A dimethoxypillar[5]arene/azastilbene host–guest recognition motif and its application in the fabrication of polypseudorotaxane

Liyun Wang[ab], Danyu Xia*[a], Jianbin Chao[a], Junjie Zhang[a], Xuehong Wei*[ab] and Pi Wang*[c]

[a]*Scientific Instrument Center, Shanxi University, Taiyuan, 030006, P. R. China; E-mail: danyuxia@sxu.edu.cn*
[b]*School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan, 030006, P. R. China*
[c]*Ministry of Education Key Laboratory of Interface Science and Engineering in Advanced Materials, Taiyuan University of Technology, Taiyuan, 030024, P.R. China; E-mail: wangpi@tyut.edu.cn*

Supporting Information (14 pages)

1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. **DMP5**[S1] was prepared according to published procedures. Compound ***trans*-G1**, **G2**, **G3**, **G4**, **G5**, **G6** and $Cu(OAc)_2$ were commercially available. NMR spectra were recorded with a Bruker Avance DMX 600 spectrophotometer. FT-IR spectra were recorded with a Thermo Scientific Nicolet iS50 instrument. XRD were performed with a Bruker D2 PHASER. Scanning electron microscopy investigations were carried out on a TASCAN (LYRA3) instrument. Atomic force microscopy experiments were performed by a Bruker Multi-Mode 8.0 instrument.

2. Partial 2 D NOESY NMR spectrum of an equimolar solution of ***DMP5*** *and* ***trans-G1***

2D NOESY NMR experiment was employed to study the relative positions of the components in complex **DMP5⊃*trans*-G1.** NOE correlation signals were observed between proton H_a of ***trans*-G1** and protons H_3 of **DMP5** (A), between proton H_b of ***trans*-G1** and protons H_1 and H_2 of **DMP5** (B and C), between proton H_c of ***trans*-G1** and protons H_3 of **DMP5** (D).

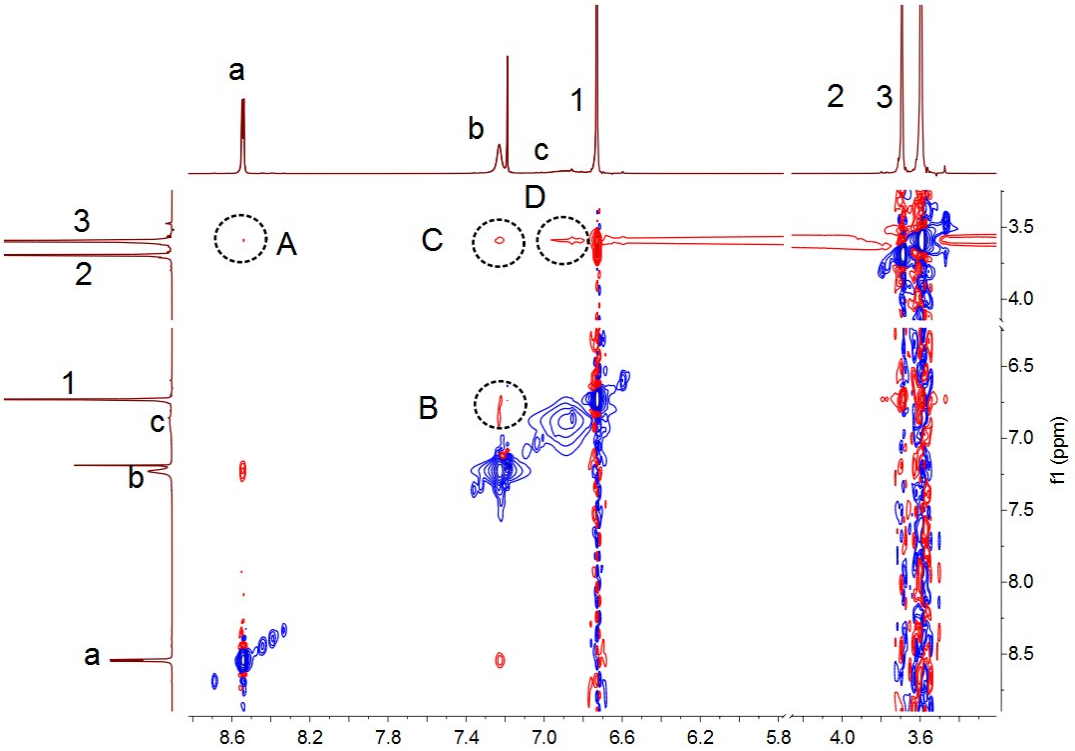

Figure S1 Partial 2D NOESY spectra of an equimolar mixture ***trans*-G1** and **DMP5** (15.0 mM) (600 MHz, $CDCl_3$, room temperature).

3. Stoichiometry and association constant determination for the complexation between ***DMP5*** *and* ***trans-G1***

To determine the stoichiometry and association constant between **DMP5** and ***trans*-G1**, ^1H NMR titration was done with solutions which had a constant concentration of ***trans*-G1** (1.00 mM) and different concentrations of **DMP5**. By a mole ratio plot, a 1:1 stoichiometry was obtained for this system. By a non-linear curve-fitting method, the association constant between the **DMP5** and ***trans*-G1** was calculated.

The non-linear curve-fitting was based on the equation: [S2]

$\Delta\delta = (\Delta\delta\infty/[G]_0)\ (0.5[H]_0 + 0.5([G]_0 + 1/Ka) - (0.5([H]_0^2 + (2[H]_0(1/Ka - [G]_0)) + (1/Ka + [G]_0)^2)^{0.5}))$ (Eq. S2)

When $\Delta\delta$ is the chemical shift change of H_c on ***trans*-G1** at $[G]_0$, $\Delta\delta_\infty$ is the chemical shift change of H_c when the guest is completely complexed, $[G]_0$ is the fixed initial concentration of the guest, and $[H]_0$ is the varying concentration of **DMP5**.

