

A poly-pseudorotaxane constructed by threading pillar[5]arene onto an ion pair recognition-based calix[4]pyrrole supramolecular polymer

Necla Bektas and Abdullah Aydogan*

Department of Chemistry, Istanbul Technical University, Maslak, 34469, Istanbul, Turkey

Email: aydoganab@itu.edu.tr

Phone: +90 (212) 285 7285, Fax: +90 (212) 285 6386

Table of Contents

General Considerations.....	2
NMR Spectra	3
Stoichiometry and Association Constant Determinations.....	9
P5A-BisPy	9
C4P-Acetate	11
C4P-BisPy.....	13
References.....	15

General Considerations

All solvents were dried before use according to standard procedures. Unless specifically indicated, all other chemicals and reagents used in this study were purchased from commercial sources and used as received. ¹H-, NEOSY-, DOSY-NMR spectra were recorded on Agilent VNMRS 500 spectrometers using TMS as an internal reference. Mass spectra were measured on a Thermo Scientific Thermo Q Exactive HR mass spectrometer equipped with a LC unit. DLS measurements were performed on a Malvern Zetasizer Nano ZS particle size analyzer equipped with a 4 mV He-Ne laser operating at $\lambda = 632$ nm, an avalanche photodiode detector with high quantum efficiency, and an ALV/LSE-5003 multiple tau digital correlator electronics system. Viscosity measurements were carried out with an Ubbelohde micro dilution viscometer (Shanghai Liangjing Glass Instrument Factory, 0.40 mm inner diameter) at 293 K. **C4P**, **P5A**, **BisPy**, and **TBASub** were synthesized according to previously reported literature procedures.¹⁻⁴

NMR Spectra

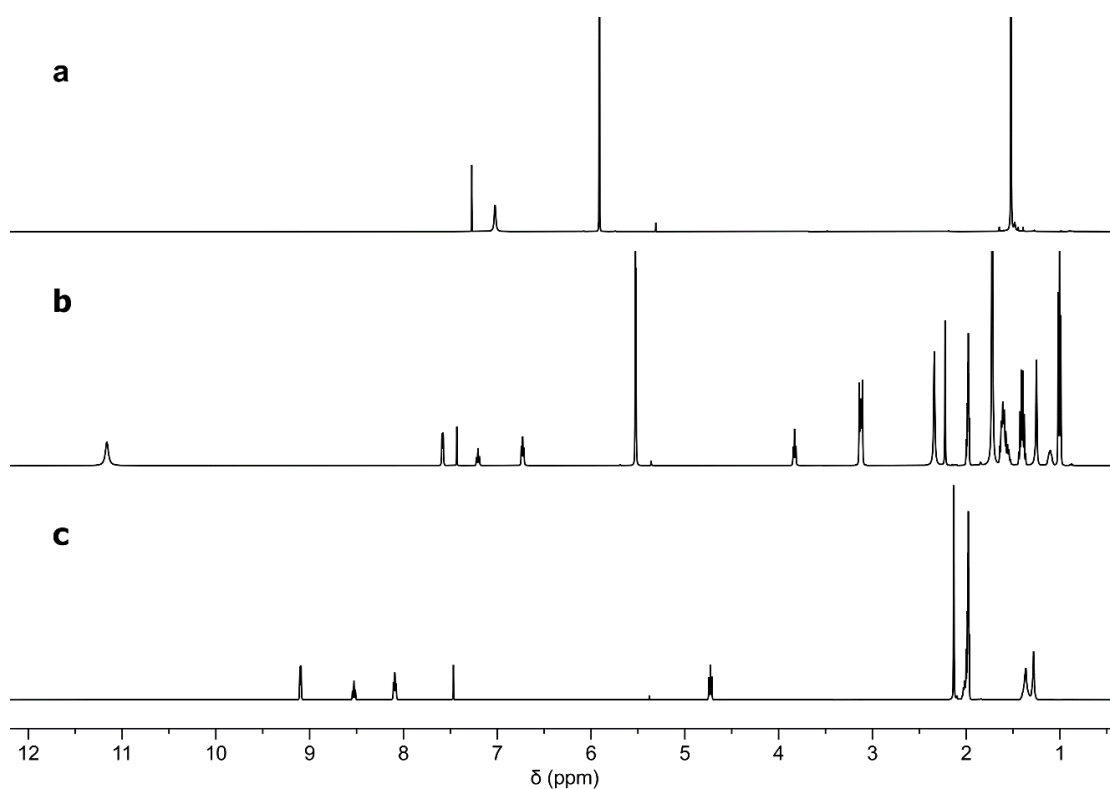


Fig. S1 ^1H -NMR spectra of (a) **C4P**, (b) **1**, and (c) **BisPy** recorded in (a) CDCl_3 , (b and c) $\text{CDCl}_3/\text{CD}_3\text{CN}$ (4:1, v/v).

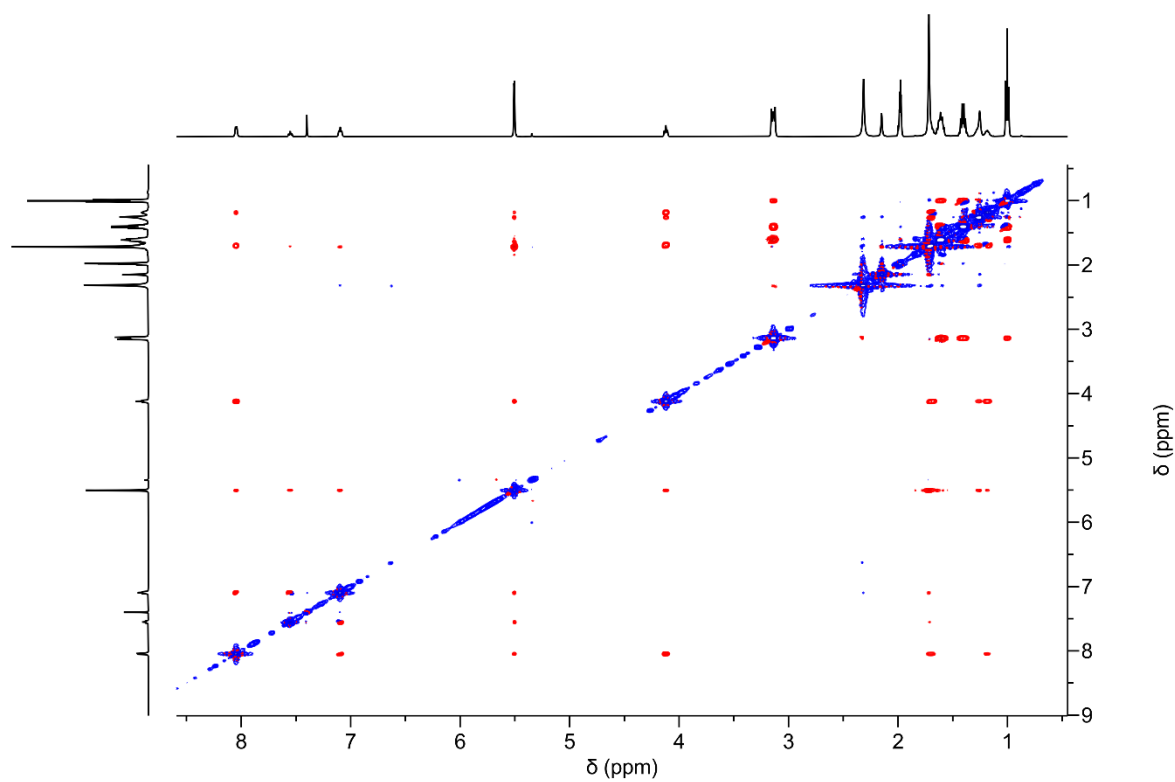


Fig. S2 NOESY-NMR spectrum of **1** recorded in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (4:1, v/v).

