

A pillar[5]arene-based anion responsive supramolecular polymer †

Chengyou Han,^a Binyuan Xia,^a Jianzhuang Chen,^a Guocan Yu,^a Zibin Zhang,^a Shengyi Dong,^a Bingjie Hu,^b Yihua Yu^b and Min Xue*^a

^a Department of Chemistry, Zhejiang University, 310027 Hangzhou, P. R. China. Fax: +86-571-8795-3189; Tel: +86-571-8795-3189; E-mail: xuemin@zju.edu.cn

^b Shanghai Key Laboratory of Magnetic Resonance, Department of Physics, East China Normal University, 200062 Shanghai, P. R. China.

Electronic Supplementary Information (4 Pages)

1. Characterization of monomer 1	S2
2. Calculated values of maximum possible polymerization degree <i>n</i> at different concentrations of 1	S4
References	S4

1. Characterization of monomer **1**

1.1 1D NMR spectrum of monomer **1**

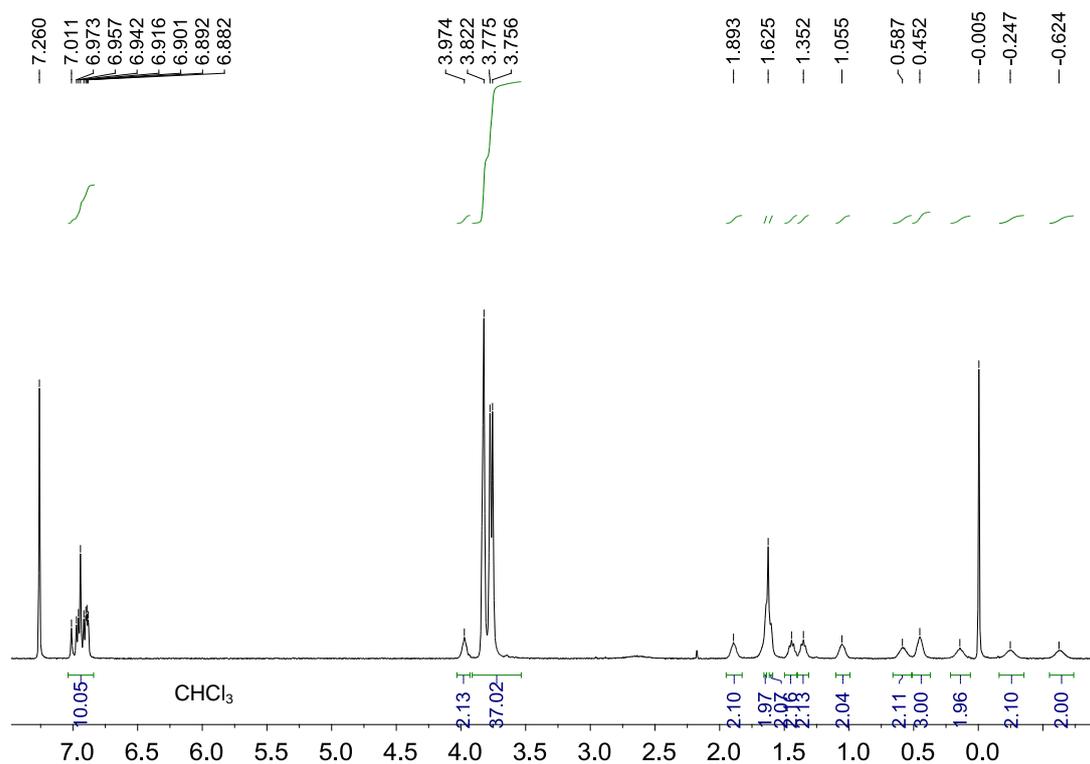


Fig. S1. ¹H NMR spectrum (400 MHz, chloroform-*d*, room temperature, 4.00 mM) of **1**.

