Supporting Information

Substituent Effects on Axle Binding in Amide Pseudorotaxanes: Comparison of NMR Titration and ITC Data with DFT Calculations

Lena Kaufmann,[a] Egor V. Dzyuba,[a] Friedrich Malberg,[b] Nora L. Löw,[a] Matthias Groschke,[a] Boris Brusilowskij,[a] Juhani Huuskonen,[c] Kari Rissanen,[c] Barbara Kirchner,*[,b] and Christoph A. Schalley*[,a]

[a] *Institut für Chemie und Biochemie, Freie Universität Berlin, Takustraße 3, 14195 Berlin, Germany.*

[b] *Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie Universität Leipzig, Linnéstraße 2, 04103 Leipzig, Germany.*

[c] *Department of Chemistry, Nanoscience Center, University of Jyväskylä, P. O. Box 35, 40014 Jyväskylä, Finland.*

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(1.) Data obtained from ^{1}H NMR titrations

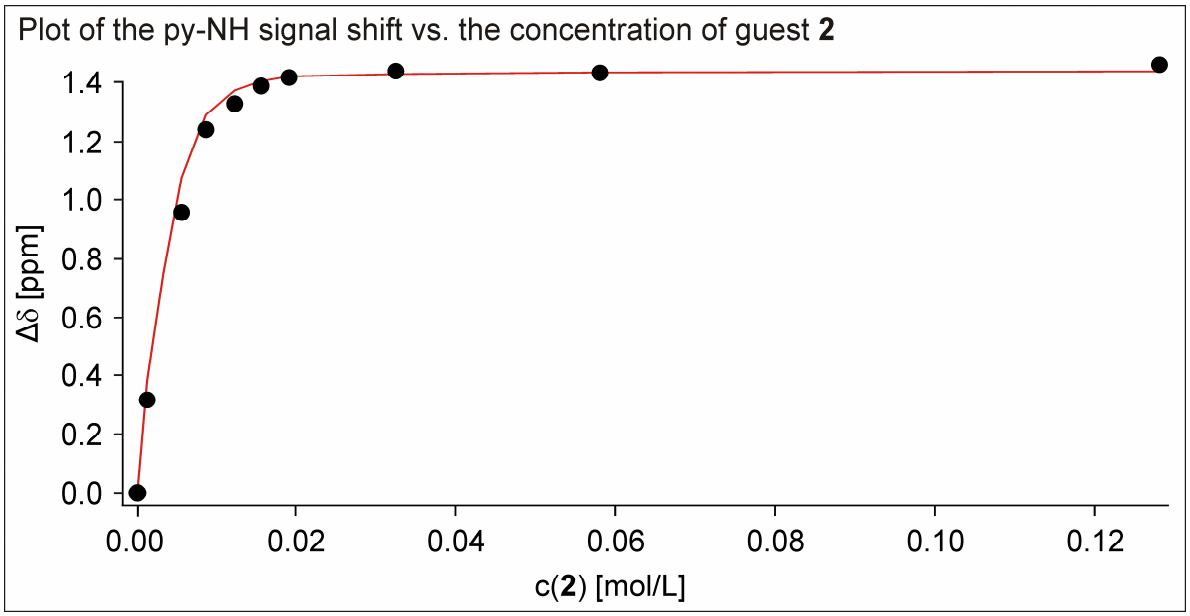

Figure S1. Titration curve obtained from ^{1}H NMR titration experiment of TLM **1a** and guest **2**. The solid line is the theoretical one.