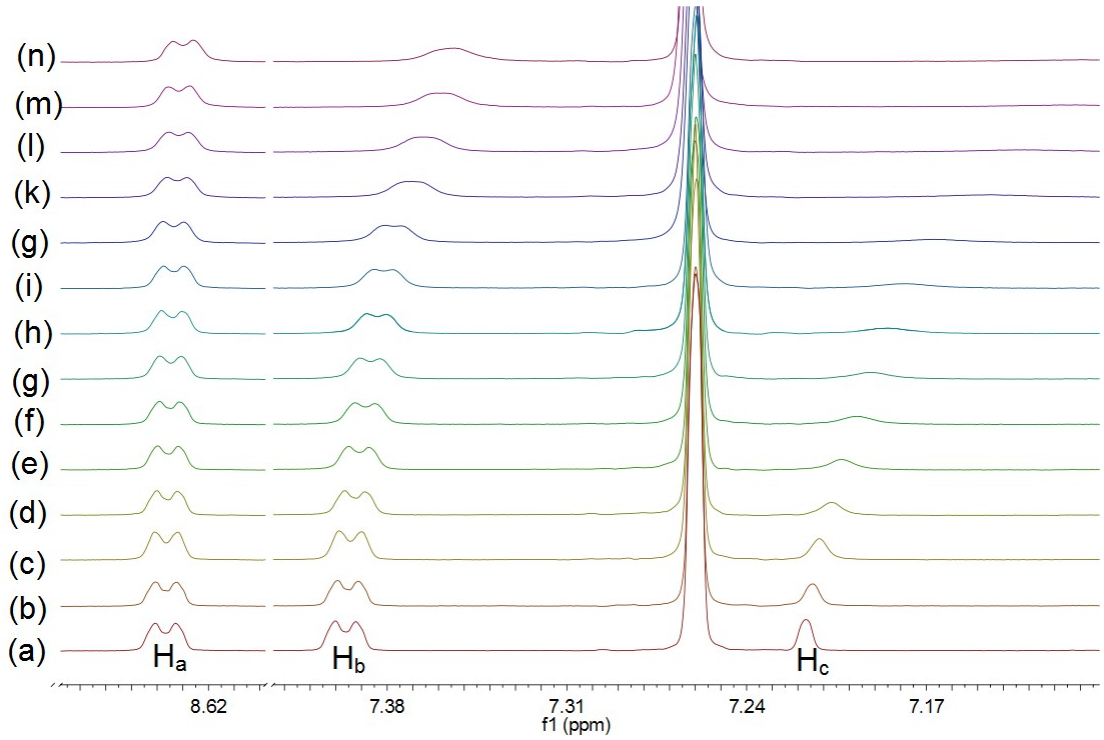

Figure S2 Partial ^{1}H NMR spectra (600 MHz, $CDCl_3$, room temperature) of ***trans*-G1** at a concentration of 1.00 mM with different concentrations of **DMP5**: (a) 0.00 mM; (b) 0.0990 mM; (c) 0.196 mM; (d) 0.385 mM; (e) 0.566 mM; (f) 0.826 mM; (g) 1.07 mM;(h) 1.38 mM; (i) 1.67 mM; (j) 2.31 mM; (k) 4.12 mM; (l) 5.24 mM; (m) 5.23 mM; (n) 6.30 mM.

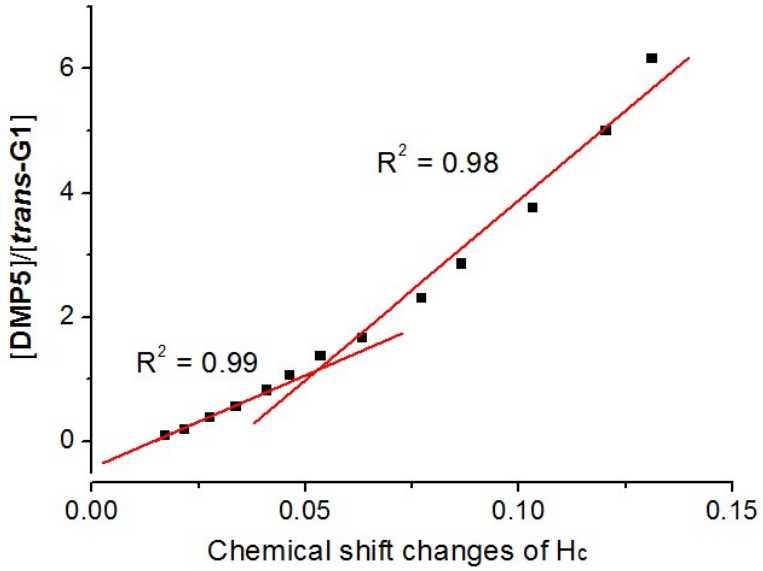

Figure S3 Mole ratio plot for the complexation between **DMP5** and ***trans*-G1**, indicating a 1:1 stoichiometry.

