Electronic Supplementary Material (ESI) for Polymer Chemistry

Supplementary Information for

Water-soluble supramolecular hyperbranched polymers based on host-enhanced π–π interaction

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1. Experimental Section

The synthetic method of BTNI is described in main body.

The cucurbit[8]uril was provided by Dr. Anthony Day from the University of New South Wales in Australia. (J. Org. Chem. 2001, 66, 8094).

BTNI: ^{13}C NMR (400 MHz, DMSO-d6, 25° C): δ_C (ppm) = 52.00, 52.76, 123.42, 123.48, 126.39, 127.33, 127.36, 128.25, 128.35, 128.43, 129.34, 129.61, 132.65, 133.23, 133.29, 136.69, 137.18.

Anal. calcd for BTNI·3H_2O: C 59.14, H 4.96, N 8.11; found C 59.20, H 4.53, N 8.23.

Materials

1,3,5-tris((1H-imidazol-1-yl)methyl)benzene (TIB) was obtained from Jinan Henghua company and used as received. 2-Bromomethyl naphthalene (purity: >96%) was obtaind from Alfa Aesar. Acetonitrile was obtained from Beijing chemical plant. （Ferrocenylmethyl）trimethyl-ammonium Iodide (FcMA) (purity:>95%) was obtaind from Tokyo Chemical Industry Co.,Ltd.

ITC studies: ITC was carried out with a Microcal VP-ITC apparatus in pH 4.75 buffer solution at 298.15 K.

Dynamic light scattering (DLS) measurement

DLS data was obtained on a Malvern Zetasizer Nano ZS90 using a monochromatic coherent He–Ne laser (633 nm) as the light source and a detector that detected the scattered light at an angle of 90° and the temperature of 20 °C.

^{1}H-NMR spectra

1H-NMR spectra was recorded on a JOEL JNM—ECA400 apparatus (400 MHz). DOSY experiments were carried out with a BRUKER AVANCE 600 NMR Spectrometer.

^{13}C-NMR spectra

^{13}C-NMR spectra was recorded on a JOEL JNM—ECA400 apparatus (400 MHz).

UV spectra

UV spectra were obtained on a Hitachi U-3010 spectrophotometer.

Fluorescence spectroscopy

Fluorescence spectroscopy was performed on a Hitachi F-7000 apparatus.

2. ^{1}H NMR for solutions of BTNI and [2BTNI-3CB[8]]

Upon addition of CB[8], signals corresponding to the hydrogen atoms of the naphthalene group moved to the high field and broadened, indicating that the naphthalene groups are encapsulated in the cavity of CB[8].

