Formation of polypseudorotaxane networks by cross-linking the quadruple hydrogen bonded linear supramolecular polymers *via* bisparaquat molecules

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1. General information

All reactions were performed in atmosphere unless noted. The commercially available reagents and solvents were either employed as purchased or dried according to procedures described in the literature. All yields were given as isolated yields. NMR spectra were recorded on a Bruker DPX 300 MHz spectrometer with internal standard tetramethylsilane (TMS) and solvent signals as internal references, CDCl₃ and CD₃CN were dried using neutral aluminium oxide. UV-Vis spectra were obtained from a Shimadzu UV-2401 spectrometer. Low-resolution electrospray ionization mass spectra (LR-ESI-MS) were obtained on Finnigan Mat TSQ 7000 instruments. Elemental analyses were obtained on Perkin-Elmer 240 instruments. NOESY and DOSY experiments were performed on a Bruker DPX 500 MHz spectrometer. Viscosity measurements were carried out with Ubbelohde micro viscometers (Shanghai Liangjing Glass Instrument Factory, 0.40 mm and 0.71 mm inner diameter) at 27 °C in chloroform/ acetonitrile (ν/ν , 1/1).

2. UV-Vis spectra of P1-D1 in chloroform/acetonitrile (1/1, v/v).



Fig. S1. UV-Vis absorption spectra of **P1**, **D1**, and the mixtures (2:1, molar ratio) of P1 and D1 in chloroform/acetonitrile (1/1, v/v).

The Fig. S1 above shows the UV-Vis absorption spectra of P1, D1, and the mixtures of P1 and D1(5.2 mM for P1 and 2.6 mM for D1) in chloroform/acetonitrile (1/1, v/v). No absorbance (above 380 nm) was observed for individual P1 and D1 respetively. In contrast, the absorption spectra of P1 and D1 mixture showed an identical band around 418 nm, which is characteristic for the charge-transfer interactions between crown ether **BPP34C10** and paraquat groups. The solutions of P1, D1 are both colorless, while their mixture presents yellow color, which confirms the host-guest recognition pair in the mixed solution.

¹H NMR spectra of solutions of individual P1, P1 with 0.50 equiv
D1 and calculation of the association ratio of the crown ether moieties and paraquat groups at different concentrations



Fig. S2. ¹H NMR spectra (300 MHz, 1 : 1 CDCl₃–CD₃CN, 24 °C) of **P1** at different concentrations: (a) 1.8 (b) 10.0, (c) 36.2, (d) 75.0, (e) 125.0 mM.

From the above specta (Fig S2), we found that the proton signals of **P1** did not shift upon the concentration, which might be due to the long flexible linker between the two Upy units.



Fig. S3. ¹H NMR spectra (300 MHz, 1 : 1 CDCl₃–CD₃CN, 24 °C) of (a) **P1**; mixtures of **P1** and 0.50 equiv **D1** at different **P1** concentrations: (b) 4.0, (c) 16.0, (d) 40.0, (e) 72.2, (f) 106.4, (g) 158.6, (h) 220 mM ; and (i) **D1**.

It was observed that when the initial concentrations increased, the chemical shift of the ethyleneoxy protons, aromatic rings of the crown ether and paraquats all had only one set of signals and shifted upfield, and their chemical shifts changed very sharply at first and then gradually slowly. It indicated that the paraquat moieties thread into the cavity of the crown ether moieties, and the percentage of complexed composition increased with increasing concentration, suggesting the cross-linking of the linear hydrogen bonded supramolecular polymers.

Moreover, on the basis of the chemical shift change of H⁴, the percentages of the complexed crown ether moieties and the paraquat units (ratio) at different initial concentrations of **P1** and 0.5 equiv **D1** were estimated, The value of the maximum chemical shift change $\Delta_0 = 0.581$ ppm, was determined by extrapolation of a plot of $\Delta = \delta - \delta_u vs$. 1/[**P1**]₀ in high initial concentration range (Table S1). It proves that the [3]pseudorotaxane stucture had been incorpatated leading to cross-linking (at least 70% based on the association ratio of 87.4% at 220 mM **P1**).

Table S1. Calculated association ratio of crown ether and paraquat unit at different concentration of monomers.

