Supporting Information

Facile Synthesis and Controlled Self-Assembly of Poly(phenyl isocyanide)-*block*-Polycarbonate Copolymers

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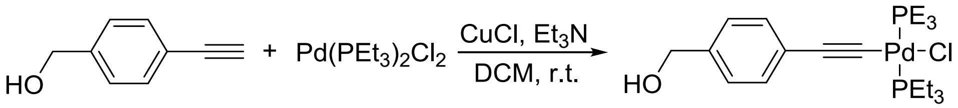
Measurements. NMR spectra were recorded using a Bruker 600 MHz spectrometer {H}. Size exclusion chromatography (SEC) was performed on SHIMADZU DGU-20A3R pump and SHIMADZU RID-20A differential refractive index (RI) detector (set at 40 °C) using KF-805L Styragel columns. Molecular weight (M_n) and polydispersity (M_w/M_n) data are reported relative to polystyrene standards. The eluent was tetrahydrofuran (THF) at a flow rate of 1.0 mL/min. FT-IR spectra were recorded on Thermo Scientific Nicolet iS10 using KBr pellets. Atomic force microscope (AFM) was performed on a Cypher S (Oxford Instruments, Asylum Research). SHIMADZU 2600i UV/vis double beam spectropolarimeter. The polymer concentration was calculated on the basis of the monomer units and was 0.20 mg/mL. Transmission electron microscopy (TEM) was performed on a JEM-2100F operating at 200 kV accelerating voltage. Scanning electron microscopy (SEM) was performed on a Regulus 8220 operating at 15.0 kV accelerating voltage. Dynamic light scattering (DLS) was recorded using a Nano-ZS 90 Zetasizer of Malvern (UK) instrument. Thermogravimetric analysis (TGA) test was performed in nitrogen atmosphere at a heating rate of 10 ^{o}C/min from 30 to 1000 ^{o}C using a Netzsch TG 209 F3 instrument. Differential scanning calorimetric (DCS) measurements were carried on a Mettler-Toledo DSC821e instrument. Samples were first heated from 30 to 300 ^{o}C at a heating rate of 10 ^{o}C/min under nitrogen atmosphere. Wide-angle X-ray scattering (WAXS) data were collected with Cu-K_α radiation ($\lambda = 1.5418$ Å) on a Bruker D8 Advance powder diffractometer fitted with a 0.6 mm fixed divergence slit, knife-edge collimator and a LynxEye area detector. L_n and L_w of each sample of monodisperse cylindrical micelles were calculated according to equation S1 and S2 as shown below (L = length of object, N = number).[1] L_n is number-average lengths and L_w is weight-average lengths. $L_\mathrm{w}/L_\mathrm{n}$ is length distribution. These values were obtained by measuring over 50 micelles using the software ImageJ.

$$L_n = \frac{\sum_{i=1}^{n} N_i L_i}{\sum_{i=1}^{n} N_i} \qquad (S1) \qquad\qquad L_w = \frac{\sum_{i=1}^{n} N_i L_i^2}{\sum_{i=1}^{n} N_i L_i} \qquad (S2)$$

Materials. All solvents were obtained from Sinopharm. Co. Ltd. and were purified by the standard procedures before use. All chemicals were purchased from Aladdin and Sigma-Aldrich. Co. Ltd., and were used as received without further purification otherwise denoted. Isocyanide monomers and the Pd(II)-OH were synthesized according to the literature.[1,2] The structures of these compounds were confirmed by ^{1}H NMR.