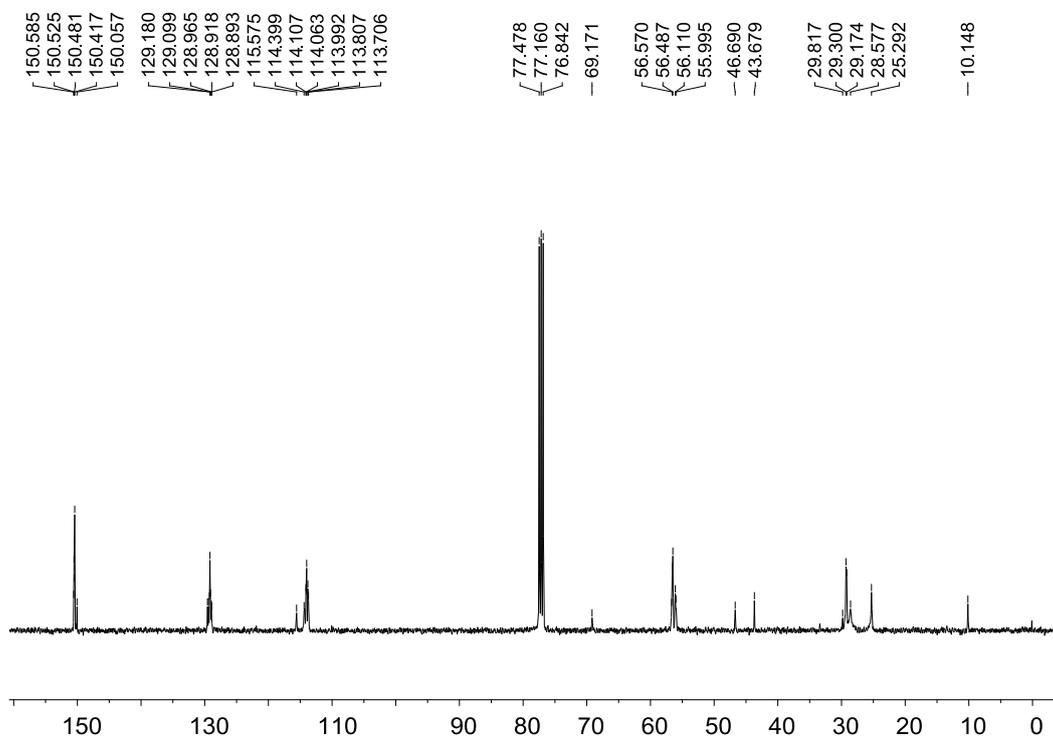


Fig. S2. ¹³C NMR spectrum (100 MHz, chloroform-*d*, room temperature, 100 mM) of **1**.

1.2 LRESIMS of monomer **1**

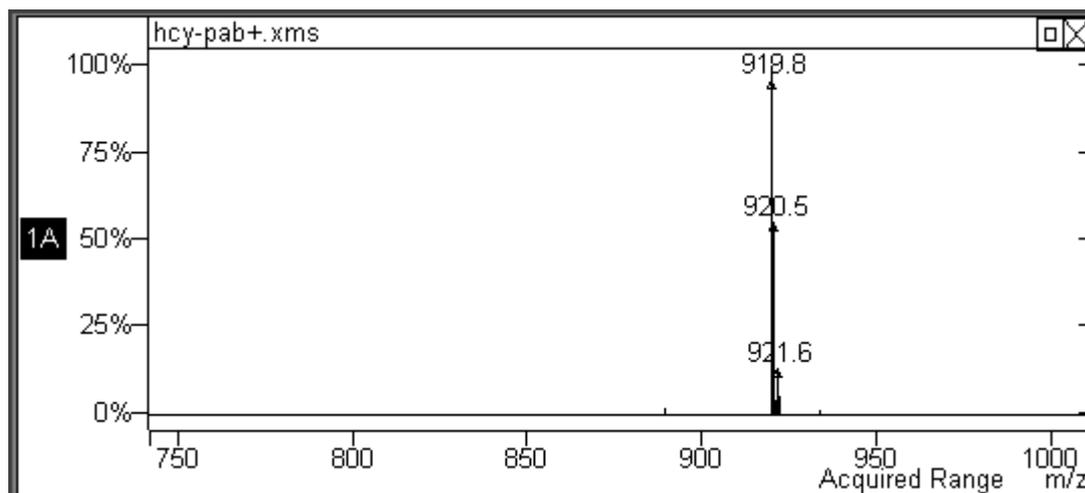


Fig. S3. Electrospray ionization mass spectrum of **1** in chloroform solution. Assignment of the main peak: m/z 919.8 $[M - PF_6]^+$ (100%).

