}. Briefly, 

\[
\text{TMPZnCl•LiCl (1.0 M in THF, 22.5 mL, 22.5 mmol, 15.0 eq.) was added to a solution of 4-picoline (1.46 mL, 15.0 mmol, 10.0 eq.) in anhydrous THF (10 mL) charged with N}_2\text{ at 25 ℃. The reaction mixture was then stirred at this temperature for 2 h. Pd(PPh}_3)_4 (520 mg, 0.45 mmol, 30% mol), 2,4,6-tris-(4-bromophenyl)-1,3,5-triazine (820 mg, 1.5 mmol, 1.0 eq.) and anhydrous 1,4-dioxane (35 mL) was added to this reaction mixture. The resulting mixture which was degassed by bubbling N}_2\text{ for 20 min, was heated to 100 ℃ and stirred for 3 days before being quenched by the addition of H}_2\text{O (100 mL) and ethylenediamine (5 mL). After stirring for an additional 30 min, the solution was extracted with CHCl}_3 (3 \times 100 mL) and dried (Na}_2\text{SO}_4). The concentrated residue was subjected to normal phase column chromatography with CHCl}_3 / MeOH (20 / 1, v/v) as the eluent, affording pure **TPPT** (402 mg, 46% yield) as a slightly yellow solid. \textsuperscript{1}H NMR (500 MHz, CDCl}_3, 298 K) \delta_H = 8.70 (d, \textit{J} = 7.7 Hz, 6H), 8.54 (d, \textit{J} = 4.6 Hz, 6H), 7.38 (d, \textit{J} = 7.7 Hz, 6H), 7.20 (d, \textit{J} = 4.5 Hz, 6H), 4.12 (s, 6H).\]
2. Synthesis of 2,4,6-tris-(4-bromomethyl-phenyl)-1,3,5-triazine / TBPT

**Figure S2.** Synthesis of TBPT

TBPT$^{33}$: Trifluoromethanesulfonic acid (4.5 mL, 51.0 mmol, 2.5 eq.) was added to an ice-bath cooled 50 mL flask, followed by the addition of 4-bromomethyl-benzonitrile (4.0 g, 20.4 mmol, 1.0 eq.) in three portions. After 5 min, the reaction mixture was warmed to room temperature and stirred under N$_2$ atmosphere for 24 h. Next, it was quenched by adding ammonium hydroxide (10% in H$_2$O, 50 mL) at 0 °C. The precipitate which formed was collected by filtration, washed with H$_2$O / Me$_2$CO and dried *in vacuo* to afford TBPT (3.4 g, 85% yield) as a white solid. $^1$H NMR (500 MHz, CDCl$_3$, 298 K) $\delta_H = 8.72$ (d, $J = 8.3$ Hz, 6H), 7.59 (d, $J = 8.3$ Hz, 6H), 4.59 (s, 6H).
3. Syntheses of 1•3CF₃CO₂ / 2•6CF₃CO₂ / 3•6CF₃CO₂

Table S1. Optimization of reaction conditions

![Chemical structures]

| Entry | Conditions | Product Yields[¹] / % |
|-------|------------|-----------------------|
|       | Solvent    | Temp. / °C | Time / d | 1•3CF₃CO₂ | 2•6CF₃CO₂ | 3•6CF₃CO₂ |
| 1     | DMF        | 50         | 3        | Trace     | Trace     | Trace     |
| 2     | MeCN       | 50         | 3        | 32        | 3         | 4         |
| 3     | MeCN       | 80         | 3        | 36        | 20        | 11        |
| 4     | MeCN / CHCl₃ (10 / 1) | 80 | 3        | 40        | 9         | 8         |
| 5[²]  | Acetylacetone | 80 | 3        | 48        | 5         | Trace     |
| 6     | MeCN       | 80         | 5        | 36        | 20        | 12        |
| 7[³]  | MeCN       | 80         | 5        | 41[⁴]     | 23[⁴]     | 13[⁴]     |

[¹] Calculated by HPLC unless otherwise noted
[²] The relative polarity of acetylacetone is higher than that of MeCN.
[³] 1.25 equiv of TBPT was used in this entry.
[⁴] Isolated yields
1•3CF₃CO₂ / 2•6CF₃CO₂ / 3•6CF₃CO₂: A catalytic amount of tetrabutylammonium iodide / TBAI (2.5 mg, 6.9 μmol, 0.2 eq.) was added to a suspension of TPPT (20.0 mg, 34.3 μmol, 1.0 eq.) and TBPT (25.0 mg, 42.9 μmol, 1.25 eq.) in anhydrous MeCN (40 mL) charged with N₂. The reaction mixture was heated at 80 °C and stirred for 5 days. After evaporation to remove all the solvent, trifluoroacetic acid / TFA (2 mL) and MeOH (10 mL) were added and stirred for an additional 30 min. The concentrated residue was loaded onto a CombiFlash® chromatography system and purified by C₁₈ reversed-phase column using a mixture of 0.1% v/v TFA in H₂O and 0.1% v/v TFA in MeCN. Fractions containing the product were combined and concentrated. The crude product was then subjected to purification on a preparative reversed-phase HPLC system with H₂O / MeCN (67 / 33, v/v, both contain 0.1% v/v TFA) as the eluent, affording 1•3CF₃CO₂ (17.9 mg, 41% yield), 2•6CF₃CO₂ (10.0 mg, 23% yield) and 3•6CF₃CO₂ (5.7 mg, 13% yield) as white solids.

