Supporting Information

Hyperbranched Supramolecular Polymer Constructed from Twisted Cucurbit[14]uril and Porphyrine via the Host-Guest Interactions

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Experimental Section

General Remarks: Metal free meso-tetrakis(4-pyridyl)porphyrin, H$_2$TPyP, was purchased from Aldrich. All other reagents and solvents were used as received. The compound of Q[14] was prepared according to the published procedure.\textsuperscript{[11]}

Measurements: $^1$H NMR spectra were recorded on a Bruker DPX 400 spectrometer in D$_2$O. Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. Steady-state fluorescence spectroscopic studies were performed on an F4500 (Hitachi). Elemental analysis was performed on an Elementar Vavio El III. Titration experiments were carried out on a Nano ITC instrument (TA, USA) at 25$^\circ$C. DLS data were obtained on a DynaPro NanoStar at 25$^\circ$C.

Preparation of 5,10,15,20-tetrakis(N-butyl-4-pyridinium)porphyrin tetrabromide (TBPyP). The mixture of metal free H$_2$TPyP (200 mg, 0.32 mmol) and 1-
bromopropane (0.39 g, 3.2 mmol) in DMF (200 mL) was refluxed for 3 h. The precipitate was filtered and washed thoroughly with diethyl ether. Further purification of the target compound was performed by recrystallization in a water/acetone mixture, giving the water soluble porphyirn compound TBPyp with the yield of 223 mg, 60%.

$^1$H NMR (400 MHz, DMSO$_{d6}$, 25°C): $\delta$ 9.59 (d, 8H, $J = 8.0$ Hz), 9.24 (s, 8H), 9.02 (d, 8H, $J = 8.0$ Hz), 4.98 (t, 8H, $J = 8$ Hz), 2.28 (t, 8H, $J = 8$ Hz), 1.64 (t, 8H, $J = 8$ Hz), 1.12 (t, 8H, $J = 8$ Hz), -3.10 (s, 2H). Anal. Calcd. for C$_{56}$H$_{58}$N$_8$Br$_4$: C, 57.85; H, 5.03; N, 9.64; found C, 57.69; H, 5.09; N, 9.71.

**DLS measurements.** The sample solution for the DLS measurements was prepared by filtering the solution through a 450 nm millipore filter into a clean scintillation vial. It is worth noting that the aqueous solution of either Q[14] or TBPyp was respectively prepared and then took the DLS measurements. Then both solutions were mixed together and the same DLS measurements were carried out. All the DLS measurements were performed at the scattering angle of 90° on a DynaPro NanoStar at 25°C.

**ITC measurements.** The association constants and thermodynamic parameters for the inclusion complexation of TBPyp with Q[14] was determined by titration calorimetry with a Nano ITC instrument (TA, USA). An aqueous solution (0.1 mM) of TBPyp was placed in the sample cell (1.3 mL). As a solution (2 mM) of the host Q[14] was added in a series of 40 injections (8 μL), the heat evolved was
recorded at $T = 298.15$ K. The heat of dilution was corrected by injecting the guest solution into deionized water and subtracting these data from those of the host-guest titration. Computer simulations (curve fitting) were performed using the Nano ITC analyze software.
Fig. S1 $^1$H NMR and $^1$H-$^1$H COSY spectra of TBPyP in D$_2$O.
Fig. S2 $^{13}$C NMR spectra of TBPyP in D$_2$O.
Fig. S3 NOSEY spectrum of TBPyP and Q[14] in the ratio of 1:2 in D$_2$O at 298.15 K.
Fig. S4 COSY spectrum of TBPyP and Q[14] in the ratio of 1:2 in D$_2$O at 298.15 K.
Fig. S5 The HSQC spectrum of TBPyP and Q[14] in the ratio of 1:2 in D₂O at 298.15 K.
Fig. S6 ITC data for the binding of Q[14] with TBPyP in aqueous solution at 298.15K.

Data:
Model Independent
N  2.087±0.011
Ka  (1.971±0.143)×10^5  M⁻¹
ΔH  -25.535±0.355  kJ/mol
ΔS  15.72  J/mol
Kd  5.074×10⁻⁶  M
Fig. S7 Diffusion coefficient of TBPyP with different ratios of Q[14].
Fig. S8  Electronic absorption spectra of 2Q[14]- TBPyP upon addition of increasing amounts of KCl.
Fig. S9 Fluorescence emission spectra of 2Q[14]-TBPypP upon addition of increasing amounts of KCl with an excitation of 422 nm.
Fig. S10 Fluorescence emission spectra of TBPyP, 2Q[14]- TBPyP, and 2Q[14]- TBPyP+KCl with an excitation of 422 nm.