Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Living polymerization of arylisocyanide initiated by phenylethynyl palladium(II) complex

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Instruments.

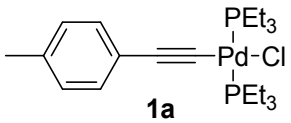
The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded using a Bruker 400 and 600 MHz {H} spectrometer. Size exclusion chromatography (SEC) was performed on Waters 1515 pump and 2414 differential refractive index (RI) detector (set at 40 °C) using a series of linear Styragel HR1, HR2 and HR4 columns. Molecular weight and polydispersity data are reported relative to polystyrene standards. The eluent was tetrahydrofuran (THF) at a flow rate of 0.3 mL/min. FT-IR spectra were recorded on Perkin-Elmer Spectrum BX FT-IR system using KBr pellets. UV-vis spectra were performed on a UNIC 4802 UV/VIS double beam spectrophotometer in 1.0 cm length quartz cell. Melting points were obtained with a Mel-Temp apparatus and are uncorrected. X-ray diffraction data of single crystals were collected on a Siemens Smart 1000 CCD diffractometer. The determination of unit cell parameters and data collections were performed with Mo-Ka radiation (l = 0.71073 Å). Unit cell dimensions were obtained with least-squares refinements and all structures were solved by direct methods using SHELXS-97. The other nonhydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed using full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F2. The hydrogen atoms were added theoretically and riding on the concerned atoms.

Materials

All solvents were purified by the standard procedures before use. THF was further dried over sodium

benzophenone ketyl, distilled onto $LiAlH_4$ under nitrogen, and distilled under high vacuum just before use. 4-Ethynyltoluene, 4-ethynylanisole, 1-ethynylbenzene, 4-(methoxycarbonyl)phenylacetylene, ethynyltrimethylsilane, *trans*-dichlorobis(triethylphosphine)palladium(II) and copper(I) chloride were purchased from Aladdin and Sigma-Aldrich, and were used as received without further purification. Isocyanide monomer **2a**, **2b**, **2c**, **2d**, **2e**, and **2f** were prepared according to the literatures and the structures were confirmed by ^{1}H NMR.[1]

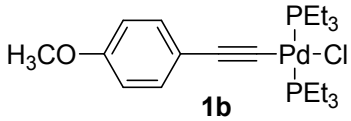
Synthetic procedure for 1a-d



1a

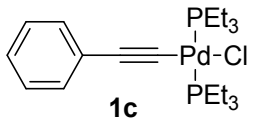
Synthesis of 1a. This Pd complex was prepared according to the reported procedure.[2] 4-Ethynyltoluene (50.0 mg, 0.43 mmol) was treated with *trans*-dichlorobis(triethylphosphine)palladium (178.0 mg, 0.43 mmol) in the presence of copper(I) chloride (2.5 mg, 0.025 mmol) as catalyst in 30 mL of diethylamine and dichloromethane (v/v = 1/1). The mixture was stirred at room temperature for 1 h. After the solvent was removed by evaporation under reduced pressure, the residue was purified by chromatography with petrol ether-ethyl acetate (10/1, v/v) as eluent. The crude product was recrystallized from petrol ether and methanol to afford **1a** as a white solid (127 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.16 (d, J = 8.8 Hz, 2H, aromatic), 7.03 (d, J = 8.8 Hz, 2H, aromatic), 2.31 (s, 3H, CH_3–Ph), 2.00–1.95 (m, 12H, P$CH_2$$CH_3$), 1.24–1.16 (m, 18H, P$CH_2$$CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 135.45, 130.58, 128.86, 124.89, 106.42, 93.59, 21.35, 15.46, 8.40. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 17.85. FT-IR (KBr, cm^{-1}): 2959 ($\nu_{C–H}$, aromatic), 2932 ($\nu_{C–H}$, aromatic), 2872 ($\nu_{C–H}$, aromatic), 2112 ($\nu_{C\equiv C}$), 1746 ($\nu_{C=C}$, aromatic), 1693 ($\nu_{C=C}$, aromatic).

Compounds **1b**,[3] **1c**,[4] and **1d** were synthesized according to the similar procedure from the reaction of 4-ethynylanisole, 1-ethynylbenzene, and 4-(methoxycarbonyl)phenylacetylene with *trans*-dichlorobis(triethylphosphine)palladium in dichloromethane and diethylamine, respectively.



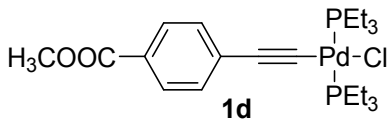
1b

1b: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.19 (d, J = 8.8 Hz, 2H, aromatic), 6.78 (d, J = 8.8 Hz, 2H, aromatic), 3.78 (s, 3H, OCH_3), 2.02–1.94 (m, 12H, PCH_2CH$_3$), 1.25–1.17 (m, 18H, PCH$_2$$CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 157.81, 131.93, 120.46, 113.79, 105.97, 92.21, 55.38, 15.52, 8.45. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 17.80. FT-IR (KBr, cm^{-1}): 3060 ($\nu_{C–H}$, aromatic), 2932 ($\nu_{C–H}$, aromatic), 2873 ($\nu_{C–H}$, aromatic), 2112 ($\nu_{C\equiv C}$), 1600 ($\nu_{C=C}$, aromatic), 1570 ($\nu_{C=C}$, aromatic).



1c

1c: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.27–7.25 (m, 2H, aromatic), 7.24–7.21 (m, 2H, aromatic), 7.16–7.14 (m, 1H, aromatic), 2.00–1.95 (m, 12H, PCH_2CH$_3$), 1.23–1.18 (m, 18H, PCH$_2$$CH_3$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 130.79, 128.18, 127.95, 125.73, 106.63, 95.16, 15.54, 8.47. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 17.95. FT-IR (KBr, cm^{-1}): 2959 ($\nu_{C–H}$, aromatic), 2933 ($\nu_{C–H}$, aromatic), 2873 ($\nu_{C–H}$, aromatic), 2113 ($\nu_{C\equiv C}$), 1750 ($\nu_{C=C}$, aromatic), 1650 ($\nu_{C=C}$, aromatic).



1d

1d: M.P.: 49.6–50.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.90 (d, J = 8.4 Hz, 2H, aromatic), 7.28 (d, J = 8.4 Hz, 2H, aromatic), 3.89 (s, 3H, $COOCH_3$), 1.99–1.96 (m, 12H, PCH_2CH$_3$), 1.25–1.17 (m,

18H, PCH_2CH_3). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 166.97, 132.60, 130.49, 129.45, 126.83, 106.66, 101.73, 52.07, 15.40, 8.38. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 18.30. FT-IR (KBr, cm^{-1}): 2970 (ν_{C-H}, aromatic), 2930 (ν_{C-H}, aromatic), 2870 (ν_{C-H}, aromatic), 2110 ($\nu_{C\equiv C}$), 1720 ($\nu_{C\equiv O}$). HRMS *m/z* calcd for $C_{22}H_{37}ClO_2P_2Pd$ $[M]^+$: 536.0992; Found: $C_{22}H_{37}ClO_2P_2Pd$, 536.0990. Anal. Calcd (%) for $C_{22}H_{37}ClO_2P_2Pd$ (536.10): C, 49.17; H, 6.94; Found: C, 49.00; H, 7.19.

Typical Polymerization Procedure of 1a–d with 2a (poly-a2a$_{100}$): A 10 mL oven-dried flask was charged with monomer **2a** (50.0 mg, 0.17 mmol), THF (0.87 mL) and a stir bar. To this stirring solution was added a solution of **1a** in THF (0.017 M, 0.10 mL) *via* a microsyringe at ambient temperature. The concentrations of monomer **2a** and initiator **1a** were 0.20 and 0.002 M, respectively ($[\mathbf{2a}]_0/[\mathbf{1a}]_0 = 100$). The reaction flask was then immersed into an oil bath at 55 °C and stirred for 10 h. After cooled to room temperature, the polymerization solution was precipitated into a large amount of methanol, collected by centrifugation, and dried in vacuum at room temperature overnight to give poly-**a2a**$_{100}$ (45.0 mg, 91% yield). SEC: $M_n = 3.1 \times 10^4$, $M_w/M_n = 1.10$. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.48–7.24 (br, aromatic), 4.58–3.42 (br, OCH_2), 1.75–0.73 (br, CH_2 and CH_3). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 165.11, 162.70, 150.50, 129.79, 127.38, 117.19, 65.03, 32.03, 29.74, 29.58, 29.46, 28.76, 26.13, 22.78, 14.19. FT-IR (KBr, cm^{-1}): 2952 (ν_{C-H}, aromatic), 2919 (ν_{C-H}, aromatic), 2852 (ν_{C-H}, aromatic), 2190 ($\nu_{C\equiv C}$), 1720 ($\nu_{C=O}$), 1599 ($\nu_{C=N}$).

Typical Procedure Used to Grow Poly(phenyl isocyanide)s of Various Molecular Weights from Palladium Complex 1a–d. Various amounts of palladium complex **1a** in THF ($[\mathbf{1a}]_0 = 0.002$ M) were added *via* a microsyringe to a series solutions of isocyanide monomer **2a** (50.0 mg, 0.17mmol) in THF. The concentration of **2a** was 0.20 M. The initial feed ratios of **2a** to **1a** were 25, 40, 55, 70, 85, and 100,

respectively. Each of the reaction mixtures were then stirred for 10 h at 55 °C and quenched by the addition of a large amount of methanol, collected by centrifugation, washed with methanol, and dried under vacuum to afford the expected polymers. The M_n and M_w/M_n of these polymers were characterized by SEC (Fig. 1a in maintext).

Typical Kinetic Study of the Polymerization of 2a with 1a-d. A mixture of **2a** (100.0 mg, 0.35 mmol) and a standard polystyrene (M_n = 2630, 50.0 mg for **1a**, and **1c**, 40.0 mg for **1b**, and **1d**) were placed in a dry ampule, and dry THF (1.36 mL) was added by a syringe. To this was added a solution of **1a** in THF (15 μM, 0.39 mL) *via* a microsyringe at ambient temperature. The concentrations of **1a** and **2a** were 0.0033 and 0.2 M, respectively. The mixture was then heated to 55 °C ([**2a**]$_0$ = 0.2 M, [**2a**]$_0$/[**1a**]$_0$ = 60). The conversion of **2a** was followed by measuring the SEC of the reaction mixture at appropriate time intervals. The peak area of the unreacted **2a** relative to that of the internal standard (PSt) was used for the determination of the conversion of **2a** on the basis of the linear calibration curve. The M_n and M_w/M_n were estimated by SEC and reported as equivalent to standard polystyrene.

References

1. (a) Y.-X. Xue, Y.-Y. Zhu, L.-M. Gao, X.-Y. He, N. Liu, W.-Y. Zhang, J. Yin, Y.-S. Ding, H.-P. Zhou and Z.-Q. Wu, *J. Am. Chem. Soc.*, 2014, **136**, 4706; (b) J. Liang, Z. Chen, J. Yin, G.-A. Yu and S. H. Liu, *Chem. Commun.,* 2013, **49**, 3567.
2. K. Osakada, T. Takizawa and T. Yamamoto, *Organometallics*, 2006, **14**, 3531.
3. K. Onitsuka, H. Ogawa, T. Joh, S. Takahashi, Y. Yamamoto and H. Yamazaki, *J. Chem. Soc., Dalt. Trans.: Inorg. Chem.,* 1991, **6**, 1531.

4. Y.-J. Kim, S.-H. Lee, S. I. Jeon, M. S. Lim and S. W. Lee, *Inorg. Chim. Acta,* 2005, **358**, 650.

Table S1. Polymerization Results of 2b–e with 1b as Initiator ($[2]_0$ = 0.2 M)[a]

Run	Monomer	$[2]_0/[1b]_0$ [b]	Solvent	T	Polymer	M_n[c]	M_w/M_n[c]	Yield[d]
1	**2b**	50	THF	55 °C	poly-**b2b**$_{50}$	Oligomers	--	--
2	**2c**	25	Toluene	90 °C	poly-**b2c**$_{25}$	5.6×10^3	1.22	90%
3	**2c**	30	Toluene	90 °C	poly-**b2c**$_{30}$	6.8×10^3	1.22	91%
4	**2c**	60	Toluene	90 °C	poly-**b2c**$_{60}$	1.4×10^4	1.27	87%
5	**2d**	50	THF	55 °C	poly-**b2d**$_{50}$	1.7×10^4	1.18	97%
6	**2d**	100	THF	55 °C	poly-**b2d**$_{100}$	3.4×10^4	1.22	95%
7	**2e**	50	THF	55 °C	poly-**b2e**$_{50}$	1.3×10^4	1.16	97%
8	**2e**	100	THF	55 °C	poly-**b2e**$_{100}$	2.7×10^4	1.15	93%

[a]The polymers were synthesized according to Scheme 1 in main text. [b]The initial feed ratio of monomer to initiator. [c]The M_n and M_w/M_n were determined by SEC and reported as equivalent to standard polystyrene. [d]Isolated yield.

