SUPPORTING INFORMATION

Periodic Polymers Based on Self-Accelerating Click Reaction

Lue Xiang+,[a,b] Zi Li+,[a,b] Jian'an Liu,[a] Jiqiang Chen,[a] Minghui Zhang,[a,c] Ying Wu,[c] Ke Zhang*,[a,b]

[a] State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100190, China.

[b] University of Chinese Academy of Sciences, Beijing 100049, China.

[c] Institute of Polymer Chemistry and Physics, Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing, 100875, China.

+ These authors contributed equally to this work.

* corresponding author: kzhang@iccas.ac.cn

Experimental

Materials

Sodium azide (NaN_3), 3-bromopropionic acid, propylamine, hexamethylenediamine, diisopropylamine, phosphorus oxychloride, potassium carbonate (K_2CO_3), magnesium sulphate ($MgSO_4$), ethyl formate, benzaldehyde, tert-butyl isocyanide, methanol (CH_3OH), dichloromethane (DCM), ethyl acetate (EA), petroleum ether (PE), hexane, *N,N*-dimethylformamide (DMF), acetone, diethyl ether, and tetrahydrofuran (THF) were purchased as regent grade from Alfa Aesar, Aldrich, Acros, J&K Chemical, or Beijing Chemical Reagent Co. and used as received unless otherwise noted. Benzaldehyde was distilled in vacuum before use. Sym-dibenzo-1,5-cyclooctadiene-3,7-diyne (DIBOD) was synthesized according to our previous publication.[1]

Characterization

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 spectrometer at room temperature.

Fourier transform infrared spectra (FT-IR) were recorded on a Thermo Nicolet Avatar-330 Spectrometer.

Ultraviolet Spectra were recorded on a TU-1901 Ultraviolet Spectrophotometer, in which DMF was used as measurement solvent.

High resolution mass spectra (HRMS) were recorded on a Bruker 9.4T Solarix FT-ICR-MS (Bruker, Germany).

Matrix-Assisted Laser Desorption/Ionization Time of Flight (MALDI-TOF) mass spectra were recorded on an Autoflex III MALDI-TOF mass spectrometer equipped with a 355 nm YAG laser. It was operated at an accelerating potential of 20 kV in linear modes. The MALDI mass spectra represent averages over 256 consecutive laser shots (3 Hz repetition rate). The polymer was dissolved in mixed solution (acetone/ethanol = 1:1) with a concentration of 5 g/L. α-Cyano-4-hydroxycinnamic acid (CCA; 23 g/L in mixed solution (acetone/ethanol = 1:1)) was used as the matrix and NaCl (saturated in mixed solution (acetone/ethanol = 1:1)) was used as the cation source. The sample was prepared by mixing 10 μL of the polymer solution with 10 μL of the matrix solution and 2 μL of the NaCl or trifluoroacetate solution. A 1 μL portion of the final solution was deposited onto the sample target and allowed to dry in air at 25°C. Internal standards (peptides or porphyrine derivatives) were used to calibrate the mass scale using the two-point calibration software 3.07.1 from Autoflex III systems.

Gel permeation chromatography (GPC) in THF was conducted on a system comprised of a Waters 1515 isocratic HPLC pump, three Agilent PLgel columns (Mixed C, Mixed C, and Mixed D), and a Waters 2414 RI detector. THF was used as the eluent at a flow rate of 1.0 mL/min. Polystyrene standards were used for the calibration.

GPC in DMF was conducted on a system comprised of a Waters 515 HPLC pump, three Agilent mixed columns (Mixed A, Mixed A and Mixed B), and a Waters 2414 RI detector. DMF with 0.01 M LiBr was used as the eluent at a flow rate of 1.00 mL/min. Polystyrene standards were used for the calibration.

GPC in DMF was conducted on a system comprised of a MODEL 12-6 isocratic HPLC pump, two Agilent PLgel columns (Mixed C and Mixed D), a DAWN HELEOSII multiangle laser light scattering (MALLS) detector (Wyatt Technology), and an Optilab T-rEX differential refractometer (Wyatt Technology). DMF with 0.01 M LiBr was used as the eluent at a flow rate of 0.5 mL/min.

