

# Supporting Information

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## SI Materials and Methods

All chemicals were purchased from commercial sources and used without further purification.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were carried out in deuterated solvents on Bruker Avance 400 and 500 Ultrashield spectrometers. Mass analyses were performed on Waters LCT Premier (ESI mode), or Bruker Maldi-TOF spectrometers. Crystal structure determination was carried out using a Bruker-Nonius diffractometer equipped with a APPEX 2 4K CCD area detector, a FR591 rotating anode with  $\text{MoK}\alpha$  radiation, Montel mirrors as monochromator and a Kryoflex low temperature device ( $T = 100\text{ K}$ ). Fullsphere data collection omega and phi scans. Programs used: Data collection Apex2 V. 1.0–22 (Bruker-Nonius 2004), data reduction Saint + Version 6.22 (Bruker-Nonius 2001) and absorption correction SADABS V. 2.10. Crystal structure solution was achieved using direct methods as implemented in SHELXTL Version 6.10 [Sheldrick GM (1998) SHELXTL Crystallographic System Ver. 5.10 (Bruker AXS, Inc, Madison, WI)] and visualized using XP program. Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on F2 using all measured intensities was carried out using the program SHELXTL Version 6.10.

**X-Ray Structure Determination.** Crystals of a methanol solvate of **2b**, could be obtained by crystallization in a saturated methanol solution at room temperature. The crystals obtained were extremely sensitive to losing solvent and were prepared in short time under inert conditions immersed in perfluoropolyether as protecting oil for manipulation. After several trials a dataset of enough quality could be obtained.

**Data Collection.** Measurements were made on a Bruker-Nonius diffractometer equipped with a APPEX 2 4K CCD area detector, a FR591 rotating anode with  $\text{MoK}\alpha$  radiation, Montel mirrors as monochromator and a Kryoflex low temperature

device ( $T = -173\text{ }^\circ\text{C}$ ). Full-sphere data collection was used with  $\omega$  and  $\varphi$  scans using Apex2 V. 1.0–22 for data collection, Saint + Version 6.22 for data reduction, and SADABS V. 2.10 for data reduction.

**Structure Solution and Refinement.** SHELXTL Version 6.10 was used.

**GPC Experiments.** GPC analysis were performed on an Agilent 1200 series HPLC with automatic injection system and a thermostated column compartment at  $25\text{ }^\circ\text{C}$ , using a UV/vis detector set at 254 nm. A PL-Gel  $300 \times 7.5\text{ mm}$   $3\text{ }\mu\text{m}$  MIXED-E column from Polymer Laboratories was used. Dichloromethane was used as eluent with a flow of 1 ml/min.

**NMR Experiments.** All experiments were carried out in  $\text{CD}_2\text{Cl}_2$  at 298K, unless otherwise specified. The experiments were determined using 1–2 mM solutions of **2**. The diffusion coefficients ( $D$ ) for **5@2b2b** mixture were measured using the PGSE technique in  $\text{CD}_2\text{Cl}_2$  at 298 K (Fig. S2). A solution containing both compounds with a small excess of **5** was prepared to observe the formation of the ternary capsule complex.

$$I = I_0 \exp[-D(\gamma\delta G)^2(\Delta - \delta/3)], \quad [1]$$

Fitting to Eq. 1 the mono-exponential plot of the attenuation of the NMR signals as a function of  $G^2$  affords the diffusion coefficient ( $D$ ) for each of the fitted signals.

Each signal was fitted using the  $T_1/T_2$  relaxation module of the TOPSPIN program. Then a linear representation of  $\ln I/I_0$  against  $\%G^2$  was fitted with a least to squares routine to obtain an estimation of the linearity of the experimental data ( $R^2$ ). All of the signals related to the species of interest were plotted and all of them showed a  $R^2$  coefficient  $>0.99$ .  $D_{(5@2b2b)} = 4.73 \times 10^{-10}$ , and  $D_{(5)} = 12.8 \times 10^{-10}$ .