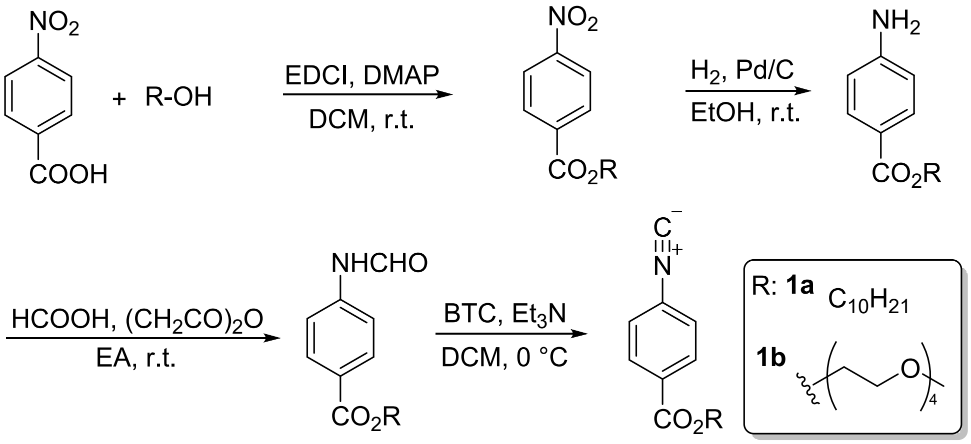
Scheme S1. Synthesis of Catalyst Pd(II)-OH



The Pd(II)-OH were prepared according to the literature.[2,3] 4-Ethynylbenzyl alcohol (50.2 mg, 0.38 mmol) was treated with trans-dichlorobis(triethylphosphine)palladium (153.0 mg, 0.37 mmol) in the presence of copper(I) chloride (0.40 mg, 0.004 mmol) as catalyst in 5.0 mL of diethylamine and dichloromethane (v/v = 1/1). The mixture was stirred at room temperature for 0.5 h. After the solvent was removed by evaporation under reduced pressure, the residue was purified by chromatography with ethyl acetate as eluent.

The crude product was recrystallized from petrol ether and methanol to afford yellow solid (158.9 mg, 85% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.25–7.22 (m, 4H, ArH), 4.64 (s, 2H, $HOC\underline{H}_2$), 2.00–1.95 (m, 12H, $P(C\underline{H}_2CH_3)_3$), 1.23–1.18 (m, 18H, $P(C\underline{H}_2C\underline{H}_3)_3$). ^{31}P NMR (243 MHz, $CDCl_3$, 25 °C): δ 18.01. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 129.80, 125.88, 64.19, 14.48, 14.39, 14.29, 12.85, 12.76, 12.67, 7.32, 7.03. MS m/z calcd for $C_{21}H_{37}OP_2Pd$ ($[M\text{-}Cl+H]^+$): 473.14; Found: 473.1349.

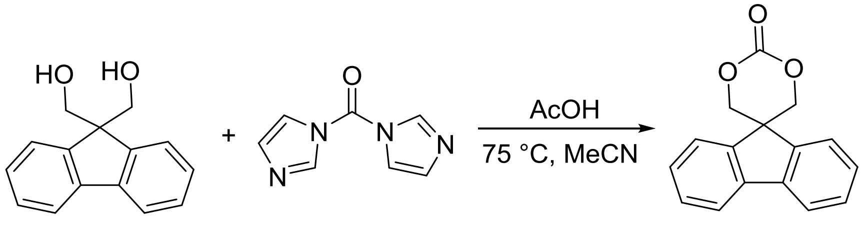
Scheme S2. Synthesis of Monomer 1a, and 1b



The monomer **1a**, and **1b** were prepared according to the literature.[2,3] The afforded monomer **1a** and **1b** were confirmed by ^{1}H NMR. **1a** faint yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.08 (d, J = 9.0 Hz, 2H, ArH), 7.44 (d, J = 8.4 Hz, 2H, ArH), 4.33 (t, J = 7.2 Hz, 2H, $CO_2C\underline{H}_2C_9H_{19}$), 1.79–1.74 (m, 2H, $CO_2CH_2C\underline{H}_2C_8H_{17}$), 1.45–1.26 (m, 14H, $CO_2C_2H_4C_7\underline{H}_{14}CH_3$), 0.88 (t, J = 6.6 Hz, 3H, CH_3).