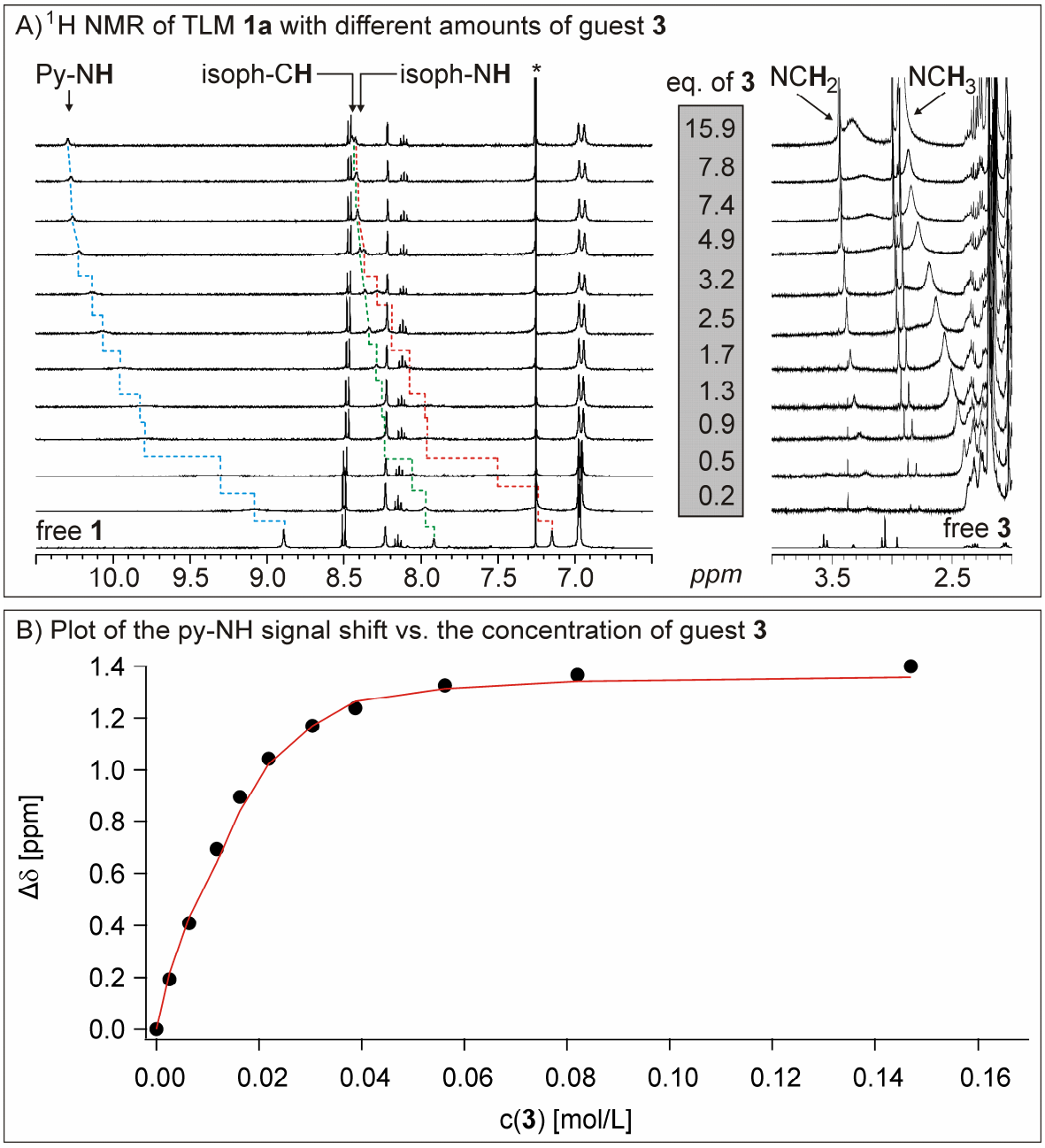

Figure S2. ^{1}H NMR spectra obtained from ^{1}H NMR titration experiment of TLM **1a** and guest **3** (A, top) and titration curve obtained from ^{1}H NMR titration experiment of TLM **1a** and guest **3** (B, bottom). The solid line is the theoretical one.

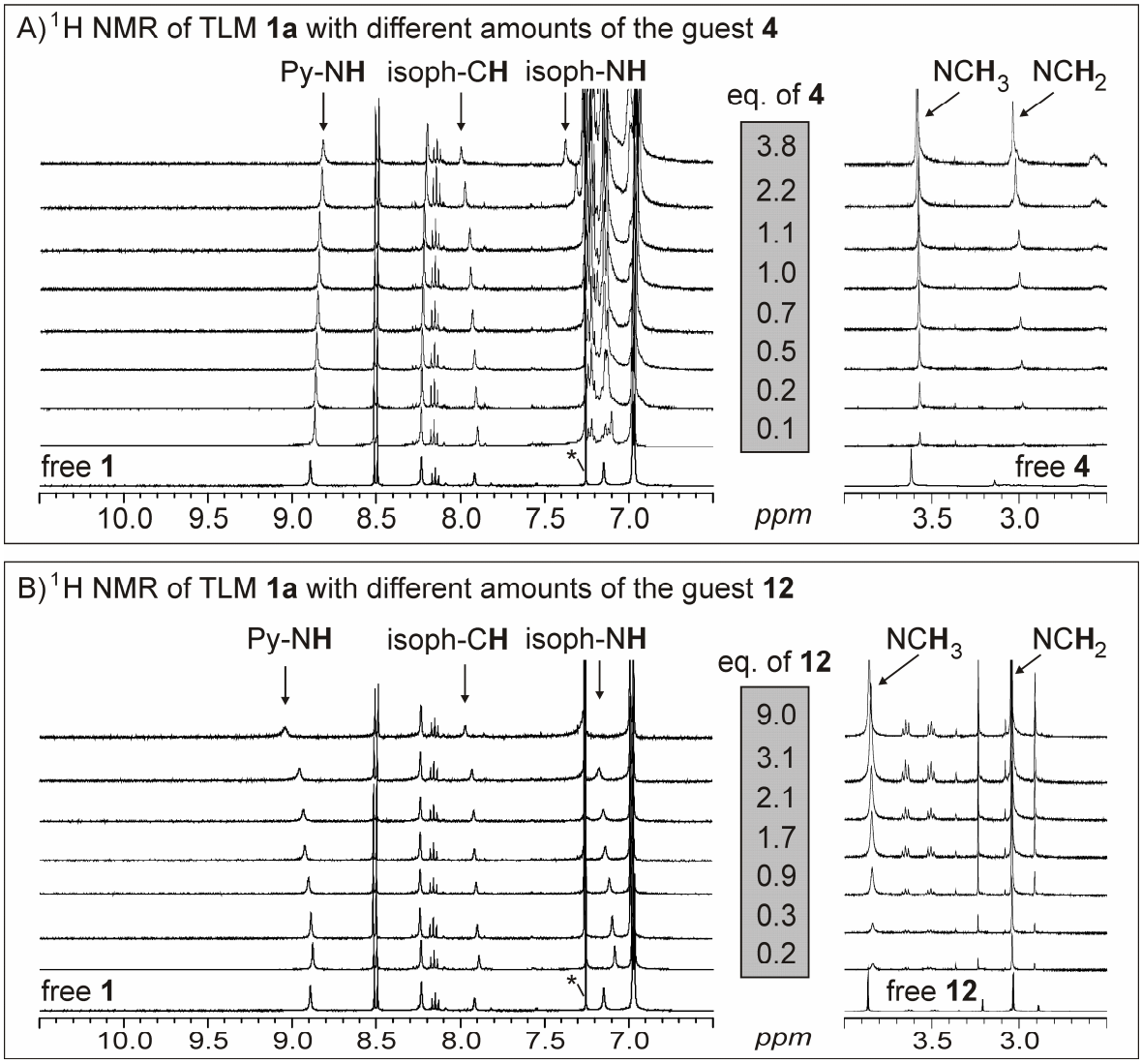

Figure S3. ^{1}H NMR spectra obtained from ^{1}H NMR titration experiments of TLM **1a** and guest **4** (A, top), and of TLM **1a** and guest **12** (B, bottom).

