Supporting Information

Studies on the structure of *N*-phenyl-substituted hexaaza[1$_6$]paracyclophane: synthesis, electrochemical properties and theoretical calculation

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Supporting information

Spectral and electrochemical results

In the differential pulse voltammograms (Figure 3), the integration areas ratio of peaks were nearly 1:1 in different electrolytes (Table 3).

Figure 4 shows the controlled potential coulometry result. Controlled potential coulometry of 1×10^{-6} mol hexamer at +0.84 V, two electrons were removed. We repeated the electrolysis experiment for four times and gave n = 2.04 ± 0.04. Figure S14 shows the controlled potential coulometry result of the linear **N6**. When $E_{appl.}$ = +0.55 V in CH_2Cl_2/TBAP solution, one electron was removed.

The number of electrons involved in the controlled potential coulometry was derived from the forward slope charge value (Q_d) of Anson's plot (Q against $t_{1/2}$) obtained in this experiment using the following equation: [S2]

$$Q_d = 2nFAD^{1/2}C_t^{1/2}/\pi^{1/2}$$

where n = electron transfer number, F = the Faraday constant (96500), A = area of the electrode (1.00 cm^2), D= diffusion coefficient in cm^2/s, C= bulk concentration in mol/cm^3.

According to the electrochemical studies, the results were another evidence that the hexamer is a cyclic oligoarylamine, although we could not obtain the single crystal of the hexamer molecule. During the process of our tries for obtaining the hexamer crystal, the color of the substrate solution changed from light-yellow to green and further to dark within several days. The color changes suggested that the hexamer was oxidized easily.

Calculated results

Energy (B3LYP/6-31-G**) = -3104.7621643 Hartree

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	4.81148364	-1.29770189	0.54856907
N	4.76406539	-2.62033372	1.08747742
C	3.57433571	-3.37489966	0.84596857
C	2.33048995	-2.88423290	1.26349016
C	1.16058503	-3.59016753	1.00839474
C	3.61601008	-4.60223631	0.17151015
C	2.44578861	-5.30349001	-0.10457534
C	1.19565602	-4.80422011	0.30163473
N	-0.00033751	-5.50604001	-0.00184904
C	4.82034141	-1.10993398	-0.84080742

C	4.81936707	0.17175851	-1.38427605
C	4.81208200	1.29718239	-0.54790274
C	4.81766949	1.10942791	0.84150193
C	4.81611788	-0.17226946	1.38495146
N	4.76531349	2.61975867	-1.08694128
C	3.57554097	3.37453843	-0.84661904
C	2.33188739	2.88345337	-1.26426098
C	1.16182954	3.58950211	-1.01018875
C	1.19652852	4.80411313	-0.30438762
C	3.61685733	4.60246355	-0.17318004
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C	-1.19652852	-4.80411313	-0.30438762
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C	-3.57554097	-3.37453843	-0.84661904
C	-2.44646331	-5.30384054	0.10184667
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C	-4.81611788	0.17226946	1.38495146
C	-4.81766949	-1.10942791	0.84150193
C	-4.81936707	-0.17175851	-1.38427605
C	-4.82034141	1.10993398	-0.84080742
C	5.77352106	-3.09425632	1.94955879
H	2.28529145	-1.94333366	1.80261174
H	0.21122709	-3.19779005	1.35468527
H	4.57325175	-4.99543911	-0.15654306
H	2.49646233	-6.23715299	-0.65369599
C	-0.00026791	-6.93219556	-0.00250210

H	4.81581849	-1.97952753	-1.49031585
H	4.82714379	0.31013007	-2.46091884
H	4.81114309	1.97901341	1.49100225
H	4.82143672	-0.31063224	2.46161191
C	5.77640704	3.09402507	-1.94692911
H	2.28697898	1.94211538	-1.80263811
H	0.21263527	3.19675500	-1.35651837
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H	-2.49684856	-6.23795586	0.65022649
H	-4.57392063	-4.99603046	0.15495327
C	0.00026791	6.93219556	-0.00250210
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H	-4.57325175	4.99543911	-0.15654306
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C	-5.77352106	3.09425632	1.94955879
H	-4.82143672	0.31063224	2.46161191
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H	-4.82714379	-0.31013007	-2.46091884
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C	7.81006854	-4.04705419	3.65846258
C	8.06624156	-3.01559725	2.75319021
C	7.06935756	-2.54534927	1.90247139
C	5.52129947	4.12883758	-2.86591209
C	6.53470078	4.59816120	-3.69870472
C	7.81604163	4.04739748	-3.65178355
C	8.07088503	3.01642353	-2.74558755
C	7.07245489	2.54590573	-1.89683367
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C	-5.52129947	-4.12883758	-2.86591209
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H	8.59275408	-4.41330168	4.31518705
H	9.05797666	-2.57516992	2.69650396
H	7.29069875	-1.75492717	1.19415070
H	4.52808837	4.55846097	-2.92762527
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H	9.06276344	2.57662268	-2.68659819
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H	-0.98251838	7.09609731	1.90644464
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H	-9.05797666	2.57516992	2.69650396
H	-7.29069875	1.75492717	1.19415070
H	-7.29273873	-1.75587564	-1.18774637
H	-9.06276344	-2.57662268	-2.68659819

H	-8.59992279	-4.41387495	-4.30695091
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References:

S1. E. Bacher, M. Bayerl, P. Rudati, N. Reckefuss, C. Muller, K. Meerholz and O. Nuyken, *Macromolecules,* 2005, **38**, 1640.

S2. R. Sivabalan, M.B. Talawar, P. Santhos, N. Senthilkumar, B. Kavitha, G.M. Gore and S. Venugopalan, *J. Haradous Materials*, 2007, **148**, 573.