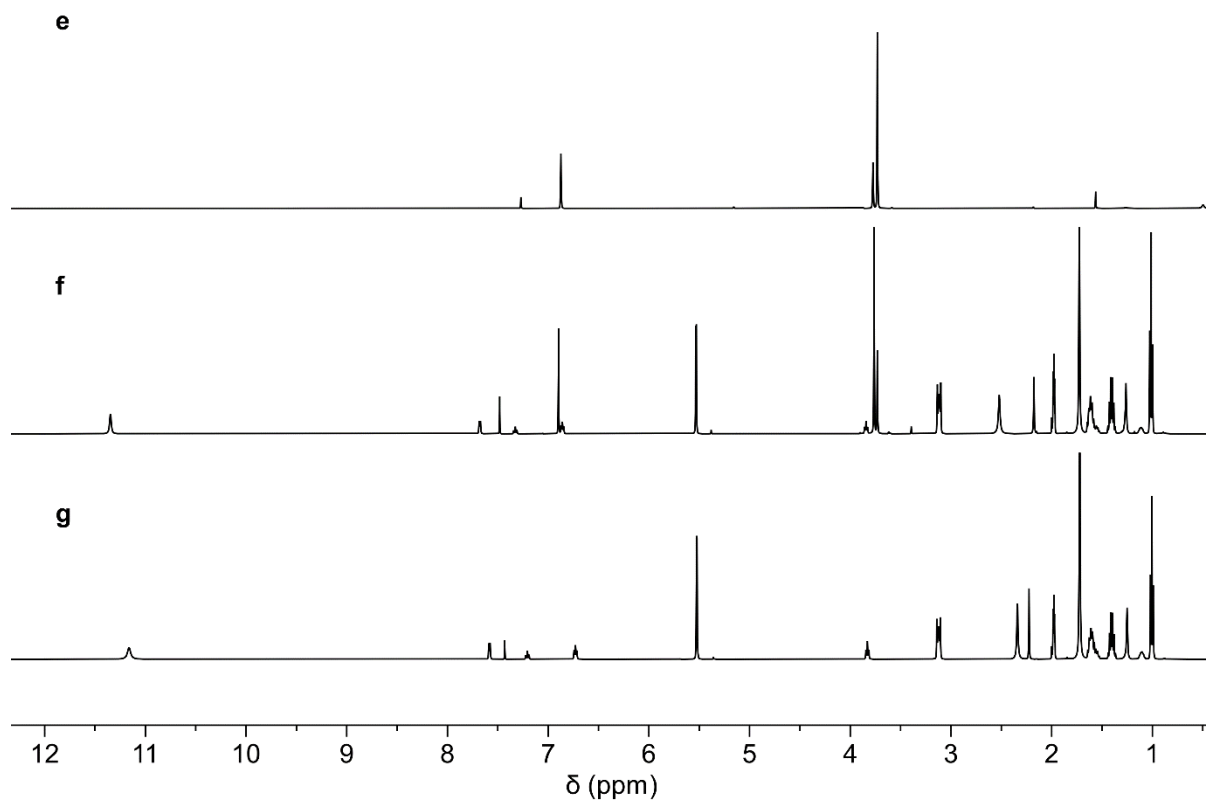


Fig. S3 ^1H -NMR spectra of (e) **P5A**, (f) **2**, and (g) **1** recorded in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (4:1, v/v).

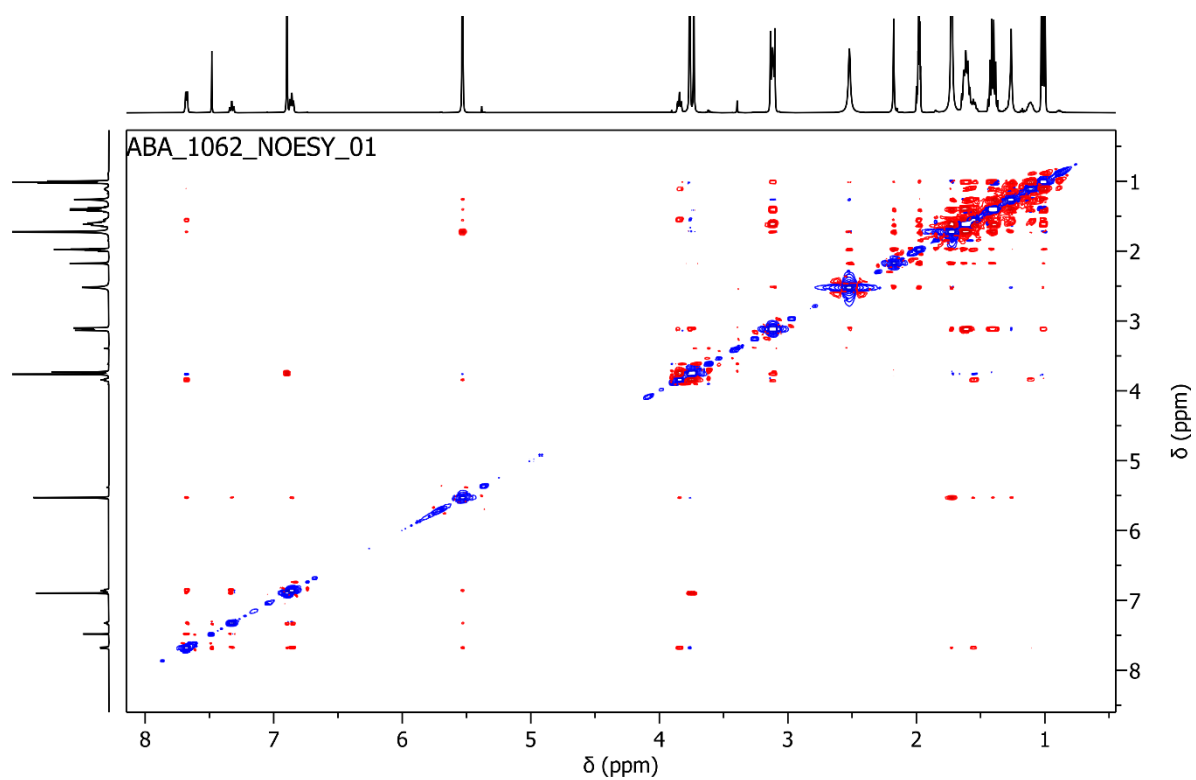


Fig. S4 NOESY-NMR spectrum of **2** recorded in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (4:1, v/v).