1•3CF₃CO₂: ¹H NMR (500 MHz, CD₃OD, 298 K) δ_H = 9.07 (d, J = 6.8 Hz, 6H, H-d), 8.58 (d, J = 7.6 Hz, 6H, H-a), 8.46 (d, J = 7.5 Hz, 6H, H-h), 8.12 (d, J = 6.8 Hz, 6H, H-e), 7.74 (d, J = 8.3 Hz, 6H, H-b), 7.50 (d, J = 8.2 Hz, 6H, H-g), 5.81 (s, 6H, H-c), 4.32 (s, 6H, H-f). ¹³C NMR (125 MHz, CD₃OD, 298 K) δ_C = 172.0 (C-15), 171.9 (C-1), 164.2 (C-9), 145.2 (C-7), 144.2 (C-11), 140.1 (C-5), 138.8 (C-2), 136.6 (C-14), 131.3 (C-3), 131.0 (C-13), 130.2 (C-4), 129.8 (C-12), 129.5 (C-8), 65.3 (C-6), 42.7(C-10). ESI-HRMS Calcd for 1•3CF₃CO₂: C₆₅H₄₈F₃N₉O₂²⁺: m/z = 521.6936 [M – 2CF₃CO₂]²⁺, found: 521.6936 [M – 2CF₃CO₂]²⁺; C₆₅H₄₈N₉³⁺: m/z = 310.1339 [M – 3CF₃CO₂]³⁺, found: 310.1344 [M – 3CF₃CO₂]³⁺.

2•6CF₃CO₂: ¹H NMR (500 MHz, CD₃OD, 298 K) δ_H = 9.62 (d, J = 7.1 Hz, 12H, H-d), 8.49 (d, J = 7.1 Hz, 12H, H-e), 7.47 (d, J = 8.2 Hz, 12H, H-h), 7.40 (d, J = 8.1 Hz, 12H, H-b), 7.29 (d, J =
8.1 Hz, 12H, H-g), 6.08 (s, 12H, H-c), 5.97 (d, J = 8.1 Hz, 12H, H-a), 4.37 (s, 12H, H-f). 13C NMR (125 MHz, CD3OD, 298 K) δC = 172.1 (C-15), 169.0 (C-1), 165.5 (C-9), 161.9 (CF3CO2), 161.6 (CF3CO2), 161.3 (CF3CO2), 161.0 (CF3CO2), 145.5 (C-7), 145.1 (C-11), 141.5 (C-5), 135.7 (C-2), 135.1 (C-14), 130.9 (C-3), 130.8 (C-13), 129.6 (C-8), 129.0 (C-12), 128.4 (C-4), 121.0 (CF3CO2), 118.7 (CF3CO2), 116.4 (CF3CO2), 114.1 (CF3CO2), 65.3 (C-6), 43.2 (C-10). ESI-HRMS Calcd for 2•6CF3CO2: C134H96F12N18O82+; m/z = 1156.3728 [M – 2CF3CO2]2+, found: 1156.3734 [M – 2CF3CO2]2+. C132H96F9N18O63+: m/z = 733.2533 [M – 3CF3CO2]3+, found: 733.2537 [M – 3CF3CO2]3+.

3•6CF3CO2: 1H NMR (500 MHz, CD3OD, 298 K) δH = 9.62 (d, J = 7.1 Hz, 6H, H-d'), 9.46 (d, J = 7.0 Hz, 6H, H-d), 8.69 (d, J = 7.0 Hz, 6H, H-e), 8.52 (d, J = 7.1 Hz, 6H, H-e'), 7.66 (d, J = 8.3 Hz, 6H, H-a), 7.58 (d, J = 8.1 Hz, 6H, H-b), 7.55 (d, J = 8.1 Hz, 6H, H-h'), 7.42 (d, J = 8.1 Hz, 6H, H-h'), 7.32 (d, J = 8.1 Hz, 6H, H-g'), 7.13 (d, J = 8.1 Hz, 6H, H-g), 6.09 (s, 6H, H-c'), 6.00 (d, J = 8.1 Hz, 6H, H-c'a'), 5.91 (d, J = 8.1 Hz, 6H, H-h), 5.89 (s, 6H, H-c), 4.59 (s, 6H, H-f), 4.39 (s, 6H, H-f'). 13C NMR (125 MHz, CD3OD, 298 K) δC = 170.7 (C-1 / C-15'), 170.6 (C-1 / C-15'), 169.1 (C-1' / C-15), 169.0 (C-1' / C-15), 165.6 (C-9' / C-9), 165.5 (C-9' / C-9), 145.5 (C-7), 145.4 (C-7'), 145.3 (C-11), 144.8 (C-11'), 141.4 (C-5'), 141.0 (C-5'), 137.0 (C-2), 135.7 (C-2'), 135.2 (C-14'), 133.9 (C-14), 131.0 (C-3), 130.9 (C-13'), 130.80 (C-3'), 130.78 (C-13), 129.63 (C-8), 129.60 (C-8'), 129.3 (C-4), 128.9 (C-12'), 128.5 (C-4'), 128.0 (C-12), 65.5 (C-6), 65.3 (C-6'), 43.1 (C-10'), 43.0 (C-10). ESI-HRMS Calcd for 3•6CF3CO2: C134H96F12N18O82+: m/z = 1156.3728 [M – 2CF3CO2]2+, found: 1156.3733 [M – 2CF3CO2]2+. C132H96F9N18O63+: m/z = 733.2533 [M – 3CF3CO2]3+, found: 733.2542 [M – 3CF3CO2]3+. 