1b yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.03 (d, J = 8.4 Hz, 2H, ArH), 7.36 (d, *J* = 8.4 Hz, 2H, ArH), 4.42 (t, *J* = 4.8 Hz, 2H, $CO_2C\underline{H}_2$, 3.77–3.46 (m, 14H, $CO_2CH_2C\underline{H}_2(OC\underline{H}_2C\underline{H}_2)_3OCH_3$), 3.30 (s, 3H, $C\underline{H}_3$).

Scheme S3. Synthesis of Monomer 2



The monomer **2** were prepared according to the literature.[4] A round-bottom flask equipped with a magnetic stirbar was charged with the 9H-Fluorene-9,9-dimethanol, CDI and dry MeCN, the reaction mixture was stirred at r.t. for 10 minutes. AcOH (16 equiv.) was added to the reaction mixture. The reaction mixture was equipped with a reflux condenser and heated to 75 °C for 1 h in a pre-heated oil bath. The resulting white solid was then dissolved in ethyl acetate and washed twice with H_2O and once with saturated brine solution, before the organic phase was dried over $MgSO_4$ and all volatiles removed in vacuo. Recrystallization from anhydrous THF yield a white crystalline solid (2.30 g, 77% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.82–7.81 (m, 2H, ArH), 7.51–7.49 (m, 4H, ArH), 7.40–7.37 (m, 2H, ArH), 4.58 (s, 4H, $C\underline{H}_2$).

Typical polymerization for stepwise polymerization procedure. All polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under dry nitrogen.

For method 1, a 10 mL oven-dried flask was charged with monomer **1a** (40.2 mg, 0.14 mmol), Pd(II)-OH (0.7 mg, 0.0014 mmol), THF (0.70 mL), and a stir bar. The concentrations of monomer **1a** and Pd(II)-OH were 0.2 mmol/ml, and 0.002 mmol/mL, respectively ($[\mathbf{1a}]_0/[\mathrm{Pd(II)\text{-}OH}]_0 = 100$). The reaction flask was then immersed into an oil bath at 55 °C and stirred for 12 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-$\mathbf{1a}_{100}$ as a yellow solid (33.4 mg, 83% yield). SEC: $M_n = 28.5$ kDa, $M_w/M_n = 1.18$. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): 7.48–6.96 (br, 2H, ArH), 5.94–5.36 (br, 2H, ArH), 4.27–3.34 (br, 2H, $OC\underline{H}_2$), 1.73–0.69 (br, 19H, $C_9\underline{H}_{19}$). FT-IR (KBr, cm^{-1}): 2964 ($\nu_{C\text{–}H}$), 2920 ($\nu_{C\text{–}H}$), 2849 ($\nu_{C\text{–}H}$), 1645 ($\nu_{OC=O}$), 1602 ($\nu_{C=N}$).

Using the resulting poly-$\mathbf{1}_{100}$-OH as the macroinitiator, added the monomer **2** and 1, 8-diazabicyclo [5.4.0]undec-7-ene (DBU) and a stir bar in THF (0.6 mL) at r.t. for 3.5 h ($[\mathbf{2}]_0/[\text{poly-}\mathbf{1a}_{100}\text{-OH}]_0 = 20$, $[\mathbf{2}]_0 = 0.2$ M). 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($\mathbf{1a}_{100}$-*b*-$\mathbf{2}_{20}$) as a yellow solid (23.6 mg, 78% yield). SEC: $M_n = 32.7$ kDa, $M_w/M_n = 1.19$. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): 7.73–6.82 (br, 3H, ArH), 5.87–5.23 (br, 2H, ArH), 4.44–3.44 (br, 4H, OCH_2), 1.86–0.57 (br, 19H, C_9H_{19}). FT-IR (KBr, cm^{-1}): 2964 ($\nu_{C\text{–}H}$), 2916 ($\nu_{C\text{–}H}$), 2848 ($\nu_{C\text{–}H}$), 1724 ($\nu_{OC=O}$), 1629 ($\nu_{OC=O}$), 1604 ($\nu_{C=N}$).