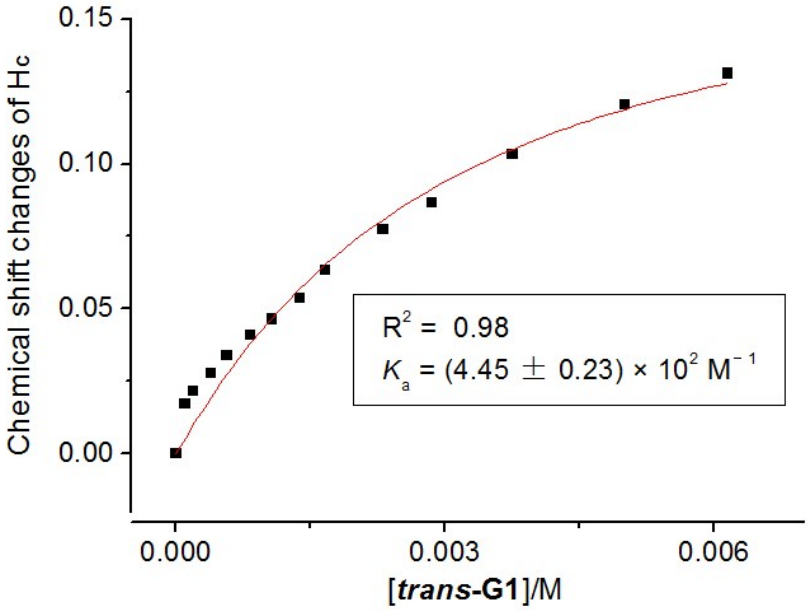

Figure S4 The chemical shift changes of H_c on ***trans*-G1** upon addition of **DMP5**. The red solid line was obtained from the non-linear curve-fitting using Eq. S1

*4. Partial [1]H NMR spectra of an equimolar solution of **DMP5** and **G2***

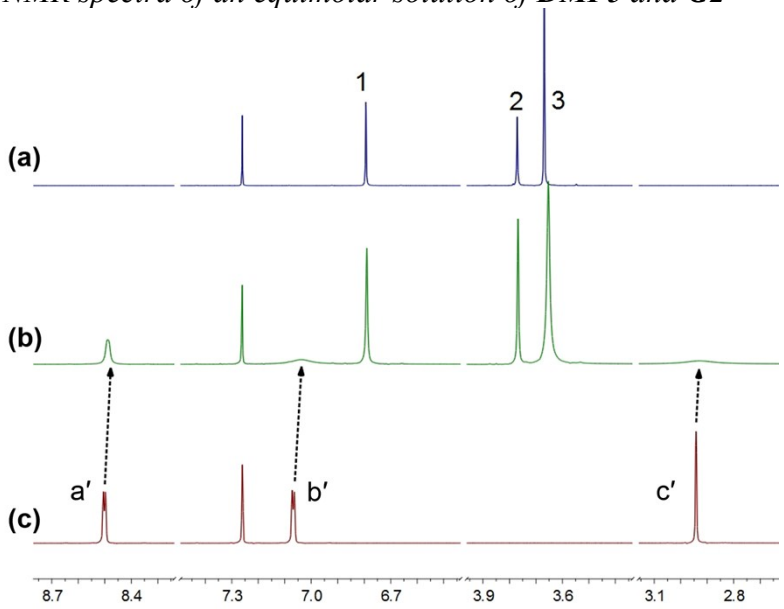

Figure S5 Partial ^{1}H NMR spectra (600 MHz, $CDCl_3$, room temperature): (a) **DMP5** (5.00 mM); (b) **G2** (5.00 mM) and **DMP5** (5.00 mM); (c) **G2** (5.00 mM).

*5. Partial 2 D NOESY NMR spectrum of an equimolar solution of **DMP5** and **G2***

2D NOESY NMR experiment was employed to study the relative positions of the components in complex **DMP5⊃G2.** NOE correlation signals were observed between proton $H_{a'}$ of **G2** and protons H_1, H_2 and H_3 of **DMP5** (A, B and C).

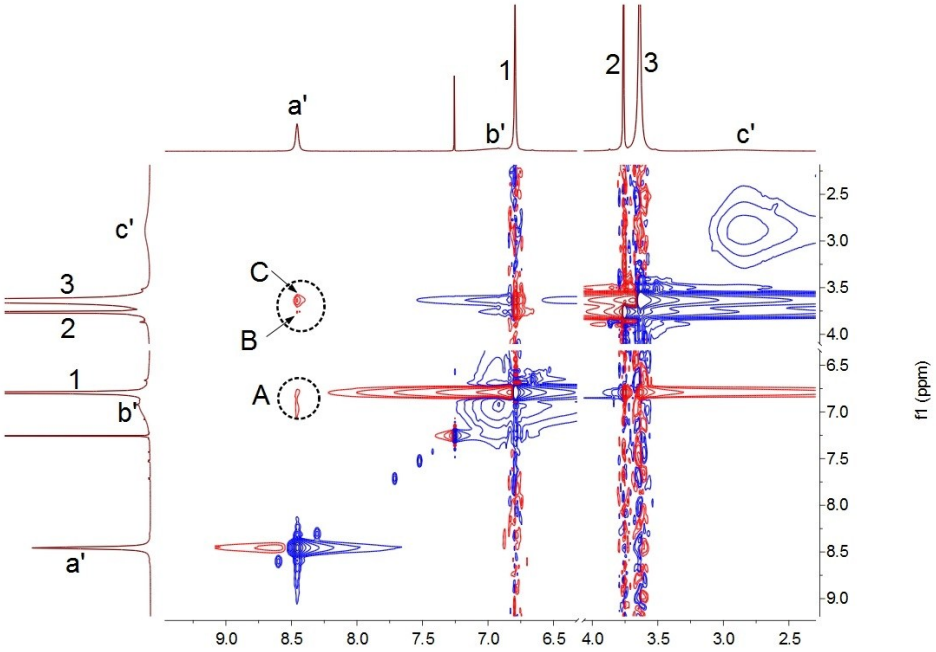

Figure S6 Partial 2D NOESY spectra of an equimolar mixture **G2** and **DMP5** (15.0 mM) (600 MHz, $CDCl_3$, room temperature).