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Section C. X-Ray Crystallography

1. Crystallographic analysis of 1•3PF₆

(a) Method: 1•3PF₆ was obtained by counterion exchange of 1•3CF₃CO₂ with NH₄PF₆ in a mixture of MeOH and H₂O. Single crystals were obtained by slow diffusion of Et₂O into a MeCN solution of 1•3PF₆ at 298 K during 2 days. A suitable crystal was selected, and the crystal was mounted on a MITIGEN holder with Paratone oil on a XtaLAB Synergy, Single source at offset/far, HyPix diffractometer. The crystal was kept at 100.2(6) K during the data collection. Employing Olex2⁴, the structure was solved with the ShelXT⁵ structure solution program using Intrinsic Phasing and refined with the XL⁶ refinement package using Least Squares minimization.

(b) Crystal parameters: Empirical formula = C₆₇H₅₄F₁₈N₁₁P₃, formula weight = 1448.12, monoclinic, space group I2/m (no. 12), a = 22.3934(6), b = 18.0518(4), c = 48.2663(14) Å, β = 102.107(3)°, V = 19077.2(9) Å³, Z = 8, T = 100.2(6) K, μ(MoKα) = 0.133 mm⁻¹, Dcalc = 1.008 g/mm³, 94128 reflections measured (4.216 ≤ 2θ ≤ 50.052), 17441 unique (Rint = 0.0752, Rsigma = 0.0533) which were used in all calculations. The final R₁ was 0.1599 (I > 2σ(I)) and wR₂ was 0.4643 (all data). CCDC number 2114507.

(c) Refinement details: Distance restraints were imposed on the disordered PF₆⁻ counterions. The enhanced rigid-bond restraint⁷ (SHELX keyword RIGU) was applied globally. Restraints on similar amplitudes separated by less than 1.7 Å were imposed on the disordered PF₆⁻ counterions.

(d) Solvent treatment details: The solvent masking procedure as implemented in Olex2 was used to remove the electronic contribution of solvent molecules from the refinement. As the exact solvent content is not known, only the atoms used in the refinement model are reported in the formula here. Total solvent accessible volume / cell = 6932.2 Å³ [36.3%), total electron count / cell = 2202.1.
**Figure S3.** X-Ray single-crystal structure of the monomeric cage 1•3PF₆. The cage is shown in royal blue. (A) Perspective view as a stick representation. (B) Perspective view as a stick representation with the corresponding semitransparent space-filling representation superimposed upon it. (C) Side-on view as a stick representation showing the distance (7.0 Å) between the two platforms. (D) Side-on view as a stick representation with the corresponding semitransparent space-filling representation superimposed upon it. (E) Plan view as a stick representation showing the “dihedral angle”. (F) Plan view as a stick representation with the corresponding semitransparent space-filling representation superimposed upon it. Irrelevant protons, PF₆⁻ counterions and solvent molecules are omitted for the sake of clarity.
2. Crystallographic analysis of 2•6CF₃CO₂

(a) **Method**: Single crystals, suitable for X-ray crystallography, were obtained by slow diffusion of iPr₂O into a MeOH solution of 2•6CF₃CO₂ at 252 K during 7 days. A suitable crystal was selected, and the crystal was mounted on a MITIGEN holder with Paratone oil on a XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at 100.01(10) K during the data collection. Employing Olex₂⁵⁴, the structure was solved with the ShelXT⁵⁵ structure solution program using Intrinsic Phasing and refined with the XL⁵⁶ refinement package using Least Squares minimization.

(b) **Crystal parameters**: Empirical formula = C₇₀H₅₃F₉N₉O₈, formula weight = 1319.21, monoclinic, space group P2₁/n (no. 14), a = 17.0044(9), b = 21.2482(18), c = 19.5071(13) Å, β = 95.204(5)°, V = 7019.1(8) Å³, Z = 4, T = 100.01(10) K, μ(CuKα) = 0.843 mm⁻¹, Dcalc = 1.248 g/mm³, 38589 reflections measured (6.164 ≤ 2Θ ≤ 117.86), 10061 unique (Rint = 0.1254, Rsigma = 0.1010) which were used in all calculations. The final R₁ was 0.1181 (I > 2σ(I)) and wR₂ was 0.3635 (all data). CCDC number 2114508.