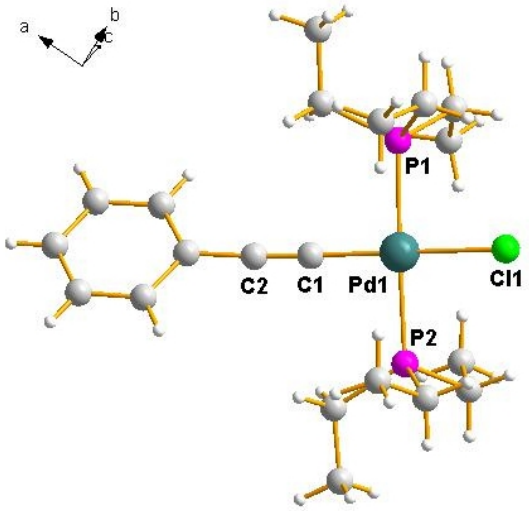


Fig. S1 Single crystal structure of Pd(II) complex **1c**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C1–C2, 1.210(5); C1–Pd, 1.947(4); Cl1–Pd, 2.3512(8); P1–Pd,

2.3136(10); P2–Pd, 2.3055(10); C1–Pd–P2, 90.58(12); C1–Pd–P2, 90.48(12); P2–Pd–P1, 176.92(5); C1–Pd–Cl1, 177.71(17); P2–Pd–Cl1, 89.10(4); P1–Pd–Cl1, 89.95(4).

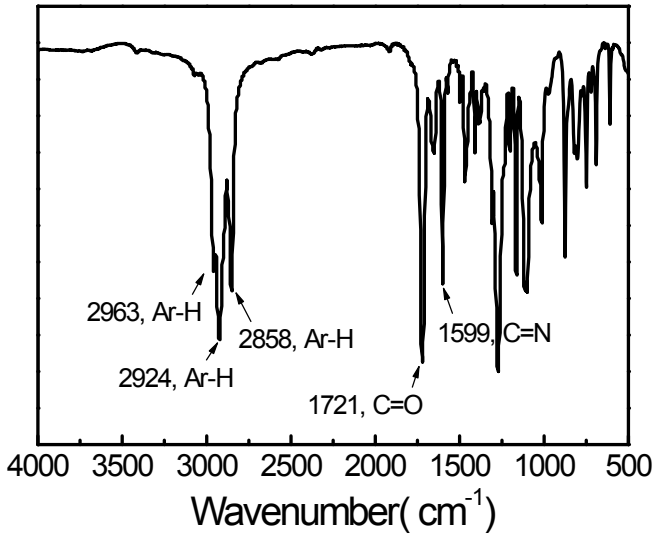


Fig. S2 FT-IR spectrum of poly-**a2a**$_{100}$ measured at 25 °C using KBr pellets.

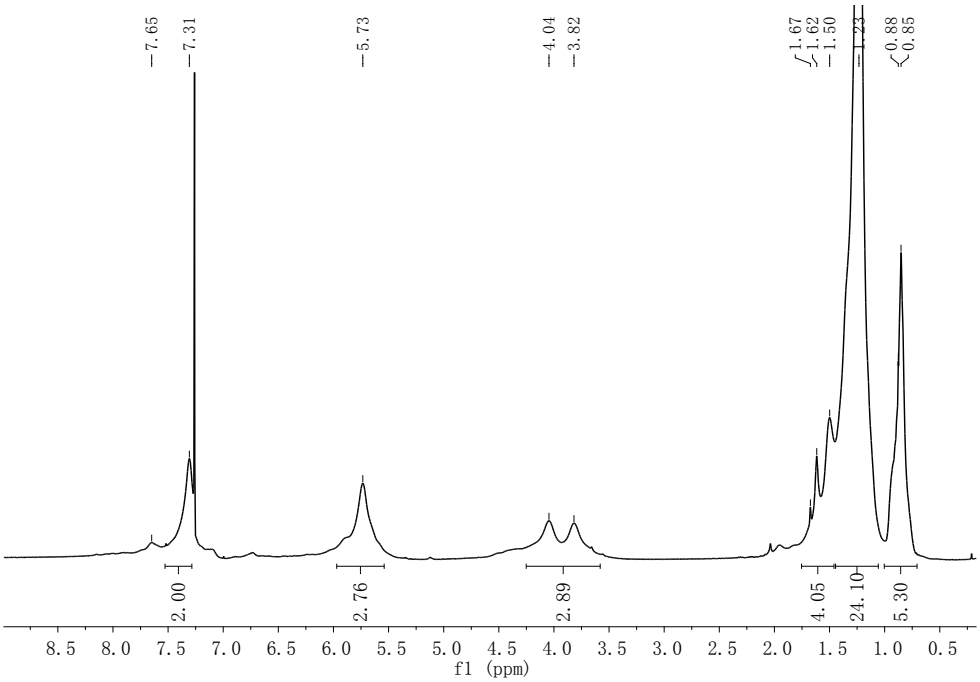


Fig. S3 ^{1}H NMR spectrum of poly-**a2a**$_{100}$ measured in $CDCl_3$ at 25 °C (400 MHz).

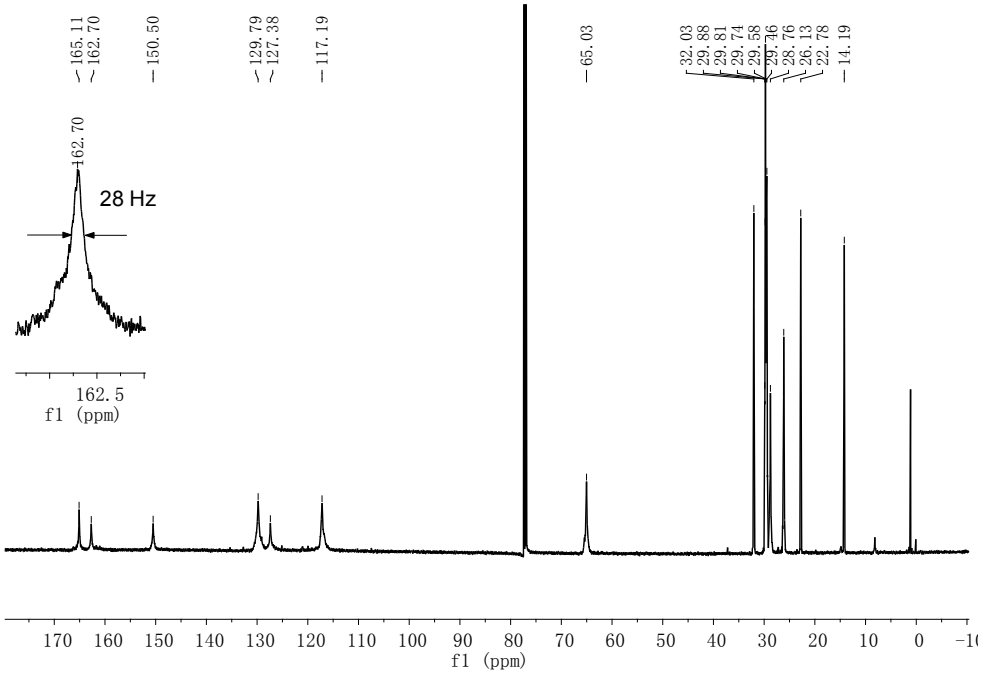


Fig. S4 ^{13}C NMR spectrum of poly-**a2a**$_{100}$ measured in $CDCl_3$ at 25 °C (150 MHz).

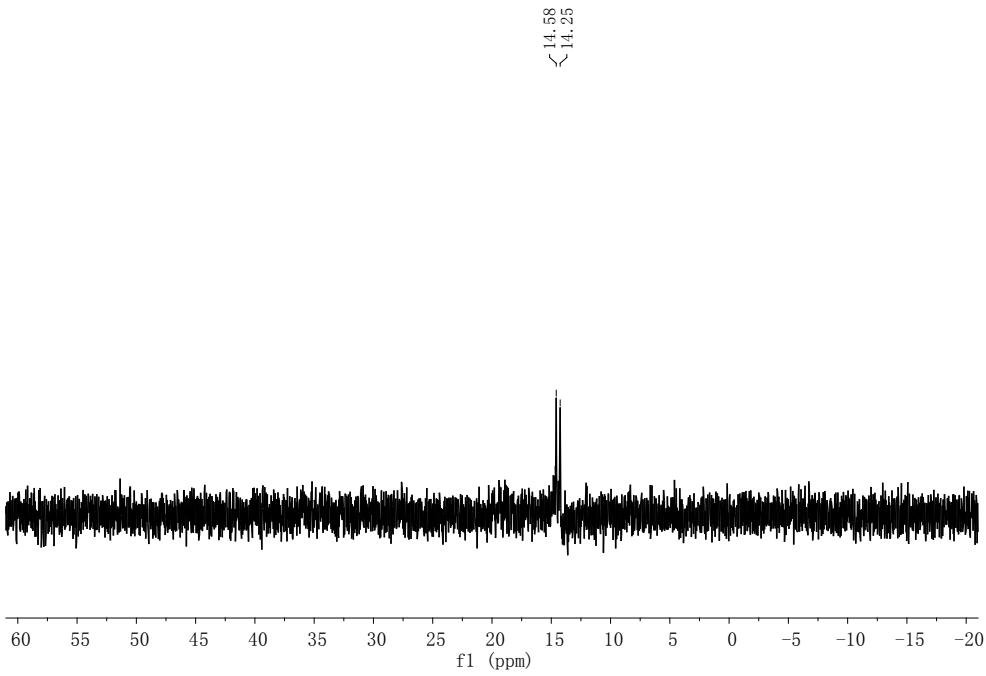


Fig. S5 ^{31}P NMR spectrum of poly-**a2a**$_{100}$ measured in $CDCl_3$ at 25 °C (121.5 MHz).

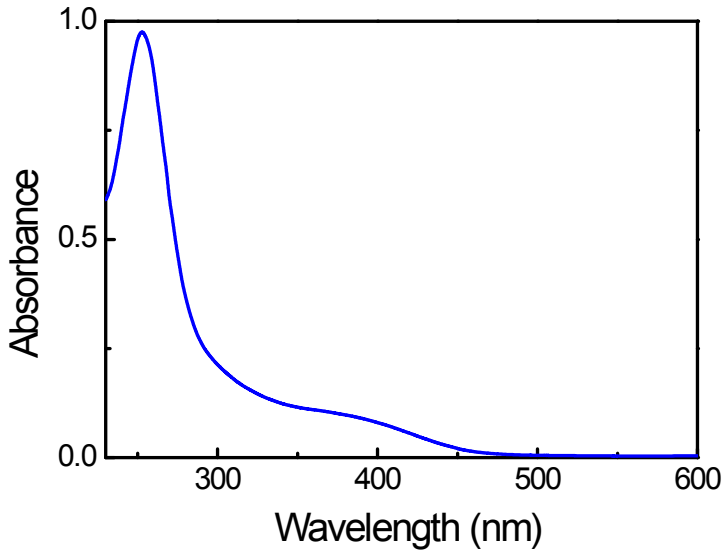


Fig. S6 UV-vis spectrum of poly-**a2a**$_{100}$ measured in $CHCl_3$ at 25 °C.

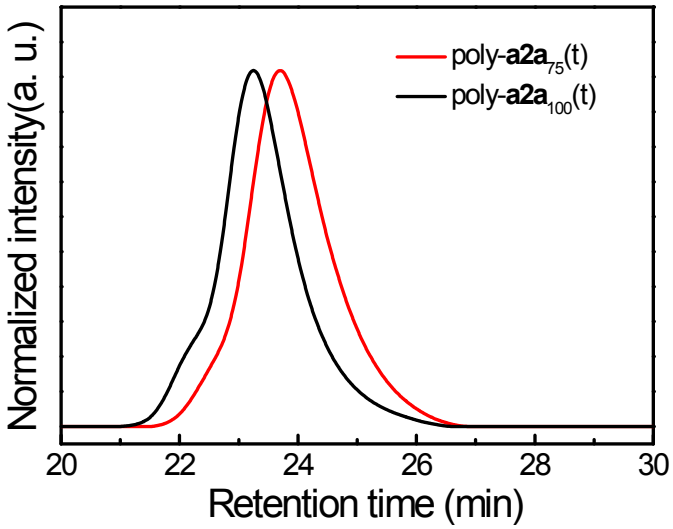


Fig. S7 SEC chromatograms of poly-**a2a**$_{75}$(t) and poly-**a2a**$_{100}$(t) prepared from **2a** with **1a** as initiator in toluene at 55°C.

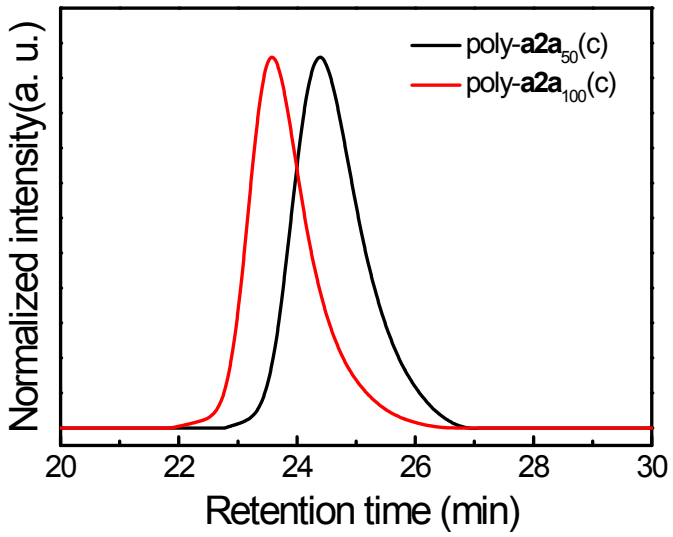


Fig. S8 SEC chromatograms of poly-**a2a**$_{50}$(c) and poly-**a2a**$_{80}$(c) prepared from **2a** with **1a** as initiator in $CHCl_3$ at 55 °C.