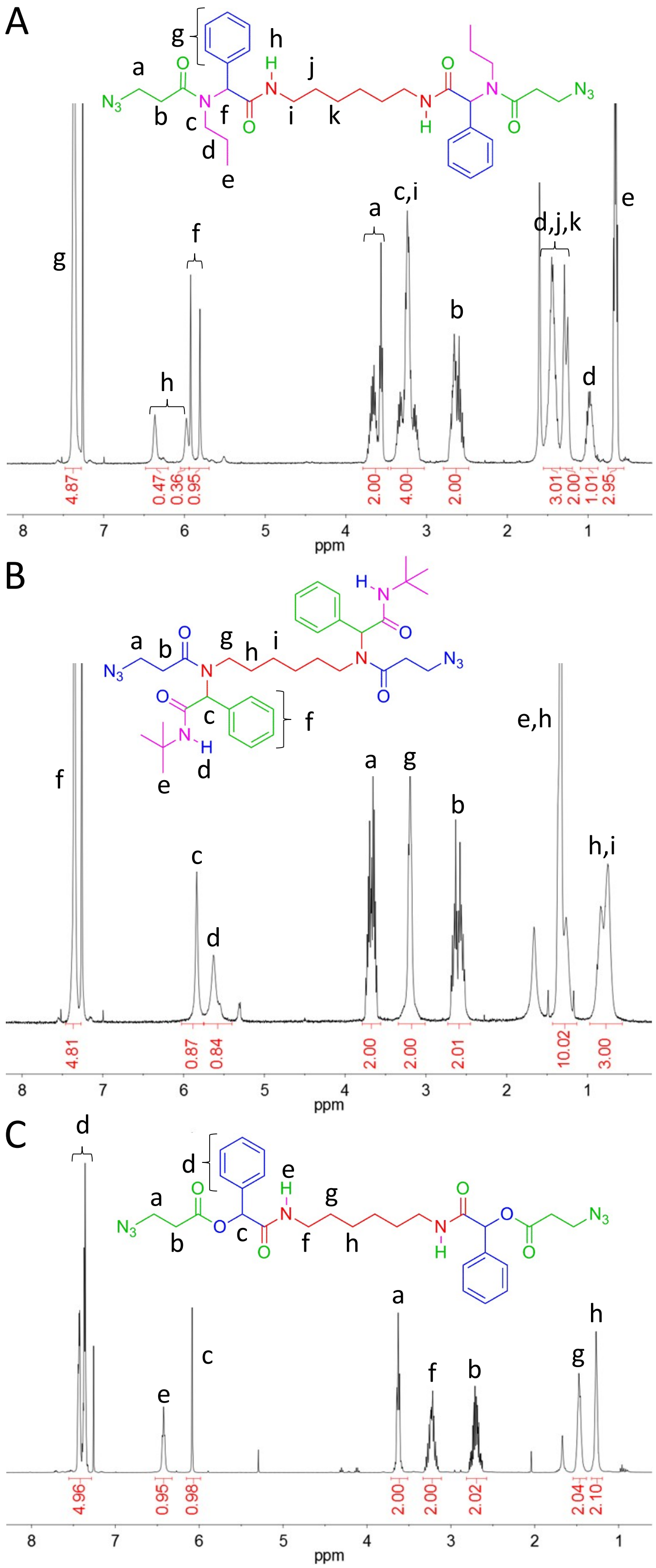

Figure S1. ^{1}H-NMR spectra of monomer **1** (A), monomer **2** (B), and monomer **3** (C) in $CDCl_3$.