(c) **Refinement details**: The enhanced rigid-bond restraint⁵⁷ (SHELX keyword RIGU) was applied on the C64-O2 and the disordered CF₃CO₂⁻ counterions. Distance restraints were also imposed on disordered CF₃CO₂⁻ counterions.

(d) **Solvent treatment details**: The solvent masking procedure as implemented in Olex2 was used to remove the electronic contribution of solvent molecules from the refinement. As the exact solvent content is not known, only the atoms used in the refinement model are reported in the formula here. Total solvent accessible volume / cell = 1091.8 Å³[15.6%], total electron count / cell = 281.8.
Figure S4. X-Ray single-crystal structure of 3D catenane 2•6CF₃CO₂. The two interlocked identical cages are shown in royal blue and pale blue. (A) Perspective view as a stick representation. (B) Perspective view as a stick representation with the corresponding semitransparent space-filling representation superimposed upon it. (C) Side-on view as a stick representation showing the plane-to-plane distances between two adjacent platforms. (D) Side-on view as a stick representation with the corresponding semitransparent space-filling representation superimposed upon it. (E) Plan view as a stick representation showing the “dihedral angles”. (F) Plan view as a stick representation with the corresponding semitransparent space-filling representation superimposed upon it. Irrelevant protons, CF₃CO₂⁻ counterions and solvent molecules are omitted for the sake of clarity.
3. Crystallographic analysis of 3•6CF₃CO₂

(a) Method: Single crystals, suitable for X-ray crystallography, were obtained by slow diffusion of iPr₂O into a MeOH solution of 3•6CF₃CO₂ at 298 K during 5 days. A suitable crystal was selected, and the crystal was mounted on a MITIGEN holder with Paratone oil on a XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at 100.01(10) K during the data collection. Employing Olex2⁵⁴, the structure was solved with the ShelXT⁵⁵ structure solution program using Intrinsic Phasing and refined with the XL⁵⁶ refinement package using Least Squares minimization.

(b) Crystal parameters: Empirical formula = C₆₃H₄₈N₉, formula weight = 931.10, monoclinic, space group C2/c (no. 15), a = 30.7366(15), b = 18.2288(8), c = 25.4634(8) Å, β = 104.092(4)°, V = 13837.6(10) Å³, Z = 8, T = 100.00(10) K, μ(CuKα) = 0.419 mm⁻¹, Dcalc = 0.894 g/mm³, 51818 reflections measured (5.682 ≤ 2Θ ≤ 146.284), 13365 unique (Rint = 0.0527, Rsigma = 0.0474) which were used in all calculations. The final R₁ was 0.1225 (I > 2σ(I)) and wR₂ was 0.4176 (all data). CCDC number 2114509.

(c) Refinement details: Distance restraints were imposed on the disordered carbon and nitrogen atoms. Restraints on similar amplitudes separated by less than 1.7 Å, as well as the enhanced rigid-bond restraint⁵⁷ (SHELX keyword RIGU), was applied on those disordered atoms. The disordered atoms were also restrained so that their Uij components approximate to isotropic.

(d) Solvent treatment details: The solvent masking procedure as implemented in Olex2 was used to remove the electronic contribution of solvent molecules and CF₃CO₂⁻ counterions from the refinement. As the exact solvent content is not known, only the atoms used in the refinement model are reported in the formula here. Total solvent accessible volume / cell = 5385.3 Å³ [38.9%], total electron count / cell = 1793.7.
Figure S5. X-Ray single-crystal structure of 3D catenane 3•6CF₃CO₂. The two interlocked identical cages are shown in royal blue and pale blue. (A) Perspective view as a stick representation. (B) Perspective view as a stick representation with the corresponding semitransparent space-filling representation superimposed upon it. (C) Side-on view as a stick representation showing the plane-to-plane distances between two adjacent platforms. (D) Side-on view as a stick representation with the corresponding semitransparent space-filling representation superimposed upon it. (E) Plan view as a stick representation showing the “dihedral angles”. (F) Plan view as a stick representation with the corresponding semitransparent space-filling representation superimposed upon it. Irrelevant protons, CF₃CO₂⁻ counterions and solvent molecules are omitted for the sake of clarity.
Section D. Molecular Modeling

Independent gradient analysis

Intramolecular interactions in 3D catenanes 2\textsuperscript{6+} and 3\textsuperscript{6+} were revealed by an independent gradient model (IGM) analysis, which is an approach\textsuperscript{58} based on pro-molecular density. Strong polar attractions and van der Waals contacts are visualized as an iso-surface with blue and green color, respectively. Single-crystal structures of 2\textsuperscript{6+} and 3\textsuperscript{6+} were used as input file. The binding surface was calculated\textsuperscript{59} by Multiwfn 3.6 program through function 20 (visual study of weak interaction) and visualized\textsuperscript{610} by Chimera software (version 1.13.1).