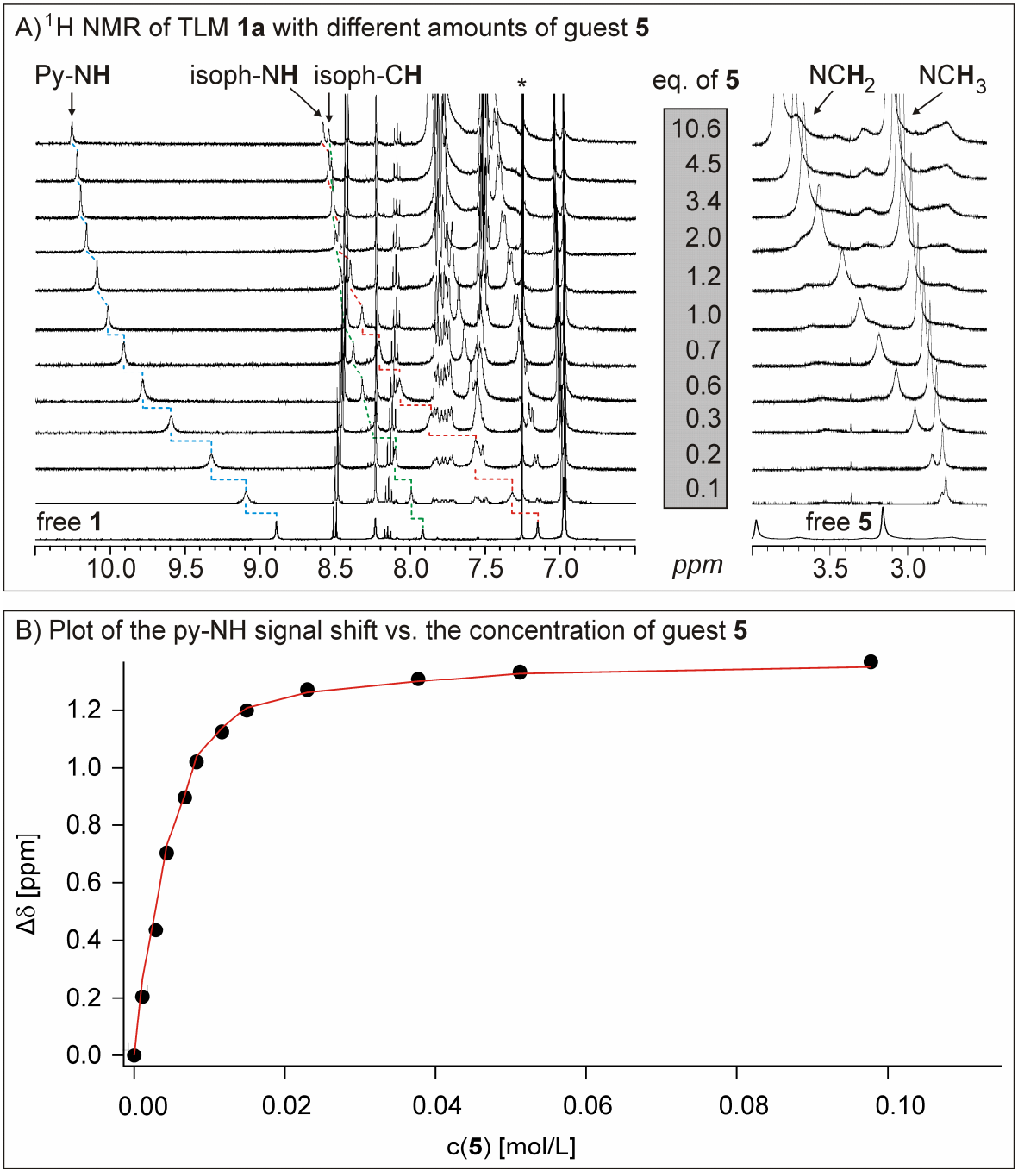

Figure S4. ^{1}H NMR spectra obtained from ^{1}H NMR titration experiment of TLM **1a** and guest **5** (A, top) and titration curve obtained from ^{1}H NMR titration experiment of TLM **1a** and guest **5** (B, bottom). The solid line is the theoretical one.

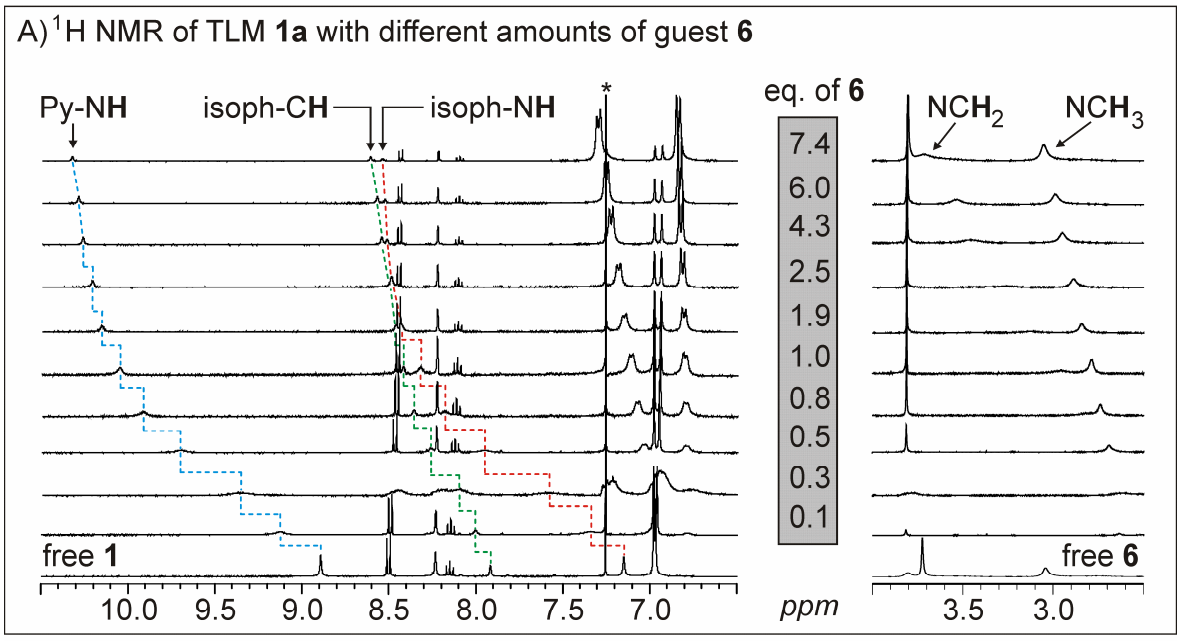

Figure S5. ^{1}H NMR spectra obtained from ^{1}H NMR titration experiment of TLM **1a** and guest **6**.