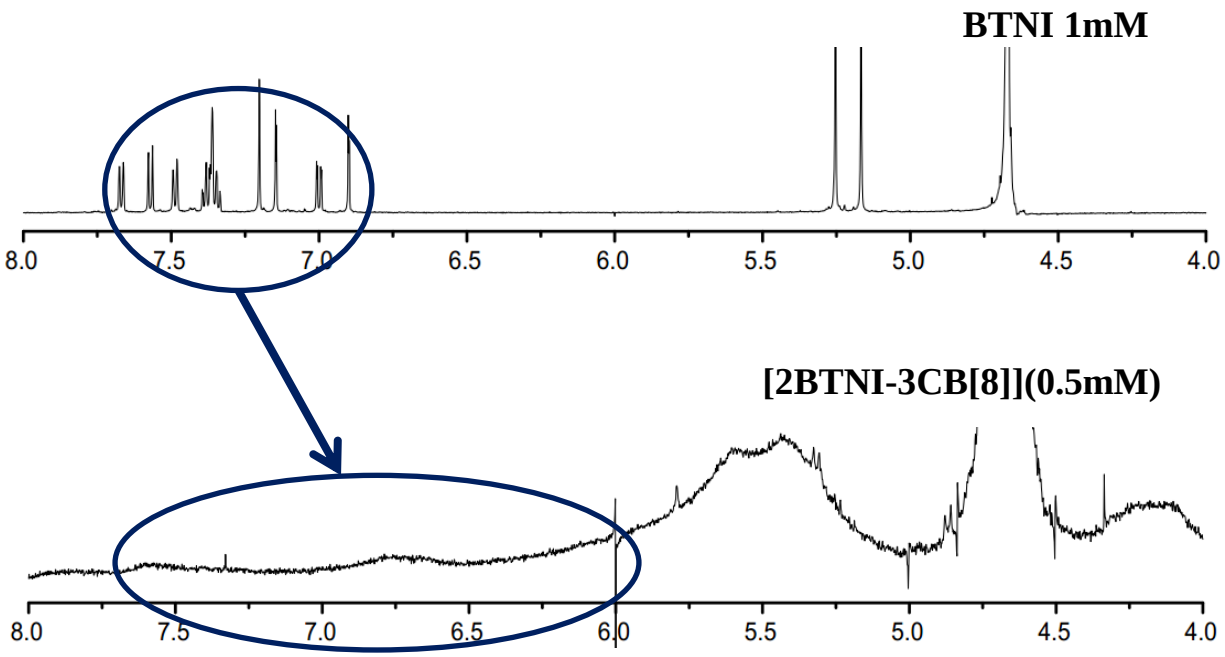


Fig. S1. ^{1}H NMR spectra of 1.0 mM BTNI and 0.5 mM [2BTNI-3CB[8]]

3. DLS for the Assembly of 2BTNI-3CB[8]

Dynamic light scattering (DLS) experiments support the formation of large supramolecular hyperbranched polymers. The average radius of the aggregates in the solution of 2BTNI-3CB[8] (0.5 mM) is measured to be around 115 nm.