Figure S6. Intramolecular binding iso-surfaces of 2\textsuperscript{6+} and 3\textsuperscript{6+}. Iso-surfaces are colored according to a BGR scheme over the range \(-0.05 < \text{sign}(\lambda_2)\rho < +0.05\) a.u. (A) Side-on view and (B) plan view of the stick representations of 2\textsuperscript{6+} as visualized by intramolecular binding isosurface. \(\Delta\kappa_{\text{inter}}(\rho) = 0.005\) a.u. Red solid circles indicate the presence of [CH\cdots\pi] interactions. (C) Side-on view and (D) plan view of the stick representations of 3\textsuperscript{6+} as visualized by intramolecular binding isosurface. \(\Delta\kappa_{\text{inter}}(\rho) = 0.005\) a.u. Scale bar: color codes for noncovalent bonding surfaces predicted by IGM analysis.
Section E. Photophysical Characterization

1. UV-Vis Absorption spectroscopy

The UV-Vis absorption spectra of the two interlocked 3D catenanes and their non-interlocked precursor 1•3CF₃CO₂ are shown in Figure S7.

![Normalized UV-Vis absorption spectra](image)

**Figure S7.** Normalized UV-Vis absorption spectra of 1•3CF₃CO₂, 2•6CF₃CO₂ and 3•6CF₃CO₂.

The normalized UV-Vis absorption spectra of 2•6CF₃CO₂ and 3•6CF₃CO₂ both show maximum absorptions at 276 nm, which are red-shifted (6 nm) compared with that (270 nm) for 1•3CF₃CO₂. This bathochromic shift is a clear indication that [π···π] stacking interactions exist in both 3D catenanes. All samples (15 µM) were recorded in MeOH at 298 K.
2. **Transient Absorption spectroscopy**

In order to gain a better understanding of how the mechanical bond influences their photophysical properties, transient absorption (TA) experiments were performed on all three compounds at femtosecond and nanosecond time resolution using the instruments described in a previous article\(^\text{S11}\). The 300 nm pump was generated using the fourth harmonic signal output of a commercial optical parametric amplifier (TOPAS-Prime, Light-Conversion, LLC). The pump pulse was depolarized to suppress polarization-dependent dynamics in the signal. The pump pulses had energies of 1 \(\mu\)J/pulse. Spectra were recorded using a customized Helios/EOS spectrometer (Ultrafast Systems, LLC). Sample \(1\cdot3\text{CF}_3\text{CO}_2\) was contained in glass cuvettes while samples \(2\cdot6\text{CF}_3\text{CO}_2\) and \(3\cdot6\text{CF}_3\text{CO}_2\) were contained in quartz cuvettes purged with bubbling nitrogen gas for 10 min each. Samples were prepared with an optical density ranging from 1.3 to 2.2 at 300 nm. Solution samples were stirred during run time to avoid degradation from localized heating. All datasets were background-subtracted to remove scatter from the pump pulse and corrected for time zero offsets and group delay dispersion using Surface Xplorer (Ultrafast Systems, LLC). The datasets were then each subjected to a global wavelength fitting analysis using sequential models. All femtosecond transient absorption datasets were fit using an A \(\rightarrow\) B \(\rightarrow\) Ground model except for those of sample \(2\cdot6\text{CF}_3\text{CO}_2\) which were fit to an A \(\rightarrow\) B model. The nanosecond transient absorption datasets were fit to a B \(\rightarrow\) Ground model. Since the B \(\rightarrow\) Ground lifetimes from the femtosecond transient absorption experiments are well beyond the \(\sim 7\) ns time range of the
experiment, the values from the nanosecond transient absorption experiment fits were used for B → Ground analysis. The B → Ground lifetimes from the femtosecond transient absorption experiments are included in the model to obtain sensible fits for the A → B lifetimes and evolution-associated spectra. The kinetic traces were fit at five wavelengths across the relevant spectral features of the species formed in each of the experiments.

Femtosecond TA spectra (Fig. S8, S10, S12) of 1•3CF₃CO₂, 2•6CF₃CO₂ and 3•6CF₃CO₂ exhibit broad singlet excited-state absorptions—denoted as species A—that span from the UV region to beyond 700 nm with maxima around 330 and 650 nm immediately after excitation at 300 nm. At time delays beyond ~100 ps, the molecules undergo intersystem crossing as peaks corresponding to the triplet state—denoted as species B—grow in at 440 and 540 nm (Fig. S8 C, S10 C, S12 C). In the global analysis, these features persist for 3.60 ± 0.06, 5.73 ± 0.12, and 4.11 ± 0.08 µs for compounds 1•3CF₃CO₂, 2•6CF₃CO₂, and 3•6CF₃CO₂, respectively, before decaying to their ground states. See Fig. S9 C, S11 C, S13 C. The singlet lifetimes are 63 ± 1, 53 ± 1, and 51 ± 1 ps for 1•3CF₃CO₂, 2•6CF₃CO₂, and 3•6CF₃CO₂, respectively. See Fig. S8 C, S10 C, S12 C. Fast triplet formation is common in systems that undergo n→π* transitions as has been observed in the s-triazine system studied by Hochstrasser and Zewail[12]. Although the T₃ → T₁ absorption spectra of these compounds show only minor differences, there is increased broadening in the 540 nm triplet feature for compounds 2•6CF₃CO₂ and 3•6CF₃CO₂, most likely as a result of [π···π] interactions between the mechanically interlocked components.
Figure S8. Femtosecond TA spectra of 1•3CF₃CO₂ in MeOH. (A) TA spectra at selected delay times. (B) Kinetic traces at selected wavelengths. (C) Evolution-associated spectra obtained by wavelength global fitting to an A → B kinetic model. State A represents the singlet excited state, state B is the triplet state. (D) Population distribution of the kinetic model.