S3. Gaussian 09, A.1 Revision, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

Supplementary information

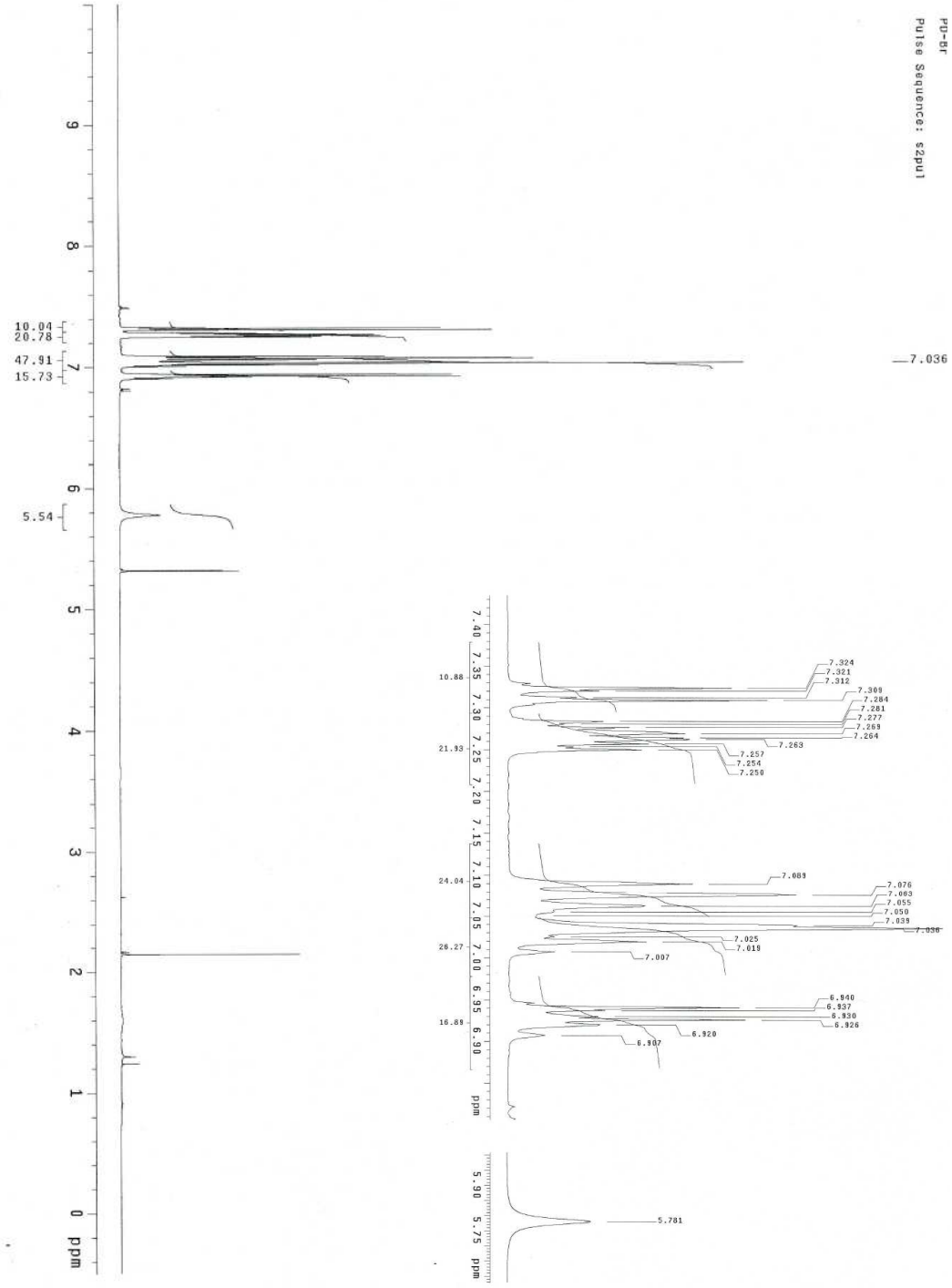


Figure S1. H^1 NMR spectra for PD-Br at room temperature.