[P1] (mM)	4.0	16.0	40.0	72.2	106.4	158.6	220
Association Ratio (%)	13.2	36.8	52.5	61.1	68.5	83.0	87.4

4. NOESY spectrum of P1 (72.2 mM) and D1 (36.1 mM) mixtures in CD₃CN/CDCl₃

The 2-D NOESY NMR spectrum (Fig. S4) of a solution of **P1**, 0.5 equiv **D1** showed the protons H^8 , and H^9 on the paraquat moiety were correlated with the ethyleneoxy protons, methylene protons H^7 and aromatic protons H^4 , H^5 , H^6 on the Crown ether moiety. And also the methylene protons H^{10} on the **D1** were correlated with the ethyleneoxy protons on the crown ether moiety. That all indicated the paraquat moiety were complexed tightly with the crown ether moiety in the solution.



Fig. S4. Partial NOESY NMR (500 MHz, chloroform-d/acetonitrile- d_3 (1/1, v/v), 24 °C) spectrum of a solution of **P1** (72.2 mM) and 0.50 equiv **D1** (36.1 mM).

5. The diffusion ordered spectroscopy (DOSY) of individual P1

Diffusion ordered spectroscopy (DOSY), was performed at 25 °C, using heptakis (2,3,6-tri-O-methyl)- β -cyclodextrin (MW = 1429 g mol⁻¹) as a internal reference in CD₃CN/CDCl₃ (*v*/*v* 1:1). **P1** (MW = 1293 g mol⁻¹). From the DOSY, we found out that the diffusion efficient of the assemblies of **P1** at 4 mM are smaller than the peralkylated β -cyclodextrin, indicating that the molecular weight of the mainly aggregates at this concentration are larger than the CD, which indicates that the dominating assemblies are the multimer at the low concentration (4.0 mM) of **P1** in the solution instead of the cyclic monomer (Fig. S5). However, in our last system,^{S4} the dominating specie is the cyclic monomer at the low concentration (below 10mM). Measurement at the 14 mM of **P1** gives further evidence to support the dominating assemblies of increasing size: the larger macrocyles (Fig. S6).







Figure S6. DOSY NMR of individual P1 at 14.0 mM

6. The determination of the K_a values of crown ether-paraquat association and the UPy dimerization

(1) Crown ether-paraquat association constant:



We use the model compound **P5** and **P0** to determine the association constant K_a of the crown ether–paraquat recognition by a competitive method developed by the Smith group.^{S1} In a 10.0 mM equimolar (1:1 CDCl₃/CD₃CN) solution of reference host **N5**, **P5** and guest **P0**, the concentration of complexed **N5**, [**N5**]_c, was 2.56 mM. $K_{a, P5-P0}$ was thus determined to be 232.8 (\pm 5.7) M⁻¹ in CHCl₃/CH₃CN (1 : 1). The error is based on errors of [**N5**]_c and $K_{a, N5-P0}$. The $K_{a, P5-P0}$ is 398 M⁻¹ in pure CH₃CN reported by stoddart's group in 2001.^{S2}

(2) UPy dimerization:

For the disscusion of the UPy dimerization constant K_a , please see our most recent work.^{S3}

7. Synthesis of the monomers P1 and D1

P5 was a reported compound,^{S2} and we replaced the benzyl group with the methoxymethyl group as the protective group to obtain **P5**.



Scheme S1 Synthesis of Monomer P1

Preparation of compound P8

To a mixture of methyl 2,5-dihydroxybenzoate (3.36 g, 20.0 mmol), anhydrous K₂CO₃ (5.52 g, 40.0 mmol), and acetone anhydrous (30 mL) were added. chloromethyl methyl ether (1.77 g , 22.0 mL) in anhydrous acetone (20 mL) dropwise at 0 °C and then stirred for 2.5 h at 25 °C. The reaction mixture was filtered, and solvent was concentrated in vacuo. The residue was purified by silica gel-chromatography by using CH₂Cl₂ as the eluent to give **P8** (3.73g, 88%) as a colorless liquid. ¹H NMR (300 MHz, CDCl₃) δ 10.4 (s, 1H), 7.49 (d, *J* = 3.1 Hz, 1H), 7.18 (dd, *J* = 9.0, 3.1 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 1H), 5.12 (s, 2H), 3.94 (s, 3H), 3.48 (s, 3H) ppm.