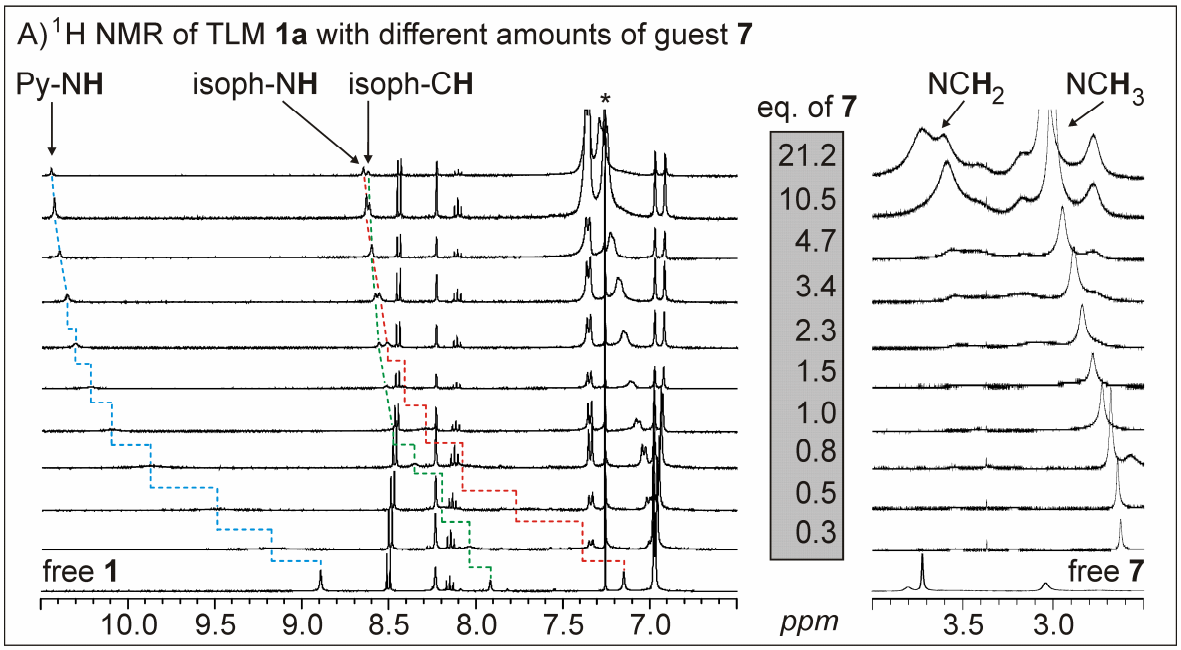

Figure S6. ^{1}H NMR spectra obtained from ^{1}H NMR titration experiment of TLM **1a** and guest **7**.

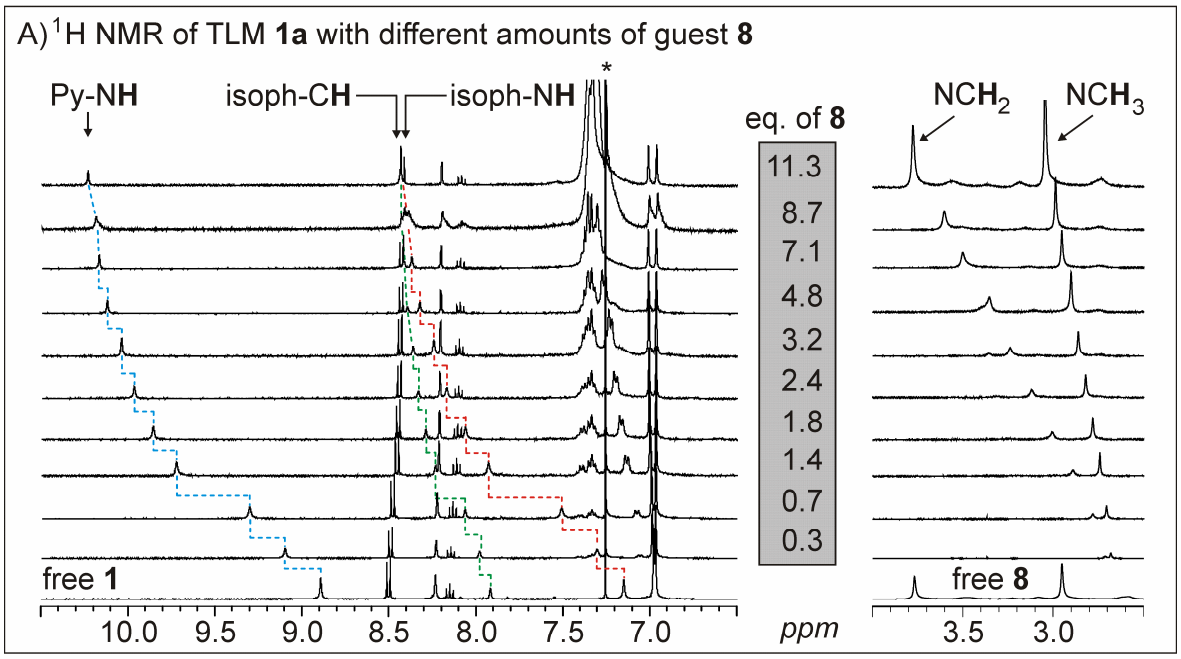

Figure S7. ^{1}H NMR spectra obtained from ^{1}H NMR titration experiment of TLM **1a** and guest **8**.

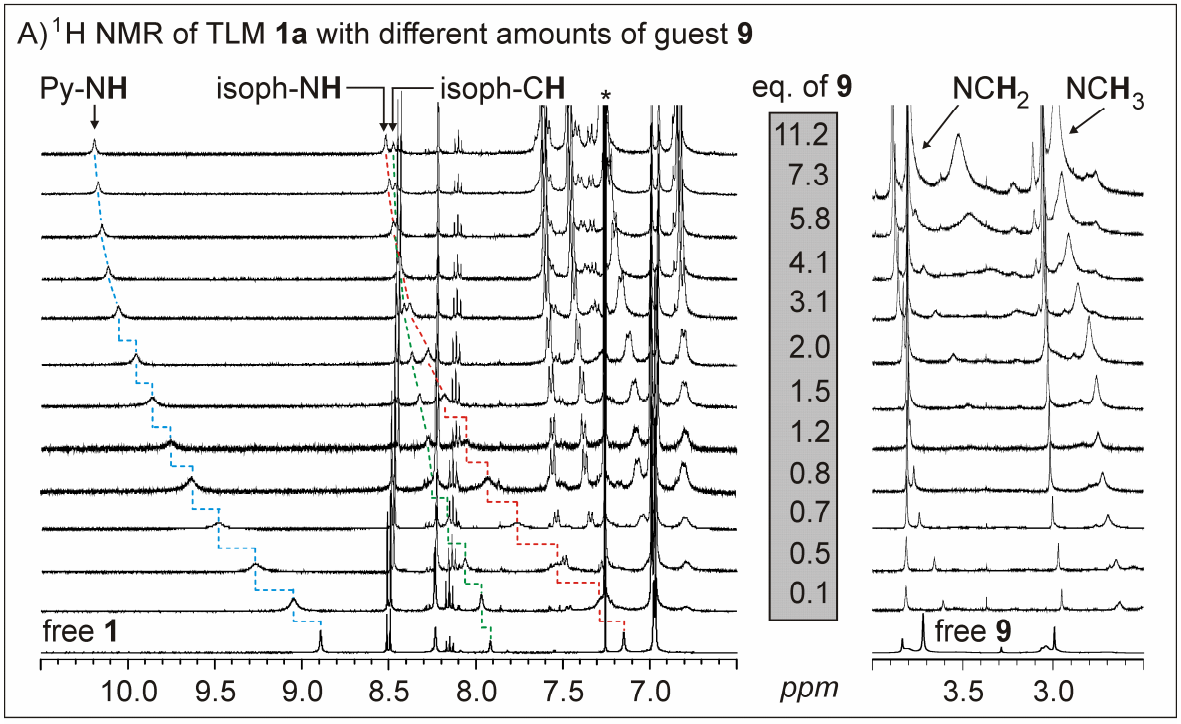

Figure S8. ^{1}H NMR spectra obtained from ^{1}H NMR titration experiment of TLM **1a** and guest **9**.