*6. Stoichiometry and association constant determination for the complexation between **DMP5** and **G2***

To determine the stoichiometry and association constant between **DMP5** and **G2**, ^{1}H NMR titration was done with solutions which had a constant concentration of **G2** (1.00 mM) and different concentrations of **DMP5**. By a mole ratio plot, a 1:1 stoichiometry was obtained for this system. By a non-linear curve-fitting method, the association constant between the **DMP5** and **G2** was calculated.

The non-linear curve-fitting was based on the equation: [S2]

$$\Delta\delta = (\Delta\delta\infty/[G]_0)\ (0.5[H]_0 + 0.5([G]_0 + 1/Ka) - (0.5([H]_0^2 + (2[H]_0(1/Ka - [G]_0)) + (1/Ka + [G]_0)^2)^{0.5})) \quad \text{(Eq. S2)}$$

When $\Delta\delta$ is the chemical shift change of $H_{c'}$ on **G2** at $[G]_0$, $\Delta\delta_\infty$ is the chemical shift change of $H_{c'}$ when the guest is completely complexed, $[G]_0$ is the fixed initial concentration of the guest, and $[H]_0$ is the varying concentration of **DMP5**.

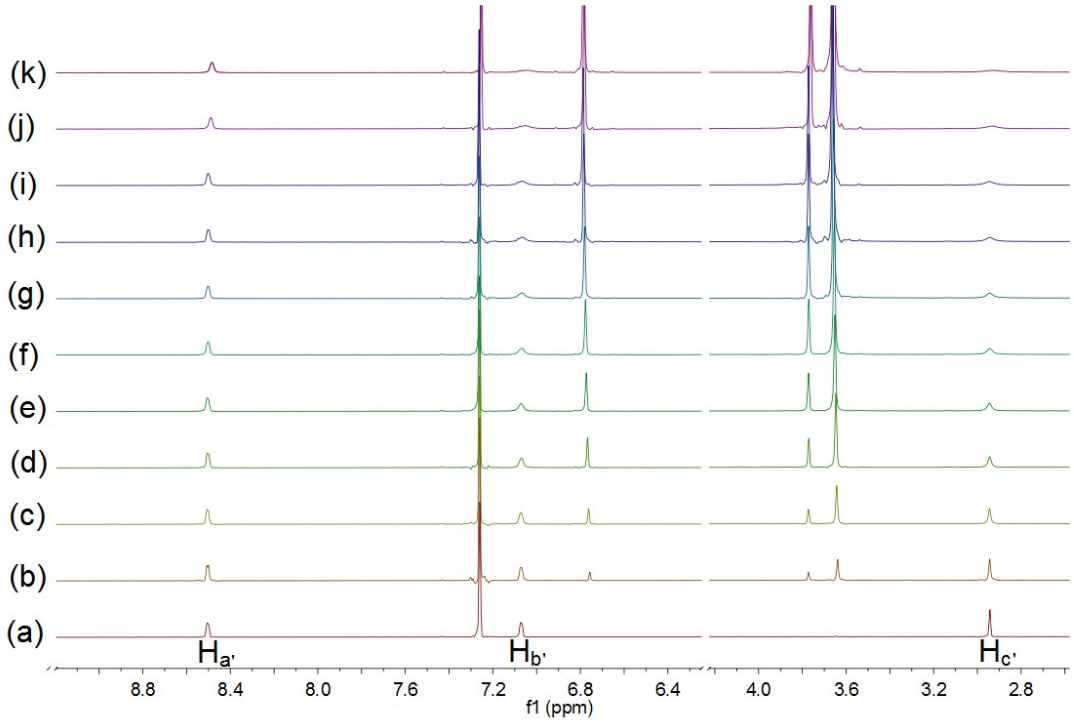

Figure S7 Partial ^{1}H NMR spectra (600 MHz, $CDCl_3$, room temperature) of **G2** at a concentration of 1.00 mM with different concentrations of **DMP5**: (a) 0.00 mM; (b) 0.0990 mM; (c) 0.196 mM; (d) 0.385 mM; (e) 0.566 mM; (f) 0.826 mM; (g) 1.07 mM;(h) 1.38 mM; (i) 1.67 mM; (j) 2.31 mM; (k) 4.12 mM.

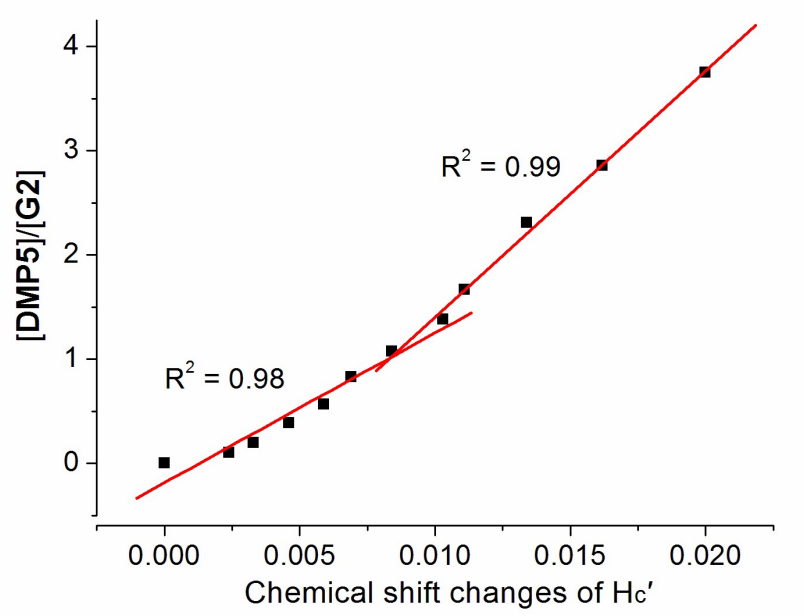

Figure S8 Mole ratio plot for the complexation between **DMP5** and **G2**, indicating a 1:1 stoichiometry.