A three neck flask was charged with anhydrous K₂CO₃ (3.85 g, 27.92 mmol), KI (0.45 g, 2.76 mmol), **P8** (2.96 g, 13.96 mmol), S2 (3.46g, 6.90 mmol) and 100 mL anhydrous CH₃CN, fitted with a condenser, was heated at reflux under nitrogen atmosphere for 24 h. After cooling down to room temperature, the reaction mixture was filtered and the solid residue was washed with CH₃CN and CH₂Cl₂. The combined organic solution was concentrated under reduced pressure. The residue was dissolved in CH₂Cl₂ (150 mL), filtered again, and the solvent was distilled off under reduced pressure. The residue was purified by silica gel-chromatography (CH₂Cl₂/MeOH 100:1) to give **P7** (3.14g, 78%) as a buff oil. ¹H NMR (300 MHz, CDCl₃) δ 7.45 (d, *J* = 3.1 Hz, 2H), 7.13 (dd, *J* = 9.0, 3.1 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 5.12 (s, 4H), 4.15 (t, *J* = 5.1 Hz, 4H), 3.90 – 3.83 (m, 4H), 3.87 (s, 6H), 3.75 (m, 4H), 3.69 (m, 4H), 3.47 (s, 6H) ppm.











A three neck flask was charged with P7 (1.0 g, 1.72 mmol), THF (18 mL), and 6N HCl (2 mL), with a condenser were heated at 50 °C for 2 h. After cooling down to room temperature, the reaction mixture was adjusted to pH 7-9 using 1N NaOH. Then the THF was evaporated in vacuo and the solution was adjusted to pH 3-4 using 1N HCl. The residue solution was extracted with CHCl₃ (30 mL \times 2), and washed with brine (40 mL). The organic phase was dried (Mg₂SO₄). After the solvent was removed with an evaporator under reduced pressure, the resulting residue was subjected to column chromatography (CH₂Cl₂/MeOH 50:1 to 20:1) to give P6 as a buff oil (0.73 g, 86%). ¹H NMR (300 MHz, CDCl₃) δ 7.25 (d, J = 2.6 Hz, 2H), 6.98 – 6.85 (dd, J = 8.8, 2.6 Hz, 2H), 6.73 (d, J = 8.8 Hz, 2H), 4.07 - 3.96 (m, 4H), 3.84 - 3.76 (m, 4H), 3.83 (s, 6H), 3.75 - 3.67 (m, 4H), 3.69 - 3.60 (m, 4H) ppm.



A three neck flask was charged with K₂CO₃ (1.95 g, 14.1 mmol), KI (50 mg), and anhydrous CH₃CN (80 mL), with a condenser, was heated under reflux under nitrogen. To this mixed solution, **P6** (0.70 g, 1.41 mmol), **S2** (0.71 g, 1.41 mmol) in anhydrous CH₃CN (50 mL) were added dropwise for 10 h. Then the reaction mixture were further heated under reflux for 3 days. After cooling down to room temperature, the reaction mixture was filtered and the solid residue was washed with CH₃CN and CH₂Cl₂. The combined organic solution was concentrated under reduced pressure. The residue was dissolved in CH₂Cl₂ (100 mL), filtered again, and the solvent was distilled off under reduced pressure. The residue was purified by silica gel-chromatography (CH₂Cl₂/MeOH 50:1) to give **P5** (0.48 g, 52%) as a buff solid. ¹H NMR (300 MHz, CDCl₃) δ 7.29 (d, *J* = 3.0 Hz, 2H), 6.92 (dd, *J* = 9.0, 3.1 Hz, 2H), 6.84 (d, *J* = 9.0 Hz, 2H), 4.09 – 3.98 (m, 8H), 3.88 – 3.81 (m, 8H), 3.84 (s, 6H), 3.75 – 3.65 (m, 16H) ppm.



Aqueous 10% sodium hydroxide solution (8 mL) was added to a solution of compound **P5** (1.55 g, 2.37 mmol) in ethanol (80 mL) and the resulting solution was stirred at 60°C for 2 h. Upon cooling to room temperature, the reaction mixture was concentrated to remove the ethanol, diluted with water, and the residue was then adjusted to pH 1 by slow addition of concentrated HCl. The aqueous solution was extracted with CH₂Cl₂ (2 × 80 mL) and the combined organic phase was washed with water (2 × 50 mL), brine (50 mL), and dried over Na₂SO₄. The solvent was removed in vacuo to afford diacid **P4** as a pale solid, which was used directly to the next step without any further purification. ¹H NMR (300 MHz, CDCl₃) δ 7.37 (d, *J* = 3.1 Hz, 2H), 7.02 (dd, *J* = 9.0, 3.2 Hz, 2H), 6.83 (d, *J* = 9.0 Hz, 2H), 4.28 – 4.19 (m, 4H), 4.03 – 3.95 (m, 4H), 3.95 – 3.89 (m, 4H), 3.89 – 3.82 (m, 4H), 3.77 – 3.66 (m, 16H) ppm.