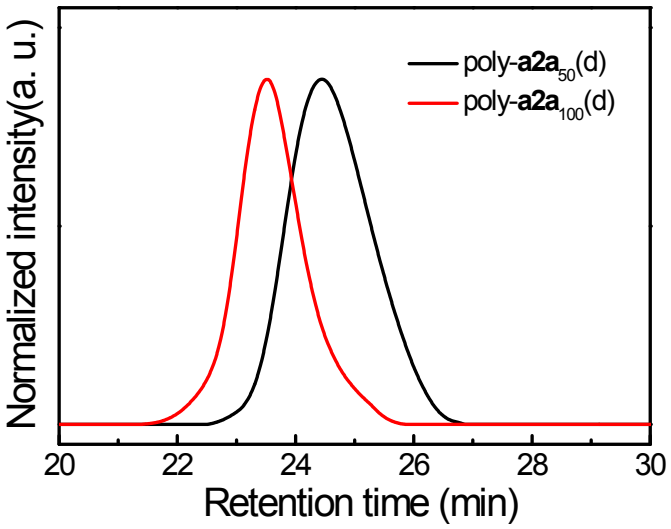


Fig. S9 SEC chromatograms of poly-**a2a**$_{50}$(d) and poly-**a2a**$_{80}$(d) prepared from **2a** with **1a** as initiator in DMF at 55 °C.

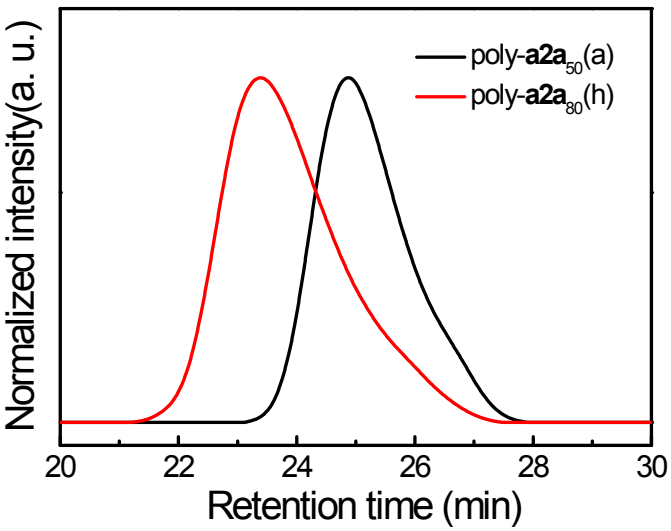


Fig. S10 SEC chromatograms of poly-**a2a**$_{50}$(a) and poly-**a2a**$_{80}$(h) prepared from **2a** with **1a** as initiator in acetone and hexane at 55 °C.

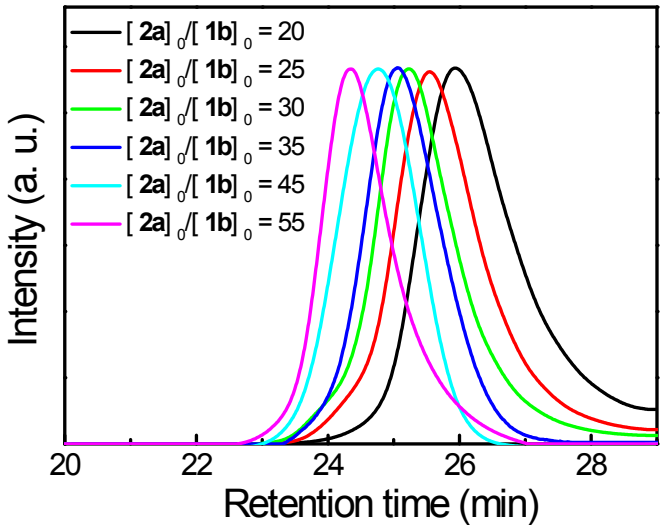


Fig. S11 SEC chromatograms of poly-**b2a**$_m$ prepared from **2a** with **1b** as initiator in THF at 55 °C with different initial feed ratios.

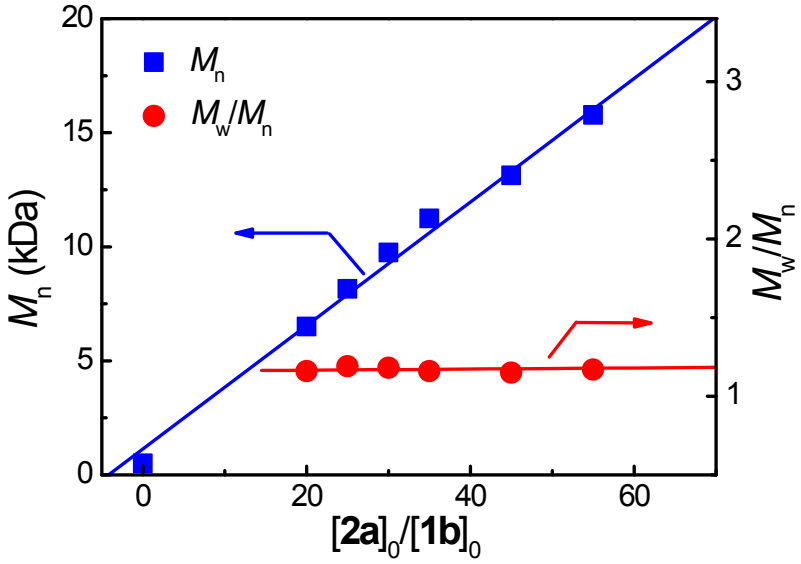


Fig. S12 Plot of M_n and M_w/M_n values of poly-**b2a**$_m$ as a function of the initial feed ratios of **2a** to **1b**. M_n and M_w/M_n were determined by SEC with polystyrene standard (SEC conditions: eluent = THF, temperature = 40 °C).

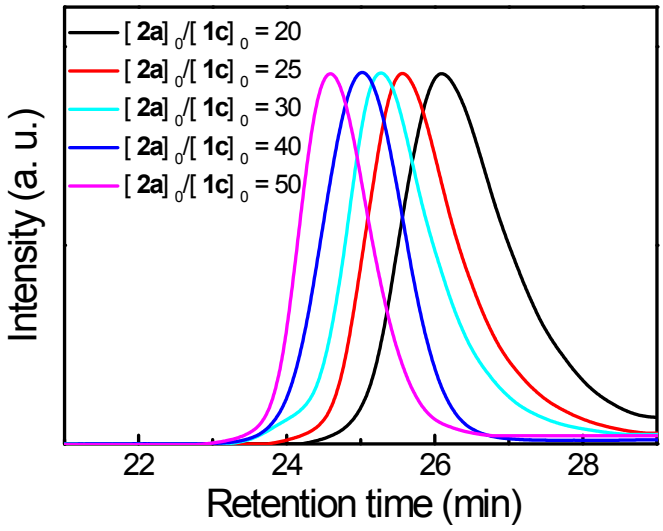


Fig. S13 SEC chromatograms of poly-**c2a**$_m$ prepared from **2a** with **1c** as initiator in THF at 55 °C with different initial feed ratios.

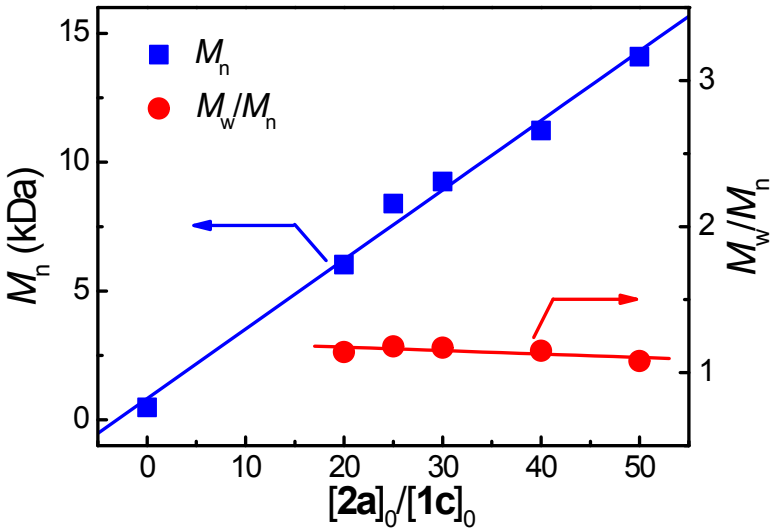


Fig. S14 Plot of M_n and M_w/M_n values of poly-**c2a**$_m$ as a function of the initial feed ratios of **2a** to **1c**. M_n and M_w/M_n were determined by SEC with polystyrene standard (SEC conditions: eluent = THF, temperature = 40 °C).

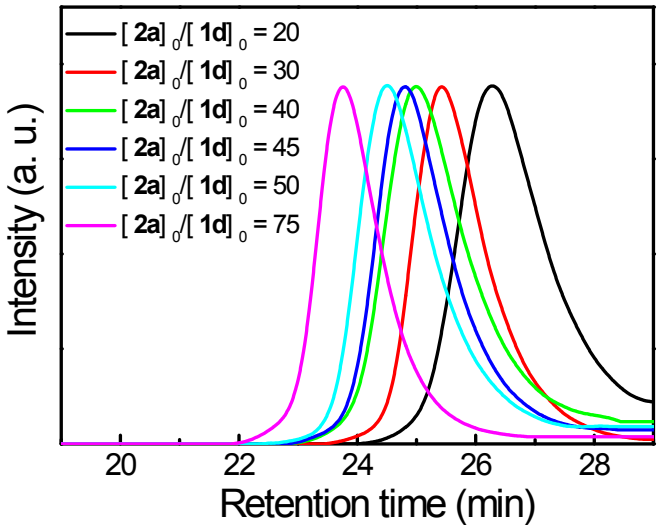


Fig. S15 SEC chromatograms of poly-**d2a**$_m$ prepared from **2a** with **1d** as initiator in THF at 55 °C with different initial feed ratios.

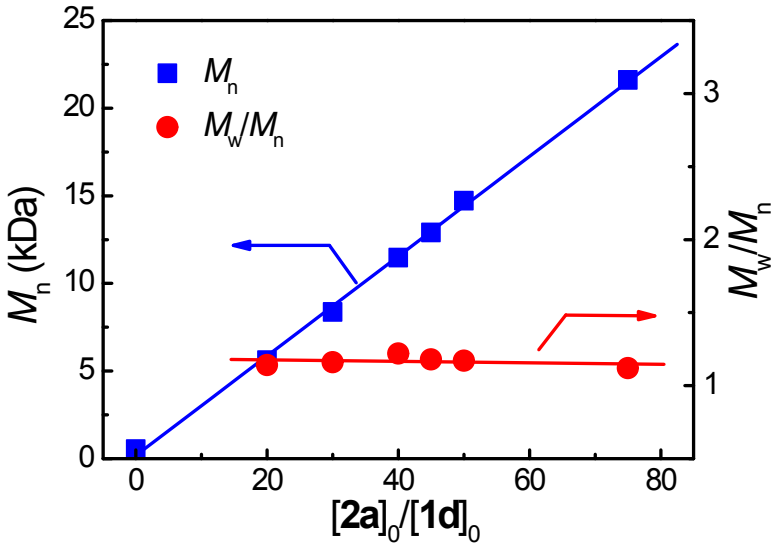


Fig. S16 Plot of M_n and M_w/M_n values of poly-**d2a**$_m$ as a function of the initial feed ratios of **2a** to **1d**. M_n and M_w/M_n were determined by SEC with polystyrene standard (SEC conditions: eluent = THF, temperature = 40 °C).

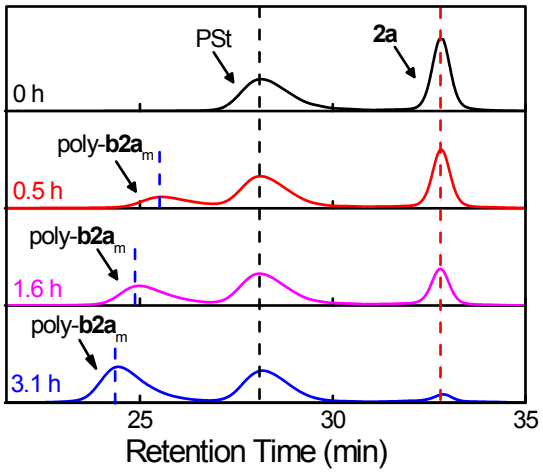


Fig. S17 Time-dependent SEC chromatograms for **1b**-initiated polymerization of **2a** in THF at 55 °C with PSt (M_n = 2630, M_w/M_n = 1.06) as internal standard ([**2a**]$_0$ = 0.2 M, [**2a**]$_0$/[**1b**]$_0$ = 60).

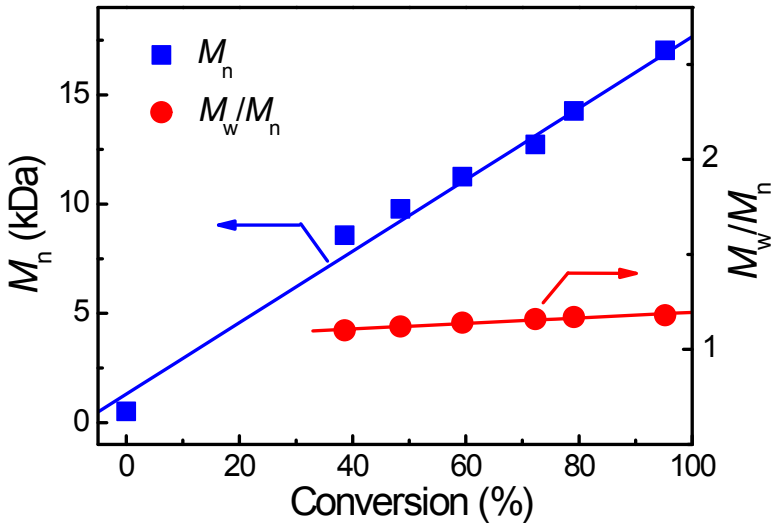


Fig. S18 Plot of M_n and M_w/M_n values as a function of conversion of **2a** with **1b** as initiator in THF at 55 °C ([**2a**]$_0$ = 0.2 M, [**2a**]$_0$/[**1b**]$_0$ = 60).