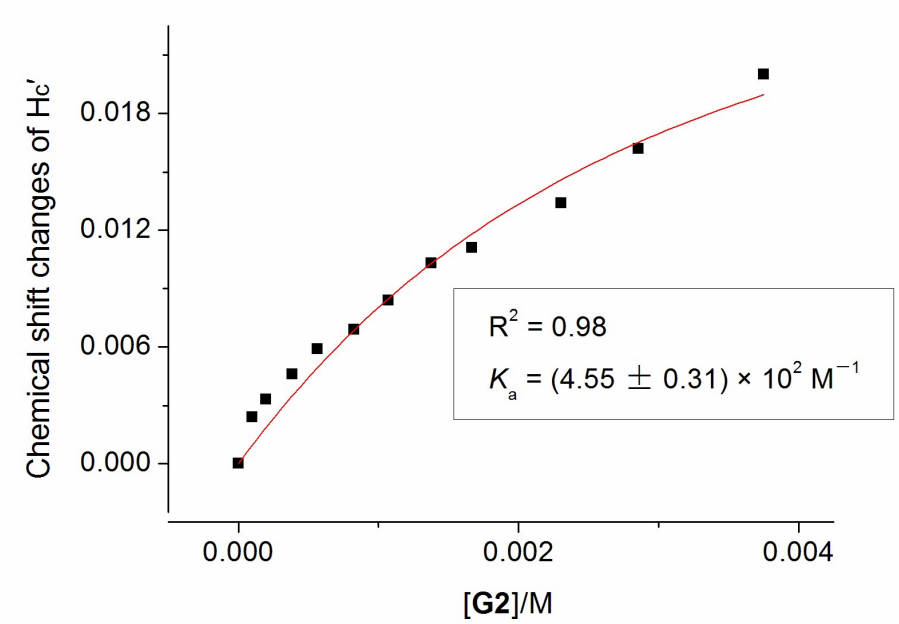

Figure S9 The chemical shift changes of $H_{c'}$ on **G2** upon addition of **DMP5**. The red solid line was obtained from the non-linear curve-fitting using Eq. S1

*7. Partial ^{1}H NMR spectra of an equimolar solution of **DMP5** and **G3***

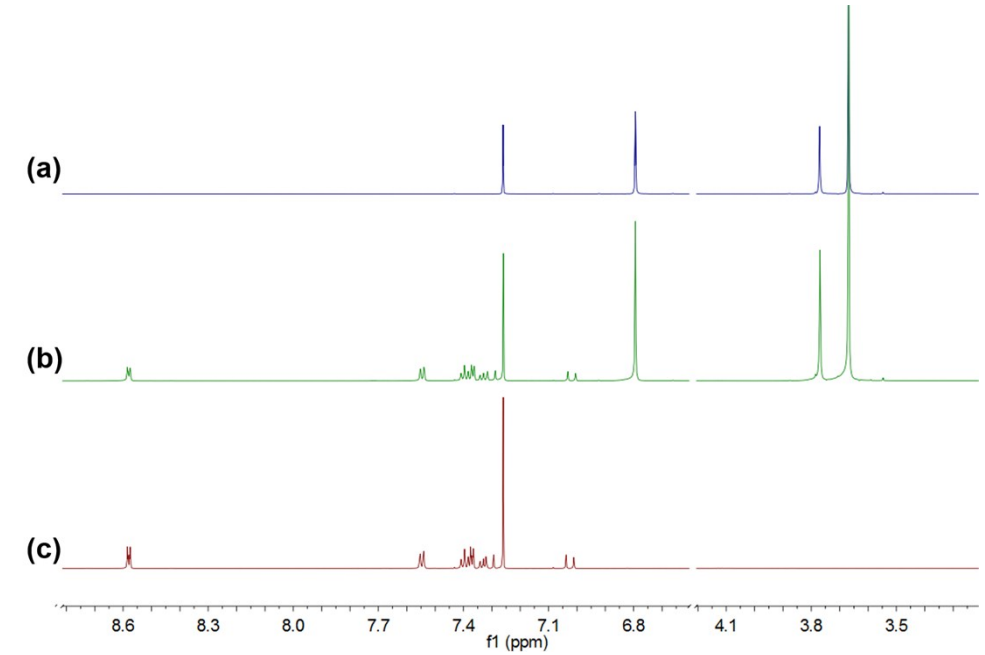

Figure S10 Partial ^{1}H NMR spectra (600 MHz, $CDCl_3$, room temperature): (a) **DMP5** (5.00 mM); (b) **G3** (5.00 mM) and **DMP5** (5.00 mM); (c) **G3** (5.00 mM).