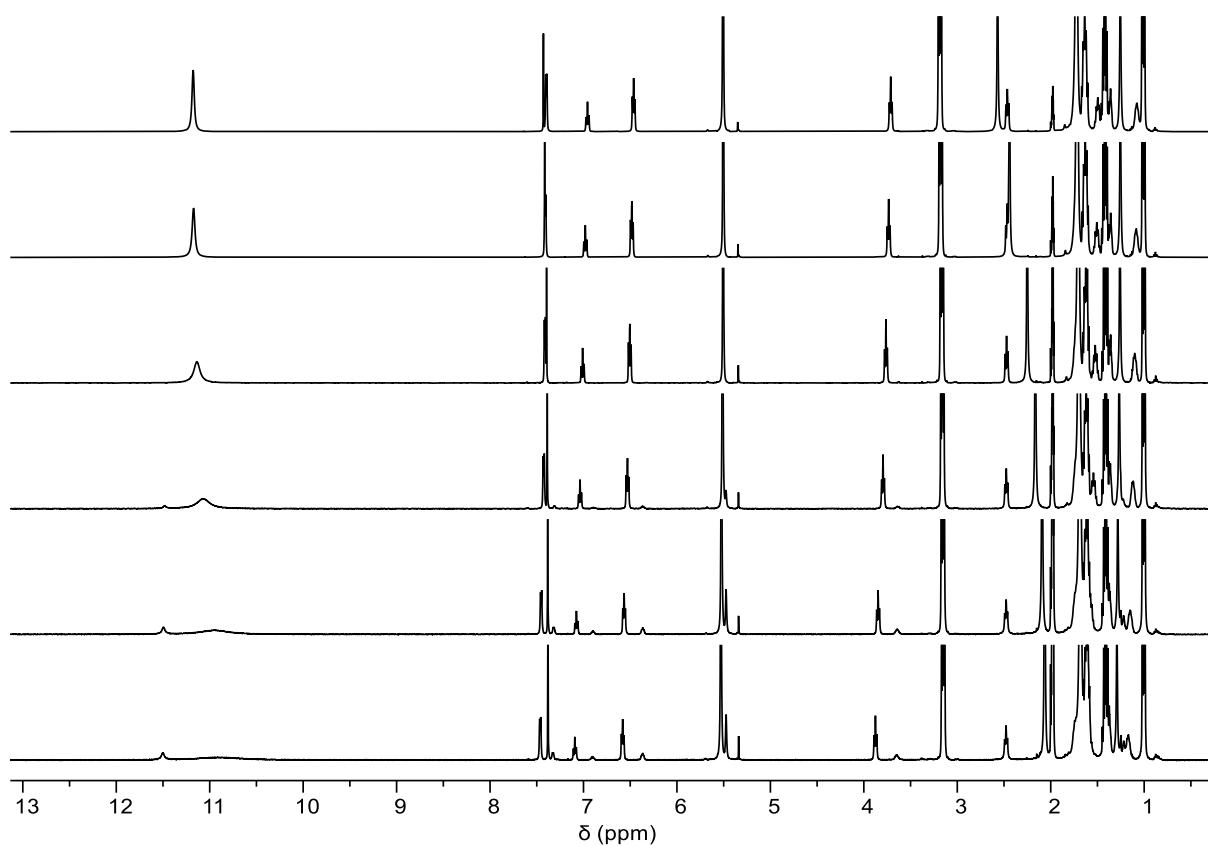


Fig. S5 ¹H NMR spectra of **3** recorded in CDCl₃/CD₃CN (4:1, v/v) at varying concentrations. Bottom to top: 3.4, 9.6, 21.7, 34.8, 77, and 121 mM (based on C₄P unit).

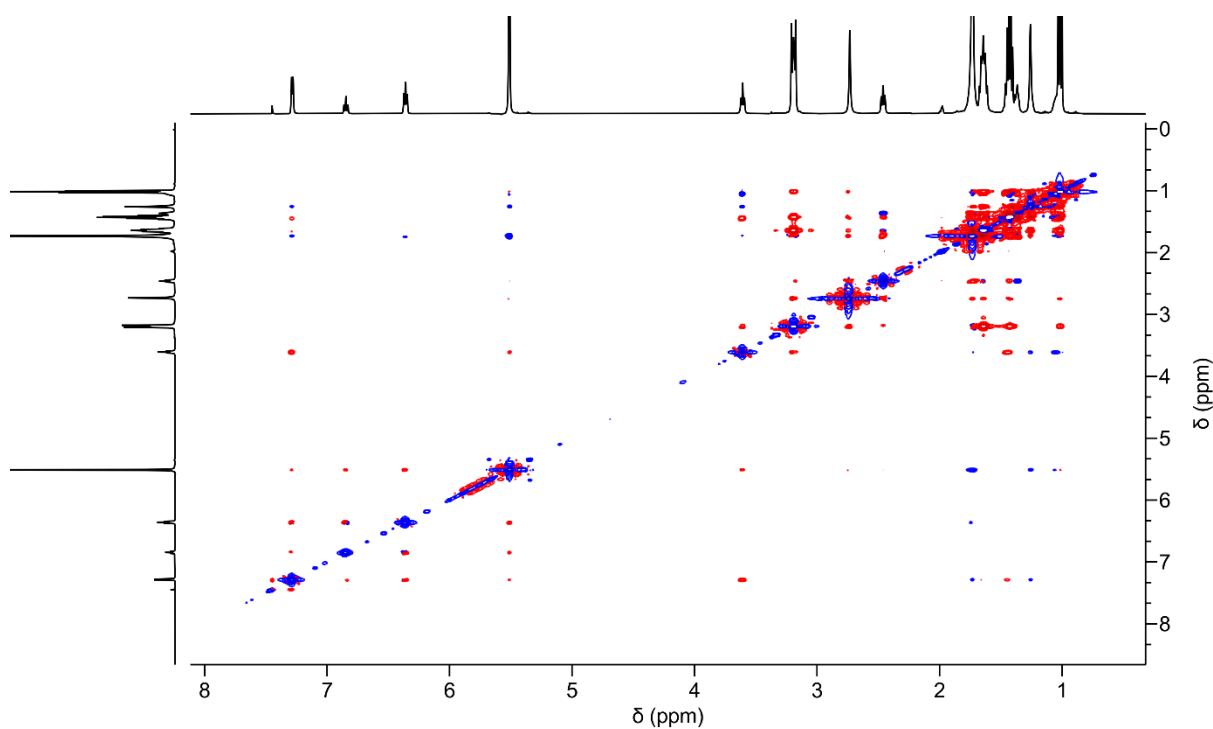


Fig. S6 NOESY-NMR spectrum of **3** recorded in CDCl₃/CD₃CN (4:1, v/v).