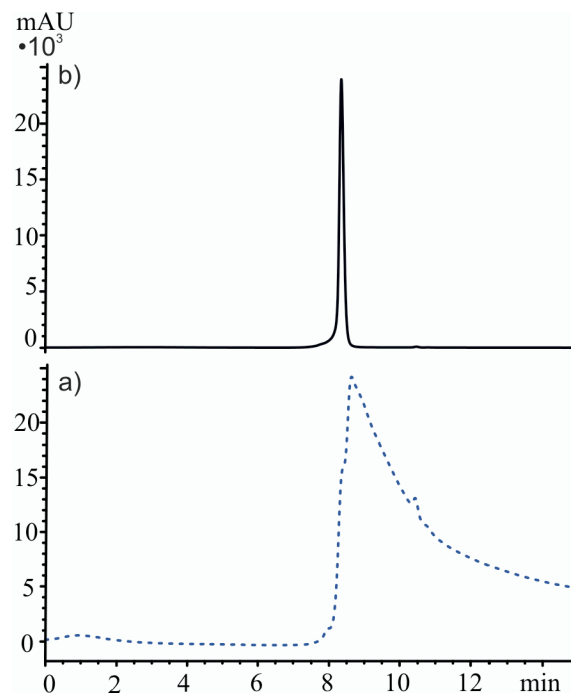


Fig. S1. GPC traces of **2b** in dichloromethane (a) and **5@2b2b** in dichloromethane (b).

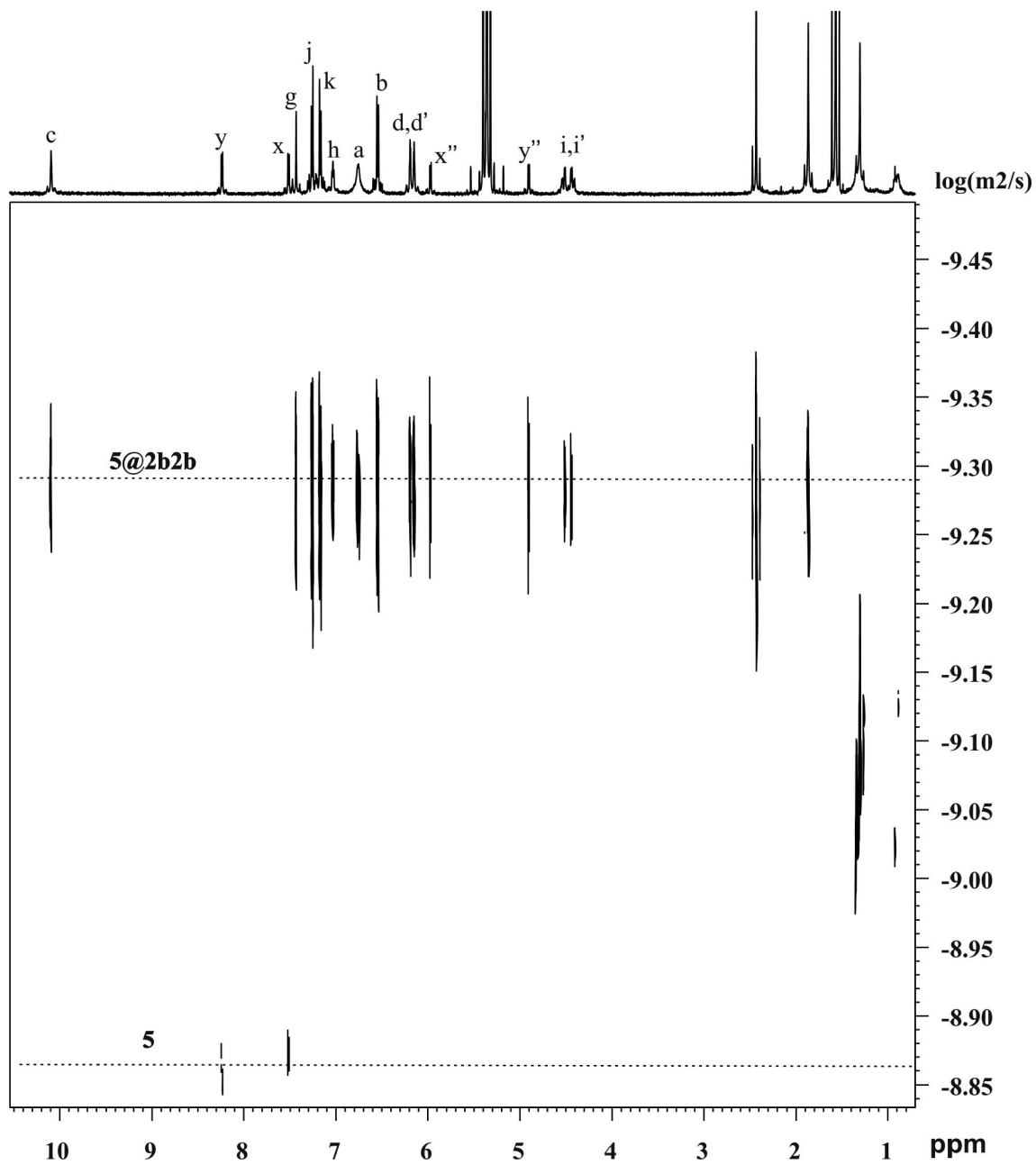


Fig. S2. DOSY-NMR of 5@2b2b in  $CD_2Cl_2$  at 298 K.