To a stirred solution of 2-(6-bromohexyl)isoindoline-1,3-dione (1.49 g, 4.80 mmol) and the prepared diacid **P4** in DMF (20 mL) was added potassium carbonate (0.53 g, 3.80 mmol) at room temperature. The mixture was then stirred at 80 °C for 12 h. Upon cooling to room temperature, the solution was filtered, washed with CH_2Cl_2 and the combined organic solution was

concentrated in vacuo to remove the solvent. The residue was exctrated with CH₂Cl₂ (50 mL × 2), washed with brine (50 mL), and dried (Na₂SO₄). After the solvent was removed under reduced pressure, the resulting residue was subjected to column chromatography (CH₂Cl₂/MeOH 50:1) to give **P3** (1.66 g, 70%) as a buff solid. ¹H NMR (300 MHz, CDCl₃) δ 7.83 (m, 4H), 7.70 (m, 4H), 7.28 (d, *J* = 2.9 Hz, 2H), 6.90 (dd, *J* = 8.9, 2.8 Hz, 2H), 6.83 (d, *J* = 9.0 Hz, 2H), 4.23 (t, *J* = 6.6 Hz, 4H), 4.07 – 4.00 (m, 8H), 3.89 – 3.78 (m, 8H), 3.67 (m, 20H), 1.79 – 1.65 (m, 8H), 1.52 – 1.37 (m, 8H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 168.4, 166.0, 152.8, 152.6, 133.9, 132.1, 123.2, 121.7, 120.0, 116.9, 116.7, 70.81, 70.78, 70.1, 69.72, 69.66, 68.2, 64.9, 37.9, 28.6, 28.5, 26.6, 25.6 ppm; ESI–MS *m/z* (%): 559.25 [M + 2NH₄]²⁺ (63), 569.50 [M + NH₄ + K]²⁺ (29), 1100.50 [M + NH₄]⁺ (100), 1121.45 [M + K]⁺ (34).





To a solution of P3 (0.98 g, 0.90 mmol) in CH_2Cl_2 (15 mL) and MeOH (15 mL) under nitrogen atmosphere, hydrazine monohydrate (0.90 mL, 14.8 mmol) was added and the mixture

was stirred at 50°C for 5h. After evaporation, the mixture was dissolved in CHCl₃ (50 mL) and washed with 3N aqueous NaOH (40 mL), water (40 mL), brine (40 mL), and dried over Na₂SO₄. The solvent was removed with an evaporator under reduced pressure to afford **P2** (0.69 g, 86%) as a pale yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 7.29 (d, *J* = 2.8 Hz, 2H), 6.91 (dd, *J* = 8.8, 2.9 Hz, 2H), 6.84 (d, *J* = 9.0 Hz, 2H), 4.25 (t, *J* = 6.5 Hz, 4H), 4.11 – 3.98 (m, 8H), 3.85 (br s, 8H), 3.70 (s, 16H), 2.69 (t, *J* = 6.7 Hz, 4H), 1.84 (*br* s, 4H), 1.77 – 1.67 (m, 4H), 1.44 (m, 12H); ¹³C NMR (75 MHz, CDCl₃) δ 166.1, 152.9, 152.7, 121.8, 119.9, 117.0, 116.7, 70.8, 70.1, 69.8, 69.7, 68.3, 65.0, 42.1, 33.4, 28.7, 26.6, 25.9; ESI-MS *m/z* (%): 412.15 [M + 2H]²⁺ (100), 423.20 [M + NH₄ + Na]²⁺ (21), 434.00 [M + 2Na]⁺ (4).