For method 1, a 10 mL oven-dried flask was charged with Pd(II)-OH, monomer **2,** 1, 8-diazabicyclo [5.4.0]undec-7-ene (DBU) and a stir bar in THF (0.6 mL) at r.t. for 3.5 h ($[\mathbf{2}]_0$/$[\text{Pd(II)-OH}]_0$ = 20, $[\mathbf{2}]_0$ = 0.2 M). 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-$\mathbf{2}_{20}$-Pd(II) as a white solid (26.3 mg, 87% yield). SEC: M_n = 5.8 kDa, M_w/M_n = 1.13. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): 7.81–7.20 (br, 8H, ArH), 4.53–4.28 (br, 4H, $OC\underline{H}_2$). FT-IR (KBr, cm^{-1}): 2964 ($\nu_{C\text{–}H}$), 1745 ($\nu_{OC=O}$).

Using the resulting poly-$\mathbf{2}_{20}$-Pd(II) as the macroinitiator, added the monomer **1** and a stir bar in THF (0.8 mL) at 55 °C for 12 h ($[\mathbf{1a}]_0$/$[\text{poly-}\mathbf{2}_{20}\text{-Pd(II)}]_0$ = 100, $[\mathbf{1}]_0$ = 0.2 M). 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($\mathbf{2}_{20}$-*b*-$\mathbf{1a}_{100}$) as a yellow solid (37.2 mg, 81% yield). SEC: M_n = 36.2 kDa, M_w/M_n = 1.15. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): 7.80–6.77 (br, 3H, ArH), 6.00–5.06 (br, 2H, ArH), 4.44–3.44 (br, 3H, OCH_2), 1.86–0.57 (br, 19H, C_9H_{19}). FT-IR (KBr, cm^{-1}): 2957 ($\nu_{C\text{–}H}$), 2920 ($\nu_{C\text{–}H}$), 2855 ($\nu_{C\text{–}H}$), 1724 ($\nu_{OC=O}$), 1648 ($\nu_{OC=O}$), 1594 ($\nu_{C=N}$).

poly($\mathbf{1b}_{100}$-*b*-$\mathbf{2}_{20}$) were prepared followed a procedure similar to above. Characteristic data for poly($\mathbf{2}_n$-*b*-$\mathbf{1b}_n$), yield 76%, SEC: M_n = 28.6 kDa, M_w/M_n = 1.19. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): 7.79–6.74 (br, 3H, ArH), 5.89–5.23 (br, 2H, ArH), 4.21–2.90 (br, 17H, $OC\underline{H}_2$ and $(C\underline{H}_2C\underline{H}_2O)_4C\underline{H}_3$). FT-IR (KBr, cm^{-1}): 2872 ($\nu_{C\text{–}H}$), 1719 ($\nu_{OC=O}$), 1651 ($\nu_{OC=O}$), 1600 ($\nu_{C=N}$).

Typical polymerization for one-pot procedure. All polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under dry nitrogen. A 10 mL oven-dried flask was charged with monomer **1a** (40.2 mg, 0.14 mmol), **2** (35.3 mg, 0.14 mmol), DBU (10.2 mg, 0.067 mmol), Pd(II)-OH (0.7 mg, 0.0014 mmol), THF (0.70 mL), and a stir bar. The concentrations of monomer **1a**, **2** and Pd(II)-OH were 0.2mmol/ml, 0.2mmol/mL, and 0.002 mmol/mL, respectively ($[\mathbf{1a}]_0/[\text{Pd(II)-OH}]_0 = 100$, $[\mathbf{2}]_0/[\text{Pd(II)-OH}]_0 = 20$). The reaction flask was then immersed into an oil bath at 55 °C and stirred for 12 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 (65.0 mg, 86.0% yield). SEC: $M_n = 33.1$ kDa, $M_w/M_n = 1.16$. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): 7.73–6.82 (br, 3H, ArH), 5.87–5.23 (br, 2H, ArH), 4.44–3.44 (br, 4H, OCH_2), 1.86–0.57 (br, 19H, C_9H_{19}). FT-IR (KBr, cm^{-1}): 2964 ($\nu_{C\text{–}H}$), 2916 ($\nu_{C\text{–}H}$), 2848 ($\nu_{C\text{–}H}$), 1724 ($\nu_{OC=O}$), 1629 ($\nu_{OC=O}$), 1604 ($\nu_{C=N}$).