*8. Partial ^{1}H NMR spectra of an equimolar solution of **DMP5** and **G4***

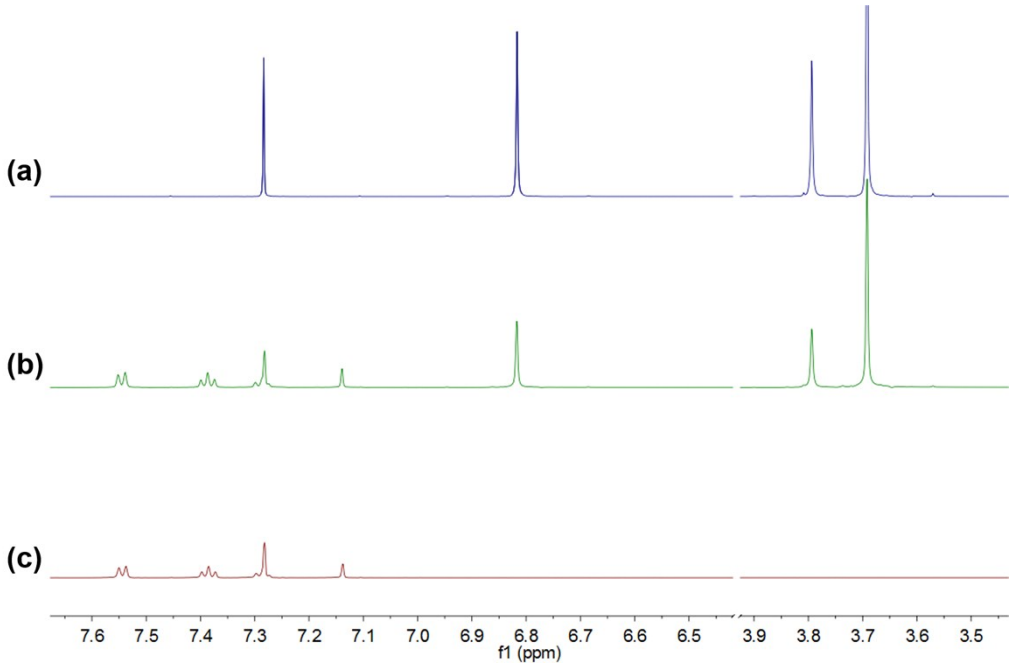

Figure S11 Partial ^{1}H NMR spectra (600 MHz, $CDCl_3$, room temperature): (a) **DMP5** (5.00 mM); (b) **G4** (5.00 mM) and **DMP5** (5.00 mM); (c) **G4** (5.00 mM).

*9. Partial ^{1}H NMR spectra of an equimolar solution of **DMP5** and **G5***

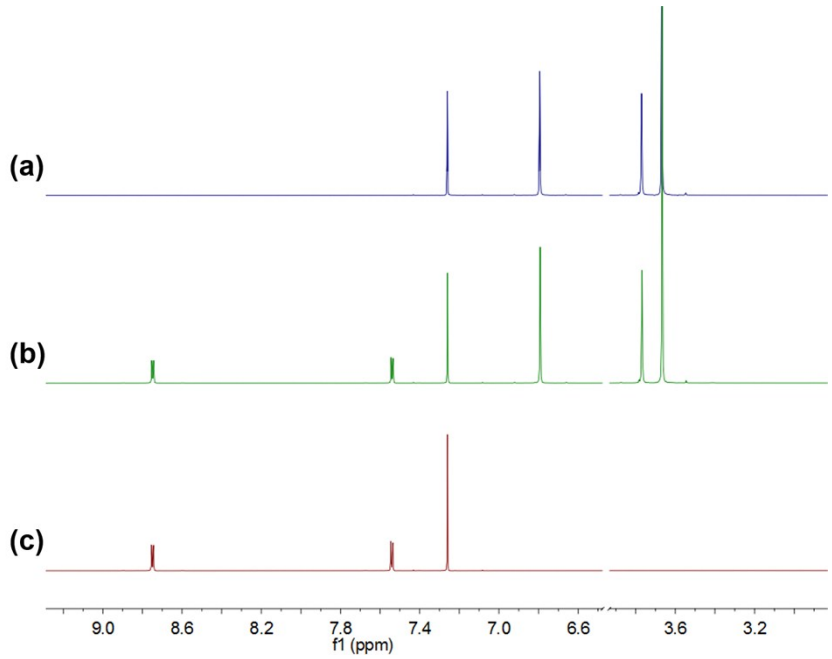

Figure S12 Partial ^{1}H NMR spectra (600 MHz, $CDCl_3$, room temperature): (a) **DMP5** (5.00 mM); (b) **G5** (5.00 mM) and **DMP5** (5.00 mM); (c) **G5** (5.00 mM).

*10. Partial ^{1}H NMR spectra of an equimolar solution of **DMP5** and **G6***

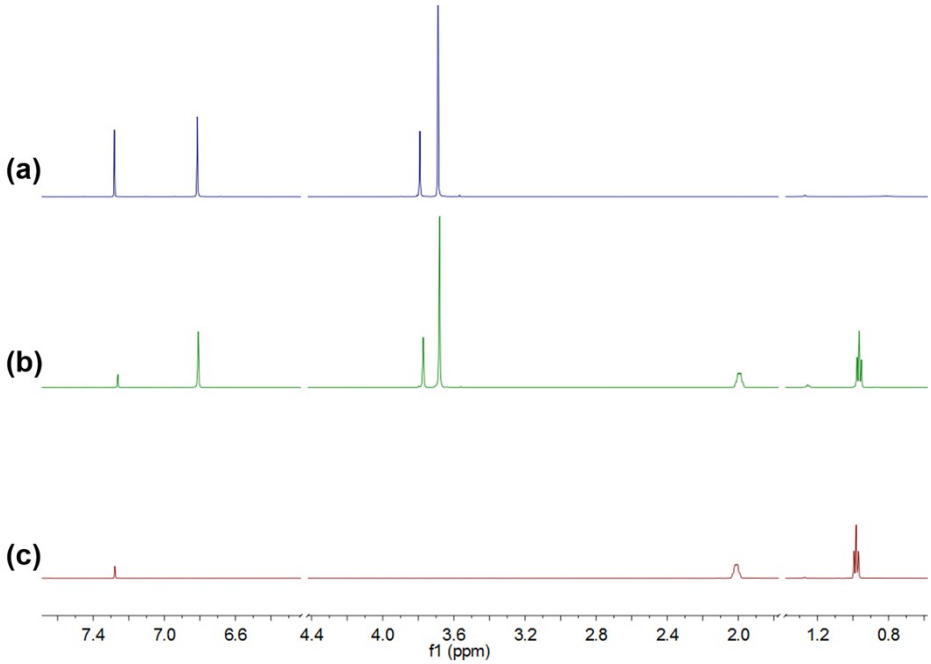

Figure S13 Partial ^{1}H NMR spectra (600 MHz, $CDCl_3$, room temperature): (a) **DMP5** (5.00 mM); (b) **G6** (5.00 mM) and **DMP5** (5.00 mM); (c) **G6** (5.00 mM).