A solution of imidazolide **P9** (0.55 g, 1.82 mmol) and **P2** (0.67 g, 0.76 mmol) in dry CHCl₃ (20 mL) was stirred for three hours under nitrogen at r.t. To the reaction mixture, CHCl₃ (50 mL) was added and the organic layer was washed with 1N HCl (20 mL), saturated NaHCO₃ (20 mL), brine (20 mL) and dried over Na₂SO₄. After the solvent was removed, the resulting residue was subjected to column chromatography CHCl₃/MeOH 80:1 (ν/ν), to give **P1** (0.76 g, 78%) as a colorless viscous solid.¹H NMR (300 MHz, DMSO-*d*₆) δ 11.44 (*br* s, 2H), 9.55 (*br* s, 2H), 7.57 (*br* s, 2H), 7.12 (d, *J* = 2.7 Hz, 2H), 6.95 (dd, *J* = 9.0, 2.8 Hz, 2H), 6.90 (d, *J* = 9.1 Hz, 2H), 5.74 (s, 2H), 4.16 (t, *J* = 6.3 Hz, 4H), 3.97 (s, 8H), 3.70 (s, 8H), 3.54 (m, 16H), 3.15 (m, 4H), 2.26 – 2.17 (m, 2H), 1.67 – 1.63 (m, 4H), 1.51 – 1.44 (m, 12H), 1.35 (s, 8H), 1.25 – 1.05 (m, 8H), 0.78 (m, 12H) ppm; ¹³C NMR (75 MHz, DMSO-*d*₆) δ 170.7, 165.7, 161.2, 154.4, 152.0, 151.6, 121.6, 119.3, 116.0, 115.9, 105.1, 70.04, 69.96, 69.3, 69.0, 68.9, 67.8, 64.4, 47.9, 33.0, 29.1, 28.1, 26.6, 26.0, 25.2, 22.2, 13.8, 11.8; ESI-MS *m*/*z* 647.45 [M + 2H]²⁺ (100%), 656.00 [M + H + Na]²⁺ (24%), 666.95 [M + 2Na]²⁺ (40%). Anal. Calcd for C₆₆H₁₀₀N₈O₁₈: C, 61.28; H, 7.79; N, 8.66; found: C, 61.48; H, 7.89, N, 8.78.



The compound D1 and D2 were obtained according to the reference methods.⁸⁵

Scheme S2 synthesis of mononmer D1

Synthesis of compound D2

A solution of 1,10-dibromodecane (1.89 g, 6.3 mmol) in CH₃CN (60 mL) was added dropwise into a stirred and refluxed solution of 4,4'-bipyridine (5.56 g, 35.7 mmol) in CH₃CN (60 mL) over 24 hours. After addition, the mixture was further stirred and refluxed for 36 hours. After it cooled, the suspension was filtered. The solid was washed with CH₃CN and then dried in an oven to afford a pale solid. It was dissolved in minimum deionized water and aqueous NH₄PF₆ (5.0 g, 30.6 mmol) was added to precipitate a white solid. The resulting solid was filtered and washed with water to afford the desired product **D2** (4.02 g, 86%). ¹H NMR (300 MHz, Acetone-d₆) δ 9.26 (d, *J* = 6.9 Hz, 4H), 8.87 (dd, *J* = 4.5, 1.6 Hz, 4H), 8.65 (d, *J* = 6.8 Hz, 4H), 8.01 (dd, *J* = 4.5, 1.7 Hz, 4H), 4.87 (t, *J* = 7.6 Hz, 4H), 2.26 – 2.11 (m, 4H), 1.56 – 1.21 (m, 12H) ppm.

Synthesis of compound D1

A solution of compound **D2** (5.94 g, 8.0 mmol) and 1-bromooctane (3.28 g, 17.0 mmol) in CH₃CN (100 mL) was refluxed for 2 days. After it cooled, the mixture was filtered. The solid was washed with CH₃CN and dried. Then excess aqueous NH₄PF₆ (4.0 g, 24.5 mmol) was added to the solution of this solid in minimal deionized water. The suspension was heated at reflux for 0.5h. After it cooled, the mixture was filtered. The solid was washed with water and dried in an oven to afford a white solid (2.50 g, 26%). ¹H NMR (300 MHz, CD₃CN) δ 8.87 (d, *J* = 5.6 Hz, 8H), 8.36(d, *J* = 5.6 Hz, 8H), 4.59 (t, *J* = 6.7 Hz, 8H), 2.00 (t, *J* = 6.9 Hz, 8H), 1.36 – 1.28 (m, 32H), 0.88 (t, *J* = 7.5, 6H) ppm; ¹³C NMR (75 MHz, CD₃CN) δ 156.0, 146.5, 128.2, 63.2, 32.4, 31.9, 29.8, 29.7, 29.6, 29.5, 26.6, 26.5, 23.4, 14.5; ESI-MS *m*/*z* (%) 169.50 [M – 4PF₆]⁴⁺ (100), 225.80 [M – 4PF₆]³⁺ (45), 339.20 [M – 4PF₆]²⁺ (51), 411.70 [M – 3PF₆]²⁺ (15); Anal. Calcd for C₄₆H₇₀F₂₄N₄P₄·2H₂O: C, 42.66; H, 5.76; N, 4.33; found: C, 42.54; H, 5.82 N, 4.53.


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1030 CD<sub>3</sub>CN
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