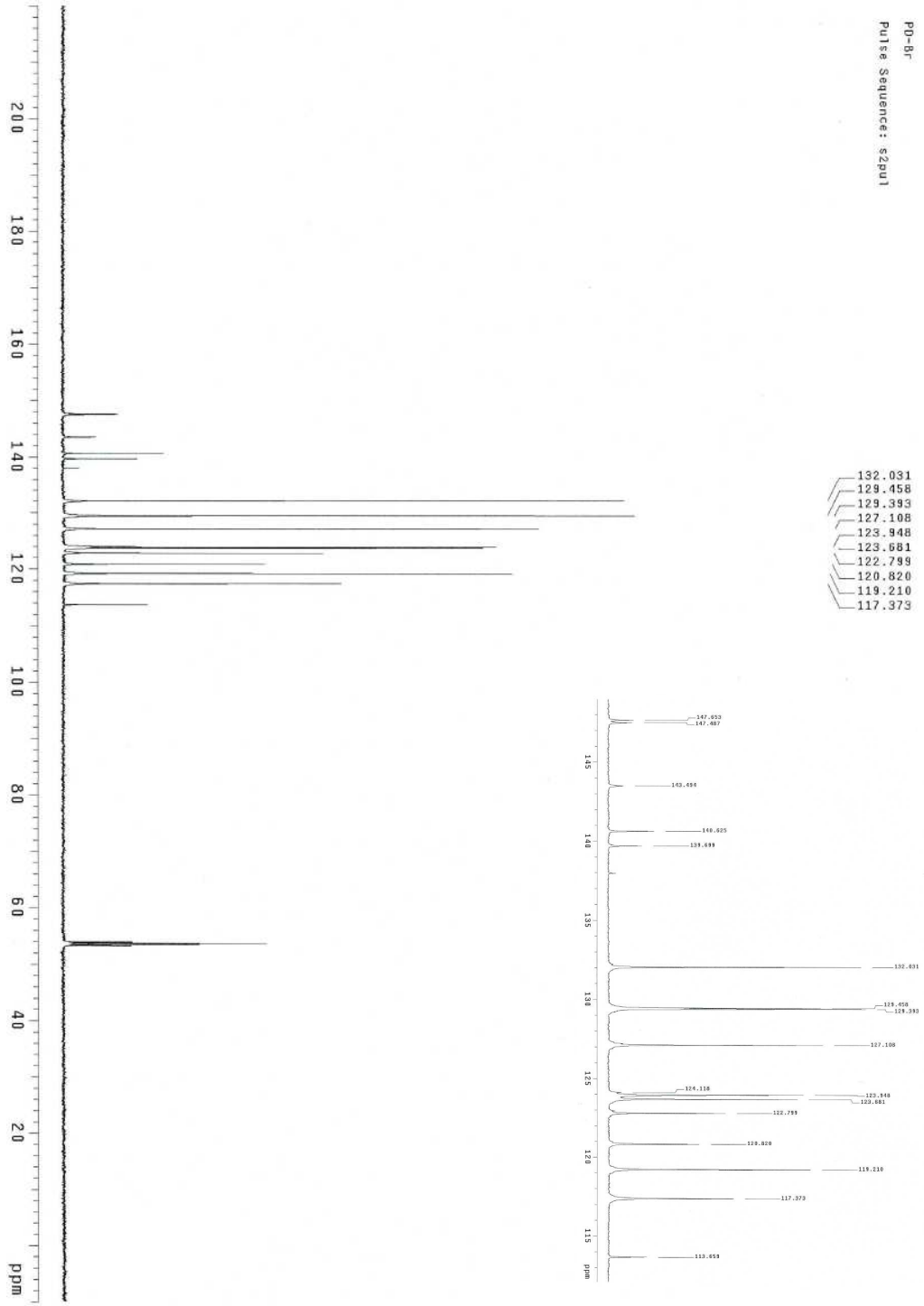


Figure S2. C^{13} NMR spectra for PD-Br at room temperature.

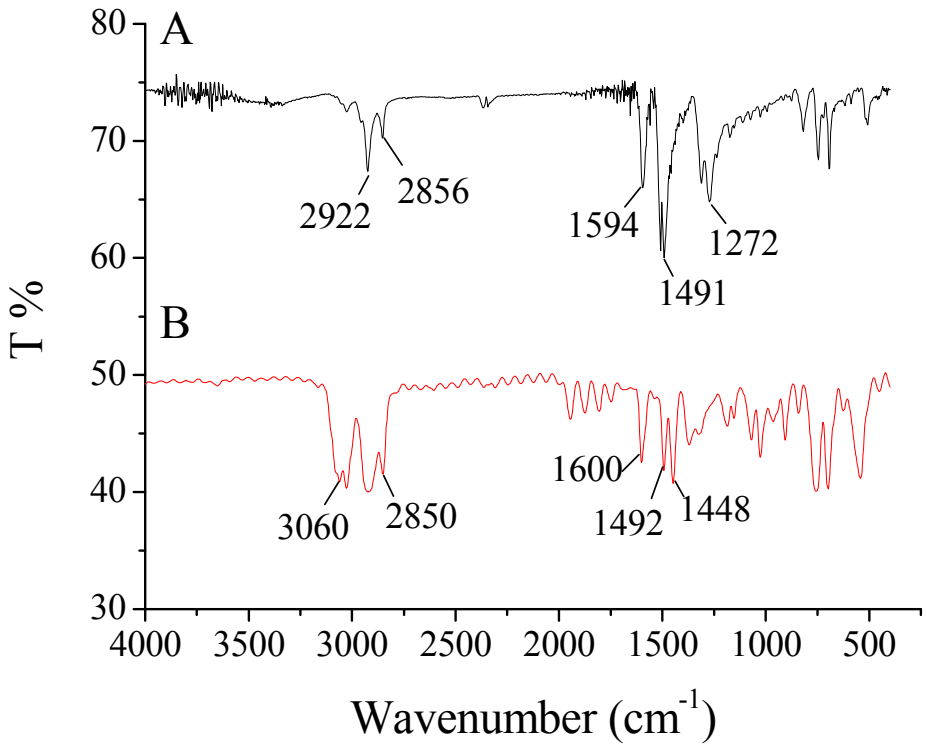


Figure S3. IR spectra of (A) hexamer and (B) polystyrene.

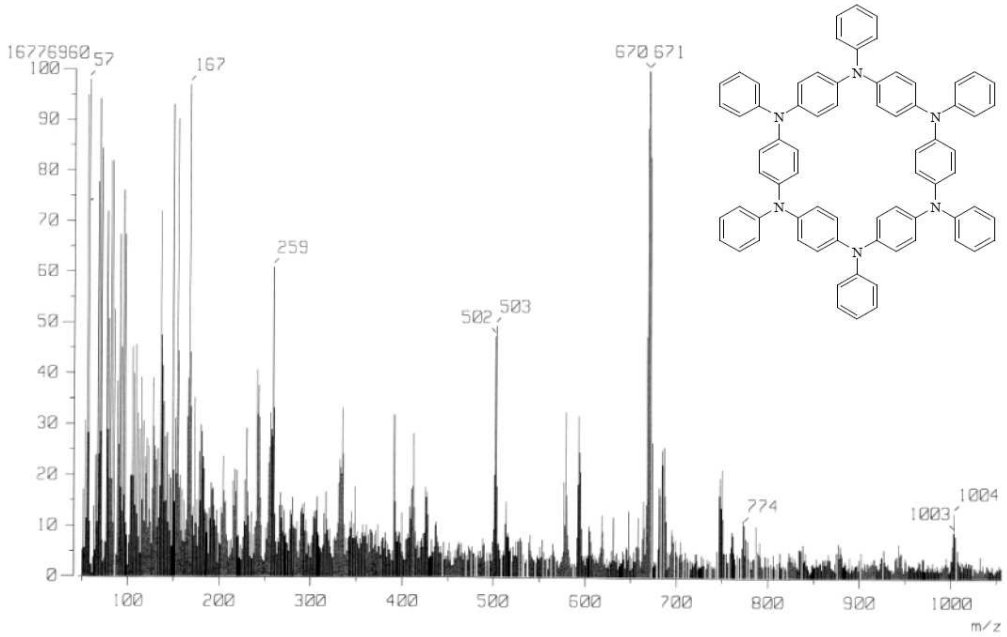


Figure S4. Ms spectra for hexamer.