Figure S9. Nanosecond TA spectra of 1•3CF₃CO₂ in MeOH. (A) TA spectra at selected delay times. (B) Kinetic traces at selected wavelengths. (C) Evolution-associated spectra obtained by wavelength global fitting to a B → Ground state kinetic model. State B represents the triplet state. (D) Population distribution of the kinetic model.
Figure S10. Femtosecond TA spectra of 2•6CF₃CO₂ in MeOH. (A) TA spectra at selected delay times. (B) Kinetic traces at selected wavelengths. (C) Evolution-associated spectra obtained by wavelength global fitting to an A → B kinetic model. State A represents the singlet excited state, state B is the triplet state. (D) Population distribution of the kinetic model.

Figure S11. Nanosecond TA spectra of 2•6CF₃CO₂ in MeOH. (A) TA spectra at selected delay times. (B) Kinetic traces at selected wavelengths. (C) Evolution-associated spectra obtained by wavelength global fitting to a B → Ground state kinetic model. State B represents the triplet state. (D) Population distribution of the kinetic model.
Figure S12. Femtosecond TA spectra of 3•6CF₃CO₂ in MeOH. (A) TA spectra at selected delay times. (B) Kinetic traces at selected wavelengths. (C) Evolution-associated spectra obtained by wavelength global fitting to an A → B kinetic model. State A represents the singlet excited state, state B is the triplet state. (D) Population distribution of the kinetic model.

Figure S13. Nanosecond TA spectra of 3•6CF₃CO₂ in MeOH. (A) TA spectra at selected delay times. (B) Kinetic traces at selected wavelengths. (C) Evolution-associated spectra obtained by wavelength global fitting to a B → Ground state kinetic model. State B represents the triplet state. (D) Population distribution of the kinetic model.
Section F. Mechanistic Study

1. Schematic representation of forming three 3D catenanes with different co-constitutions

Figure S14. Three 3D catenanes with different co-constitutions can be formed as a result of reaction of TPPT with TBPT. The theoretical probabilities of forming $2^{6+}$, $3^{6+}$ and $4^{6+}$ are 25, 50 and 25%, respectively.
2. DFT Calculations performed on the of three 3D catenanes with different co-constitutions

The relative energies of 3D catenanes 2\textsuperscript{6+}, 3\textsuperscript{6+}, and 4\textsuperscript{6+} were investigated computationally by density functional theory (DFT) calculations. In all cases, their structures were optimized using the APFD\textsuperscript{S13} functional, which explicitly includes dispersion forces while maintaining a manageable demand on computational resources, and the 6-31G(d) basis set. Frequency calculations were used at the same level of theory to validate all located stationary points, ensuring that there were no negative frequencies for minima. Frequency calculations also provided the sum of the electronic and thermal free energies, which were used to compute the relative energies of each 3D catenane.

![Figure S15](image.png)

**Figure S15.** Relative energies of the three 3D catenanes with different co-constitutions calculated by DFT. The 3D catenane 4\textsuperscript{6+} has the lowest relative energy (0 kcal/mol), compared with that of 2\textsuperscript{6+} (20.8 kcal/mol) and 3\textsuperscript{6+} (11.5 kcal/mol). The 3D catenane 4\textsuperscript{6+}, however, was not observed under all the attempted experimental conditions.
3. Proposed suit[3]ane-based mechanism

Figure S16. Proposed suit[3]ane-based mechanism. The reaction of TPPT with TBPT gives a tricationic monomeric cage $1^{3+}$, we envisioned that this compound can act as a suit which opens up entrances to its cavity at elevated temperatures (80 °C) and allows the slippage of TBPT inside to produce $[\text{Suit}[3]\text{ane}\cdot\text{TBPT}]^{3+}$ as an intermediate. The subsequent reaction with TPPT from the bottom and top side of this intermediate affords the 3D catenanes $2^{6+}$ and $3^{6+}$, respectively, by Reaction Pathway A. Since TPPT is relatively more bulky than TBPT, the formation of a similar $[\text{Suit}[3]\text{ane}\cdot\text{TPPT}]^{3+}$ intermediate is disfavored kinetically as a result of steric hindrance. Thus, neither $3^{6+}$ nor $4^{6+}$ can be formed by Reaction Pathway B.
4. Suit[3]ane intermediate identification