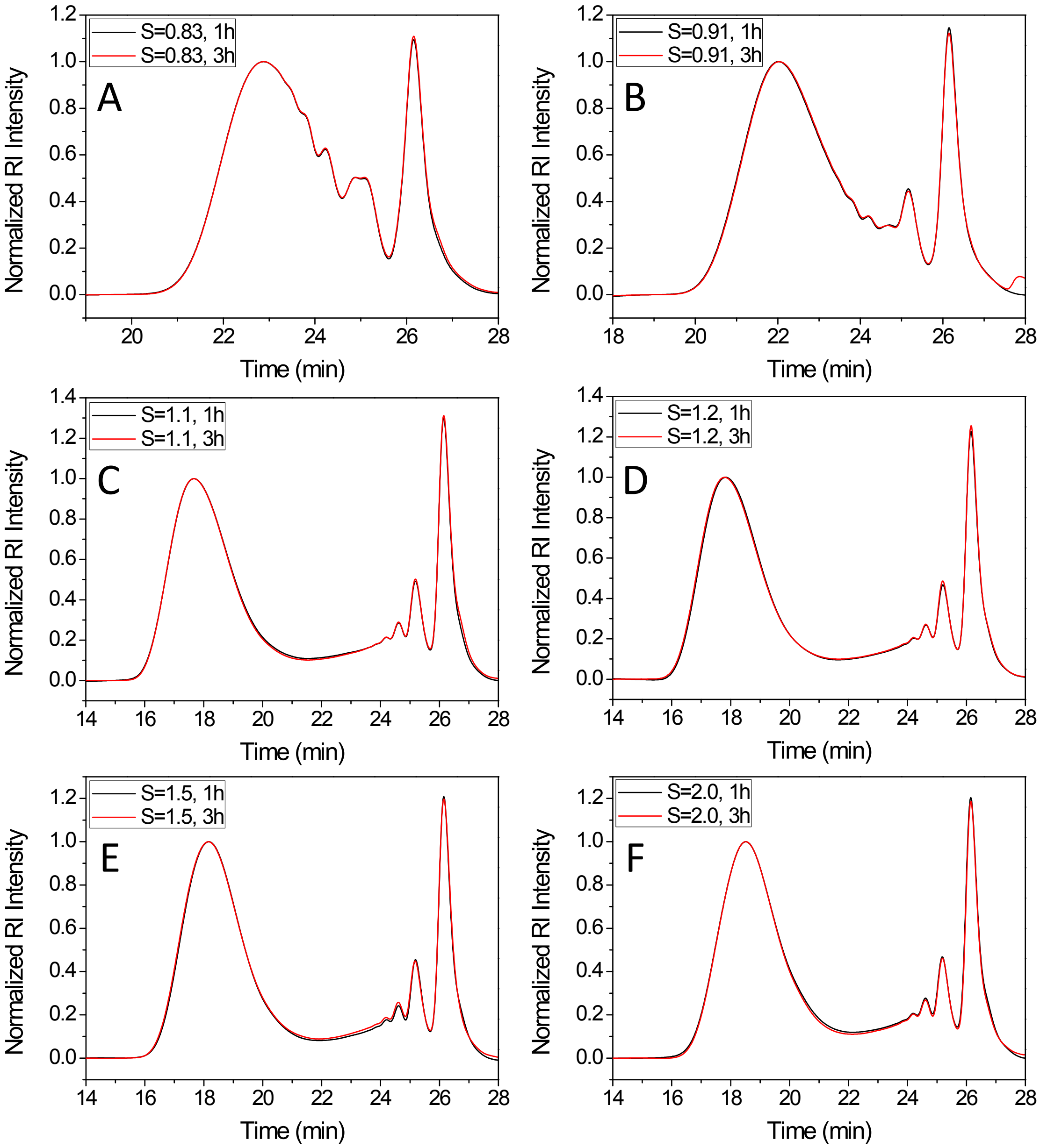

Figure S2. GPC curves of periodic polymer **1** from varied S ([DIBOD]$_0$/[monomer **1**]$_0$) values of 0.83 (A), 0.91 (B), 1.1 (C), 1.2 (D), 1.5 (E), and 2.0 (F) and different reaction time of 1 h (black) and 3 h (red), in which the polymerizations were all performed at room temperature in DMF with [monomer **1**]$_0$ = 0.2 M. THF was used as the eluent and PS standards were used for the calibration.