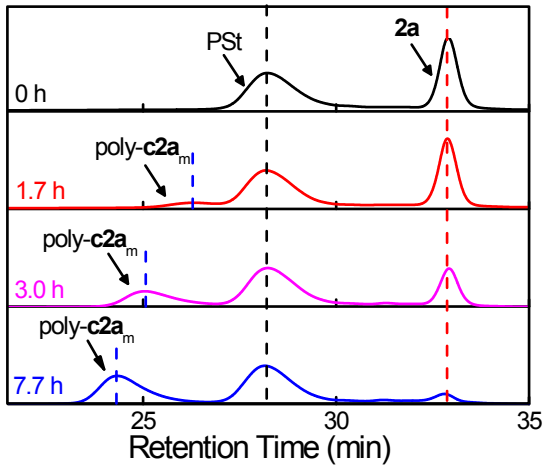


Fig. S19 Time-dependent SEC chromatograms for **1c**-initiated polymerization of **2a** in THF at 55 °C with PSt (M_n = 2630, M_w/M_n = 1.06) as internal standard ([**2a**]$_0$ = 0.2 M, [**2a**]$_0$/[**1c**]$_0$ = 60).

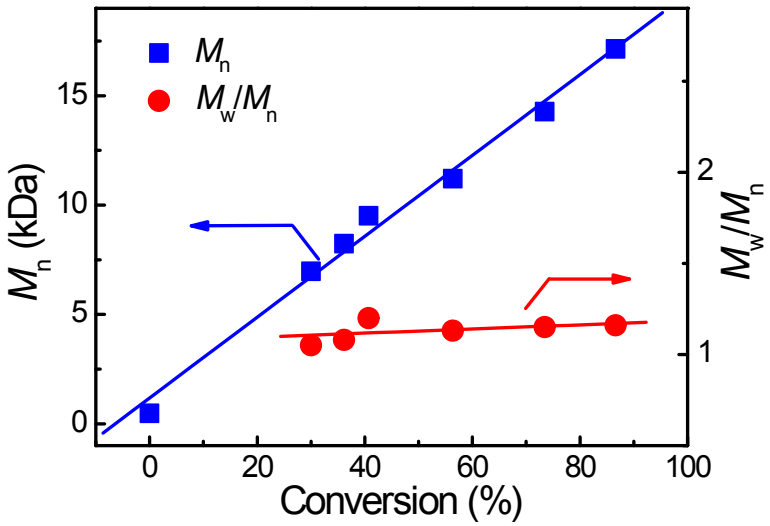


Fig. S20 Plot of M_n and M_w/M_n values as a function of conversion of **2a** with **1c** as initiator in THF at 55 °C ([**2a**]$_0$ = 0.2 M, [**2a**]$_0$/[**1c**]$_0$ = 60).

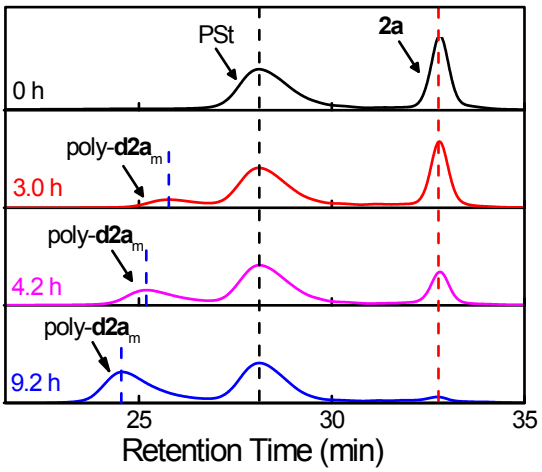


Fig. S21 Time-dependent SEC chromatograms for **1d**-initiated polymerization of **2a** in THF at 55 °C with PSt (M_n = 2630, M_w/M_n = 1.06) as internal standard ([**2a**]$_0$ = 0.2 M, [**2a**]$_0$/[1**d**]$_0$ = 60).

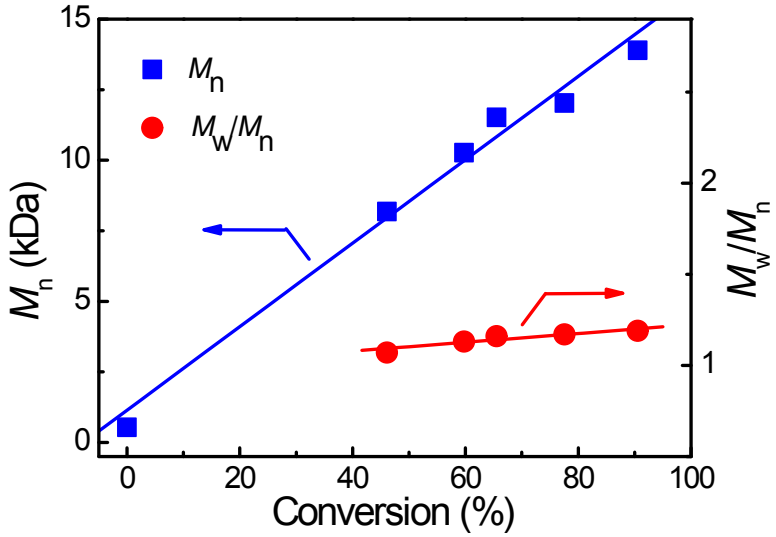


Fig. S22 Plot of M_n and M_w/M_n values as a function of conversion of **2a** with **1d** as initiator in THF at 55 °C ([**2a**]$_0$ = 0.2 M, [**2a**]$_0$/[**1d**]$_0$ = 60).

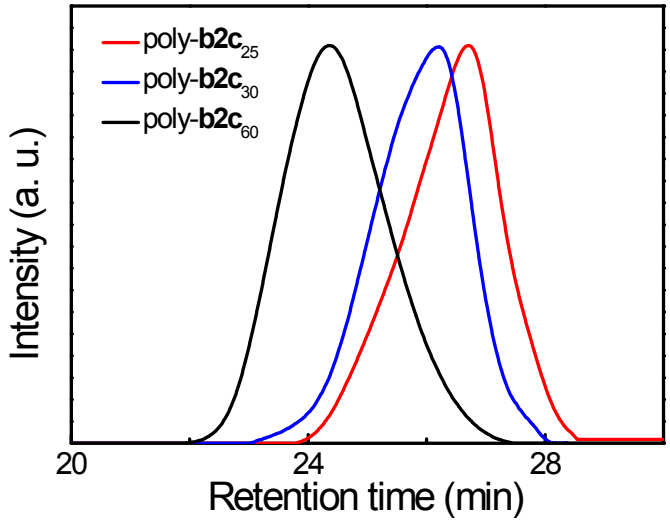


Fig. S23 SEC chromatograms of poly-**b2c**$_{25}$, poly-**b2c**$_{30}$, and poly-**b2c**$_{60}$ prepared from **2c** with **1b** as initiator in toluene at 90 °C.

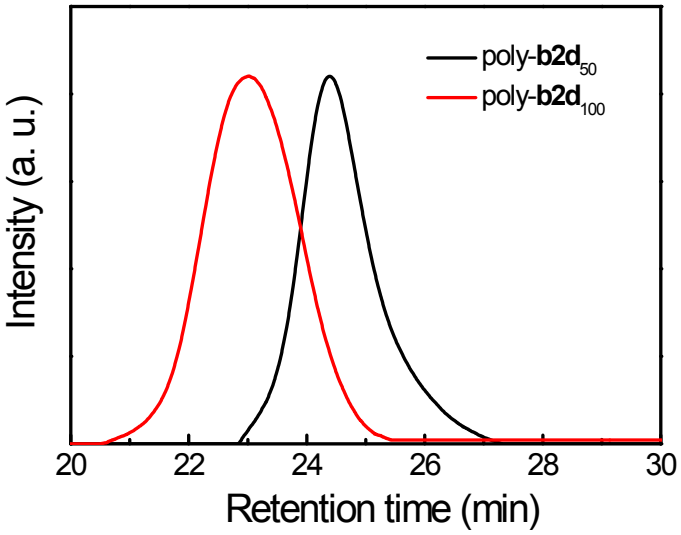


Fig. S24 SEC chromatograms of poly-**b2d**$_{50}$ and poly-**b2d**$_{100}$ prepared from **2d** with **1b** as initiator in THF at 55 °C.

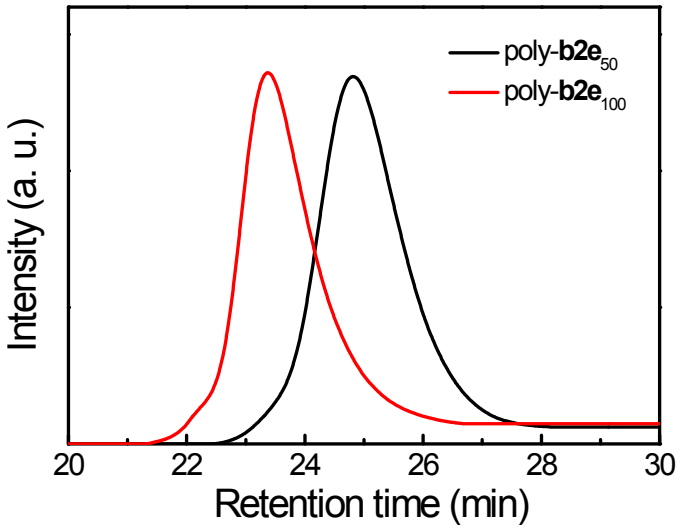


Fig. S25 SEC chromatograms of poly-**b2e**$_{50}$ and poly-**b2e**$_{100}$ prepared from **2e** with **1b** as initiator in THF at 55 °C.

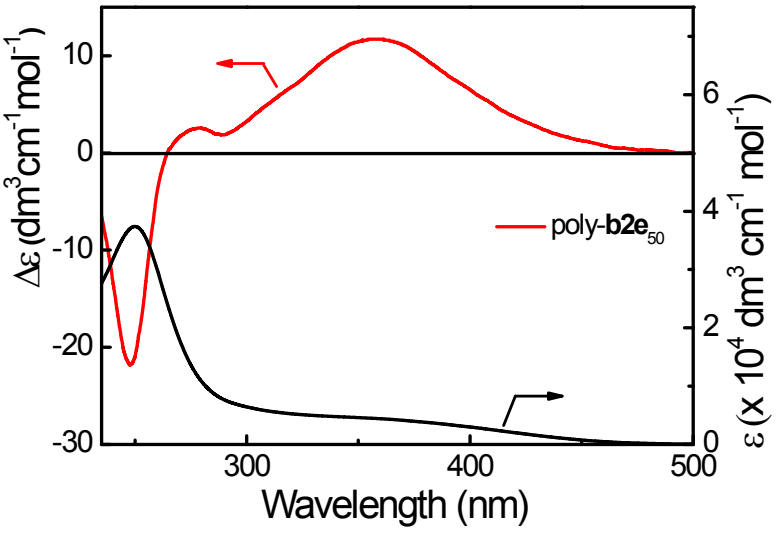


Fig. S26 CD and UV-vis spectra of poly-**b2e**$_{50}$ measured in THF at room temperature.

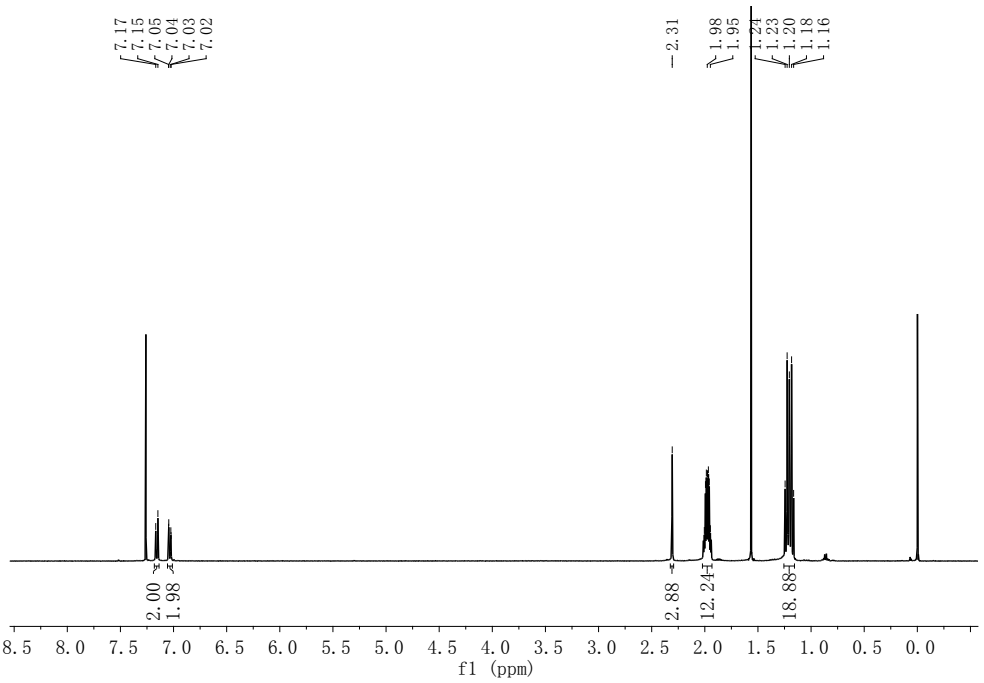


Fig. S27 ^{1}H NMR spectrum of **1a** measured in $CDCl_3$ at 25 °C (400 MHz).