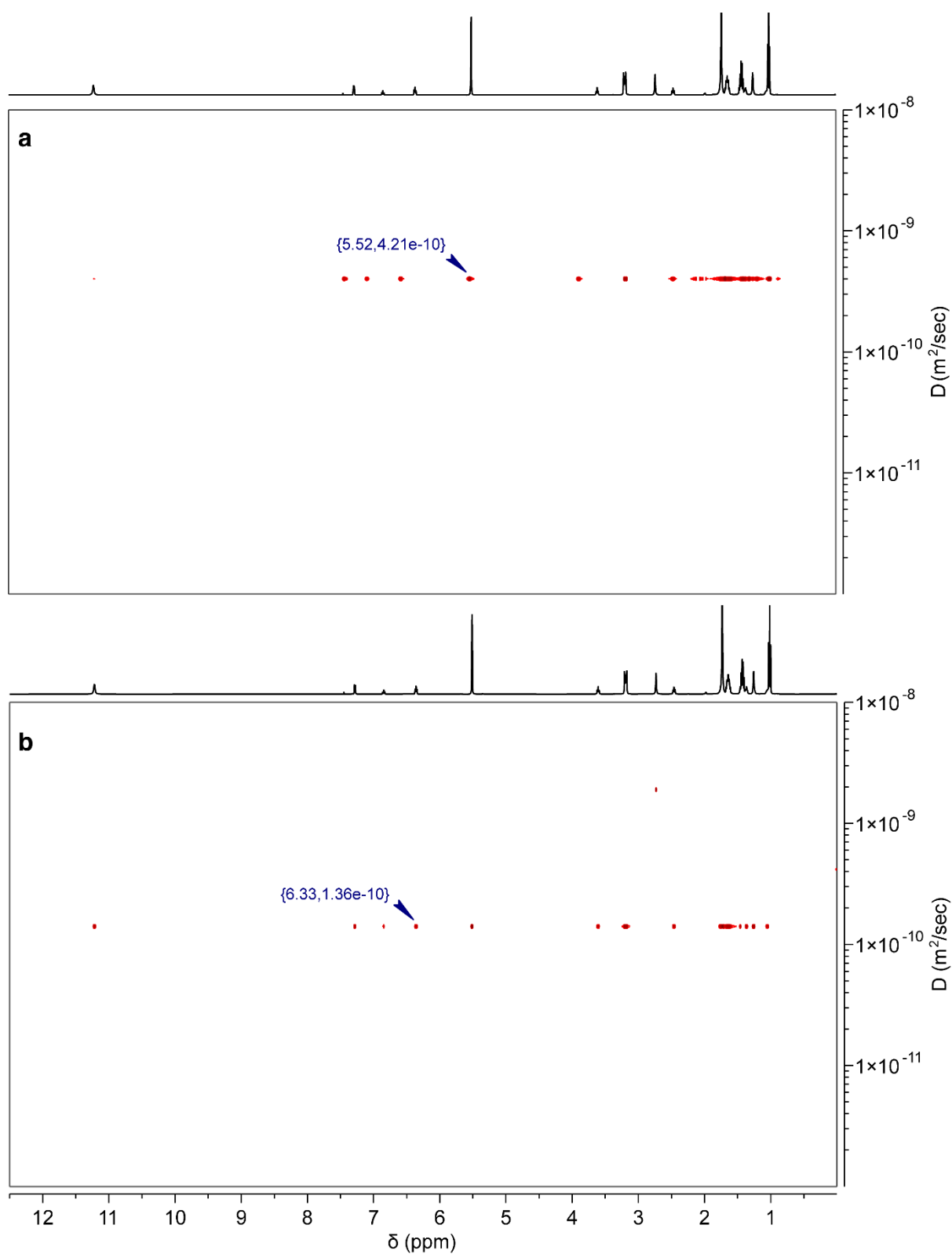


Fig. S7 DOSY-NMR spectra of **3** recorded in CDCl₃/CD₃CN (4:1, v/v) at 25 °C: (a) 6 and (b) 140 mM concentrations.

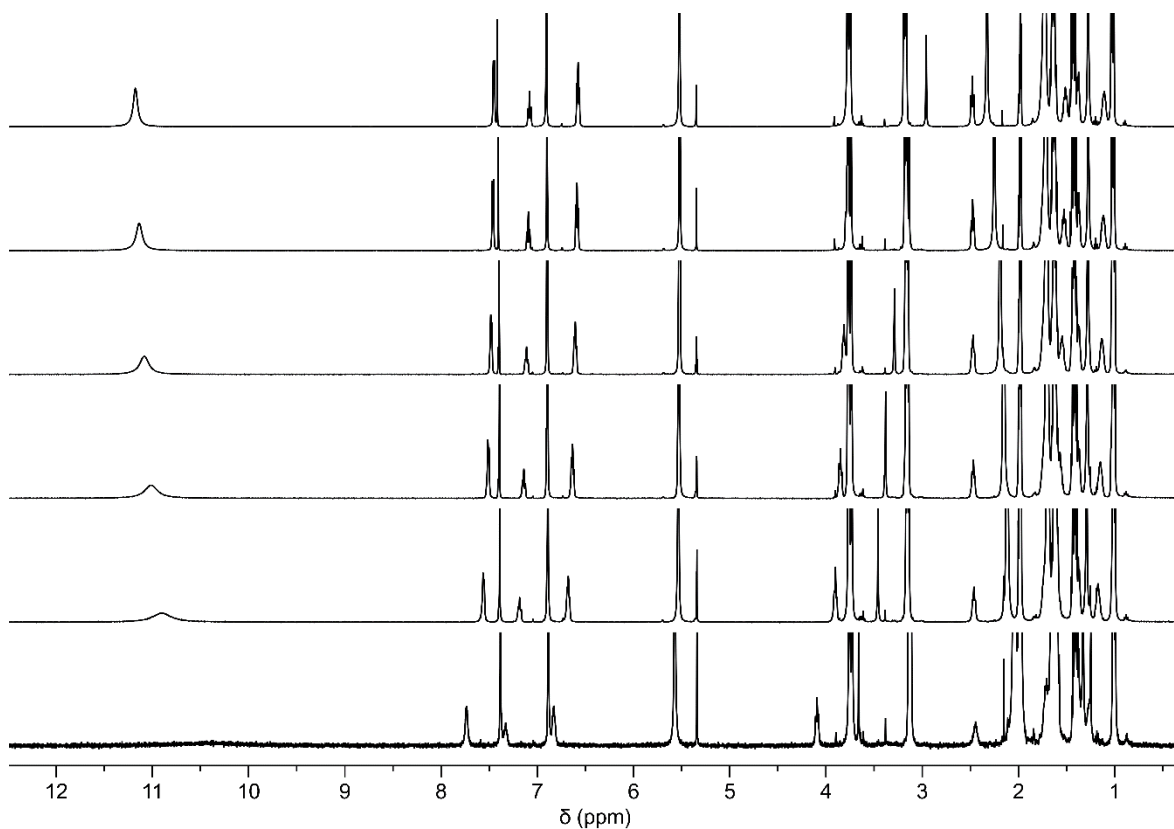


Fig. S8 ¹H NMR spectra of **4** recorded in CDCl₃/CD₃CN (4:1, v/v) at varying concentrations. Bottom to top: 2.87, 10.9, 14.4, 26.7, and 37.4c mM (based on C4P unit).