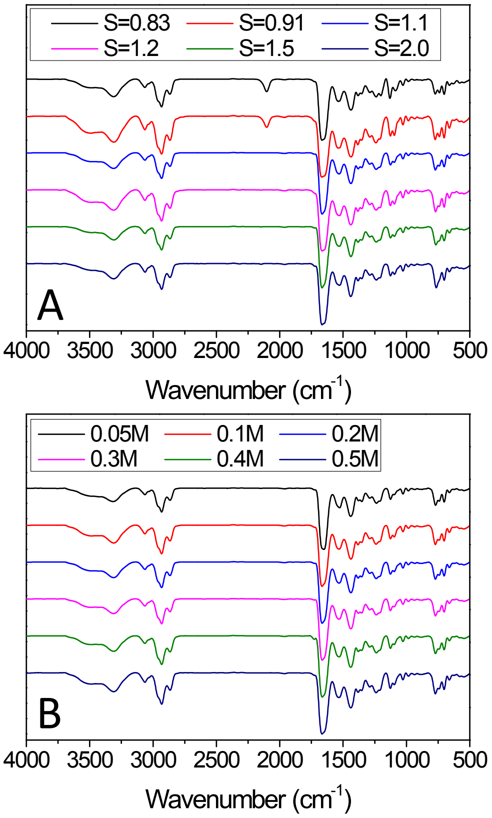

Figure S3. FT-IR spectra of raw periodic polymer **1** and **1'** from varied S (A) and [monomer **1**]$_0$ (B).

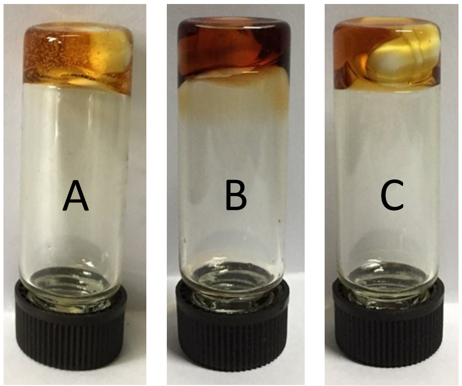

Figure S4. Photographs of in-situ polymerization solution of polymer **1** (A), **2** (B), and **3** (C), in which the S and initial molar concentration of monomers **1-3** were used as 1.1 and 0.5 M, respectively.

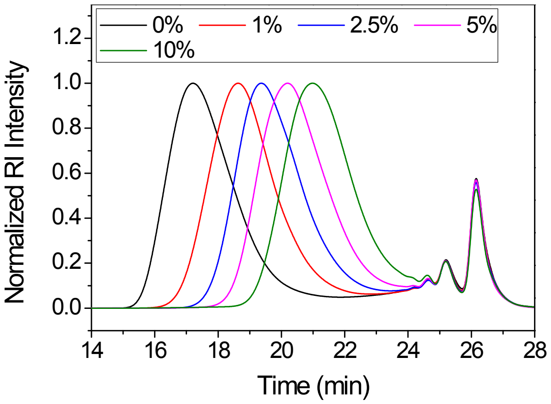

Figure S5. GPC curves of raw polymer **1** from [monomer **1**]$_0$ = 0.5 M, S =1.1, and varied [3-azidopropanoic acid]$_0$/[monomer **1**]$_0$ = 0% (black), 1% (red), 2.5% (blue), 5% (magenta), and 10% (olive). THF was used as the eluent and PS standards were used for the calibration.