*11. 2D DOSY NMR spectra of **DMP5** + **trans-G1** and **DMP5** + **trans-G1** + Cu(II)*

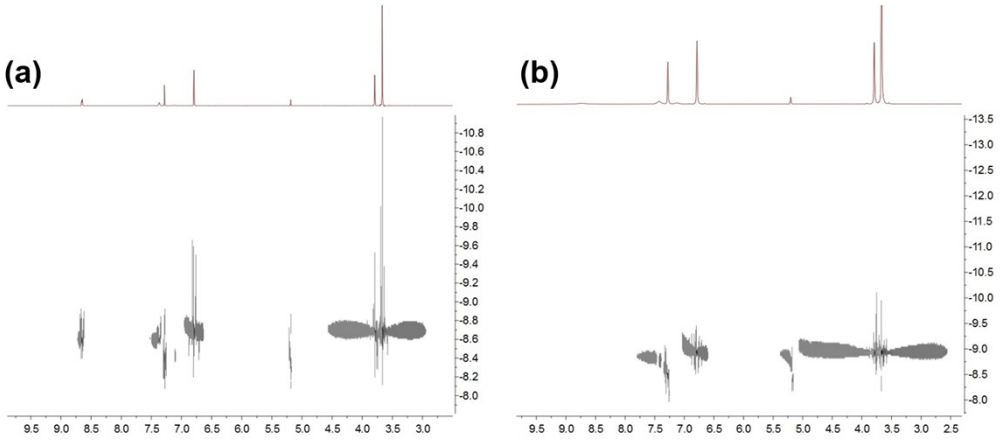

Figure S14 Partial DOSY NMR spectra (600MHz, $CDCl_3$, room temperature) : (a) a mixture of **DMP5** + ***trans*-G1** at 5.00 mM; (b) a mixture of **DMP5** + ***trans*-G1** + Cu(II) at 5.00 mM.

According to the literature,[S3] we used the Stokes-Einstein relation to estimate the average degree of polymerization (DP):

$DP(DOSY) \approx (D(polymer) / D(monomer))^3 = 11.4$

12. FT-IR spectroscopy experiments

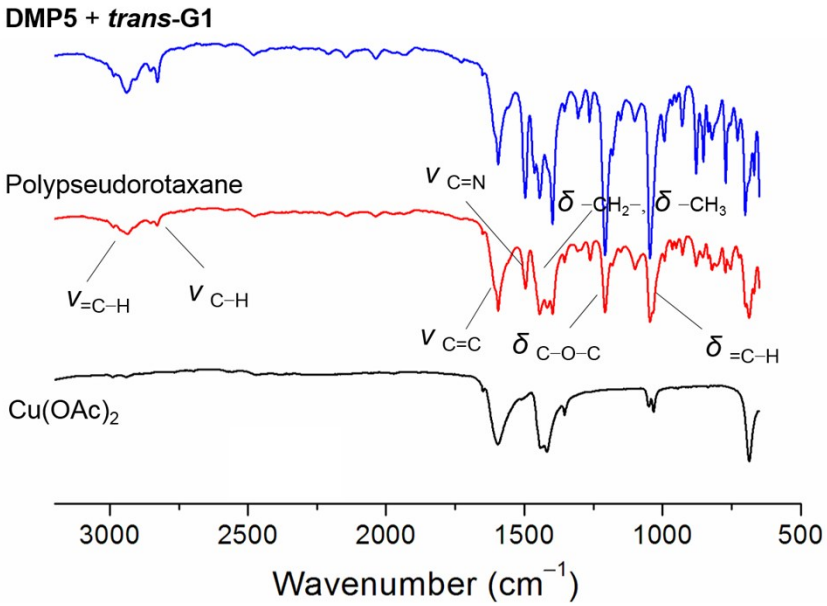

Figure S15 FT-IR spectra of **DMP5** + ***trans*-G1**, the polypseudorotaxane and $Cu(OAc)_2$ The stretching vibration and bending vibration were noted as ν and δ, respectively.

13. Powder X-ray diffraction (XRD) analysis

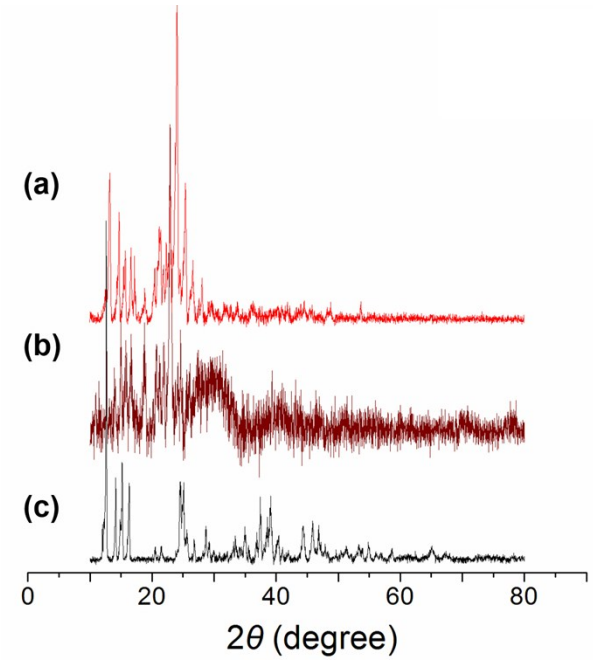

Figure S16 X-ray powder diffraction patterns: (a) **DMP5** + ***trans*-G1**; (b) the polypseudorotaxanes; (c) $Cu(OAc)_2$.