1.3 2D COSY spectrum of monomer **1**

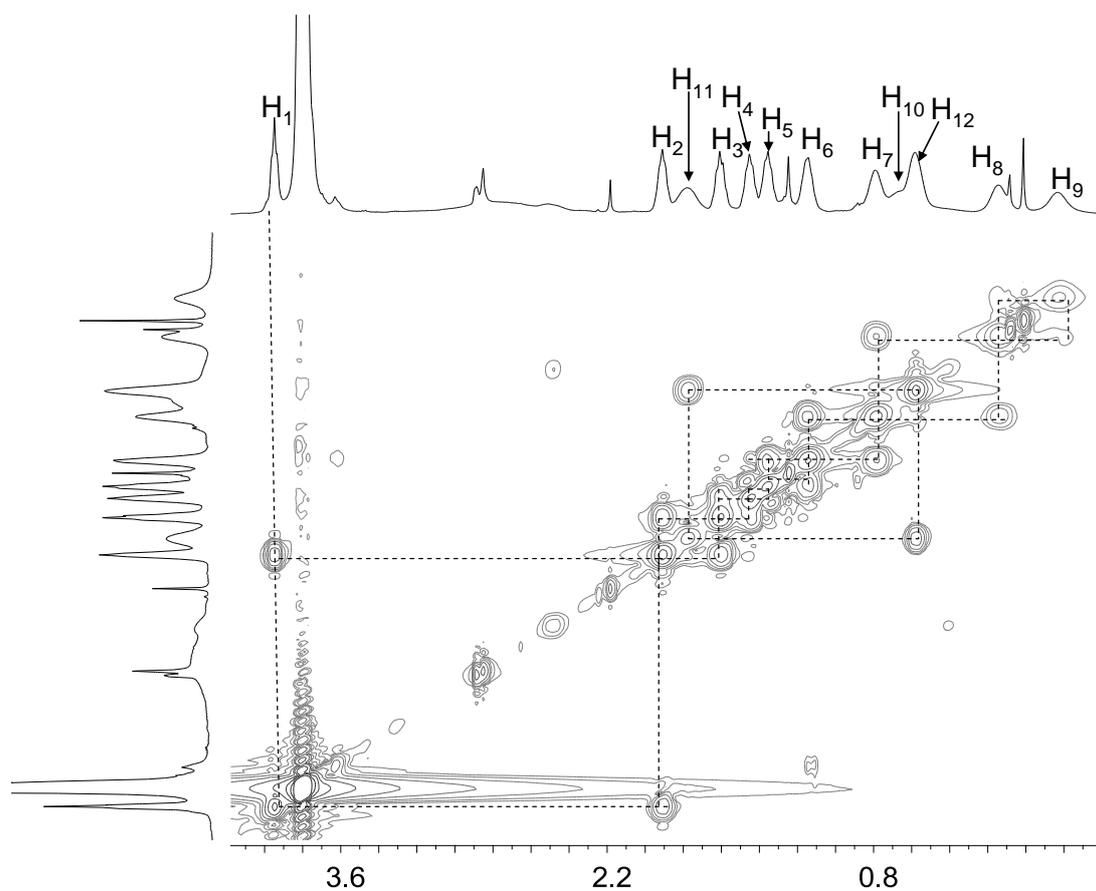


Fig. S4. 2D COSY spectrum (400 MHz, chloroform-*d*, room temperature, 100 mM) of monomer **1**.

2 Calculated values of maximum possible polymerization degree n at different concentrations of **1**

Using the Carothers equation (1)^{S1} and assuming that the same average association constant (1090 M⁻¹ for the model system) holds for each successive step (isodesmic) and that cyclic species can either be ignored or taken into account, the average degree of polymerization, n , is easily derived as being related to the equilibrium constant K_a and the initial monomer concentration as follows:^{S2}

$$n = 1/(1 - p) \quad (1)$$

If we now define p = extent of complexation,

$$K_a = p[\text{H}]_0 / (1 - p)^2 [\text{H}]_0^2.$$

Solving this quadratic equation leads to

$$1 - p = \{ (1 + 4K_a[\text{H}]_0)^{1/2} - 1 \} / 2K_a[\text{H}]_0$$

$$n = 1/(1 - p) = 2K_a[\text{H}]_0 / \{ (1 + 4K_a[\text{H}]_0)^{1/2} - 1 \}$$

$$n = K_a^{1/2} [\text{H}]_0^{1/2} \quad (2)$$

In this system p is the extent of complexation and $[\text{H}]_0 = [\mathbf{1}]_0$. Therefore, degrees of polymerization calculated in this way represent maximum values that in practice will be reduced by formation of cyclics and possibly by reduction in the association constant as the suprapolymer grows (“attenuation”). As the concentration increases, the calculated size of aggregates increases to large values. For example, at $[\mathbf{1}]_0 = 500$ mM, $p = 95.8\%$ and $n = 23.8$, indicating the formation of aggregates of increasing sizes.

Table S1. Calculated Parameters for the supramolecular polymers.

[monomer 1] ₀ (mM)	p	max n^* Eq. 1	molar mass (KDa)	max n^* Eq. 2
1.00	0.397 ± 0.050	1.66 ± 0.14	1.77 ± 0.14	1.04 ± 0.15
15.0	0.781 ± 0.028	4.57 ± 0.58	4.87 ± 0.61	4.04 ± 0.58
62.5	0.886 ± 0.016	8.77 ± 1.18	9.34 ± 1.26	8.25 ± 1.19
125	0.918 ± 0.012	12.2 ± 1.7	13.0 ± 1.8	11.7 ± 1.7
250	0.941 ± 0.008	17.0 ± 2.4	18.1 ± 2.5	16.5 ± 2.4
500	0.958 ± 0.006	23.8 ± 3.4	25.4 ± 3.6	23.3 ± 3.4

* Errors were calculated from the error in K_a ($1.09 (\pm 0.31) \times 10^3 \text{ M}^{-1}$)

References:

- S1. C. H. Carothers, *Trans. Faraday Soc.*, 1936, **32**, 39–53.
 S2. (a) H. W. Gibson, N. Yamaguchi and J. W. Jones, *J. Am. Chem. Soc.*, 2003, **125**, 3522–3533; (b) F. Huang, D. S. Nagvekar, X. Zhou and H. W. Gibson, *Macromolecules*, 2007, **40**, 3561–3567.