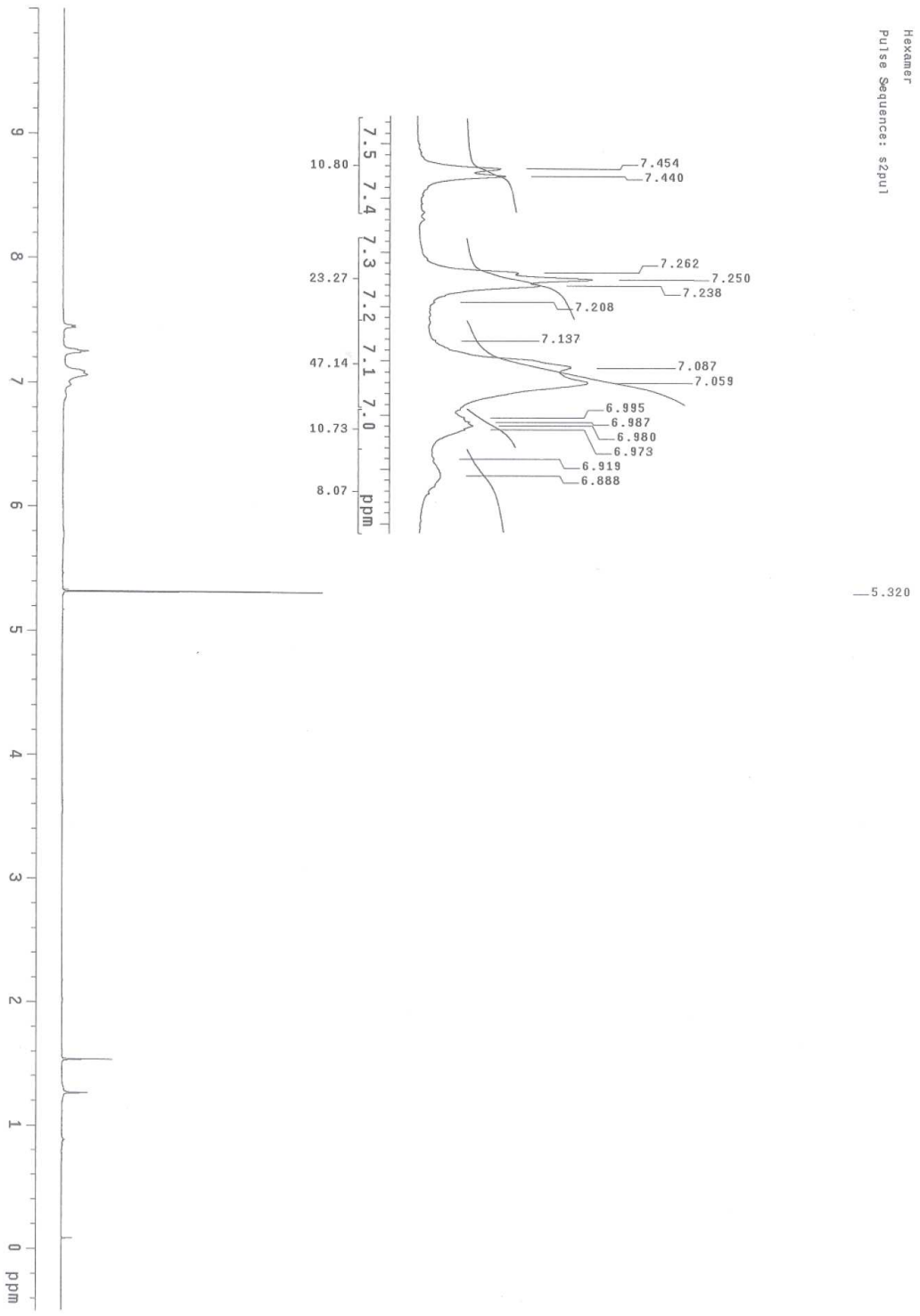


Figure S5. H^1 NMR spectra for hexamer at room temperature.