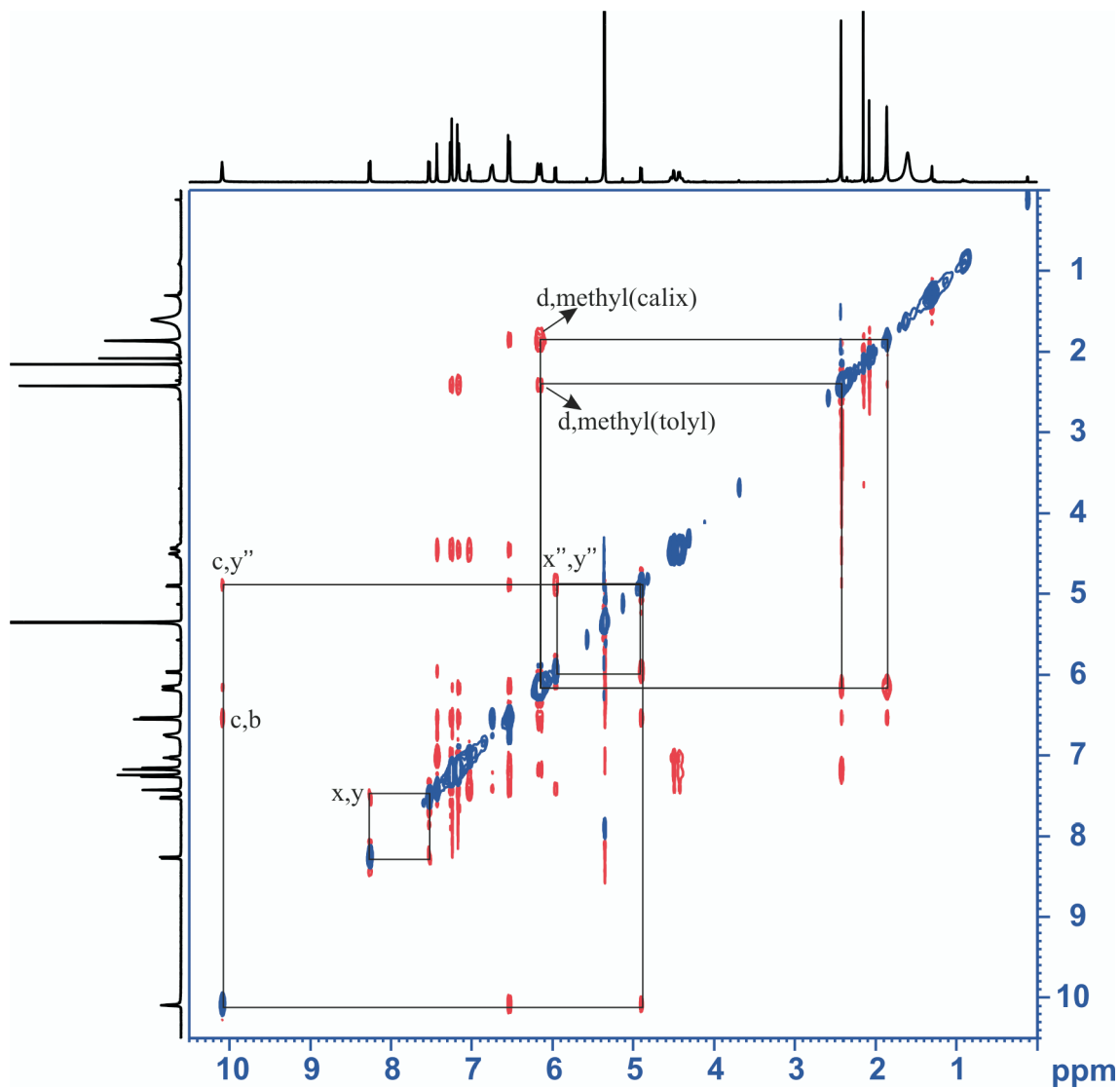


Fig. S3. <sup>1</sup>H,<sup>1</sup>H-2D ROESY (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 1.7 mM) spectrum of 5@2b2b. Some cross peaks of interest have been boxed.