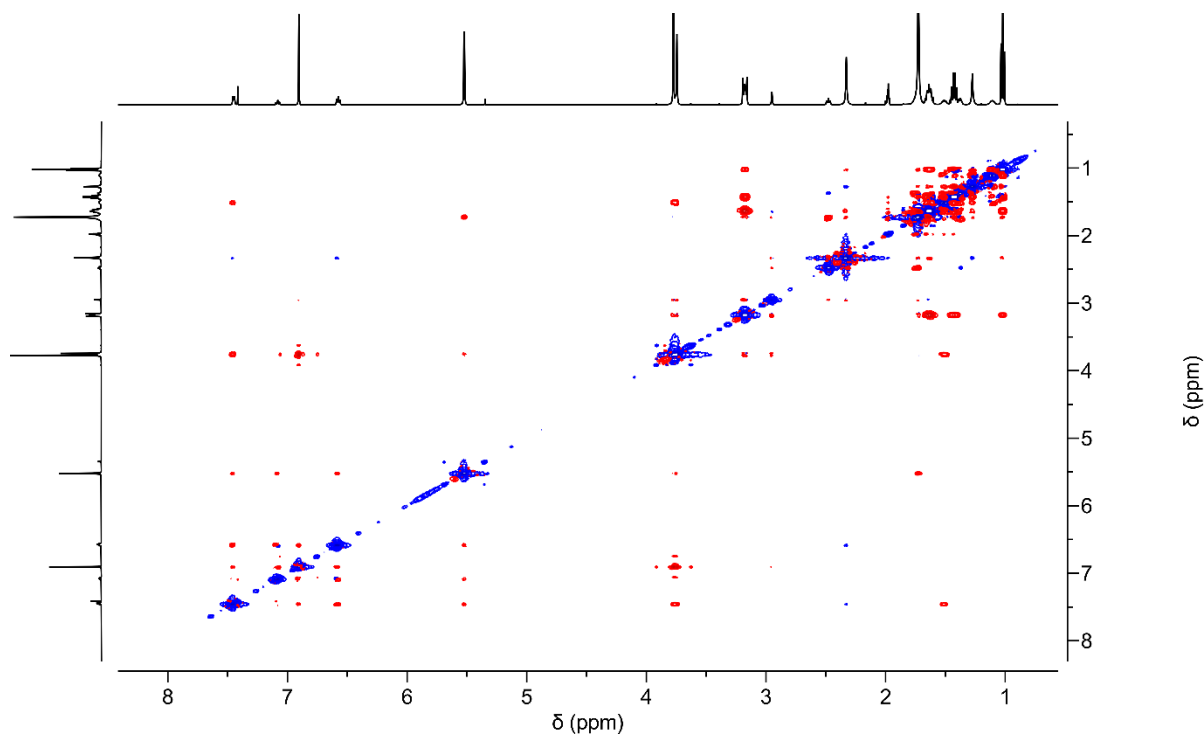


Fig. S9 NOESY-NMR spectrum of **4** recorded in CDCl₃/CD₃CN (4:1, v/v).

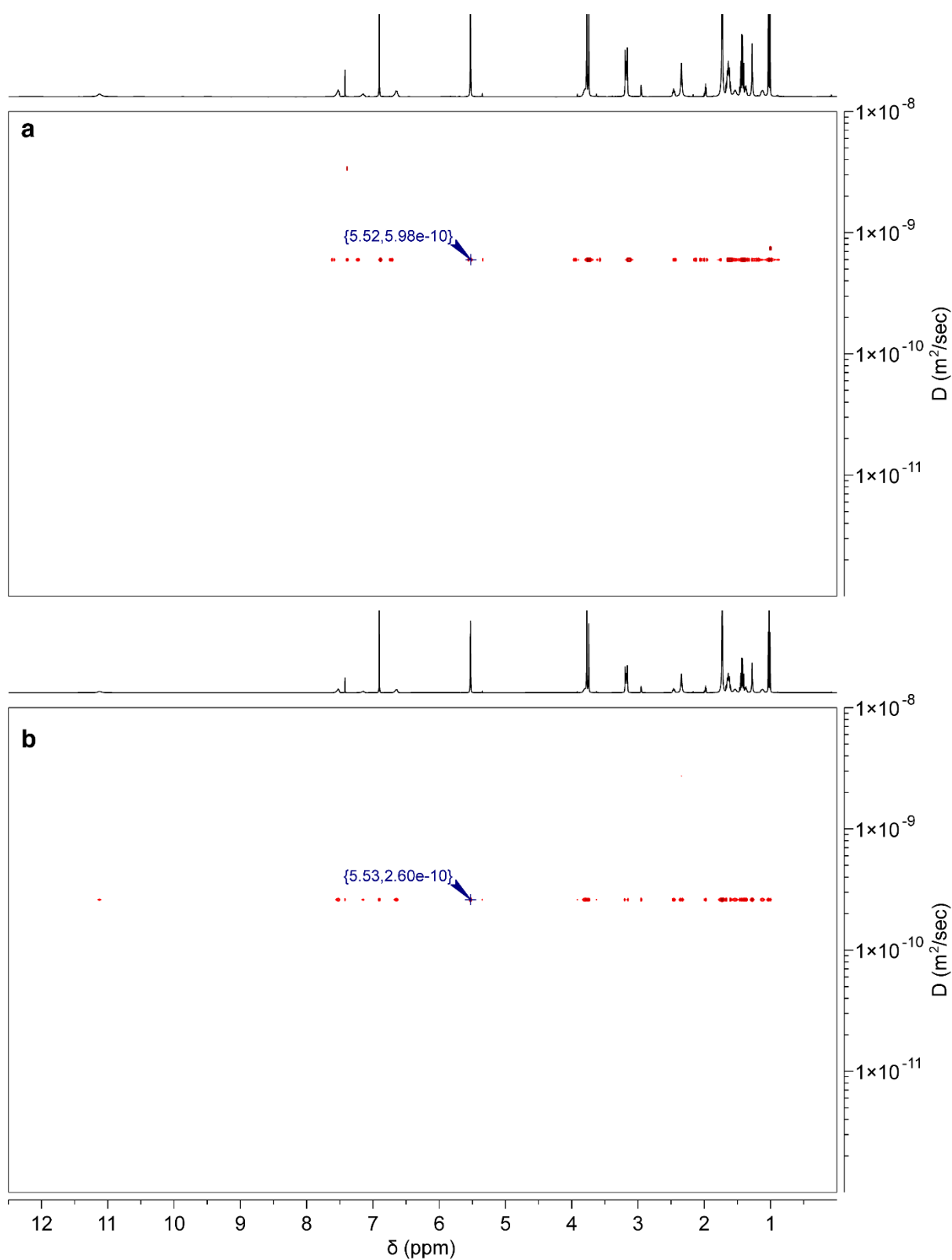


Fig. S10 DOSY-NMR spectra of **4** recorded in CDCl₃/CD₃CN (4:1, v/v) at 25 °C: (a) 3.0 and (b) 37.4 mM concentrations.

Stoichiometry and Association Constant Determinations

The following equation⁵ was used to fit the binding data obtained from NMR titrations.

$$\Delta\delta = (\delta_{max} - \delta_{free}) \frac{[1 + K([H]_0 + [G]_0)] - \sqrt{[1 + K([H]_0 + [G]_0)]^2 - 4K^2[H]_0[G]_0}}{2K[H]_0} \quad (1)$$

P5A-BisPy

To determine the stoichiometry and association constant between **P5A** and **BisPy**, ¹H NMR titrations were performed in CDCl₃/CD₃CN (4:1, v/v) solutions which had a constant concentration of **P5A** (3.99 mM) and varying concentrations of **BisPy**. By a non-linear curve-fitting method, the association constant between **P5A** and **BisPy** was determined to be $1.1 \times 10^2 \pm 26.6 \text{ M}^{-1}$ and the complexation stoichiometry between **P5A** and **S1** was found to be 1 as depicted in Figs. S12 and S13.