4.1. Preparation of the suit[3]ane intermediate

**Figure S17.** Preparation of [Suit[3]ane•TBPT•3Br] or [Suit[3]ane•TPPT•3Br] by the reaction of 1•3Br with TBPT or TPPT under the same conditions

**Method:** 1•3Br was obtained by counterion exchange of 1•3PF₆ with tetrabutylammonium bromide / TBABr in MeCN. A catalytic amount of TBAI (0.3 mg, 0.9 µmol, 0.2 eq.) was added to a suspension of 1•3Br (5.0 mg, 4.3 µmol, 1.0 eq.), TBPT (10.0 mg, 17.1 µmol, 4.0 eq.) or TPPT (10.0 mg, 17.1 µmol, 4.0 eq.) in anhydrous MeCN (10 mL) charged with N₂. The resulting mixture was heated at 80 °C and stirred for 4 days. After cooling to room temperature, the concentrated residues were dissolved in CD₃OD and used directly for recording ^1H NMR spectra.
**Figure S18.** $^1$H NMR Spectra (500 MHz, CD$_3$OD, 298 K) comparison of crude products obtained from the reaction of 1·3Br with TBPT (A) or TPPT (B). (A) The doublets at 9.50 ($J = 7.0$ Hz) and 6.36 ppm ($J = 8.2$ Hz) indicate that a [Suit[3]ane·TBPT·3Br] intermediate with TBPT trapped inside of the cavity of 1·3Br has been formed. (B) Neither downfield nor upfield shifted doublets can be detected, indicating that TPPT cannot be trapped inside of the cavity of 1·3Br to form the [Suit[3]ane·TPPT·3Br] intermediate under the same reaction conditions. The small peaks found between 9.20 ppm and 7.10 ppm may result from the decomposition of 1·3Br at high temperature in the presence of TPPT, itself a weak base.

**4.2. Attempts to isolate the suit[3]ane intermediate**

**Method:** The crude product obtained from the reaction of 1·3Br with TBPT was subjected to counterion exchange with TFA, followed by C$_{18}$ reversed-phase column purification using a mixture of 0.1% v/v TFA in H$_2$O and 0.1% v/v TFA in MeCN. Fractions containing Suit[3]ane·TBPT·3CF$_3$CO$_2$ were combined and concentrated. The residue dissolved in MeOH was analyzed by mass spectrometry.
Figure S19. ESI-MS showing Suit[3]ane•TBPT•3CF₃CO₂ is water-labile and can be easily hydrolyzed. The mass spectra of Suit[3]ane•TBPT•3CF₃CO₂ were recorded after column purification and stored at room temperature for 0 h (A), 12 h (B) and 96 h (C). The m/z signals at around 505 (light red), 485 (light green), 464 (light blue) and 443 (light purple) correspond to those of [Suit[3]ane•TBPT]³⁺, its hydrolyzed by-products [Suit[3]ane•OH]³⁺, [Suit[3]ane•2OH]³⁺ and [Suit[3]ane•3OH]³⁺, respectively.
4.3. Capturing of the suit[3]ane intermediate