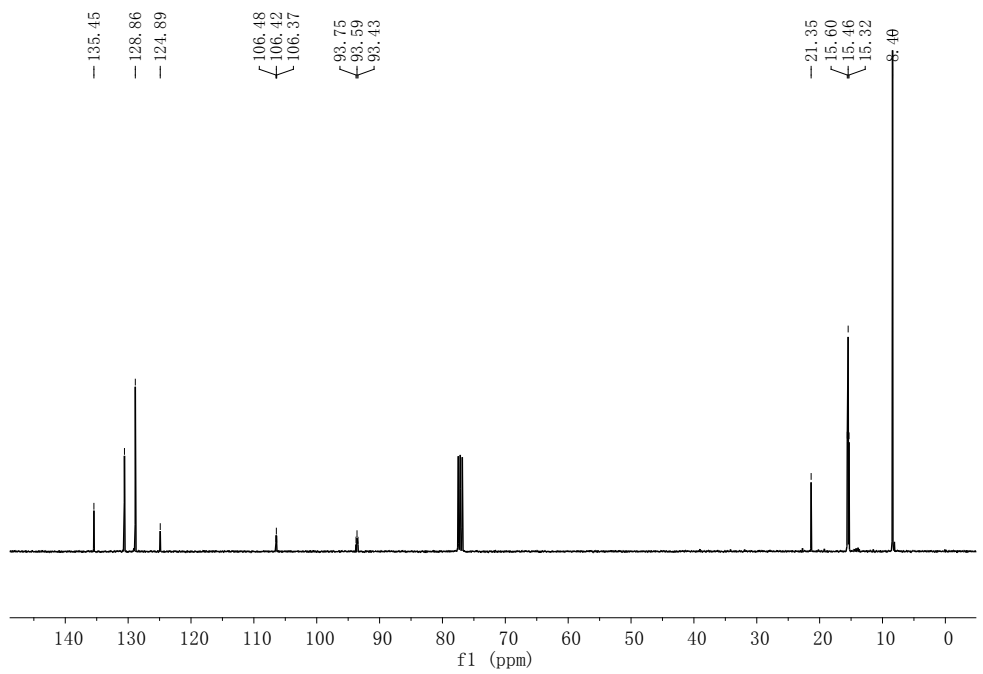


Fig. S28 ^{13}C NMR spectrum of **1a** measured in $CDCl_3$ at 25 °C (100 MHz).

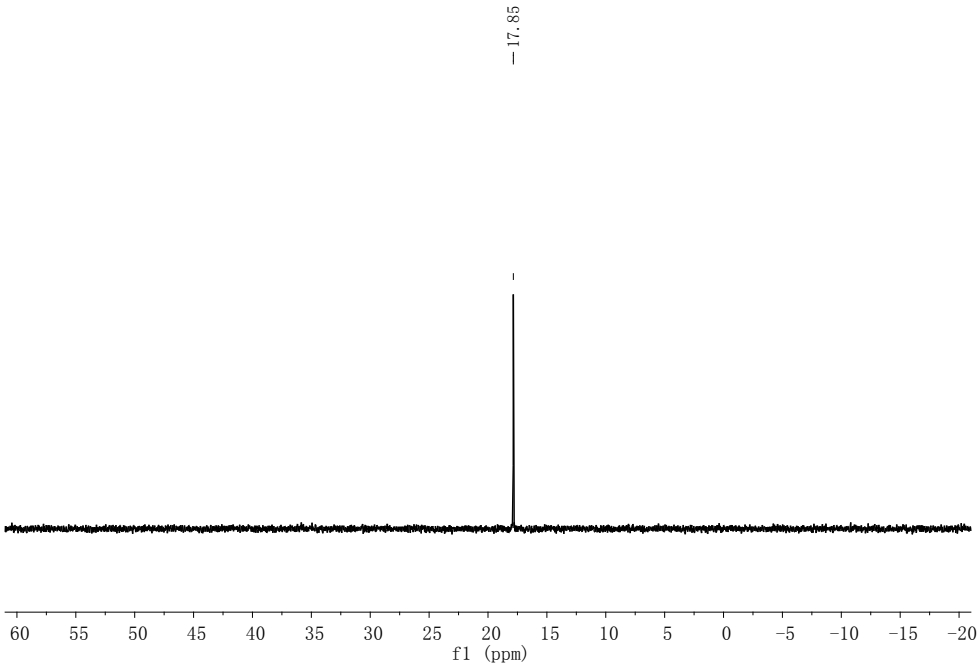


Fig. S29 ^{31}P NMR spectrum of **1a** measured in $CDCl_3$ at 25 °C (121.5 MHz).

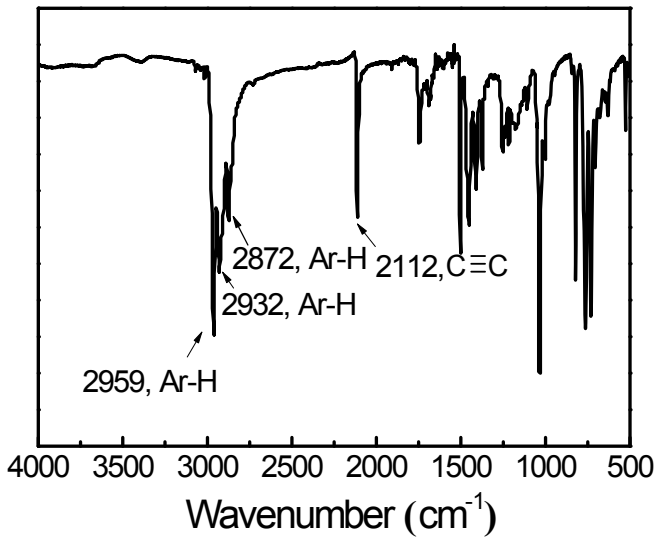


Fig. S30 FT-IR spectrum of **1a** measured at 25 °C using KBr pellets.

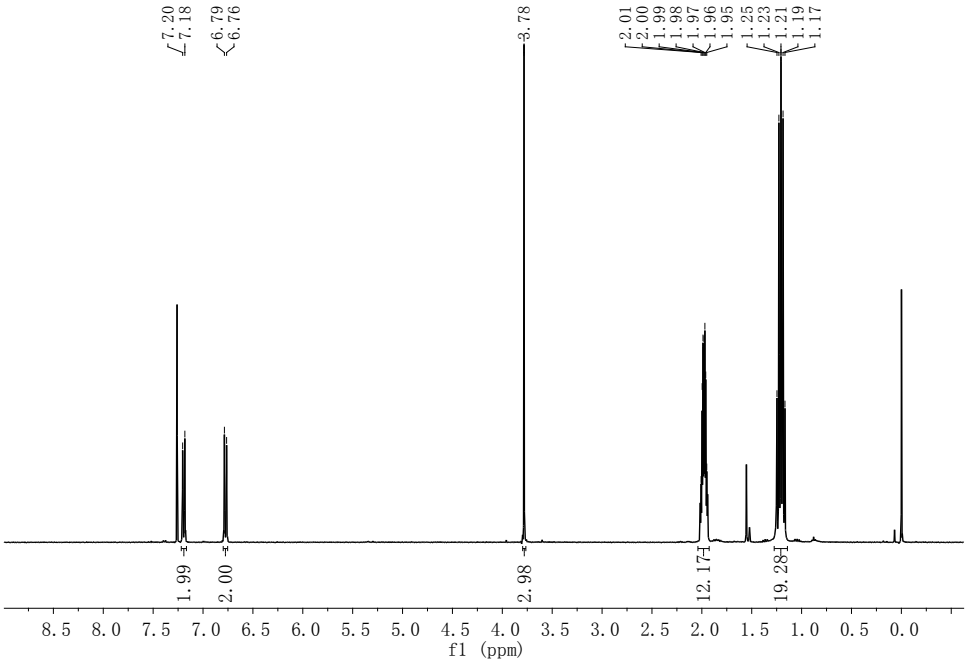


Fig. S31 ^{1}H NMR spectrum of **1b** measured in $CDCl_3$ at 25 °C (400 MHz).

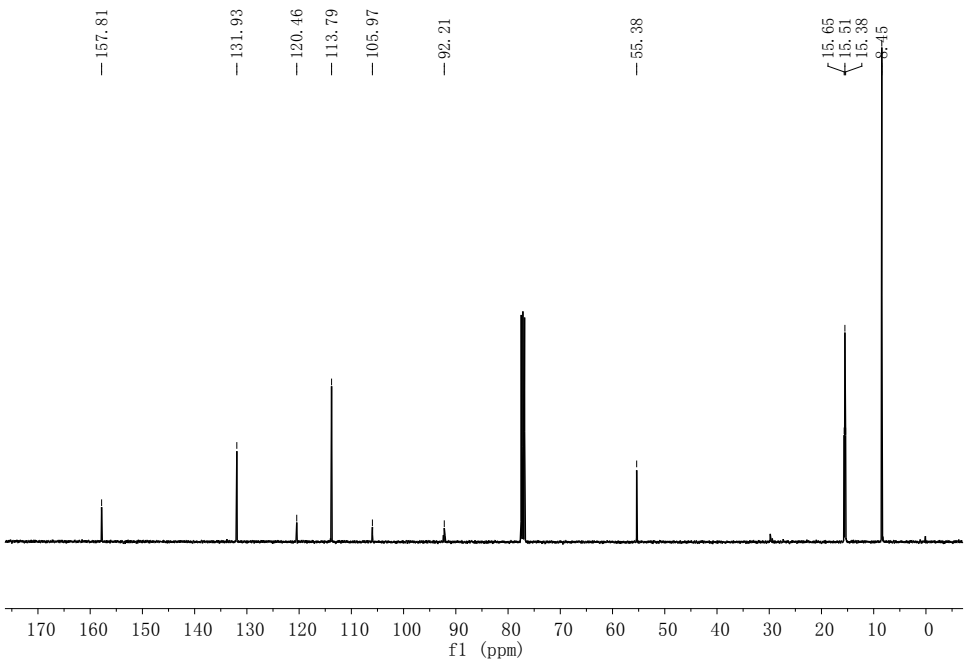


Fig. S32 ^{13}C NMR spectrum of **1b** measured in $CDCl_3$ at 25 °C (100 MHz).

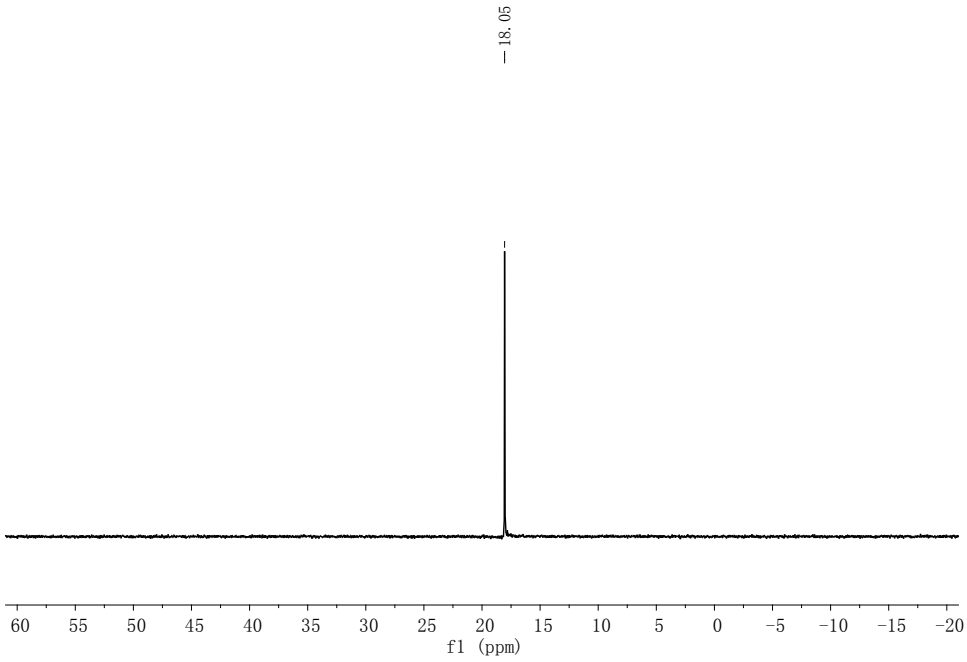


Fig. S33 ^{31}P NMR spectrum of **1b** measured in $CDCl_3$ at 25 °C (121.5 MHz).

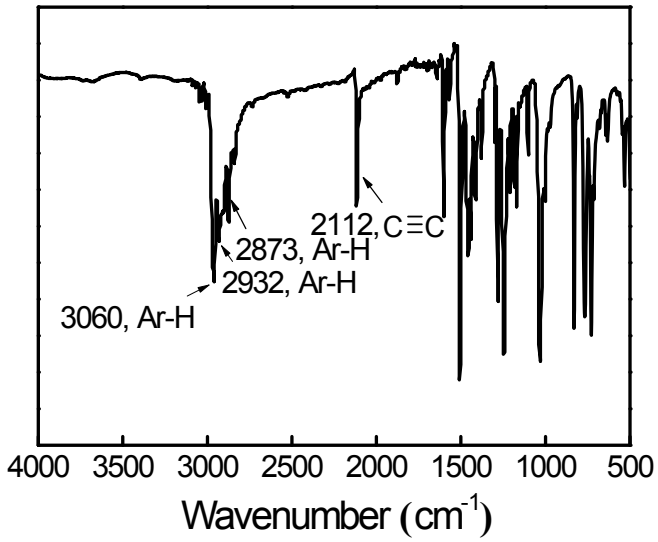


Fig. S34 FT-IR spectrum of **1b** measured at 25 °C using KBr pellets.