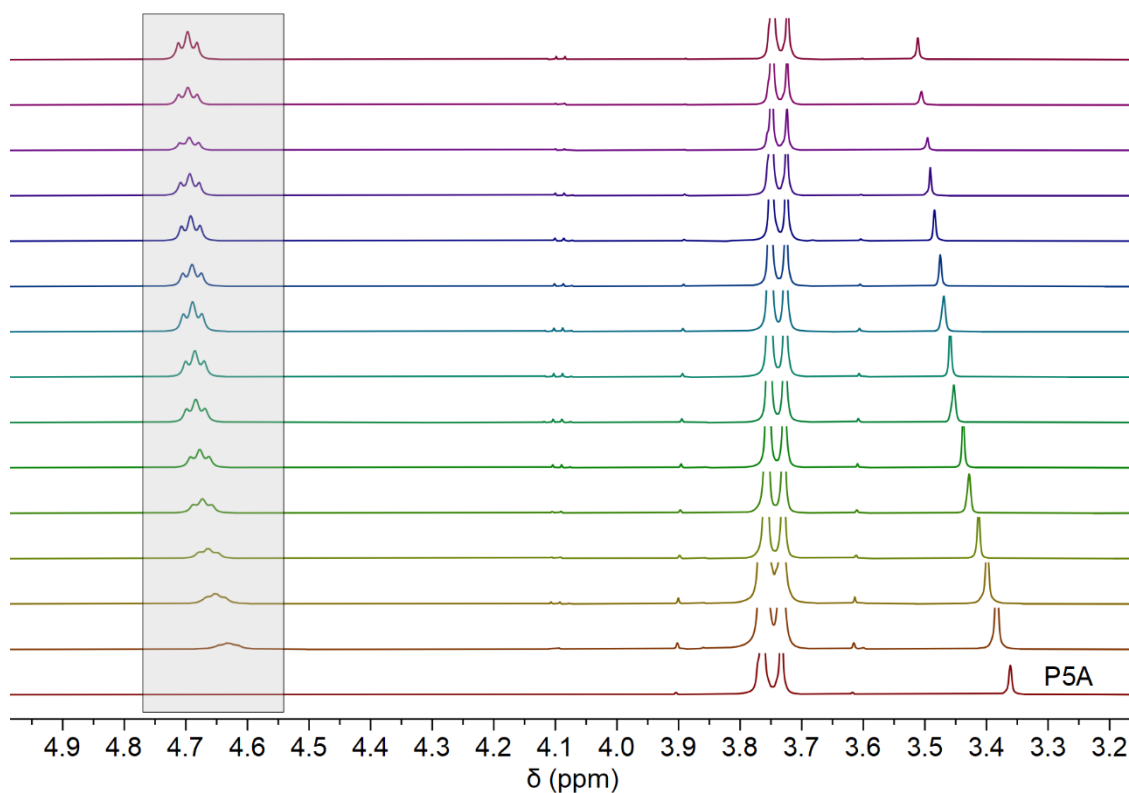


Fig. S11 Partial ¹H NMR spectra (500z MHz, CDCl₃/CD₃CN, 4:1, v/v, 25 °C) of **P5A** at a constant concentration of 3.99 mM. Chemical shift changes of Py-CH₂- proton signal at 4.611 ppm upon addition of **BisPy** at 0.28, 0.59, 0.86, 1.11, 1.35, 1.65, 1.9, 2.22, 2.47, 2.72, 2.97, 3.21, 3.45, 3.68 equivalents from bottom to top.

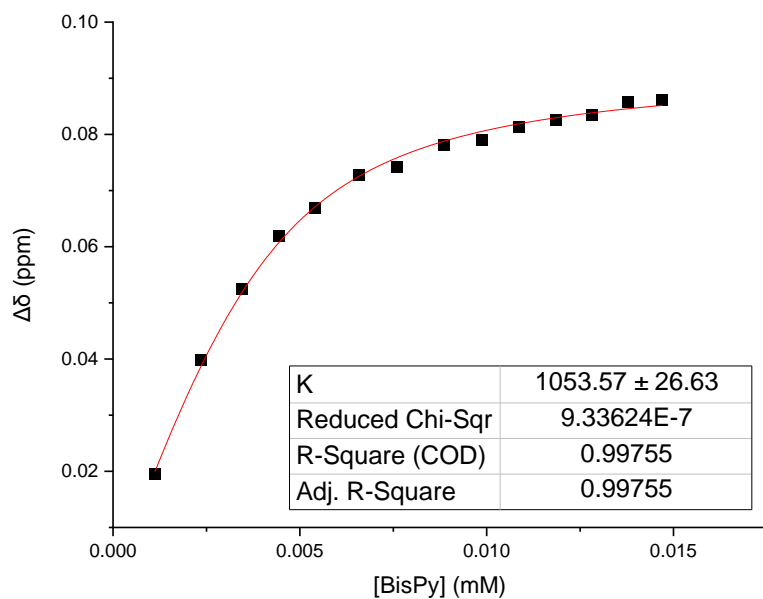


Fig. S12 Chemical shift changes of N-CH₂- protons belonging to **BisPy**. The red solid line was obtained from a non-linear curve fitting based on 1:1 binding scheme and equation (1).

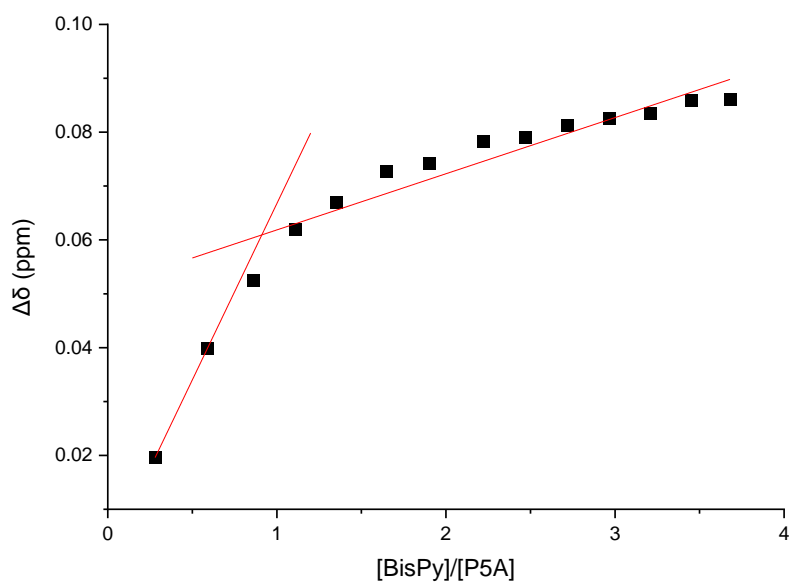


Fig. S13 Molar ratio plot for the interaction of **P5A** with **BisPy**, indicating a 1:1 stoichiometry

C4P-Acetate

To determine the stoichiometry and association constant between **C4P** and ⁻OAc, ¹H NMR titrations were performed in CDCl₃/CD₃CN (4:1, v/v) solutions which had a constant concentration of **C4P** (4.46 mM) and varying concentrations of tetrabutylammonium acetate (**TBAOAc**). By a non-linear curve-fitting method, the association constant between **C4P** (Host) and ⁻OAc (Guest) was determined to be $1.8 \times 10^3 \pm 148 \text{ M}^{-1}$ and the complexation stoichiometry between **C4P** and ⁻OAc was found to be 1 (Figs. S15 and S16).