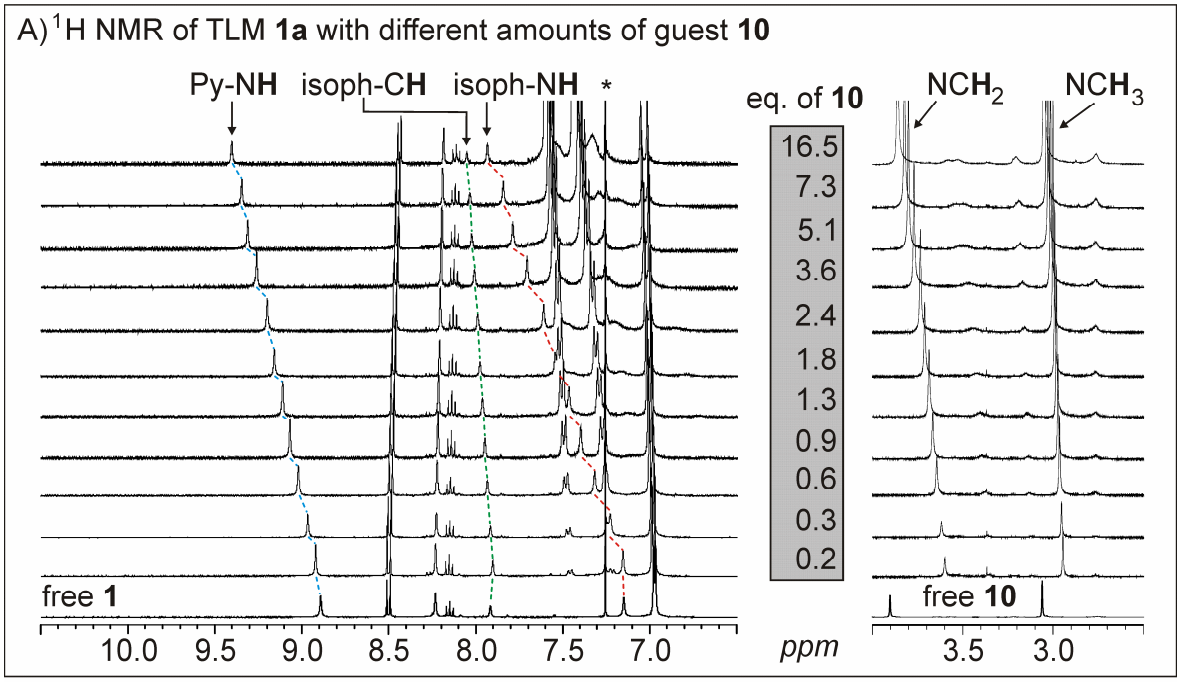

Figure S9. ^{1}H NMR spectra obtained from ^{1}H NMR titration experiment of TLM **1a** and guest **10**.

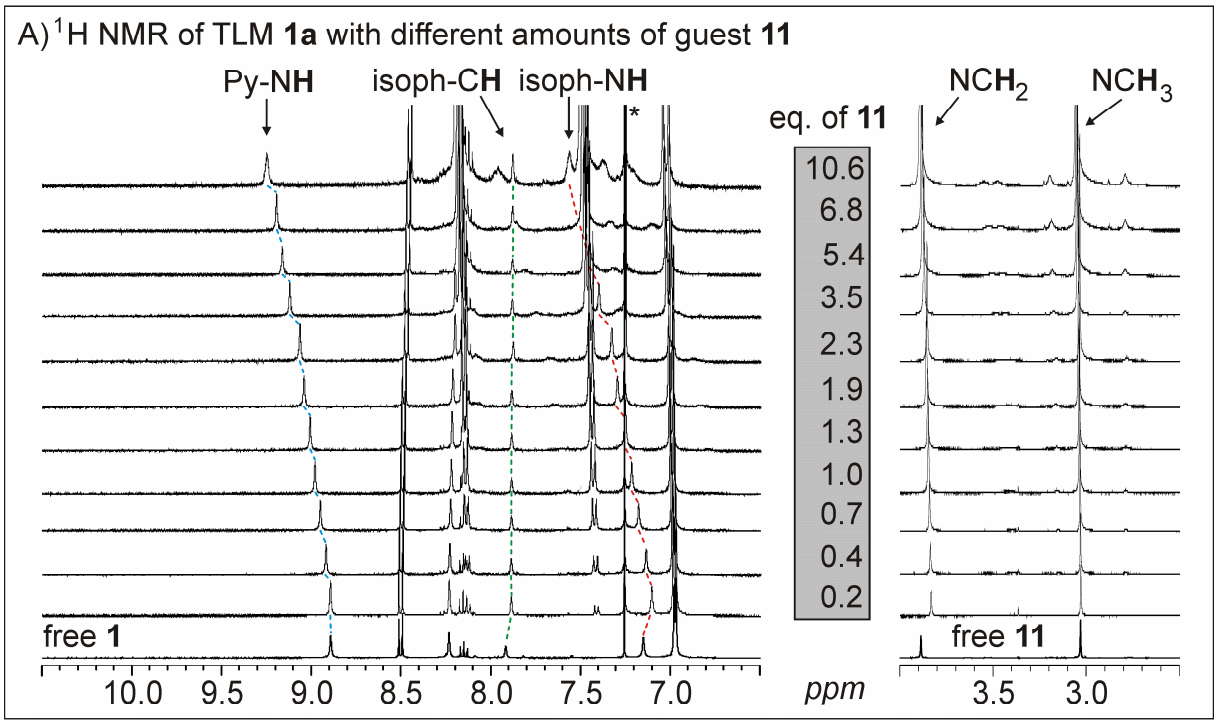

Figure S10. ^{1}H NMR spectra obtained from ^{1}H NMR titration experiment of TLM **1a** and guest **11**.

(2.) Data obtained from ITC experiments.