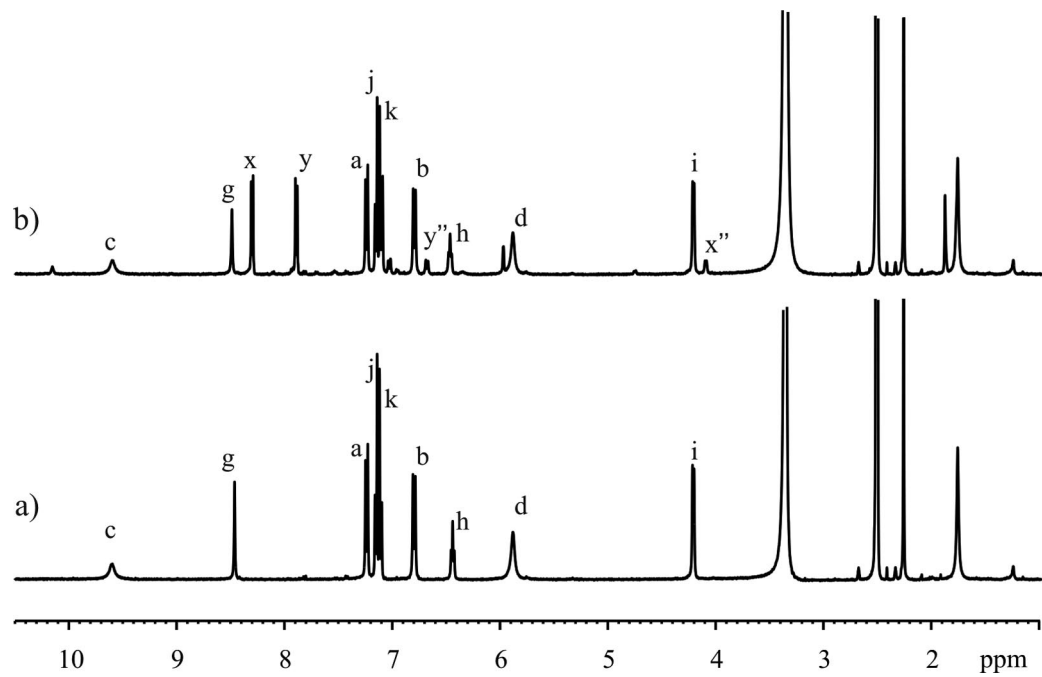
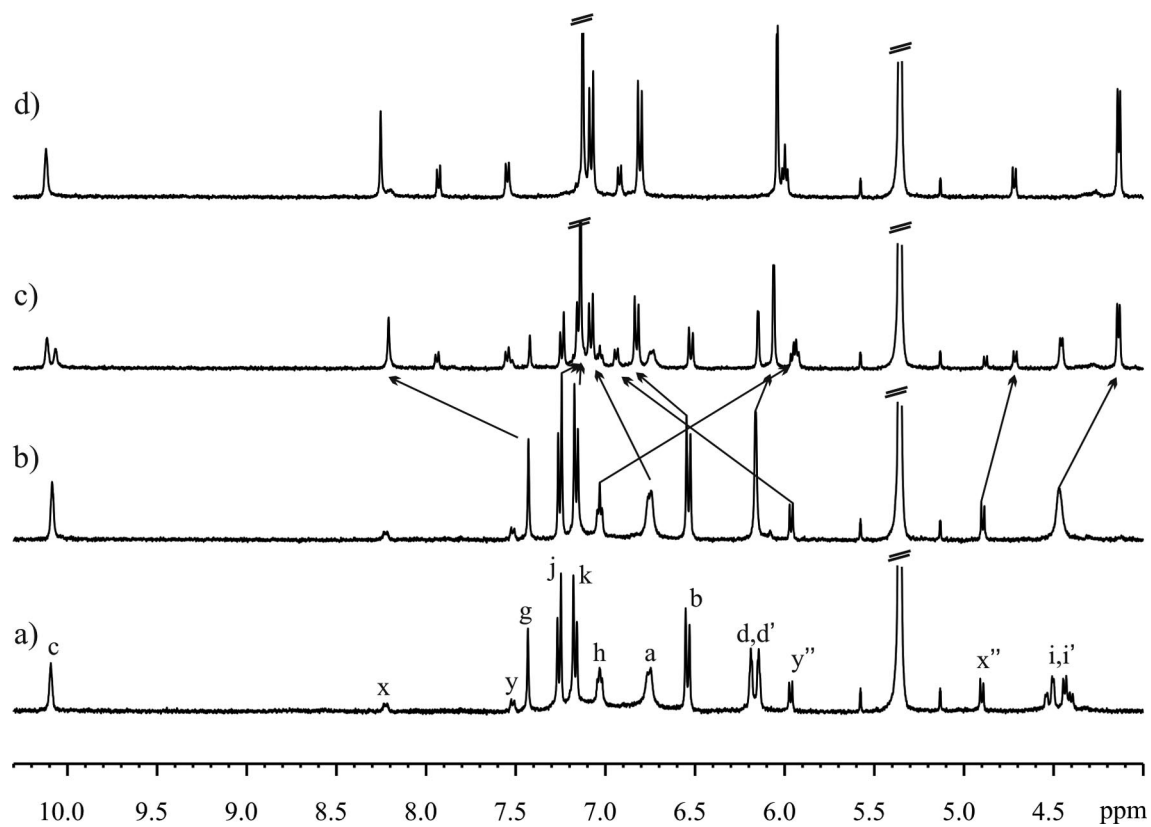
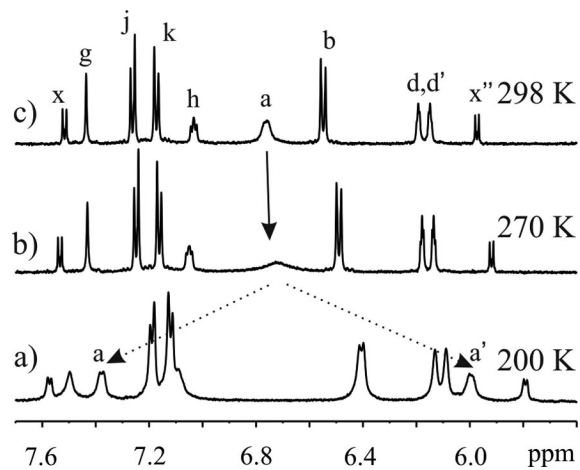