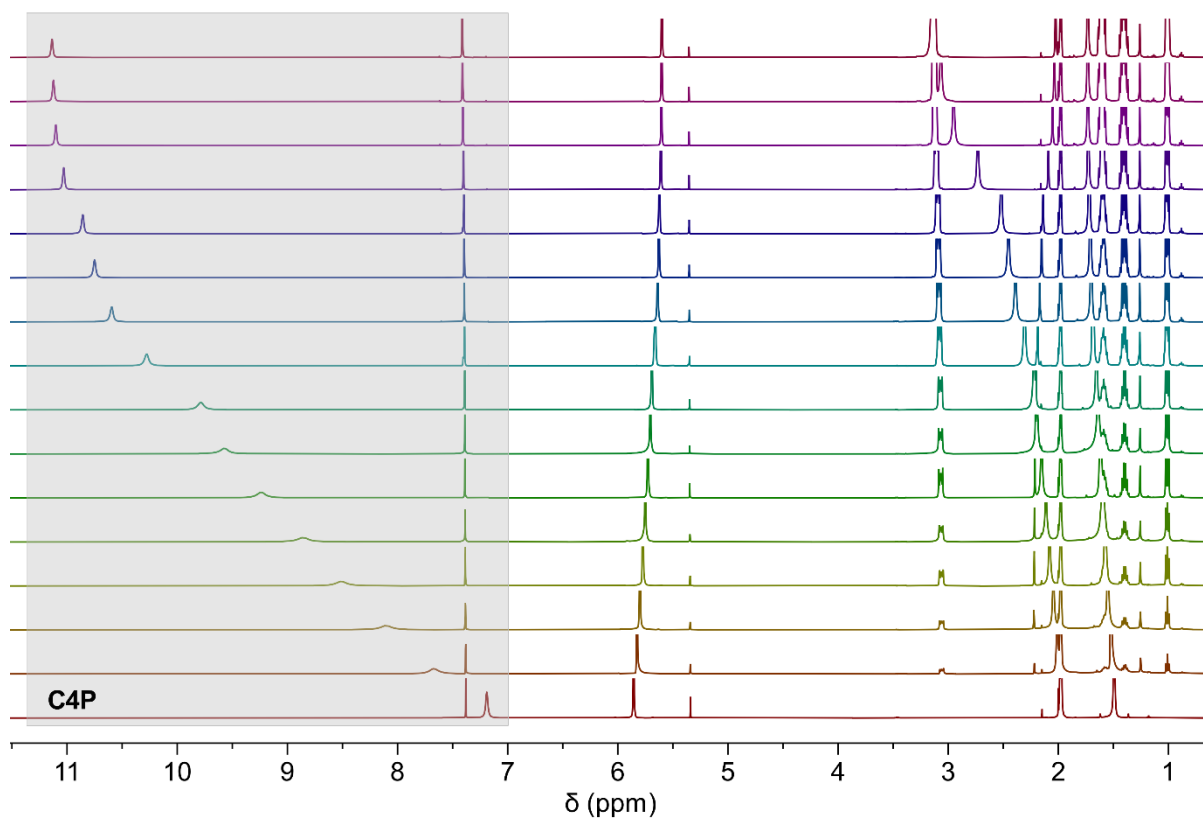


Fig. S14 Partial ¹H NMR spectra (500 MHz, CDCl₃/CD₃CN, 4:1, v/v, 25 °C) of **C4P** at a constant concentration of 4.46 mM upon addition of **TBAOAc** mixture at 0, 0.14, 0.24, 0.35, 0.46, 0.54, 0.65, 0.73, 0.89, 1.1, 1.25, 1.51, 2.59, 3.24, 3.96, 4.33 equivalents from bottom to top.

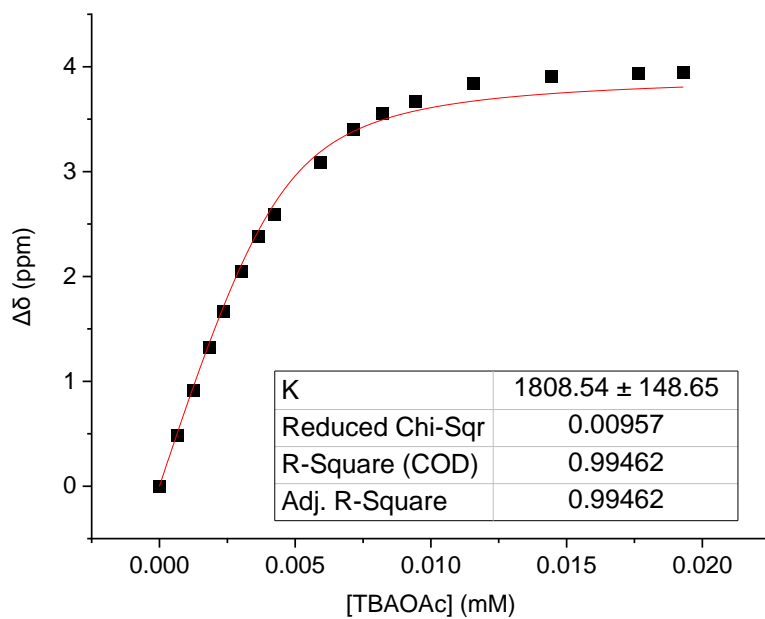


Fig. S15 Chemical shift changes of one of the pyrrole NH protons (initially at 7.19 ppm) belonging to **C4P** (15.6 mM) upon addition of **TBAOAc**. The red solid line was obtained from a non-linear curve fitting using the equation (1).

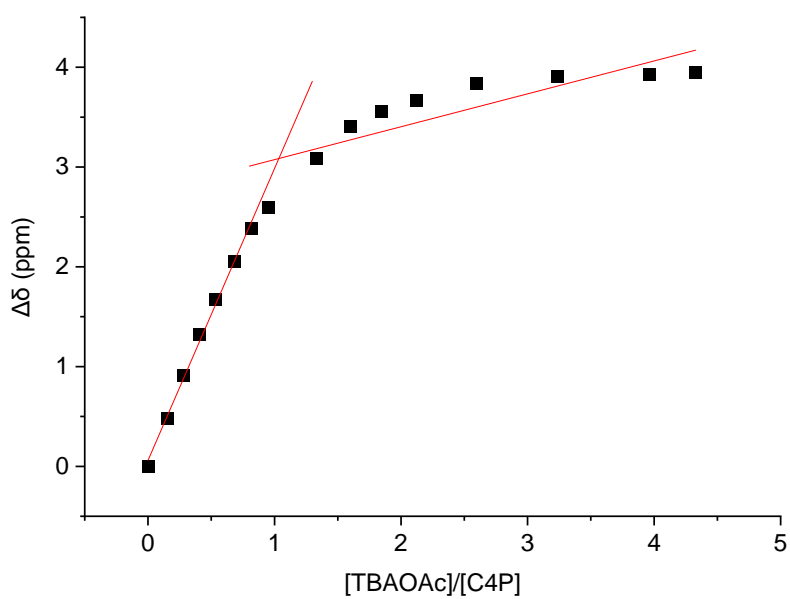


Fig. S16 Molar ratio plot for the interaction of **C4P** with **TBAOAc**, indicating a 1:1 stoichiometry.

C4P-BisPy

To determine the stoichiometry and association constant between π -electron cup of $^-$ OAc bound **C4P** and Py units of **BisPy**, ^1H NMR titrations were performed in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (4:1, v/v) solutions which had a constant concentration of **C4P** (9.3 mM) and varying concentrations of **BisPy**. By a non-linear curve-fitting method, the association constant between **C4P** (Host) and **BisPy** (Guest) was determined to be $3.1 \times 10^3 \pm 260 \text{ M}^{-1}$ and the complexation stoichiometry between **C4P** and **BisPy** was found to be 1 (Figs. S18 and S19).