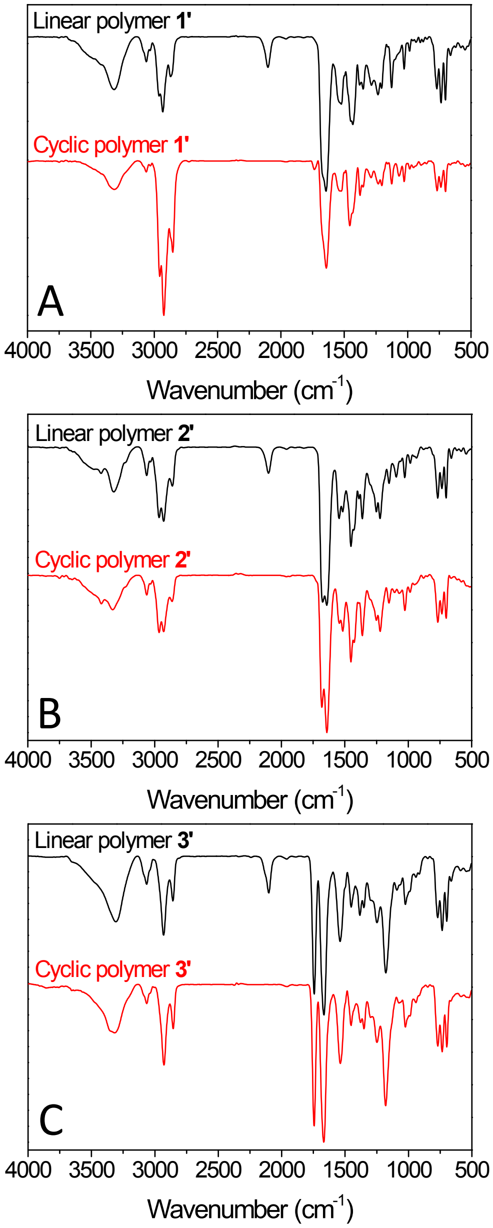

Figure S6. FT-IR spectra of periodic linear (black) and cyclic (red) polymers **1'** (A), **2'** (B) and **3'** (C).