14. *AFM images of the polypseudorotaxane*

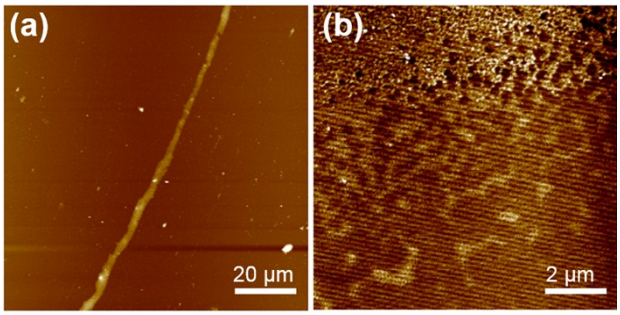

Figure S17 *AFM images: (a) fibers drawn from a high concentration solution of mixtures of* ***DMP5⊃trans-G1*** *and Cu(II) in the molar ratio of 1:1 in chloroform; (b) the powder obtained by drying of the polypseudorotaxane solution.*

15. ^1H NMR spectroscopy experiments of photo-responsive property of the polypseudorotaxane

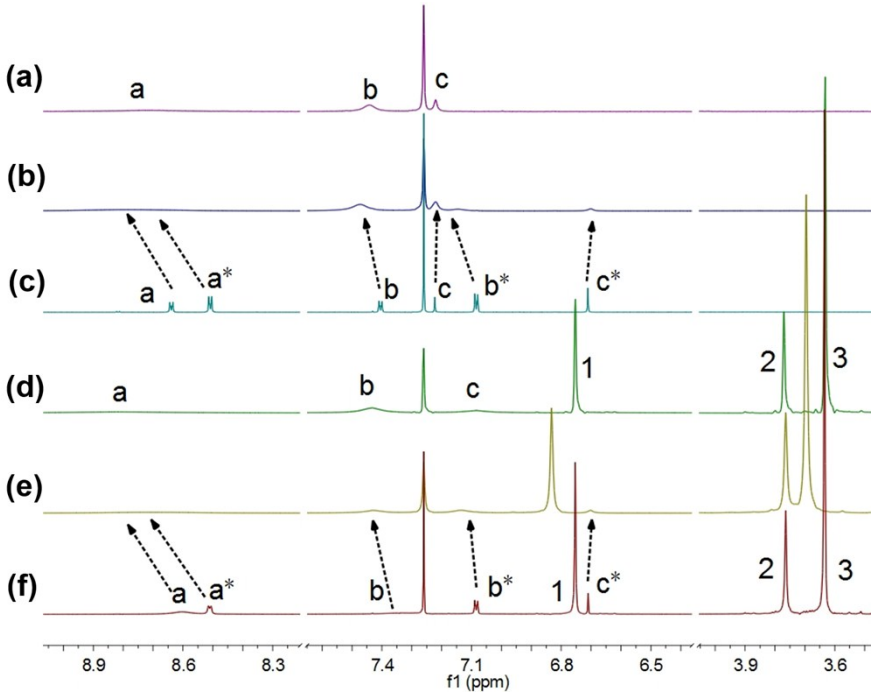

Figure S18 Partial ^1H NMR spectra (600 MHz, $CDCl_3$, room temperature): (a) ***trans*-G1**-based coordination polymer; (b) after irradiation with UV light at 365 nm of a; (c) ***trans*-G1** (5.00 mM) after irradiation with UV light at 365 nm; (d) **DMP5⊃*trans*-G1**-based polypseudorotaxane; (e) after irradiation with UV light at 365 nm of d; (f) **DMP5⊃*trans*-G1** (5.00 mM) after irradiation with UV light at 365 nm.

16. AFM image of the polypseudorotaxane after photo irradiation

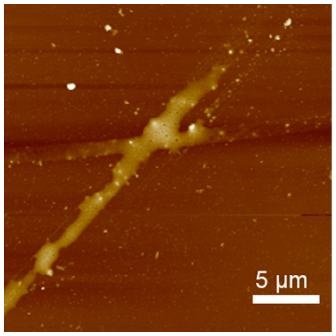

Figure S19 AFM image of the polypseudorotaxane after irradiation with UV light at 365 nm.

References:

S1. T. Ogoshi, S. Kanai, S. Fujinami, T. Yamagishi and Y. Nakamoto, *J. Am. Chem. Soc*., 2008, **130**, 5022–5023.

S2. K. A. Connors, *Binding Constants*; Wiley: New York, 1987; P. S. Corbin, Ph.D. Dissertation, University of Illinois at Urbana-Champaign, Urbana, IL, 1999; P. R. Ashton, R. Ballardini, V. Balzani, M. Belohradsky, M. T. Gandolfi, D. Philp, L. Prodi, F. M. Raymo, M. V. Reddington, N. Spencer, J. F. Stoddart, M. Venturi and D. J. Williams, *J. Am. Chem. Soc.*, 1996, **118**, 4931–4951.

S3. H. Xing, H. Wang, X. Yan and X. Ji, *Dalton Trans.*, 2015, **44**, 11264–11268