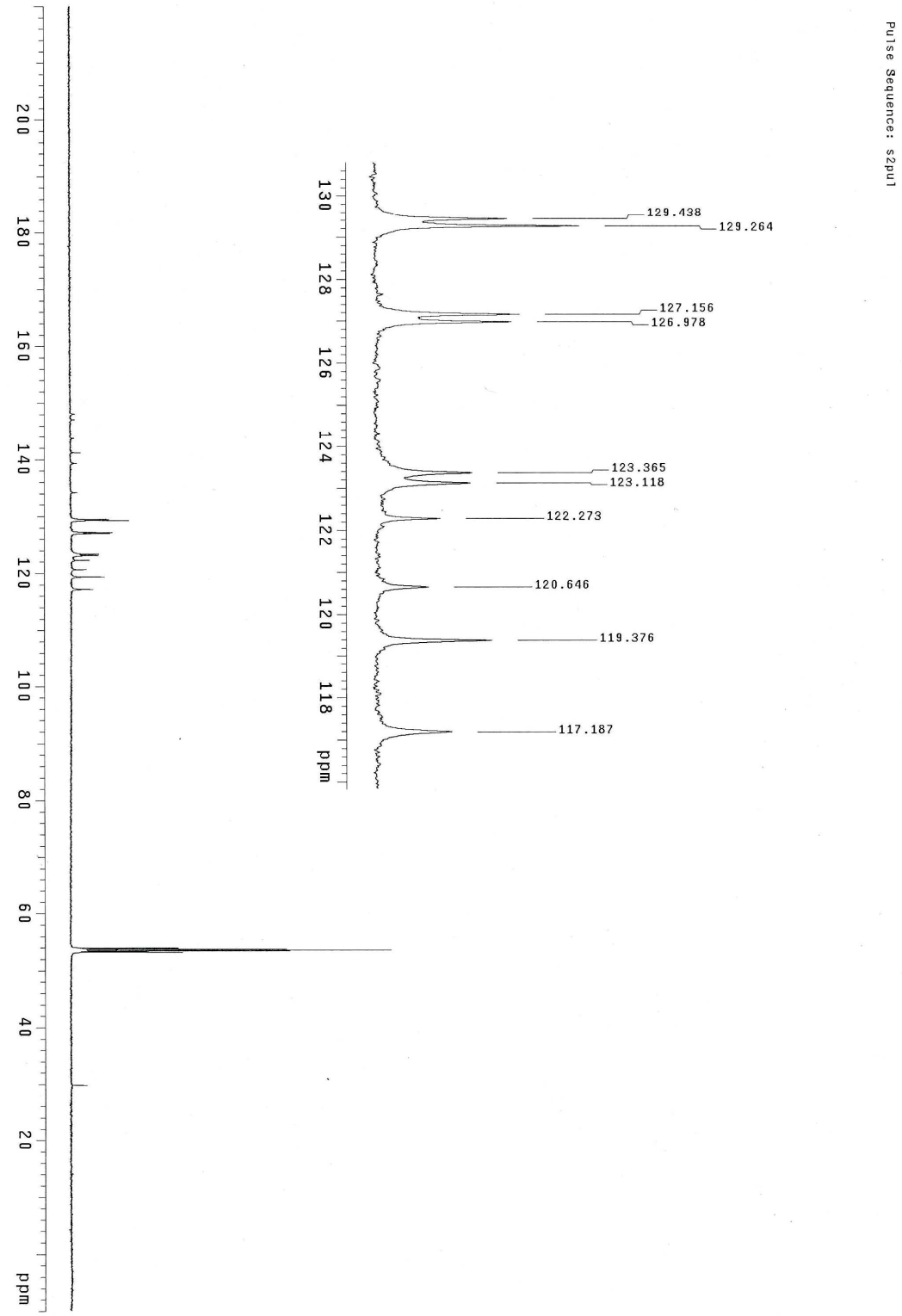


Figure S6. C^{13} NMR spectra for hexamer at room temperature.

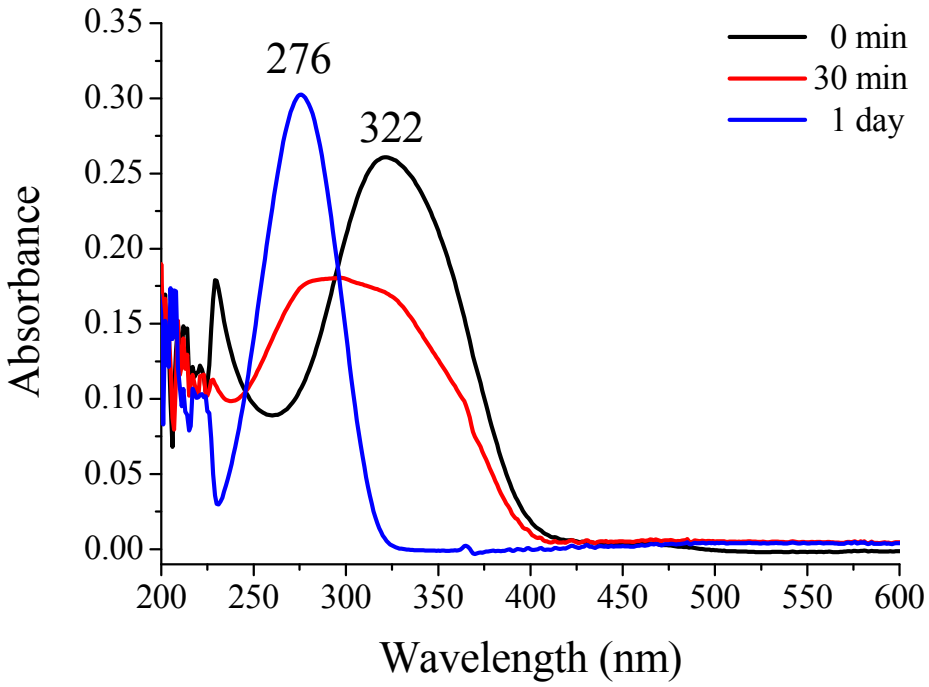


Figure S7. The UV-Vis spectra change of the hexamer in the CH_2Cl_2.