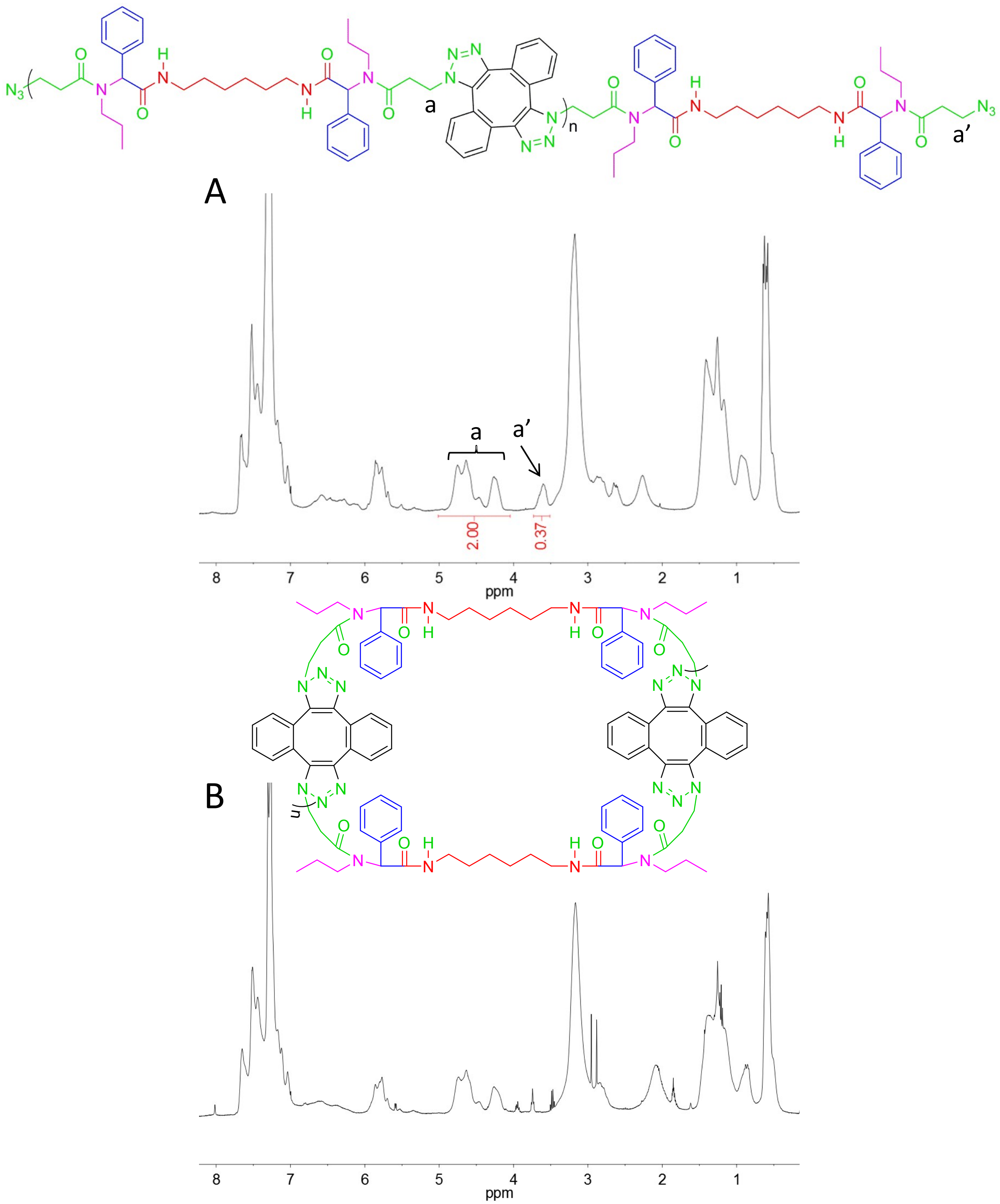

Figure S7. ^{1}H-NMR spectra of linear (A) and cyclic (B) polymer **1'** in $CDCl_3$.

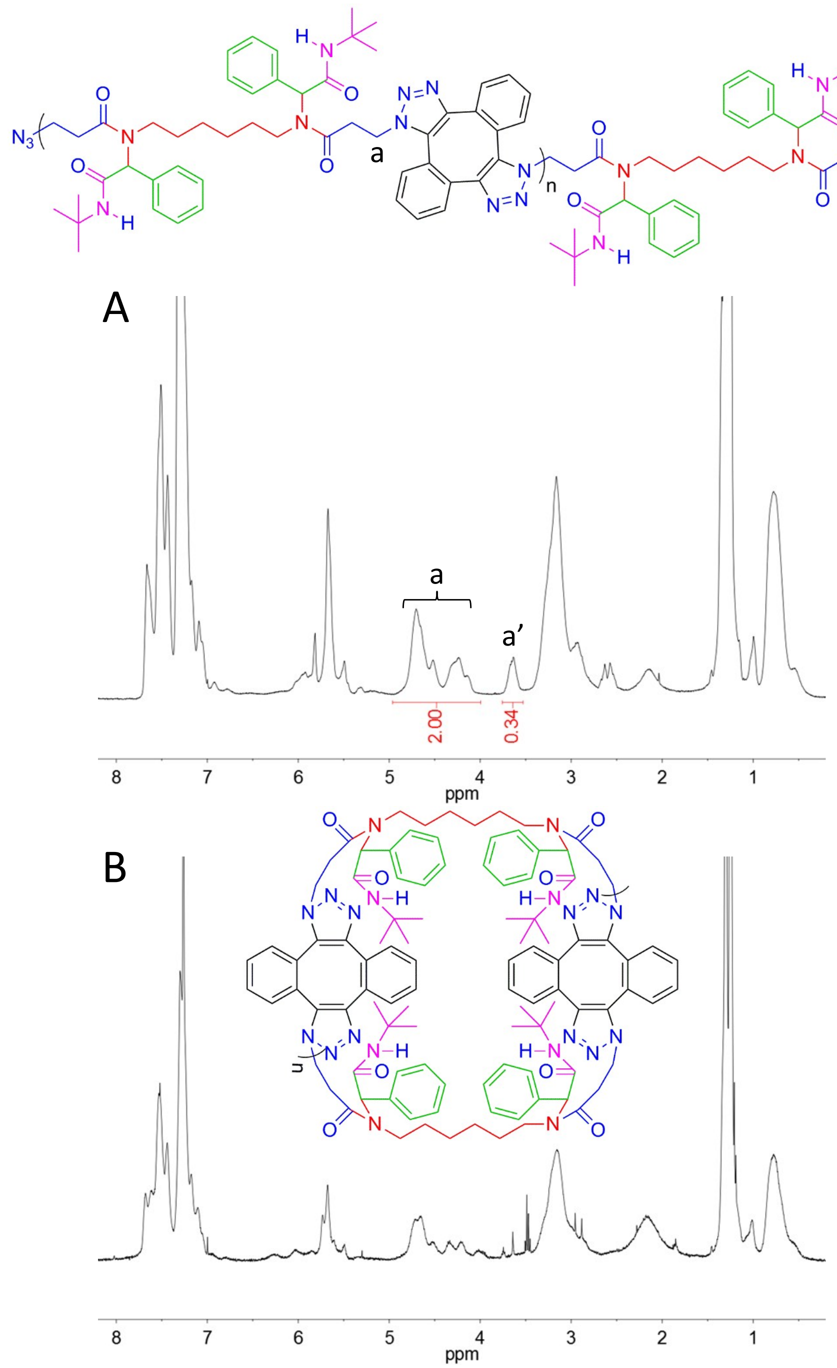

Figure S8. ^{1}H-NMR spectra of linear (A) and cyclic (B) polymer **2'** in $CDCl_3$.