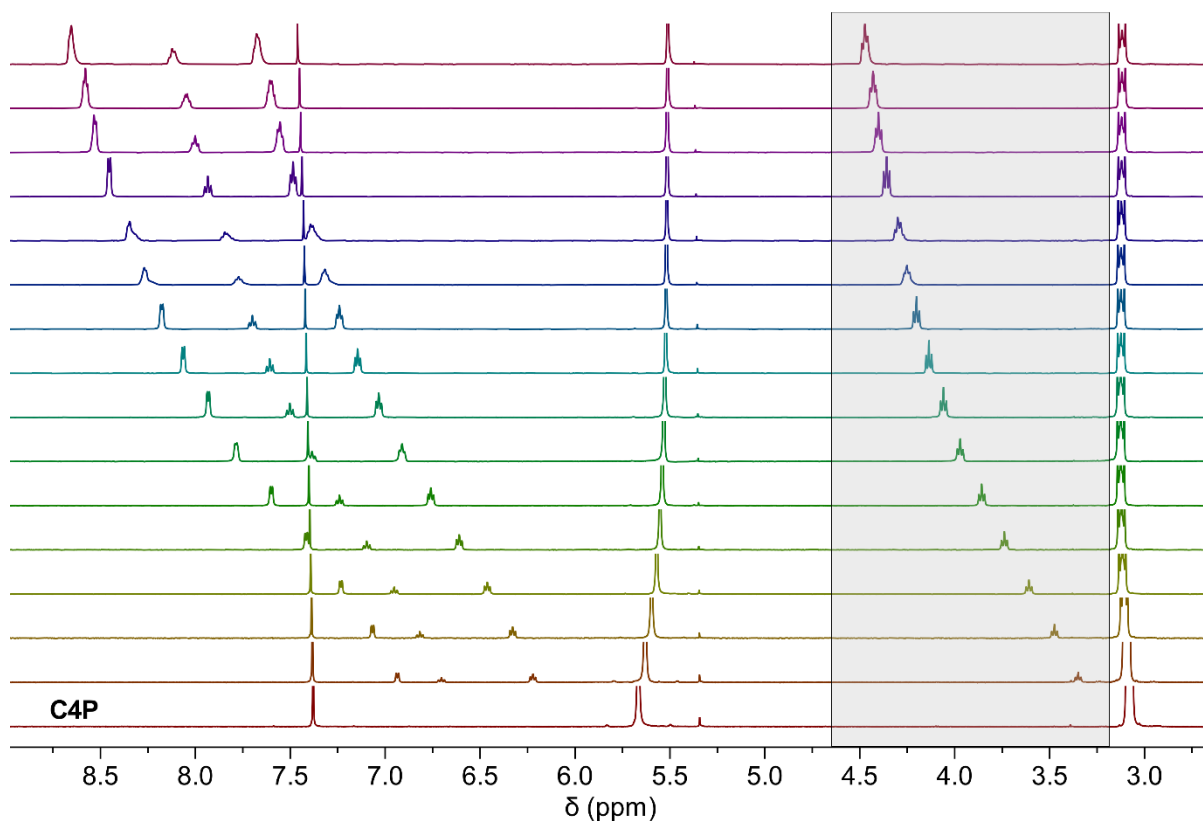


Fig. S17 Partial ^1H NMR spectra (500 MHz, $\text{CDCl}_3/\text{CD}_3\text{CN}$, 4:1, v/v, 25 $^\circ\text{C}$) of **C4P** at a constant concentration of 9.33 mM upon addition of **BisPy** at 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.4, 1.7, 2.0 equivalents from bottom to top.

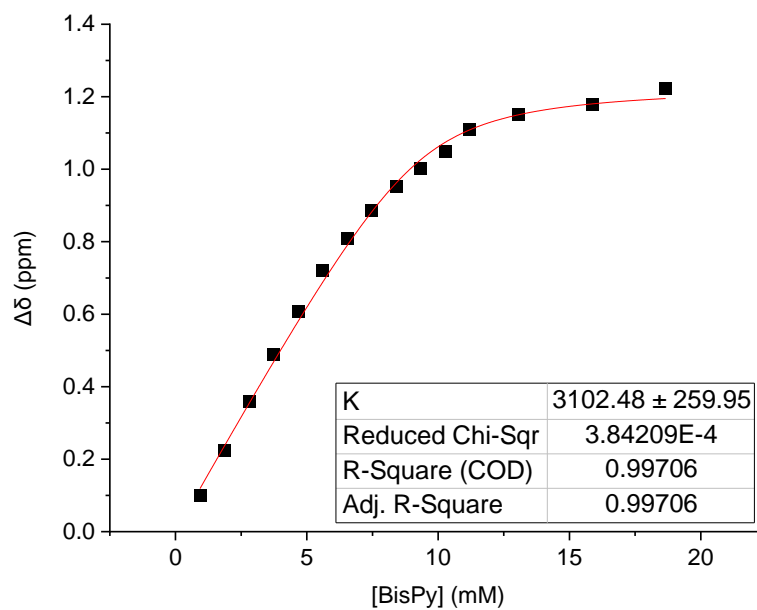


Fig. S18 Chemical shift changes of $-\text{Py}-\text{CH}_2-$ protons belonging to **BisPy** upon addition of **BisPy** into a **C4P** (9.3 mM) solution. The red solid line was obtained from a non-linear curve fitting using the equation (1).

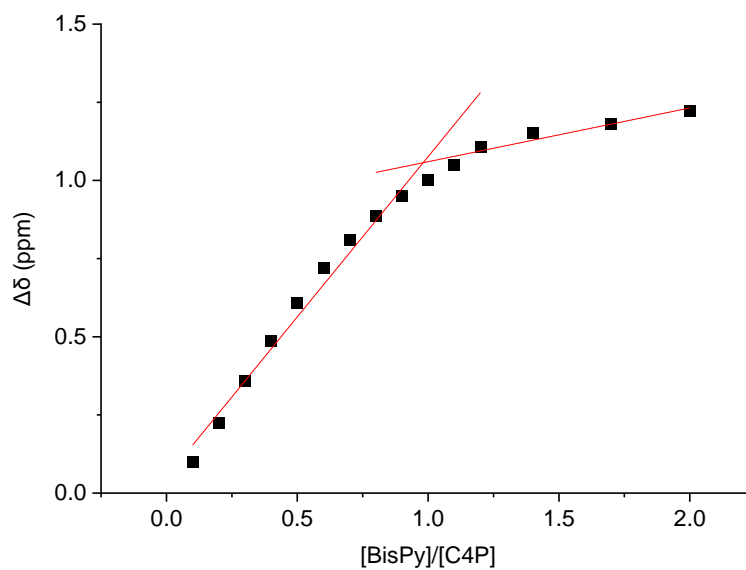


Fig. S19 Molar ratio plot for the interaction of **C4P** with **BisPy**, indicating a 1:1 stoichiometry.

References

1. Ogoshi, T.; Kanai, S.; Fujinami, S.; Yamagishi, T.-a.; Nakamoto, Y., para-Bridged Symmetrical Pillar[5]arenes: Their Lewis Acid Catalyzed Synthesis and Host–Guest Property. *J. Am. Chem. Soc.* **2008**, *130* (15), 5022-5023.
2. Li, C.; Xu, Q.; Li, J.; Feina, Y.; Jia, X., Complex interactions of pillar[5]arene with paraquats and bis(pyridinium) derivatives. *Org. Biomol. Chem.* **2010**, *8* (7), 1568-1576.
3. Yuvayapan, S.; Aydogan, A., Supramolecular calix[4]pyrrole polymers from a complementary pair of homoditopic host–guest molecules. *Chem. Commun.* **2019**, *55* (60), 8800-8803.
4. Baeyer, A., Ueber ein Condensationsproduct von Pyrrol mit Aceton. *Berichte der deutschen chemischen Gesellschaft* **1886**, *19* (2), 2184-2185.
5. Hristova, Y. R.; Smulders, M. M. J.; Clegg, J. K.; Breiner, B.; Nitschke, J. R., Selective anion binding by a “Chameleon” capsule with a dynamically reconfigurable exterior. *Chemical Science* **2011**, *2* (4), 638-641.