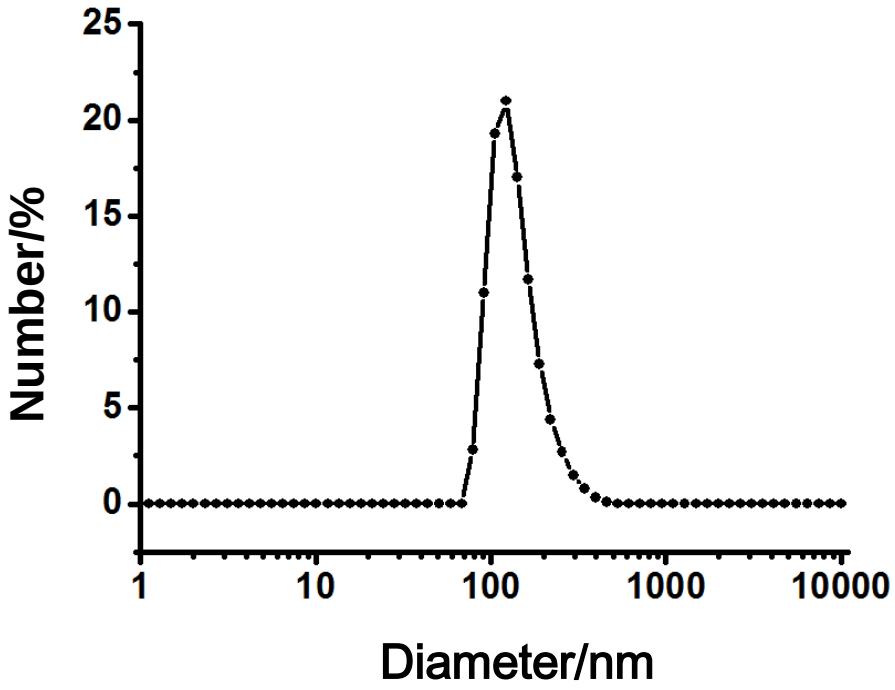
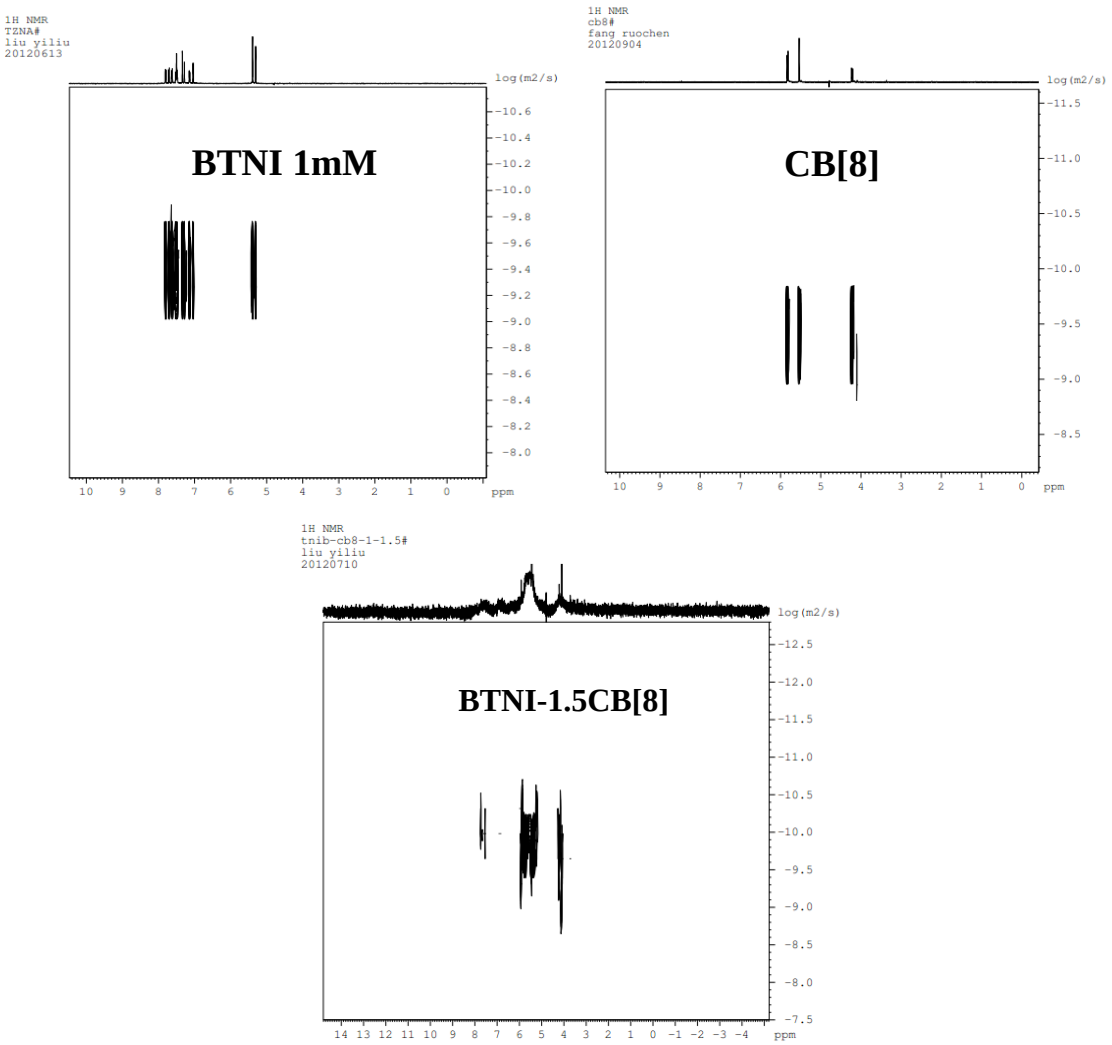


Fig. S2. DLS data of 0.5 mM [2BTNI-3CB[8]]

4. Diffusion-ordered NMR Spectroscopy data

The average diffusion coefficients of BTNI and CB[8] were measured to be 3.23×10^{-10} m^2s^{-1} and 2.95×10^{-10} m^2s^{-1}, respectively. However, after complexation in 2:3 ratio, the NMR signals of both BTNI and CB[8] show a single diffusion coefficient with a value of 8.63×10^{-11} m^2s^{-1}, which suggests that the two building blocks diffuse as one entity. The significant decrease of diffusion coefficient also implies that large polymeric species are formed. Simply assuming that the formed supramolecular polymers are spherical aggregates, the average size of 2BTNI-3CB[8] complexes is equal to 40 times of CB[8].