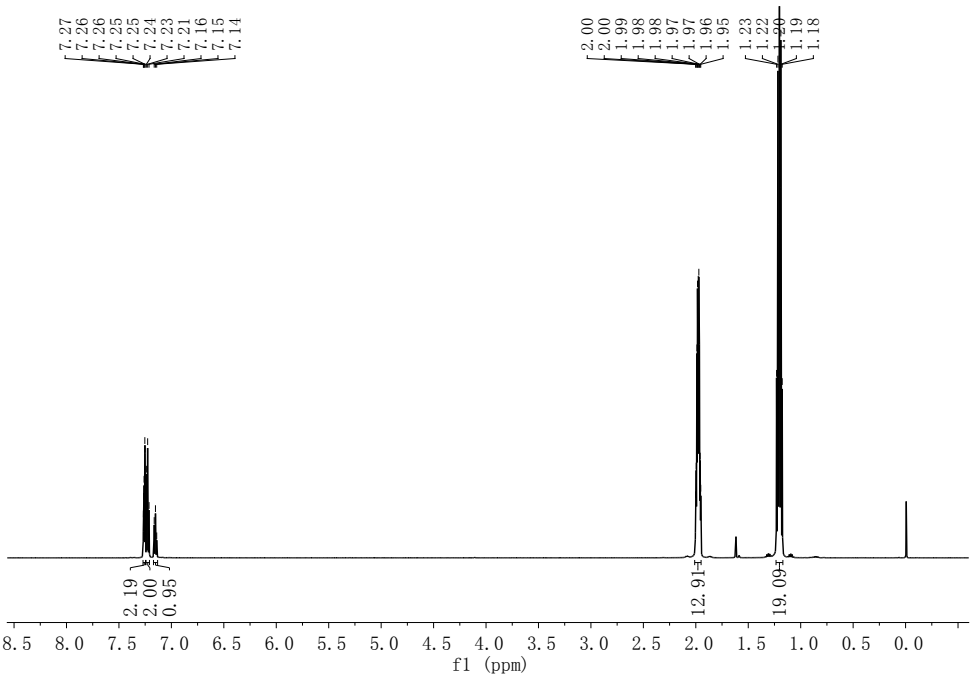


Fig. S35 ^{1}H NMR spectrum of **1c** measured in $CDCl_3$ at 25 °C (600 MHz).

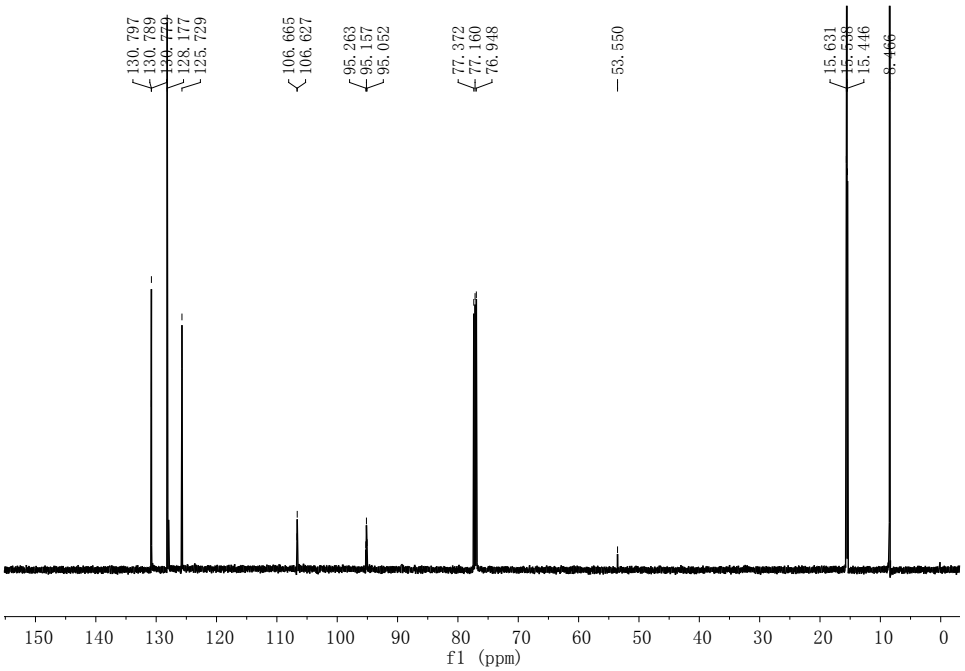


Fig. S36 ^{13}C NMR spectrum of **1c** measured in $CDCl_3$ at 25 °C (150 MHz).

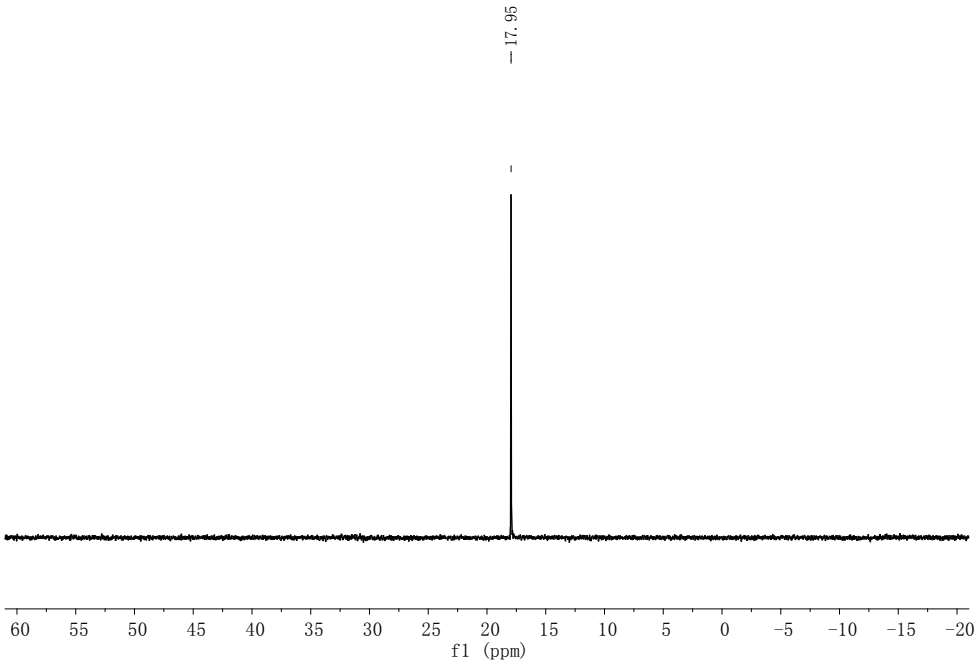


Fig. S37 ^{31}P NMR spectrum of **1c** measured in $CDCl_3$ at 25 °C (121.5 MHz).

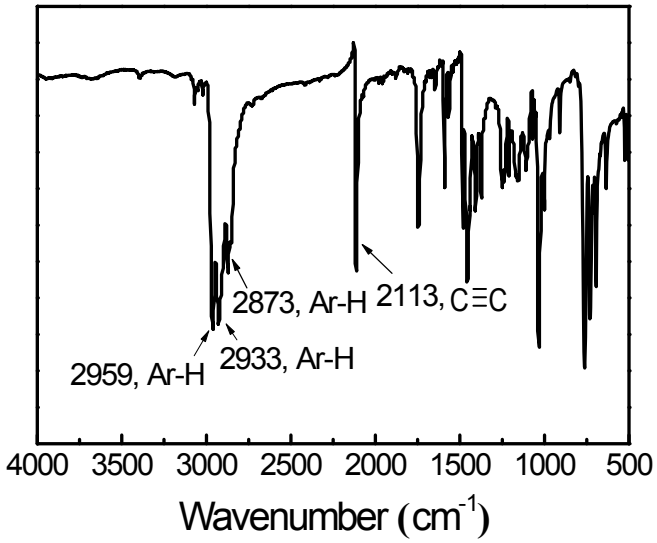


Fig. S38 FT-IR spectrum of **1c** measured at 25 °C using KBr pellets.

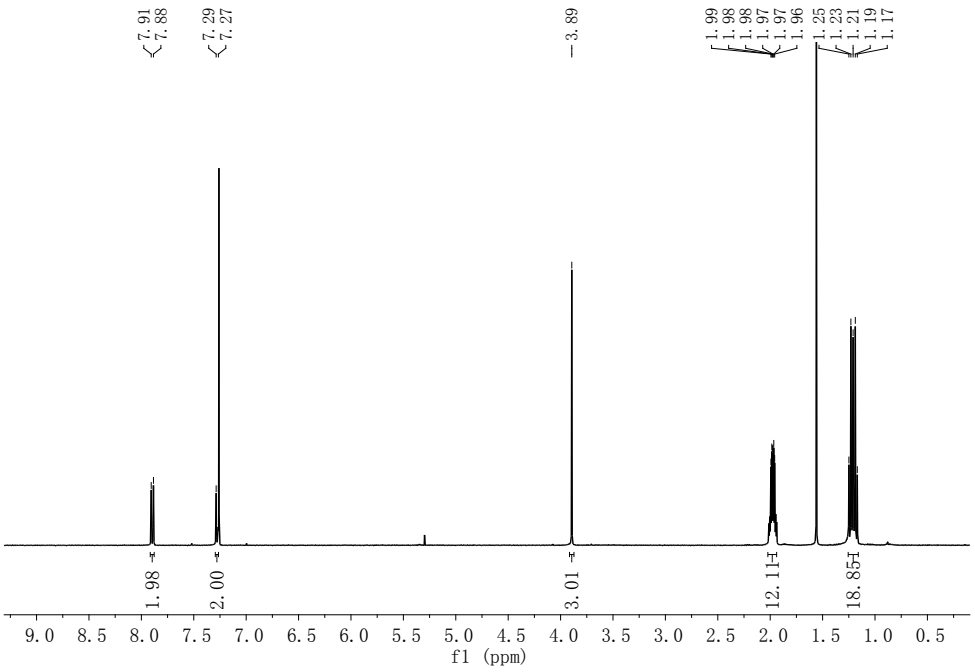


Fig. S39 ^{1}H NMR spectrum of **1d** measured in $CDCl_3$ at 25 °C (400 MHz).

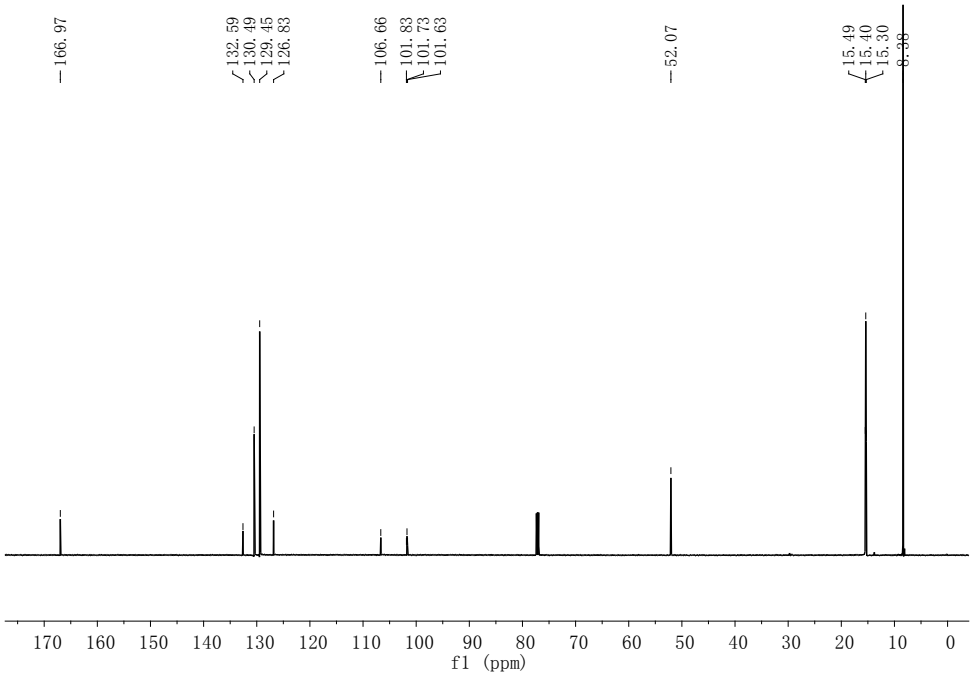


Fig. S40 ^{13}C NMR spectrum of **1d** measured in $CDCl_3$ at 25 °C (150 MHz).