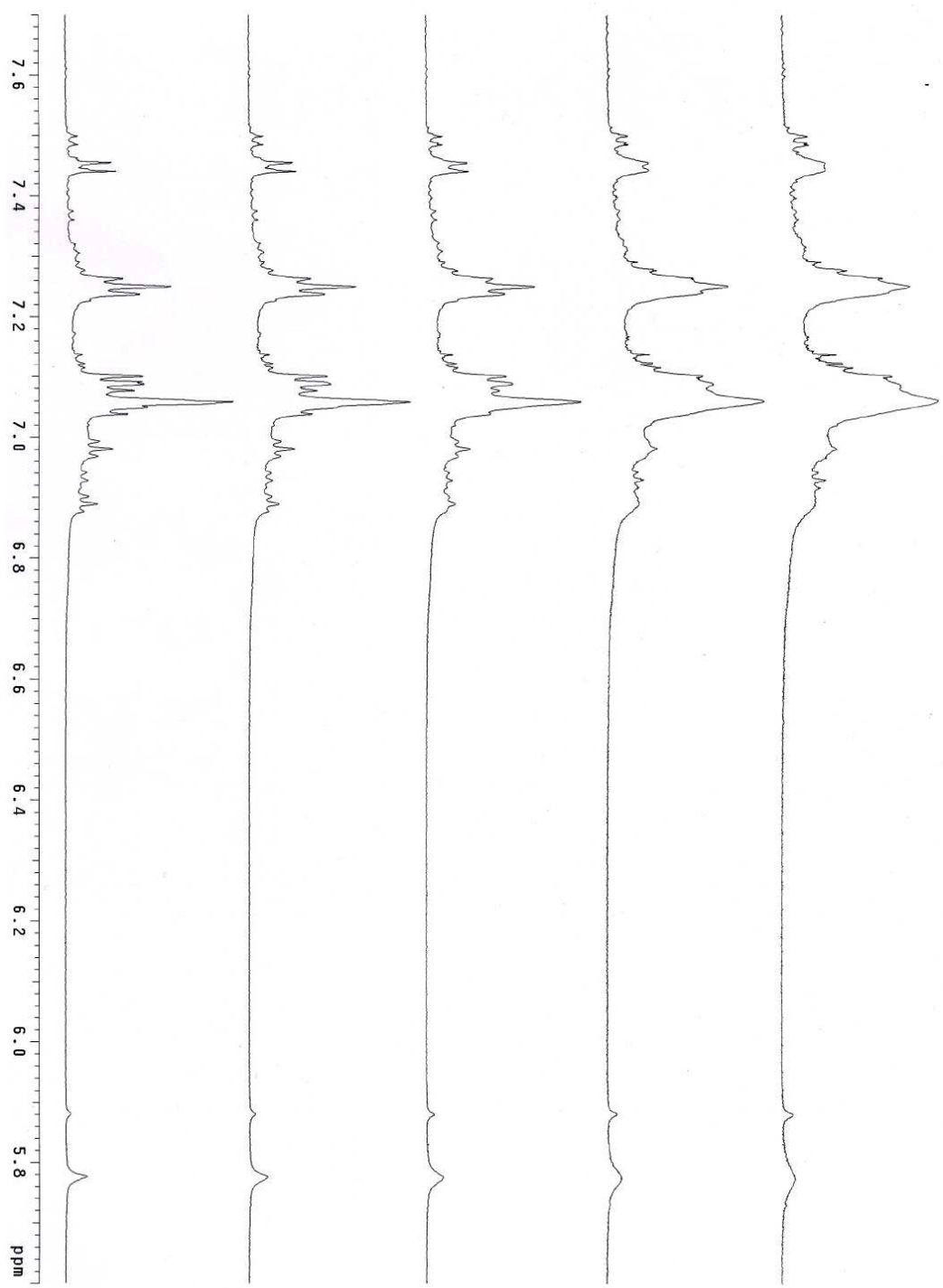


Figure S8. The NMR spectra change (every 10 min. from bottom to up) of the hexamer in the CD_2Cl_2 at 0 ℃.

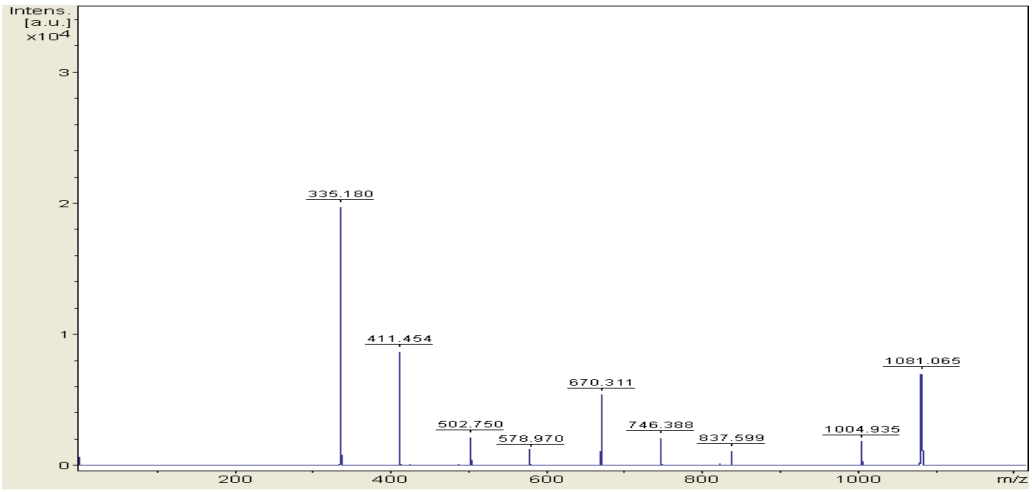


Figure S9. Mass spectrum for linear **N6**.