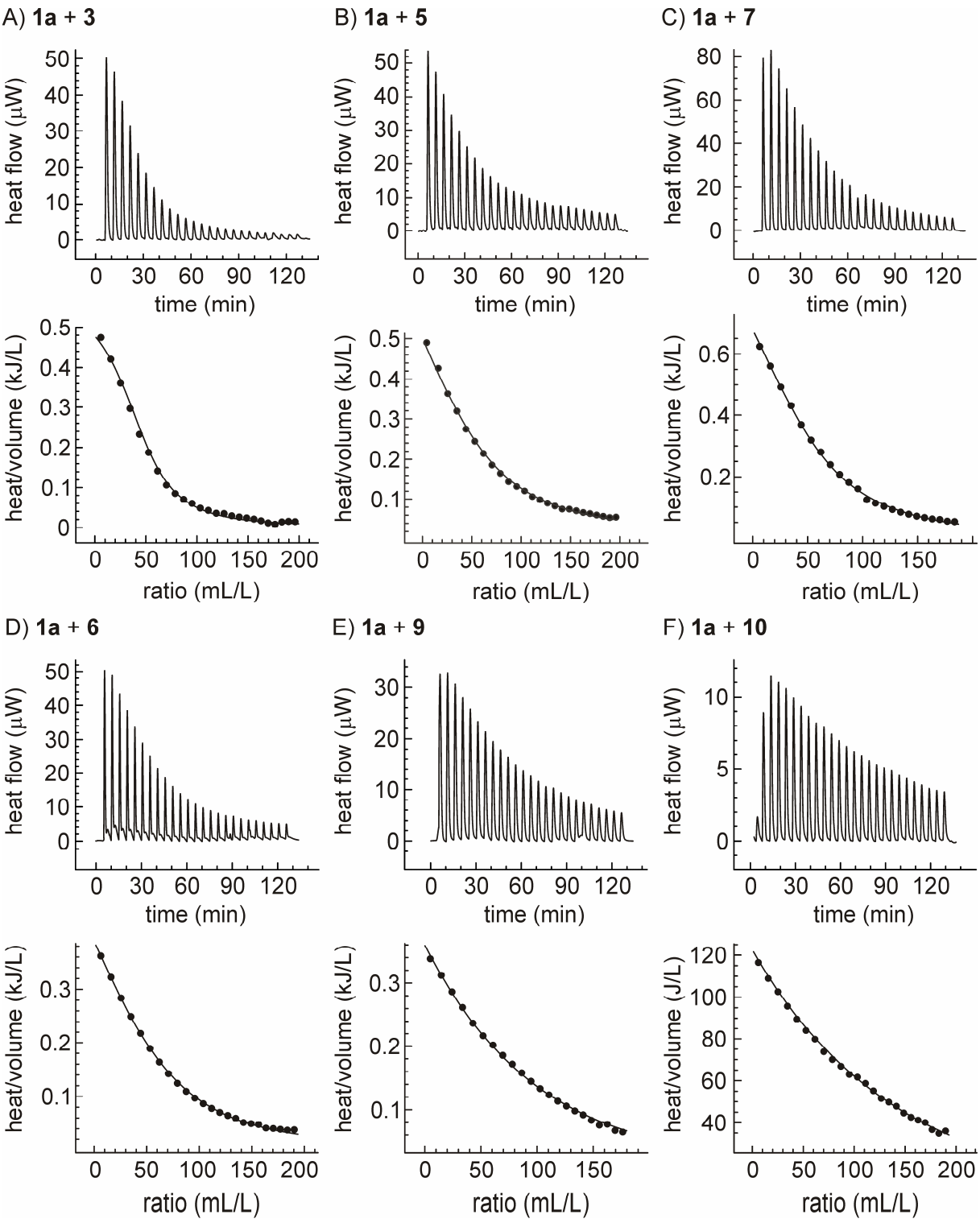

Figure S11. Data obtained from separate ITC experiments of **1a** and guests **3**, **5** and **7** (A, B, C, top row) and **6**, **9** and **10** (D, E, F, bottom row).

(3.) Crystallographic Data

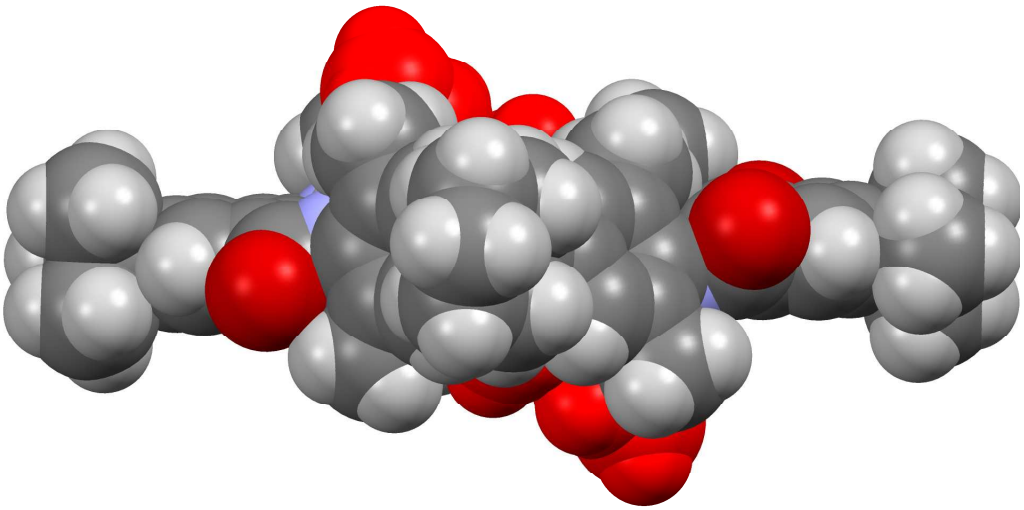

Figure S12. Crystal structure of **2@1b** in space-filling representation (side view).