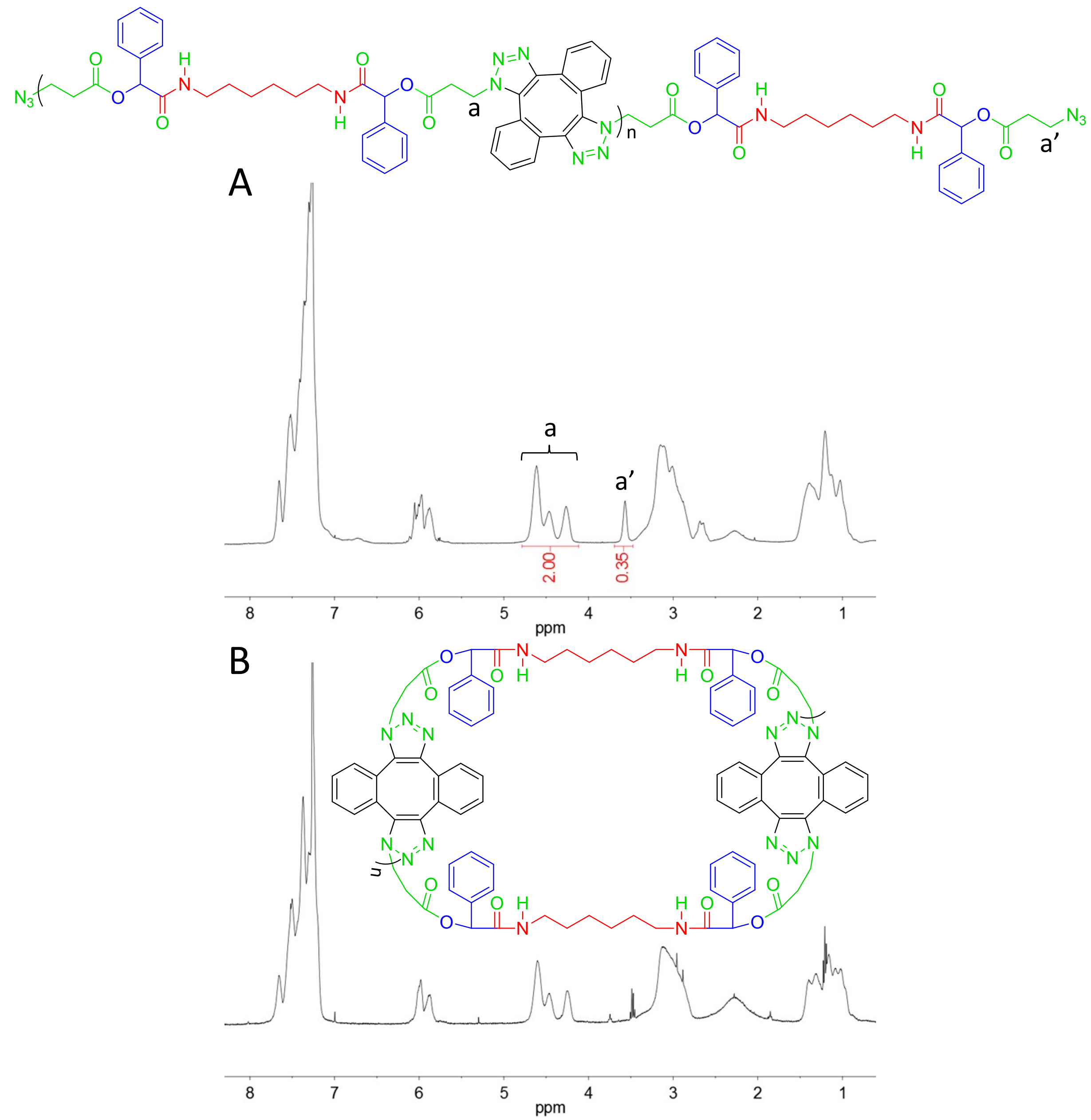

Figure S9. ^{1}H-NMR spectra of linear (A) and cyclic (B) polymer **3'** in $CDCl_3$.