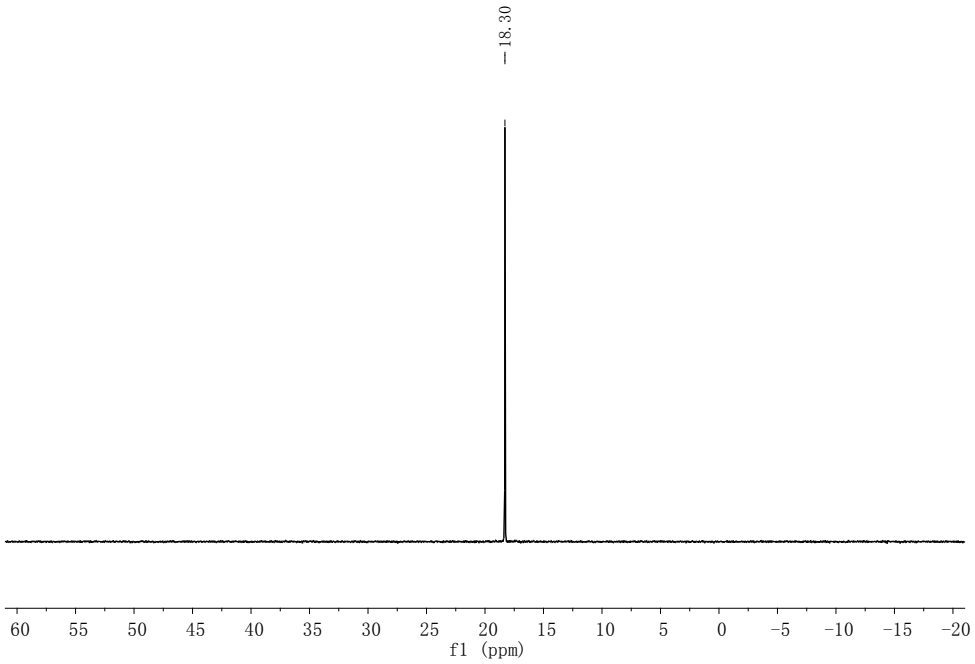


Fig. S41 ^{31}P NMR spectrum of **1b** measured in $CDCl_3$ at 25 °C (121.5 MHz).

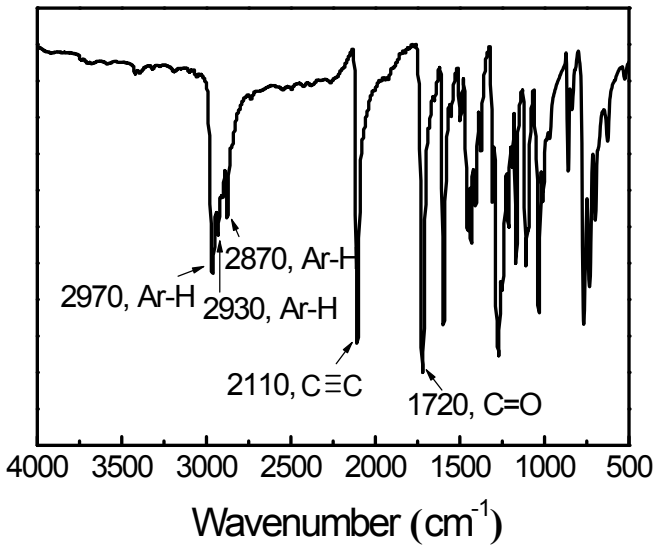


Fig. S42 FT-IR spectrum of **1d** measured at 25 °C using KBr pellets.

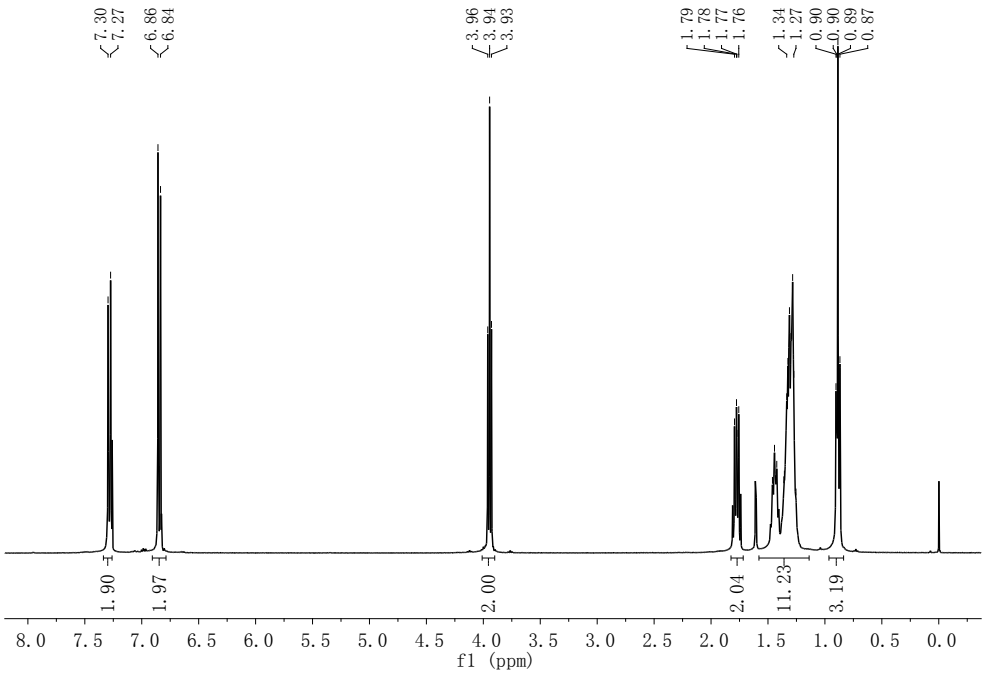


Fig. S43 ^{1}H NMR spectrum of **2c** measured in $CDCl_3$ at 25 °C (400 MHz).

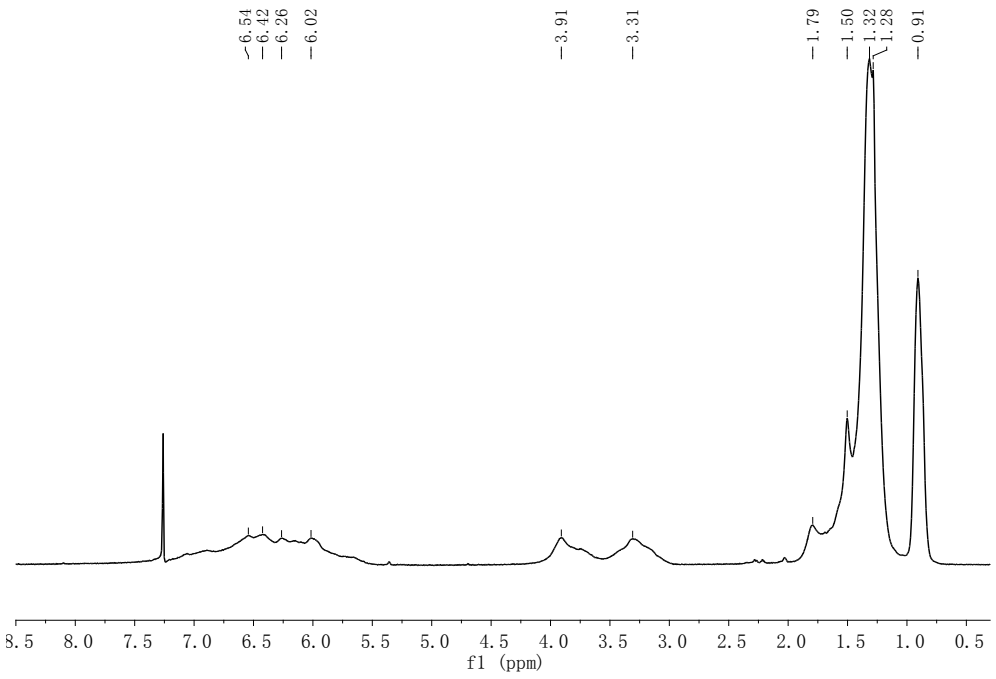


Fig. S44 ^{1}H NMR spectrum of poly-**b2c**$_{60}$ measured in $CDCl_3$ at 25 °C (600 MHz).

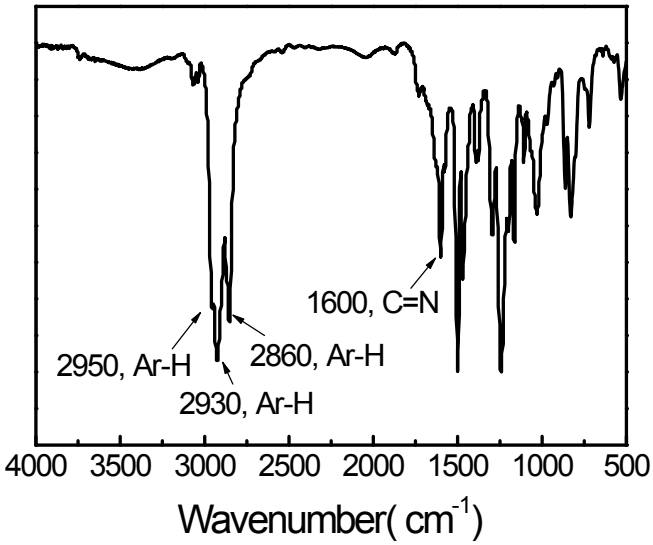


Fig. S45 FT-IR spectrum of poly-**b2c**$_{60}$ measured at 25 °C using KBr pellets.

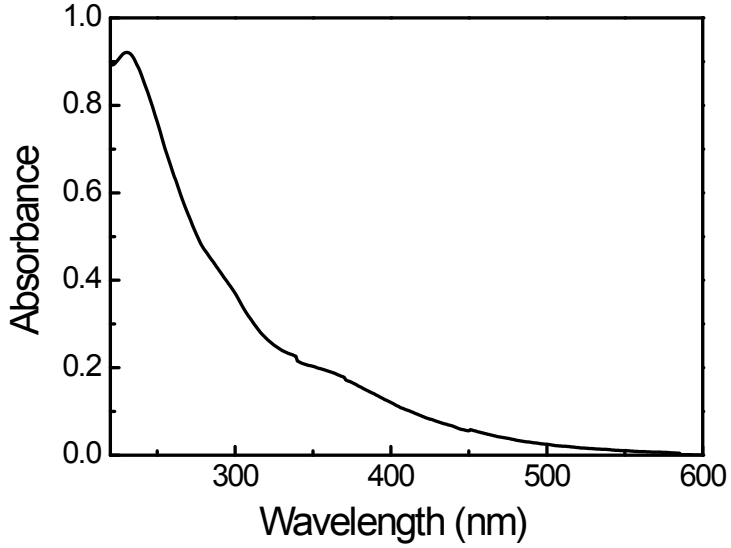


Fig. S46 UV-vis spectrum of poly-**b2c**$_{60}$ measured in $CHCl_3$ at 25 °C.

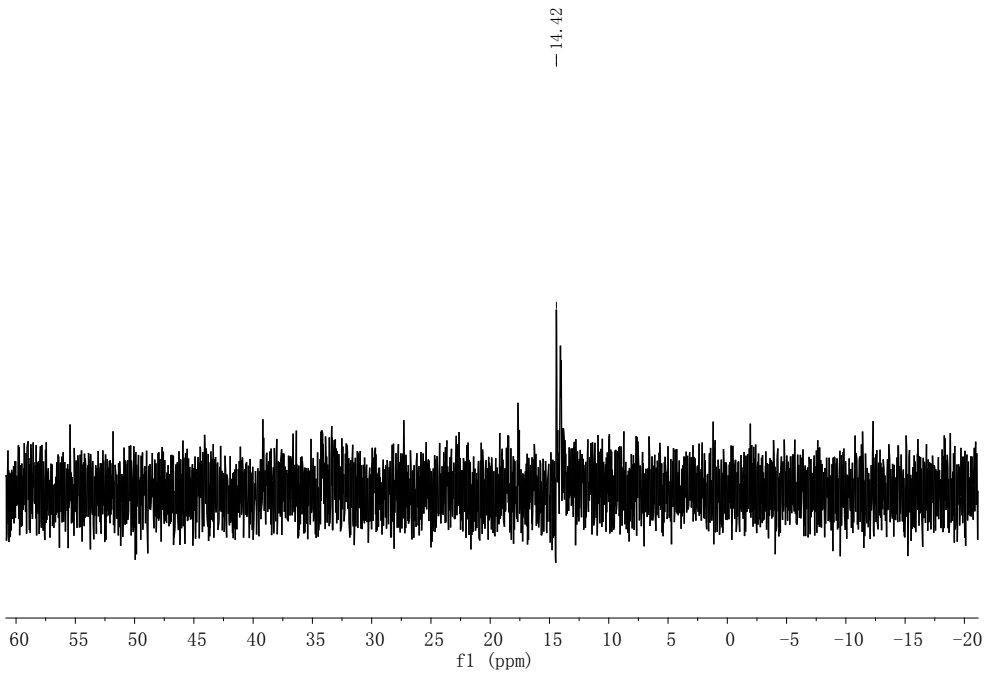


Fig. S47 ^{31}P NMR spectrum of poly-**b2c**$_{60}$ measured in $CDCl_3$ at 25 °C (121.5 MHz).