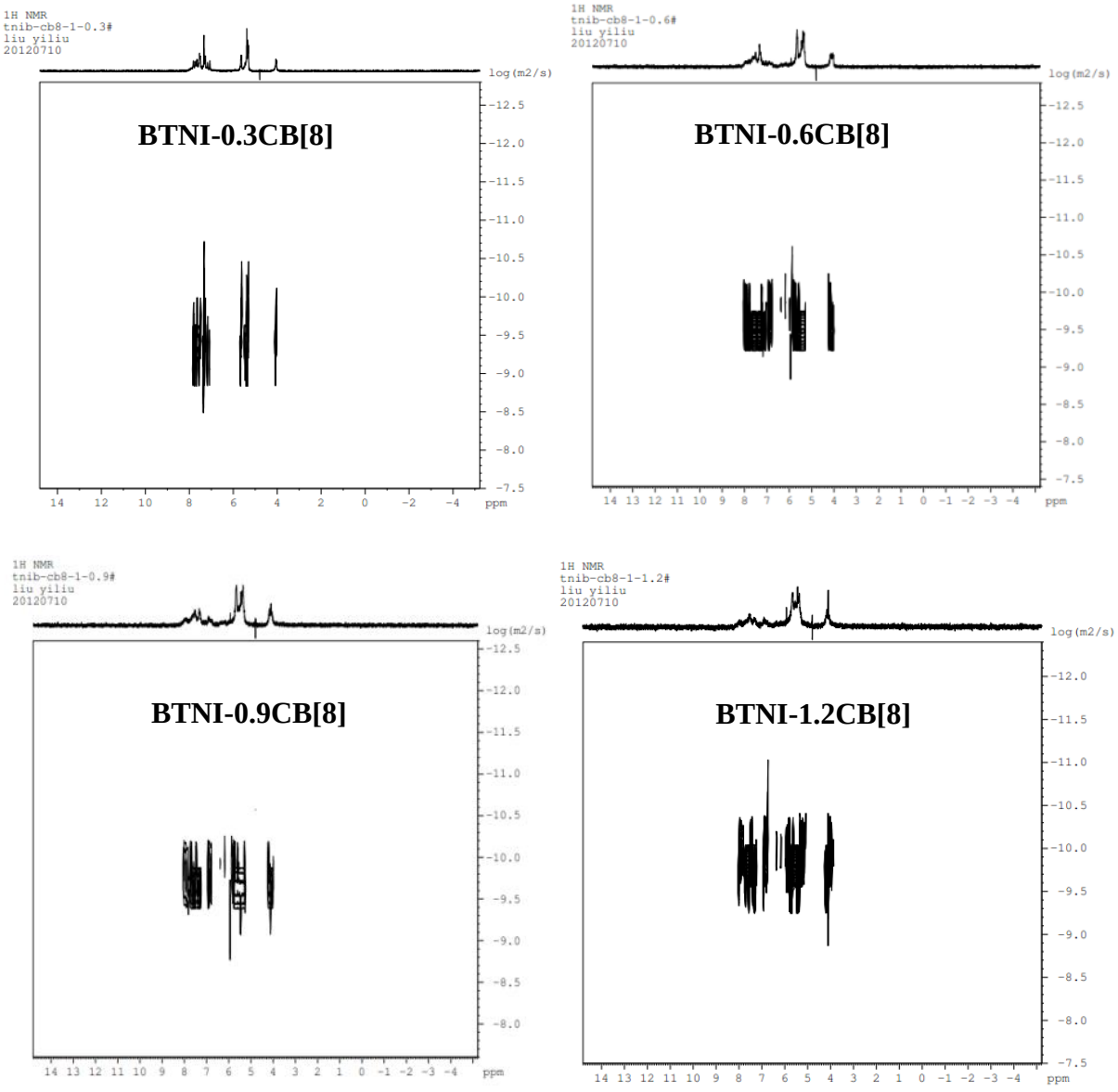


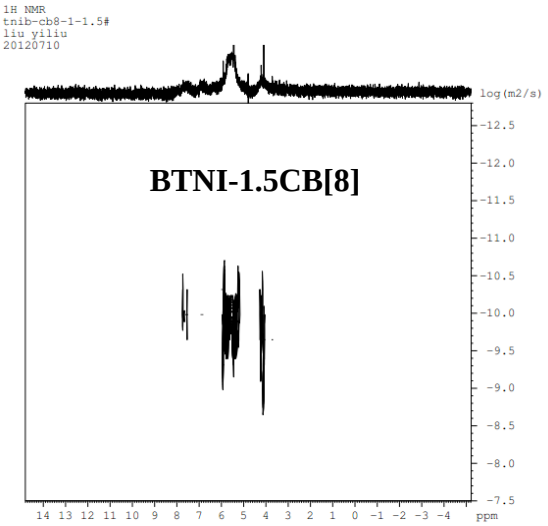
	$D_{avg}(10^{-10}\ m^2s^{-1})$
BTNI	**3.23**

CB[8] **2BTNI-3CB[8]**	**2.95** **0.86**

DOSY for BTNI with different ratios of CB[8]

With the increase of the ratio of CB[8] to BTNI, the diffusion coefficients of the complexes decrease. Therefore, the supramolecular polymerization can be adjusted by tuning of the ratio of BTNI and CB[8].