Figure S20. Capturing of [Suit[3]ane•TBPT•3Br] by reacting it with pyridine

Suit[3]ane•TPyPT•6CF₃CO₂: TBPT (10.0 mg, 17.1 µmol, 1.0 eq.) was added to a suspension of 1•3Br (20.0 mg, 17.1 µmol, 1.0 eq.) and a catalytic amount of TBAI (1.3 mg, 3.4 µmol, 0.2 eq.) in anhydrous MeCN (20 mL) charged with N₂. The reaction mixture was heated at 80 °C and stirred for 2 days before adding anhydrous pyridine (4.1 µL, 51.0 µmol, 3.0 eq.). The resulting mixture was stirred at 80 °C for 1 day. The sequential addition of TBPT (10.0 mg, 17.1 µmol, 1.0 eq.) and pyridine (4.1 µL, 51.0 µmol, 3.0 eq.) was repeated 3 times. After evaporation to remove all the solvent, TFA (1 mL) and MeOH (5 mL) was added and stirred for an additional 30 min. The concentrated residue was loaded onto a CombiFlash® chromatography system and purified on a C₁₈ reversed-phase column using a mixture of 0.1% v/v TFA in H₂O and 0.1% v/v TFA in MeCN.
Fractions containing the product were combined and concentrated to afford **Suit[3]ane•TPyPT•6CF₃CO₂** (2.2 mg, 6% yield) as a white solid. $^1$H NMR (500 MHz, CD₃OD, 298 K) $\delta_H = 9.56$ (d, $J = 5.8$ Hz, 6H, H-l), 9.50 (d, $J = 6.9$ Hz, 6H, H-d), 8.85 (t, $J = 7.8$ Hz, 3H, H-n), 8.52 – 8.50 (m, 12H, H-m / H-e), 7.62 – 7.58 (m, 12H, H-a / H-b), 7.50 (d, $J = 8.1$ Hz, 6H, H-j), 7.43 (d, $J = 8.2$ Hz, 6H, H-h), 7.28 (d, $J = 8.2$ Hz, 6H, H-g), 6.42 (d, $J = 8.2$ Hz, 6H, H-i), 6.29 (s, 6H, H-k), 5.92 (s, 6H, H-c), 4.41 (s, 6H, H-f). $^{13}$C NMR (125 MHz, CD₃OD, 298 K) $\delta_C = 170.7$ (C-1 / C-15), 169.7 (C-16), 165.5 (C-9), 148.2 (C-24), 146.2 (C-22), 145.6 (C-7), 145.2 (C-11), 141.2 (C-5), 139.7 (C-20), 137.1 (C-2), 136.4 (C-17), 135.1 (C-14), 131.1 (C-3), 131.0 (C-18), 130.9 (C-13), 130.4 (C-23), 129.63 (C-19), 129.58 (C-8), 129.4 (C-4), 129.1 (C-12), 65.4 (C-6 / C-21), 43.0 (C-10). ESI-HRMS Calcd for **Suit[3]ane•TPyPT•6CF₃CO₂**: $C_{108}H_{81}F_9N_{15}O_6^{3+}$: $m/z = 618.2111$ [$M - 3CF₃CO₂$]$^{3+}$, found: 618.2093 [$M - 3CF₃CO₂$]$^{3+}$; $C_{110}H_{81}F_{12}N_{15}O_8^{2+}$: $m/z = 983.8095$ [$M - 2CF₃CO₂$]$^{2+}$, found: 983.8081 [$M - 2CF₃CO₂$]$^{2+}$.

**Figure S21.** ESI-MS of **Suit[3]ane•TPyPT•6CF₃CO₂**. The corresponding theoretical peaks (blue) of [**Suit[3]ane•TPyPT•3CF₃CO₂**]$^{3+}$ and [**Suit[3]ane•TPyPT•4CF₃CO₂**]$^{2+}$ were found to be consistent with the experimental peaks (red).
Section G. NMR Spectroscopy

Figure S22. Annotated $^1$H NMR spectrum of 1•3CF$_3$CO$_2$
Figure S23. Annotated $^{13}$C NMR spectrum of 1•3CF$_3$CO$_2$
Figure S24. Annotated $^1$H-$^1$H COSY NMR spectrum of 1•3CF$_3$CO$_2$
Figure S25. Annotated $^1$H-$^{13}$C HSQC NMR spectrum of 1•3CF$_3$CO$_2$
Figure S26. $^1$H-$^{13}$C HMBC NMR spectrum of 1•3CF$_3$CO$_2$
Figure S27. Annotated $^1$H NMR spectrum of 2•6CF$_3$CO$_2$
Figure S28. Annotated $^{13}$C NMR spectrum of $2\cdot6\text{CF}_3\text{CO}_2^-$
Figure S29. Annotated $^1$H-$^1$H COSY NMR spectrum of 2•6CF$_3$CO$_2$
Figure S30. Annotated $^1$H-$^{13}$C HSQC NMR spectrum of 2•6CF$_3$CO$_2$
Figure S31. $^1$H-$^{13}$C HMBC NMR spectrum of 2•6CF$_3$CO$_2$
Figure S32. Annotated $^1$H-$^1$H NOSEY NMR spectrum of 2•6CF$_3$CO$_2$
Figure S33. Annotated $^1$H NMR spectrum of 3•6CF$_3$CO$_2$
Figure S34. Annotated $^{13}$C NMR spectrum of 3•6CF$_3$CO$_2$
Figure S35. Annotated $^1$H-$^1$H COSY NMR spectrum of $3\cdot6$CF$_3$CO$_2$
Figure S36. Annotated $^1$H-$^{13}$C HSQC NMR spectrum of 3•6CF$_3$CO$_2$
Figure S37. $^1$H-$^{13}$C HMBC NMR spectrum of 3•6CF$_3$CO$_2$
Figure S38. Annotated $^1$H-$^1$H NOSEY NMR spectrum of 3•6CF$_3$CO$_2$
Figure S39. Annotated $^1$H NMR spectrum of Suit[3]ane•TPyPT•6CF$_3$CO$_2$
Figure S40. Annotated $^{13}$C NMR spectrum of Suit[3]ane•TPyPT•6CF$_3$CO$_2$
Figure S41. Annotated $^1$H-$^1$H COSY NMR spectrum of $\text{Suit}[3]\text{ane}\cdot\text{TPyPT}\cdot6\text{CF}_3\text{CO}_2$
Figure S42. Annotated $^1$H-$^{13}$C HSQC NMR spectrum of Suit[3]ane•TPyPT•6CF$_3$CO$_2$
Figure S43. $^1$H-$^{13}$C HMBC NMR spectrum of Suit[3]ane•TPyPT•6CF$_3$CO$_2$
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