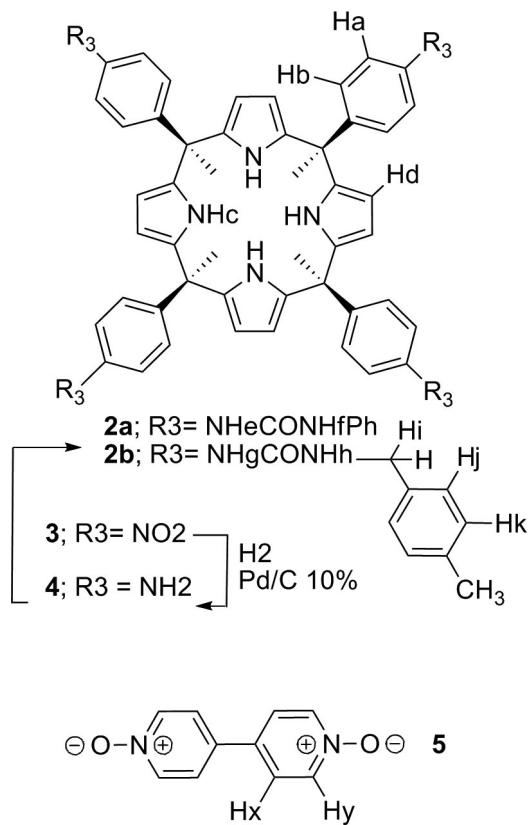
Fig. S4.  $^1\text{H}$  NMR (400 MHz) spectra of: **2b**, 1.3 mM in  $\text{DMSO-}d_6$  (a) and **2b**, 1.3 mM in  $\text{DMSO-}d_6$  + 2 eq of **5** (b).



**Fig. S5.** Selected regions of  $^1\text{H}$  NMR (400 MHz) spectra of 5@2b2b (1 mM) at 298K.in:  $\text{CD}_2\text{Cl}_2$  (a),  $\text{CD}_2\text{Cl}_2 + 5 \mu\text{l}$  of  $\text{DMSO-}d_6$  (b),  $\text{CD}_2\text{Cl}_2 + 20 \mu\text{l}$  of  $\text{DMSO-}d_6$  (c), and  $\text{CD}_2\text{Cl}_2 + 40 \mu\text{l}$  of  $\text{DMSO-}d_6$  (d).



**Fig. S6.** Selected region of the  $^1\text{H}$  NMR spectra of a solution of 5@2b2b in  $\text{CH}_2\text{Cl}_2\text{-}d_2$  at 200 K (a), 270 K (b), and 298 K (c). Primed numbers indicate diastereotopic protons, second primed numbers indicate protons corresponding to encapsulated 5. See [Scheme S1](#) for proton assignments.



Scheme S1. Molecular structures of compounds 2-5.