Typical procedure for self-assembly of poly($\mathbf{1b}_m$-*b*-$\mathbf{2}_n$) copolymer.[5] A solution of 40.0 mg in THF (4.0 mg/mL in THF) was prepared in a small sample vial and the mixed THF/MeOH (v/v = 2/8) solvents were added dropwise (0.2 mg/mL). The solution was aged for 3 days, and then subjected to AFM, SEM, TEM, DLS, UV-vis.

Typical procedure for self-assembly of poly($\mathbf{1b}_m$-*b*-$\mathbf{2}_n$) copolymer and poly-$\mathbf{2}_n$ homopolymer blend solution.[6] A solution of poly($\mathbf{1b}_{100}$-*b*-$\mathbf{2}_{20}$) and poly-$\mathbf{2}_{20}$ with different mass ratio in THF (4.0 mg/mL in THF) was prepared in a small sample vial and the mixed

THF/MeOH (v/v = 2/8) solvents were added dropwise (0.2 mg/mL). The solution was aged for 3 days, and then subjected to AFM, SEM, TEM, DLS, UV-vis.

Procedure for seed micelles preparation. A vial containing the micelle colloidal solution (THF/MeOH = 2/8) was flushed with nitrogen and capped with a rubber septum. The sonotrode was introduced into the colloidal solution through the rubber septum after the solution was cooled to 0 °C. The colloidal solution was then subjected to ultrasound with stirring for 1 h. SEM of the fragmented micelles (seed micelles) are shown in Figure 5b.

Procedure for self-seeding. Seven equivalent batches (300 μL) of THF/MeOH (2/8) solutions containing micelle fragments were transferred into new vials. These solutions were annealed in an oil bath at various temperatures (35, 40, 45, 50, 55, and 60 °C). After 2 h, each solution was quenched into another oil bath at 25 °C and allowed to age at 25 °C for 3 days. Afterwards, these samples were subjected to TEM and AFM measurements.

AFM Sample preparation. The micelle samples were prepared by spin-coating 20 μL solution of micelles on silica wafer substrate. Imaging was conducted in air at ambient temperature.

SEM Sample preparation. The micelle samples were prepared by spin-coating 20 μL solution of micelles on silica wafer substrate and dry in the air, gold was sputtered on the sample surface.

TEM Sample preparation. The samples for TEM were prepared by drop-casting one drop (ca. 10 μL) of the micelle colloidal solution onto a carbon coated copper grid which was placed on a piece of filter paper to remove excess solvent.

Table S1. Results for the Synthesis Homopolymers and Copolymers

run	polymer	M_n (kDa)	M_w/M_n	Yield (%)
1	poly-$\mathbf{1a}_{100}$	28.5	1.18	83
2	poly($\mathbf{1a}_{100}$-*b*-$\mathbf{2}_{20}$)	32.7	1.19	78
3	poly-$\mathbf{2}_{20}$	5.8	1.13	87
4	poly($\mathbf{2}_{20}$-*b*-$\mathbf{1a}_{100}$)	36.2	1.15	81
5	poly($\mathbf{1a}_{100}$-*b*-$\mathbf{2}_{20}$)	33.1	1.16	86
6	poly($\mathbf{1a}_{10}$-*b*-$\mathbf{2}_{10}$)	5.0	1.16	82
7	poly($\mathbf{1a}_{20}$-*b*-$\mathbf{2}_{20}$)	10.4	1.18	87
8	poly($\mathbf{1a}_{30}$-*b*-$\mathbf{2}_{30}$)	15.1	1.20	81
9	poly($\mathbf{1a}_{40}$-*b*-$\mathbf{2}_{40}$)	19.0	1.19	83
10	poly($\mathbf{1a}_{50}$-*b*-$\mathbf{2}_{50}$)	25.9	1.16	86

[a]These polymers were synthesized according to Scheme 1. [b]M_n and M_w/M_n values were determined by SEC with equivalent to polystyrene standards. [c]The isolated yields.