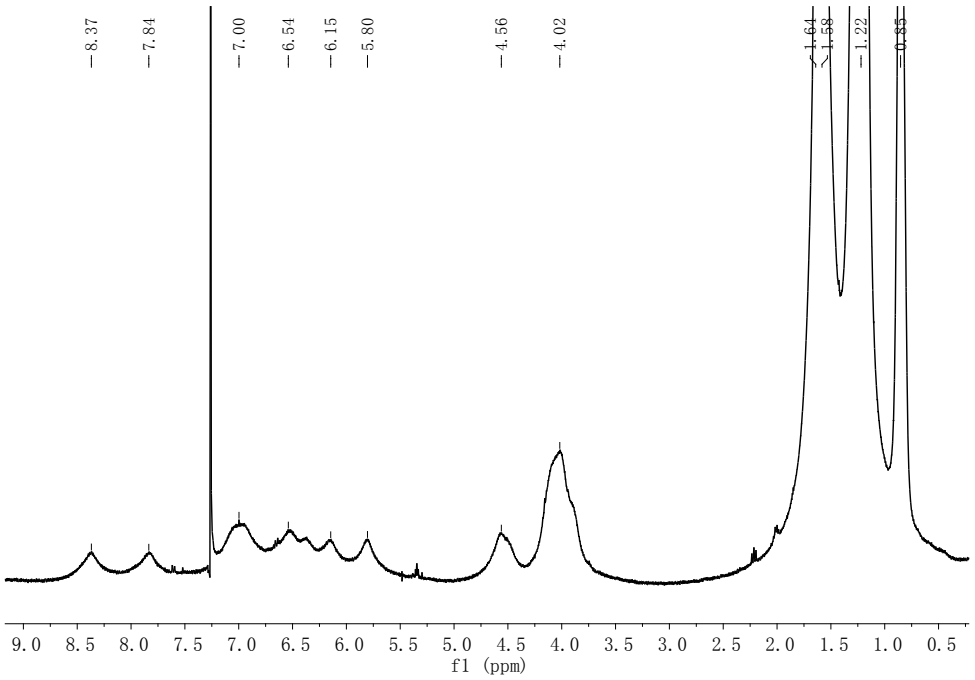


Fig. S48 ^{1}H NMR spectrum of poly-**b2d**$_{50}$ measured in $CDCl_3$ at 25 °C (600 MHz).

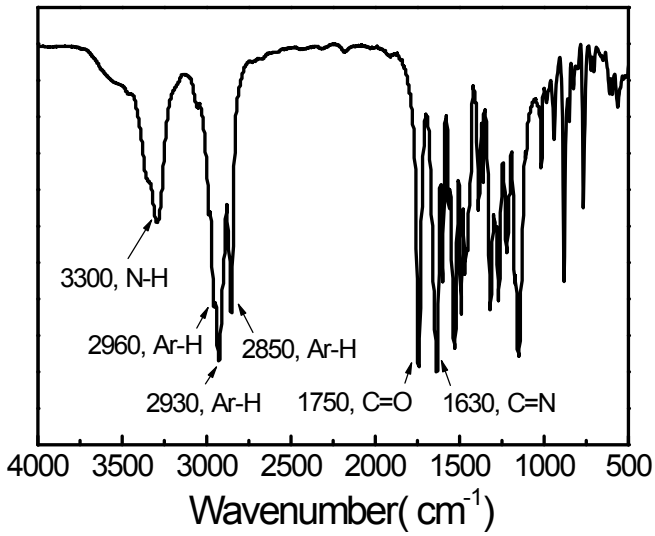


Fig. S49 FT-IR spectrum of poly-**b2d**$_{50}$ measured at 25 °C using KBr pellets.

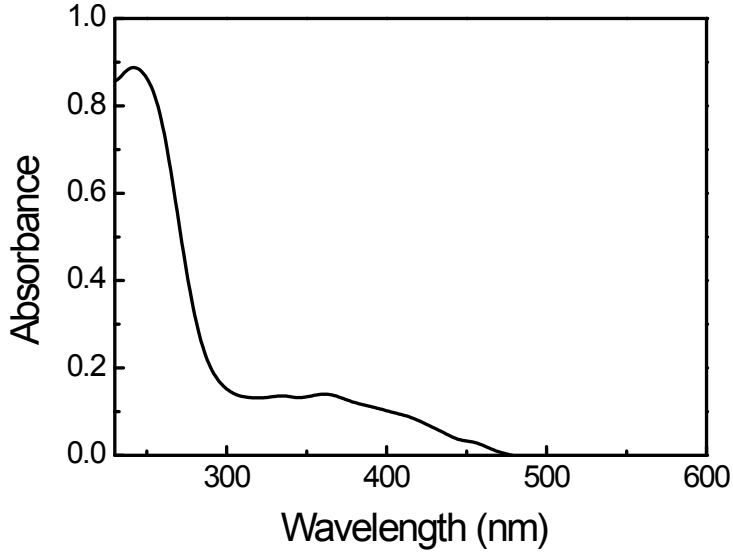


Fig. S50 UV-vis spectrum of poly-**b2d**$_{50}$ measured in $CHCl_3$ at 25 °C.

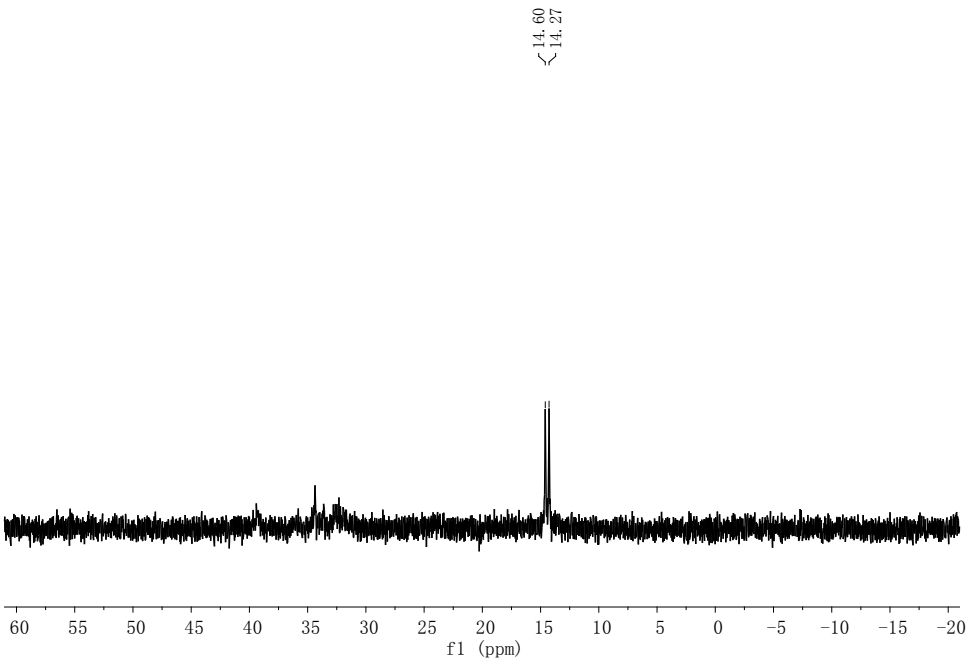


Fig. S51 ^{31}P NMR spectrum of poly-**b2d**$_{50}$ measured in $CDCl_3$ at 25 °C (121.5 MHz).

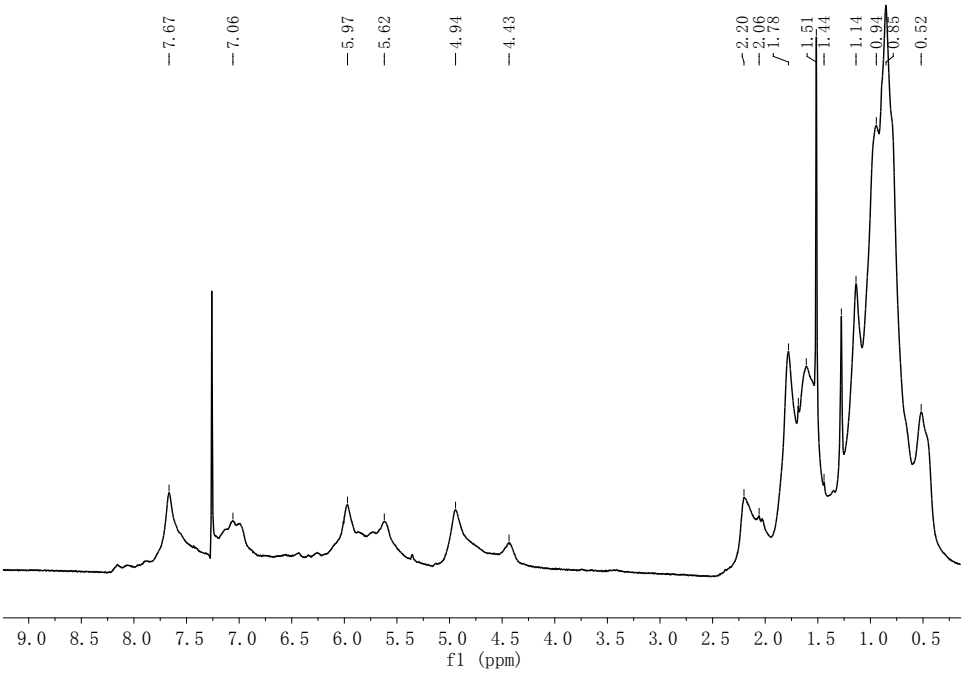


Fig. S52 ^{1}H NMR spectrum of poly-**b2e**$_{50}$ measured in $CDCl_3$ at 25 °C (600 MHz).

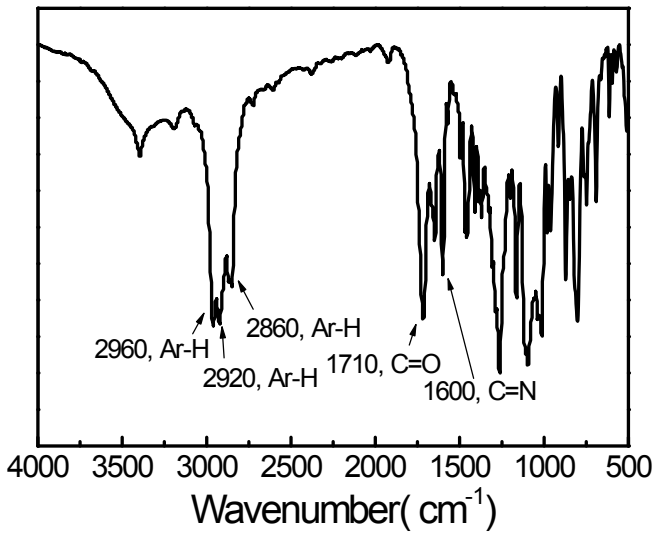


Fig. S53 FT-IR spectrum of poly-**b2e**$_{50}$ measured at 25 °C using KBr pellets.

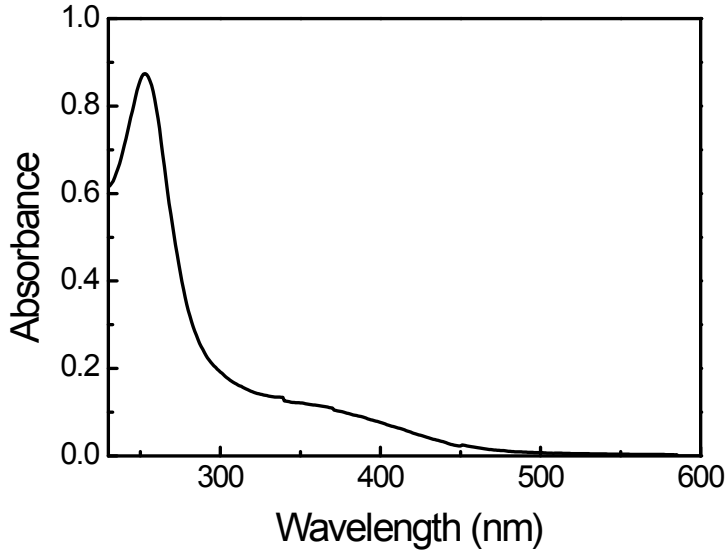


Fig. S54 UV-vis spectrum of poly-**b2e**$_{50}$ measured in $CHCl_3$ at 25 °C.

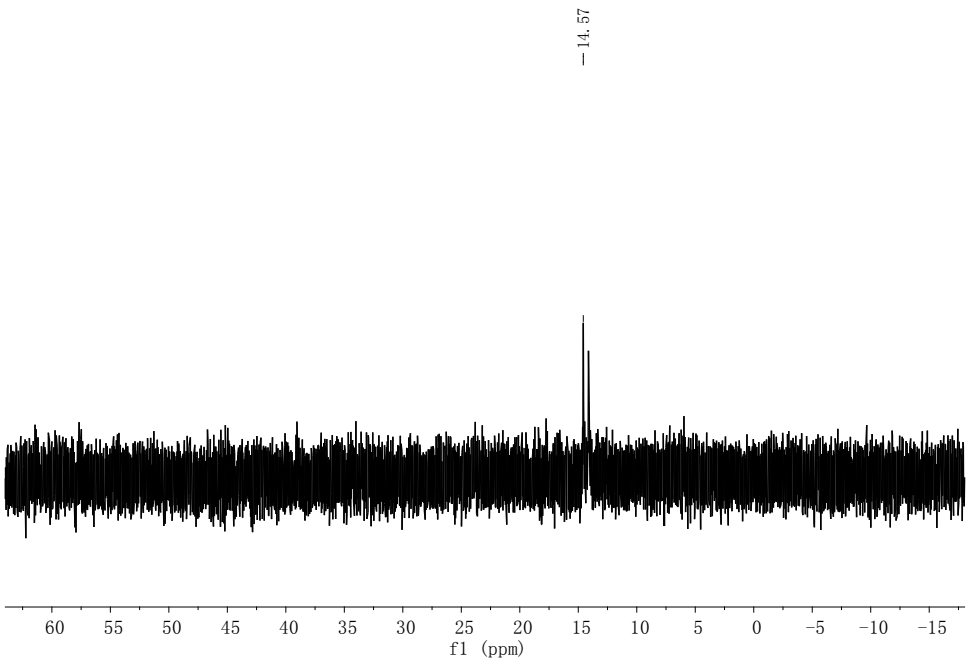


Fig. S55 ^{31}P NMR spectrum of poly-**b2e**$_{50}$ measured in $CDCl_3$ at 25 °C (121.5 MHz).