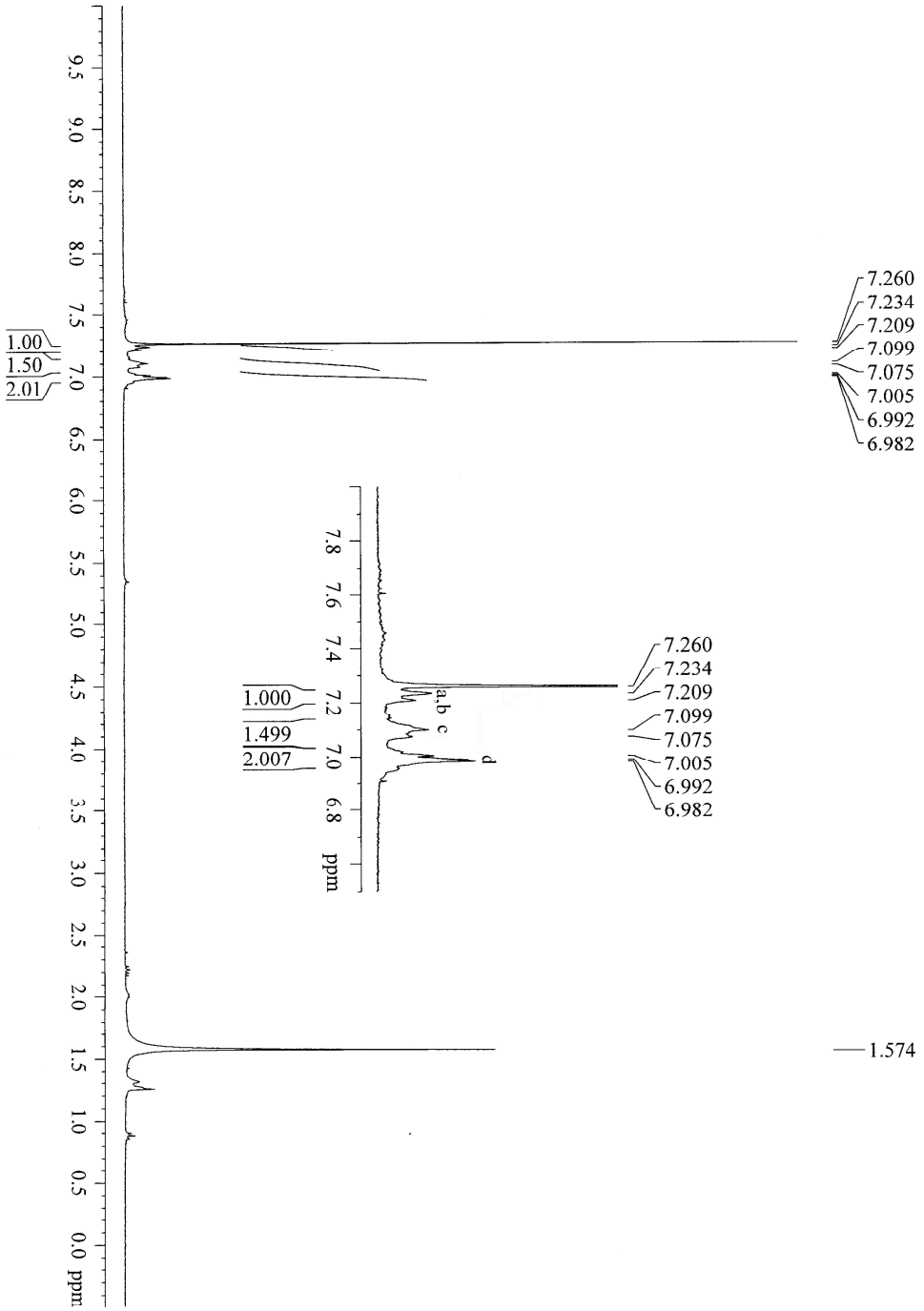


Figure S10. H^1 NMR spectra for linear **N6** at room temperature.

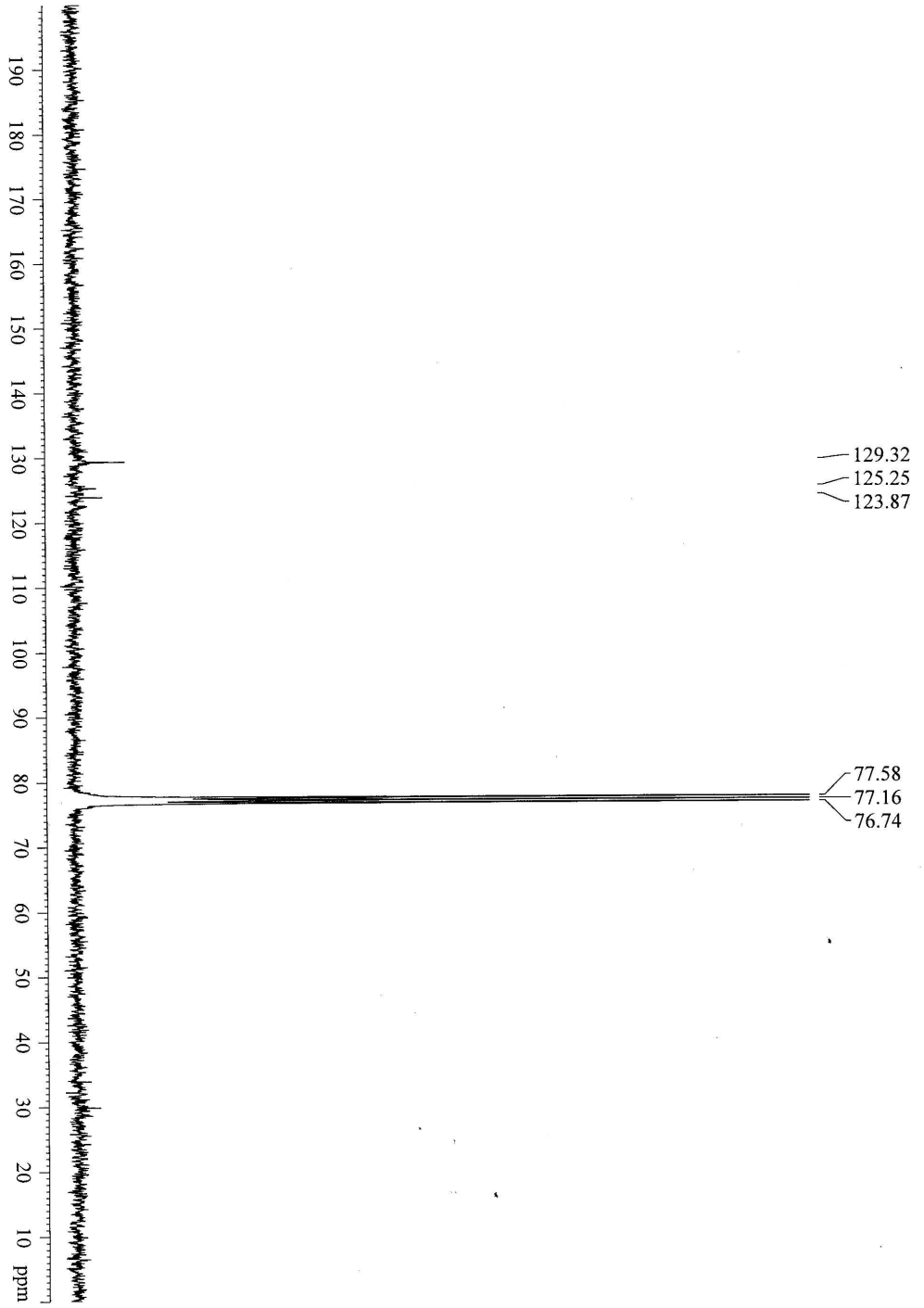


Figure S11. C^{13} NMR spectra for linear **N6** at room temperature.