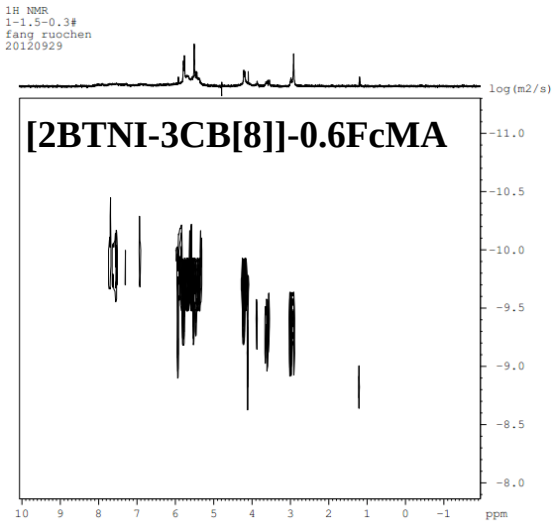


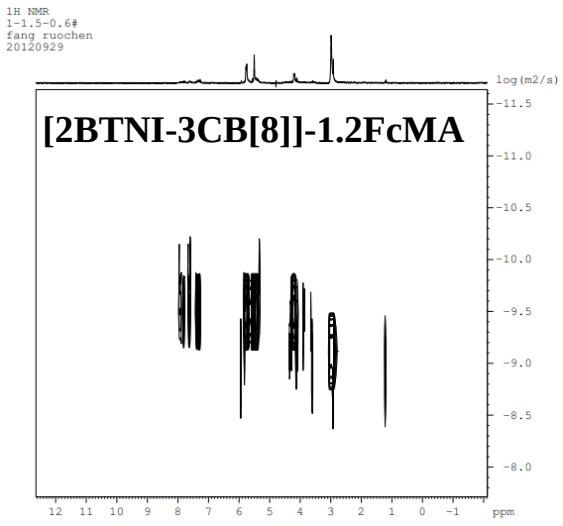


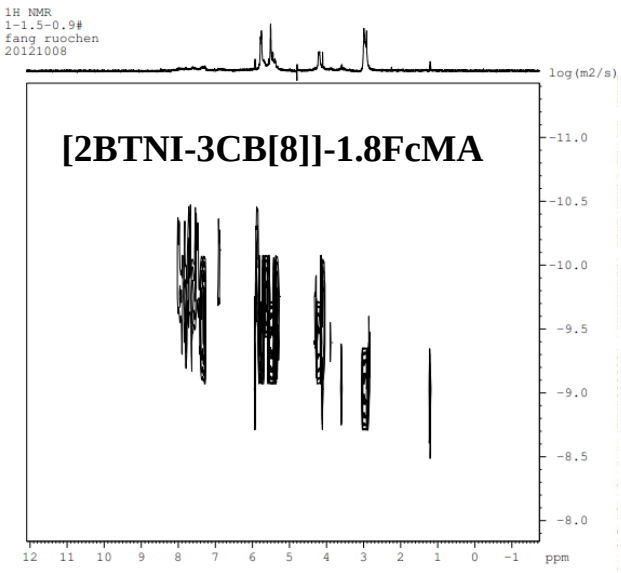
Molar ratio of CB[8]	$D_{avg}(10^{-10}\ m^2s^{-1})$
0	3.23
0.3	2.64
0.6	1.80
0.9	1.50
1.2	1.17
1.5	0.86

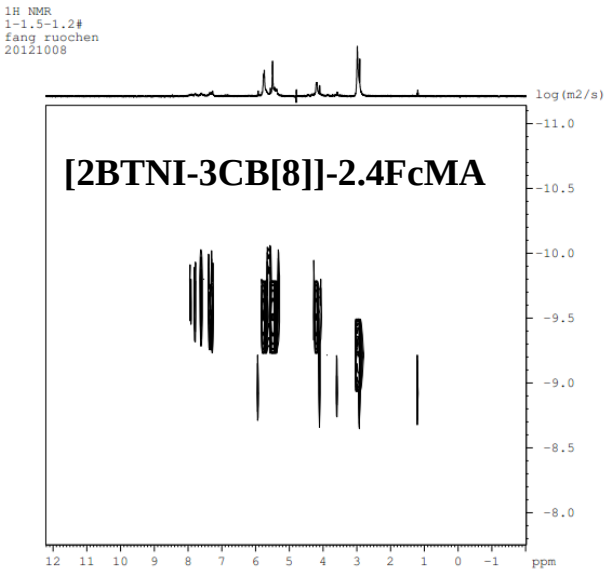
DOSY for [2BTNI-3CB[8]] with different ratios of FcMA

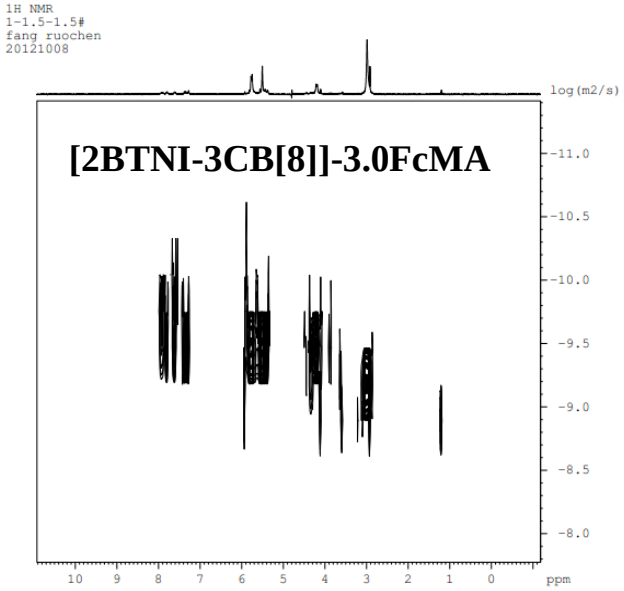
Upon adding FcMA, diffusion coefficient increases, indicating that the size of the supramolecular hyperbranched polymers decrease. It means that the introduction of FcMA into the solution do induce a depolymerization process











Molar ratio of FcMA	$D_{avg}(10^{-10}\ m^2s^{-1})$
0	0.86
0.6	0.90
1.2	0.95
1.8	1.08
2.4	1.50
3.0	1.74