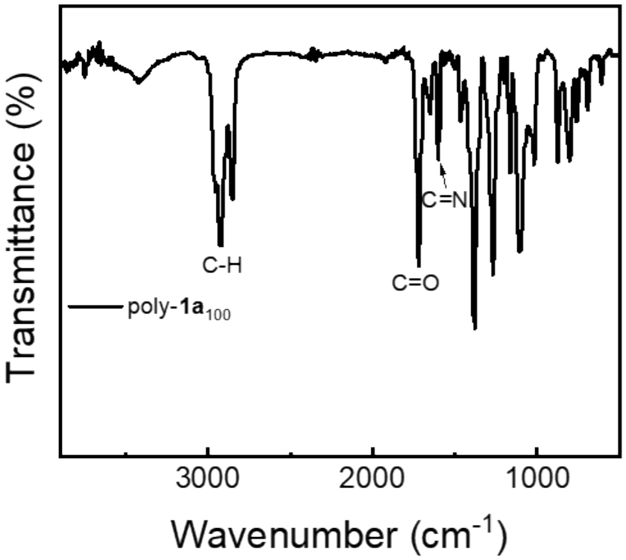


Figure S1. FT-IR spectra of poly-**1a**$_{100}$ measured at 25 °C using KBr pellets.

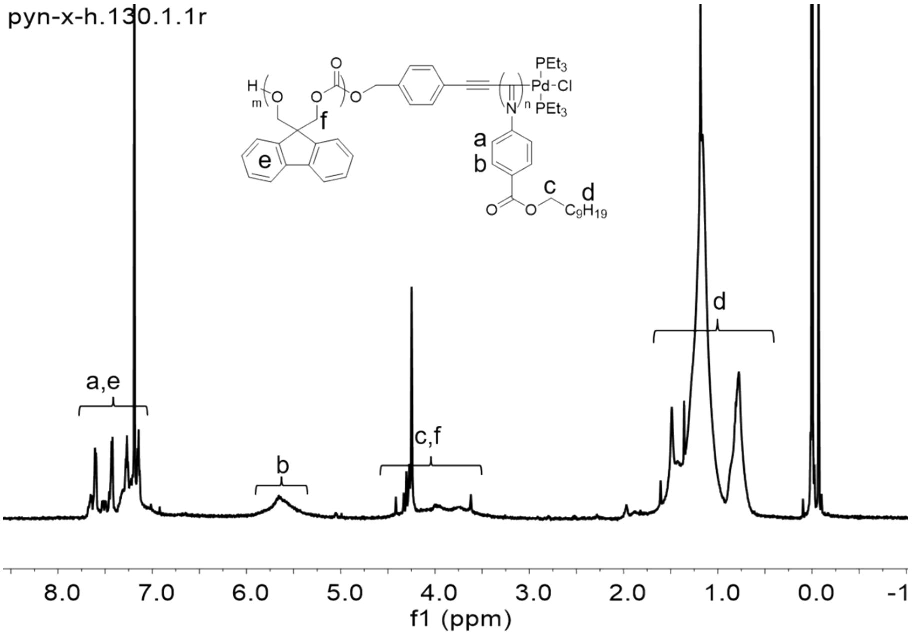


Figure S2. ^{1}H NMR (600 MHz) spectrum of poly(**1a**$_{100}$-*b*-**2**$_{20}$) for stepwise measured in CDCl$_3$ at 25 °C.