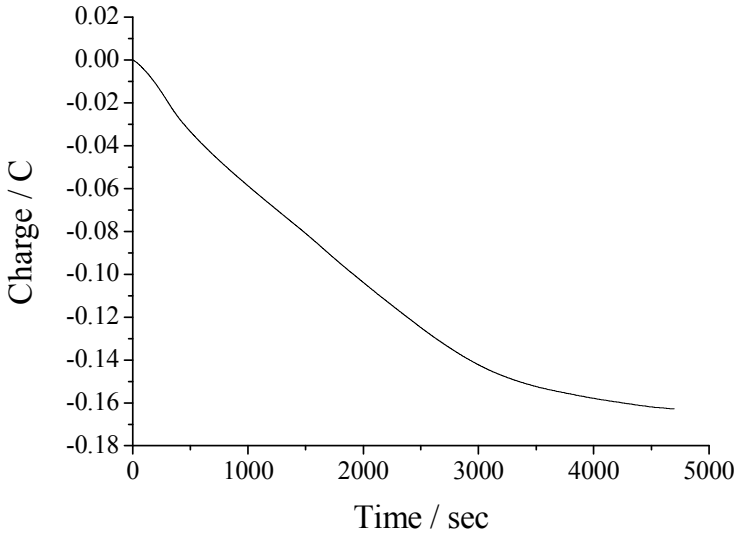


Figure S12. Controlled potential coulometry at $E_{appl.}$ = +0.55 V vs Ag/AgCl for linear **N6** (1.9 x 10^{-6} mol) in CH_2Cl_2 (0.1 M TBAP).

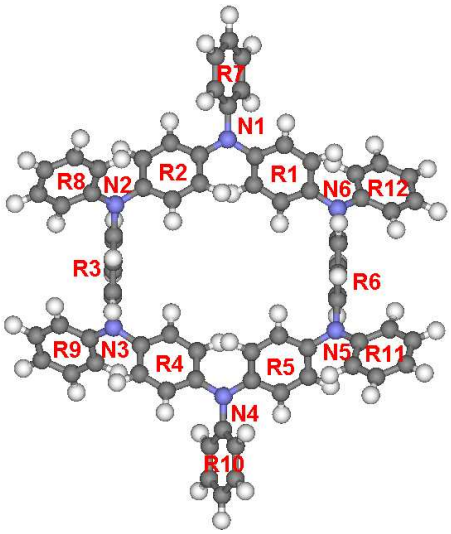


Figure S13. Optimized structure of the hexamer calculated based on B3LYP/6-31G** level; N: blue, C: gray, H: white.

Table S1. The position (m/z value) of peak and the corresponding species for the mass spectrum of the hexamer.

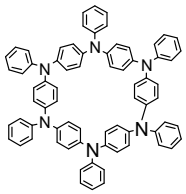
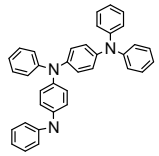
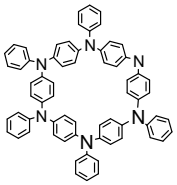
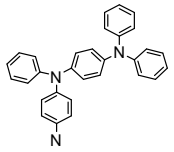
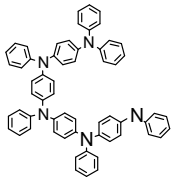
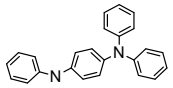
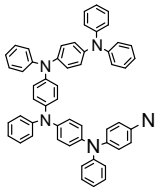
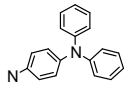
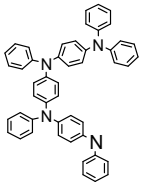
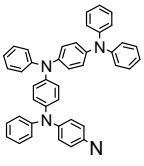
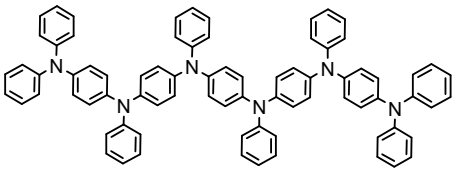
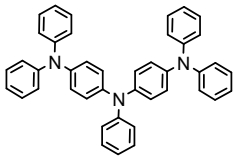
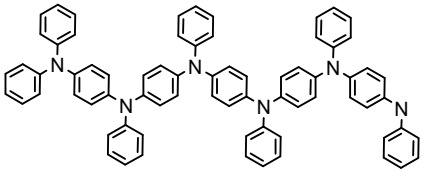
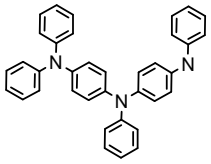
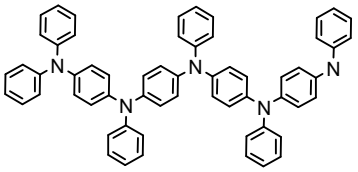
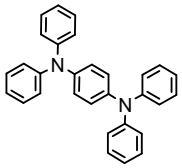
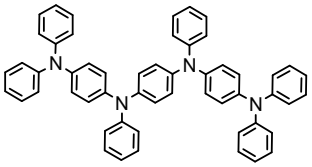
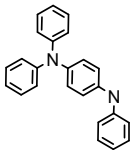
Peak at m/z	Corresponding species	Peak at m/z	Corresponding species
1002		503	
927		425	
836		335	
760		258	
670		168	
593		91	

Table S2. The position (m/z value) of peak and the corresponding species for the mass spectrum of the linear **N6**.

Peak at m/z	Corresponding species	Peak at m/z	Corresponding species
1081.056		578.970	
1004.935		502.750	
837.599		411.454	
746.388		335.180	
670.311