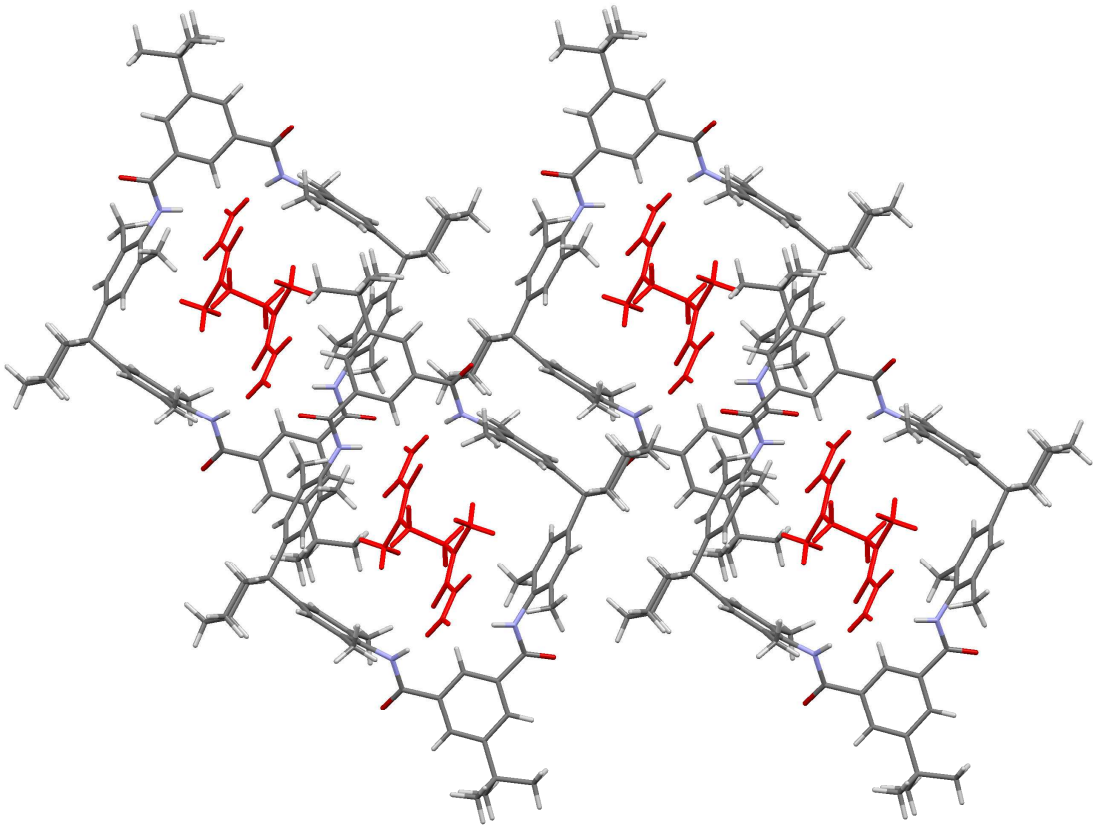

Figure S13. Crystal structure of **2@1b**. Crystal packing seen perpendicular to the overall macrocycle plane.

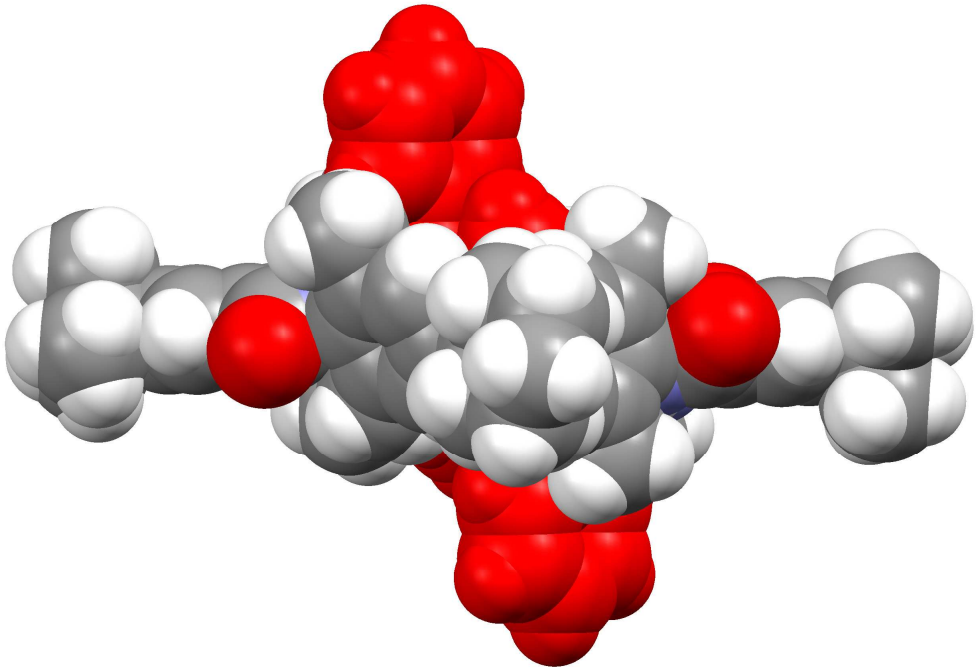

Figure S14. Side-view of a space filling representation of the crystal structure of **8@1b**. The axle is highlighted in red.

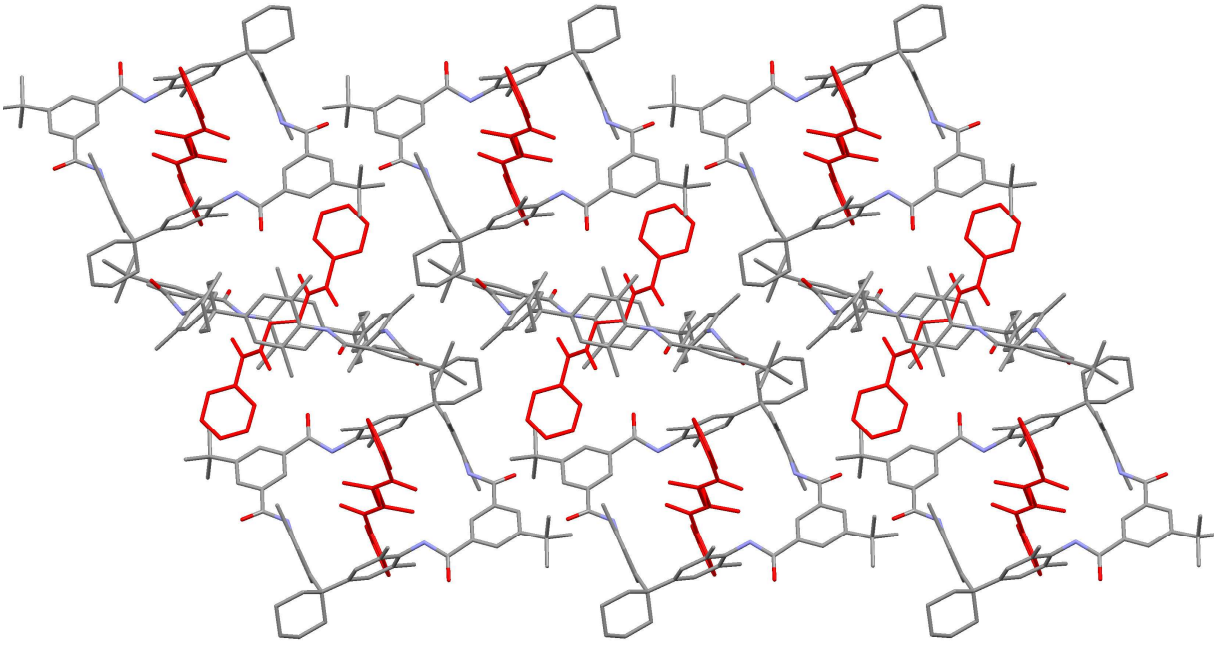

Figure S15. Packing diagram of **8@1b** showing the alternating orientations of the pseudorotaxanes.