Table S1. Synthesis and characterization of raw periodic polymers **1**, **1'**, **2**, **2'**, **3**, **3'**.

Run[a)]	$[\text{Monomer}]_0$[b)] (mol/L)	S[c)]	$M_{n,theory}$[d)] (g/mol)	$M_{n,GPC}$[e)] (g/mol)	PDI[e)]	Polymer[e)] (%)	Oligomer[e)] (%)
1	0.2	0.83	4632	4670	1.39	68.39	31.61
2	0.2	0.91	9131	6190	1.70	76.08	23.92
3	0.2	1.1	9131	123100	1.91	63.44	36.56
4	0.2	1.2	4632	117800	1.87	66.70	33.30
5	0.2	1.5	2177	94780	1.88	66.49	33.51
6	0.2	2.0	1291	75480	1.86	66.26	33.74
7	0.05	1.1	9131	44290	1.45	18.64	81.36
8	0.1	1.1	9131	75150	1.85	46.36	53.64
9	0.3	1.1	9131	142800	1.86	72.74	27.26
10	0.4	1.1	9131	158200	1.86	76.50	23.50
11	0.5	1.1	9131	170200	1.89	77.99	22.01
12	0.5	1.1	9428	178600	1.93	68.89	31.11
13	0.5	1.1	8259	392800	2.10	80.86	19.14
14	0.2	0.83	4782	4430	1.34	59.00	41.00
15	0.2	0.83	4189	14780	1.35	70.34	29.66

[a)] The polymerization was performed at room temperature in air using DMF as solvent. [b)] Initial molar concentration of bis-azide monomers. [c)] Initial molar ratio of DIBOD and bis-azide monomers. [d)] Calculated from the equation of $M_0 \times (1 + r)/(1 + r - 2rp)$ with $p = 1$. [e)] Calculated from GPC characterization. Runs 1 and 2 were assigned to polymers **1'**; Runs 3-11 were assigned to polymers **1**; Run 12 was assigned to polymer **2**; Run 13 was assigned to polymer **3**; Run 14 was assigned to polymer **2'**; Run 15 was assigned to polymer **3'**.

Table S2. Synthesis and characterization of raw periodic polymers **1**.

Run[a]	[Monomer 1]$_0$[b] (mol/L)	S[c]	Ratio[d] (%)	$M_{n,theory}$[e] (g/mol)	$M_{n,GPC}$[f] (g/mol)	PDI[f]	Polymer[f] (%)	Oligomer[f] (%)
1	0.5	1.1	0	9131	170200	1.89	77.99	22.01
2	0.5	1.1	1	9078	62630	1.84	80.24	19.76
3	0.5	1.1	2.5	9143	34000	1.80	81.61	18.39
4	0.5	1.1	5	9250	21000	1.75	82.90	17.10
5	0.5	1.1	10	9466	12720	1.70	84.24	15.76

[a] The polymerization was performed at room temperature in air using DMF as solvent. [b] Initial molar concentration of monomer **1**. [c] Initial molar ratio of DIBOD and monomer **1**. [d] Initial molar ratio of 3-azidopropanoic acid and monomer **1**. [e] Calculated from the equation of $M_0 \times (1 + r)/(1 + r - 2rp)$ for run 1 with $p = 1$, $r = 1/S$; Calculated from the equation of $M_0 \times 2/(2 - pf_{avg})$ for run 2 to run 5 with $p = 1$and $f_{avg} = 2 \times (2 + \text{Ratio})/(1 + 1.1 + \text{Ratio})$. [f] Calculated from GPC characterization.

References

(1) Sun, P.; Chen, J. Q.; Liu, J. A.; Zhang, K. *Macromolecules* **2017**, *50*, 1463.