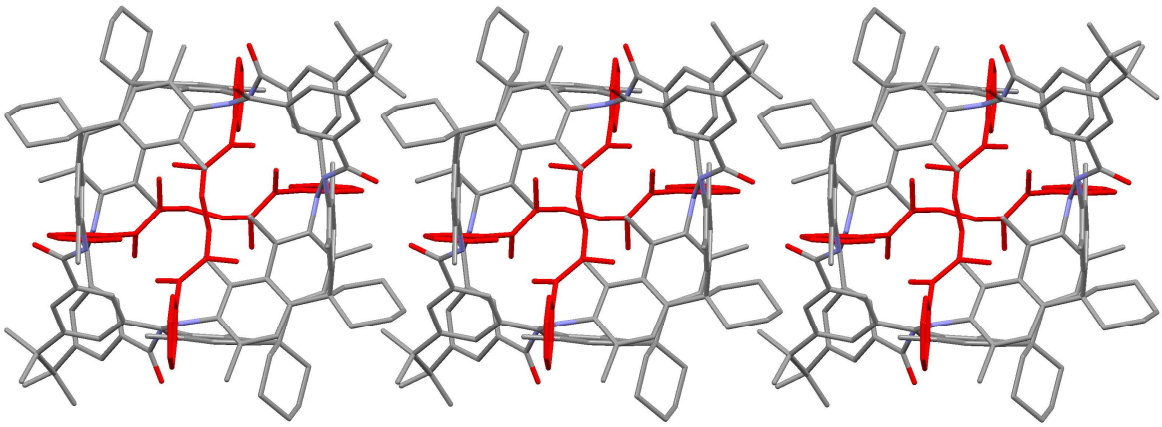

Figure S16. View along the crystallographic *c* axis of the crystal structure of **8@1b**.

(4.) Theoretical Calculations

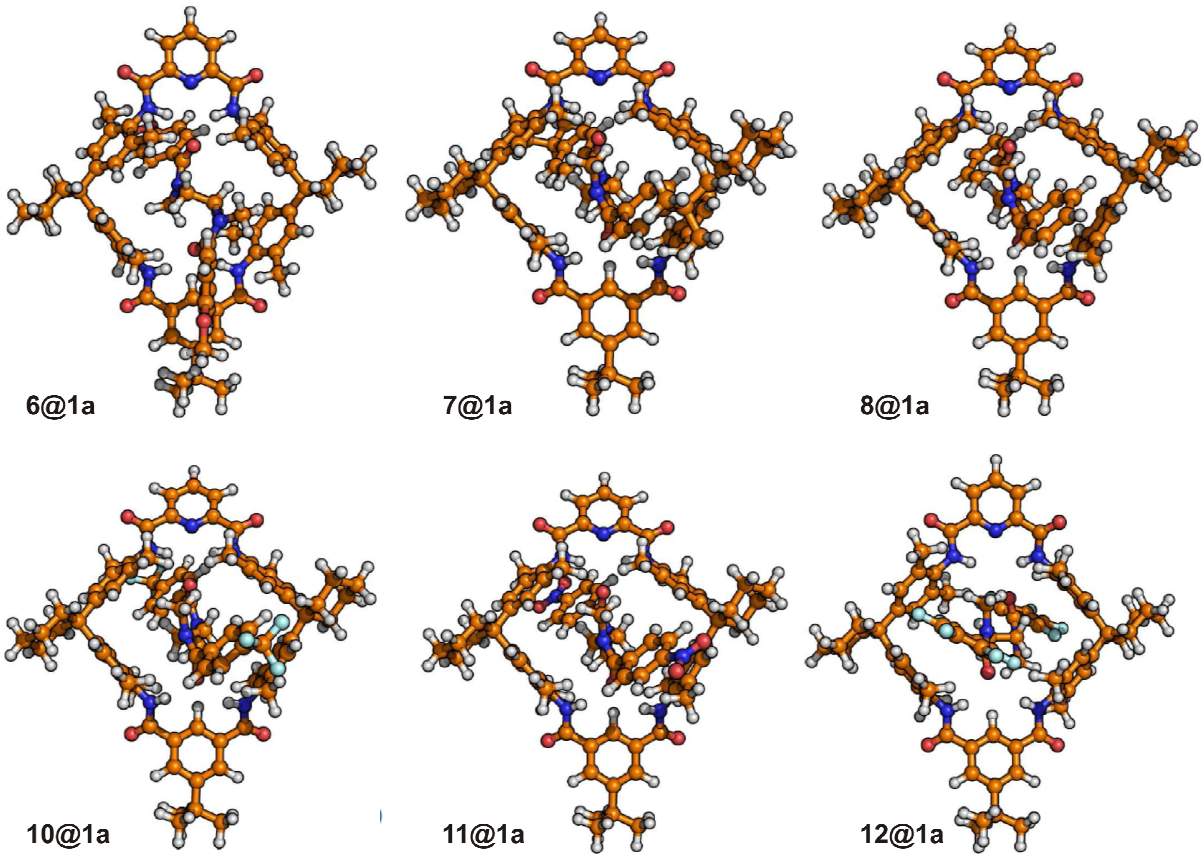

Figure S17. Calculated structures of the pseudorotaxanes with symmetrical aryl-substituted axles.

Table S1. Shared electron number for all hydrogen bonds of pseudorotaxanes with symmetrical aryl-substituted axles.

axle	**SENs of individual hydrogen bonds**				
	$\sigma_{HO}(py1)$ [e]	$\sigma_{HO}(py2)$ [e]	$\sigma_{HO}(iso1)$ [e]	$\sigma_{HO}(iso2)$ [e]	σ_{total} **[e]**
6	0.0258	0.0183	0.0378	0.0387	**0.1206**
7	0.0196	0.0250	0.0192	0.0165	**0.0803**
8	0.0196	0.0227	0.0183	0.0164	**0.0770**
10	0.0165	0.0177	0.0180	0.0166	**0.0688**
11	0.0173	0.0174	0.0131	0.0148	**0.0626**
12	0.0089	-	0.0126	0.0020	**0.0235**