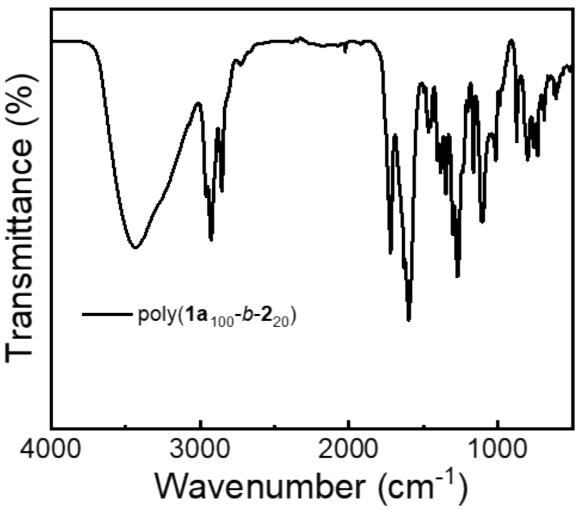


Figure S3. FT-IR spectra of poly($\mathbf{1a}_{100}$-b-$\mathbf{2}_{20}$) for stepwise measured at 25 °C using KBr pellets.

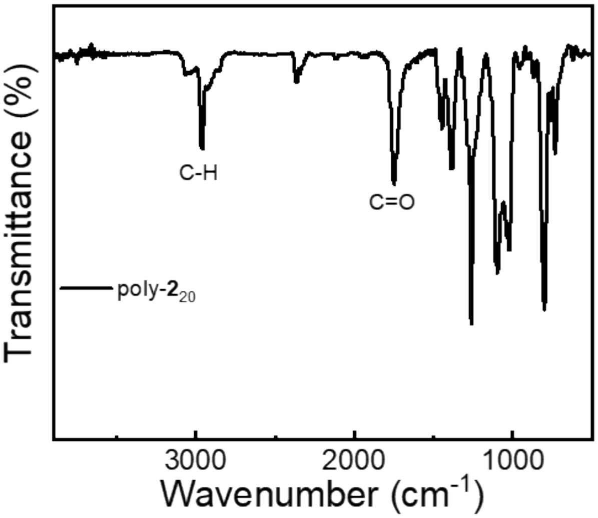


Figure S4. FT-IR spectra of poly-$\mathbf{2}_{20}$ for stepwise measured at 25 °C using KBr pellets.

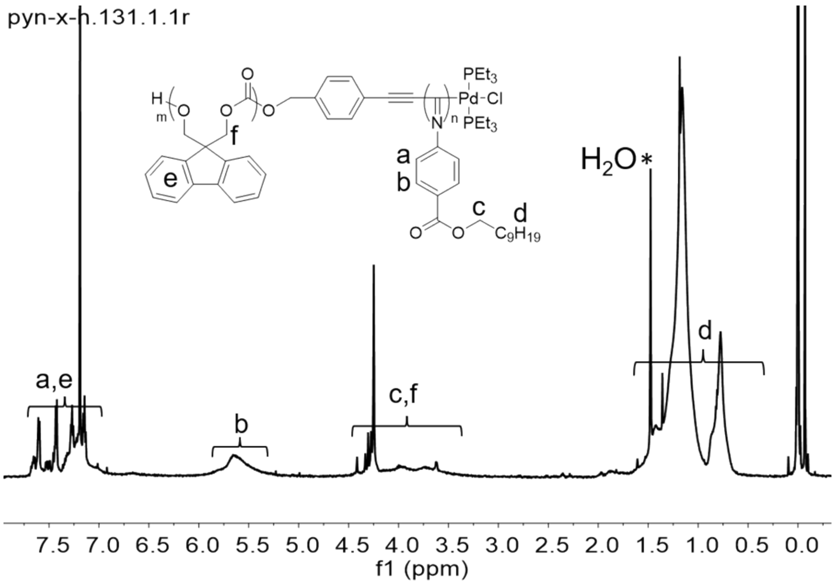


Figure S5. ^{1}H NMR (600 MHz) spectrum of poly($\mathbf{2}_{20}$-*b*-$\mathbf{1a}_{100}$) measured in $CDCl_3$ at 25 °C. The asterisk denotes a residual solvent peak.

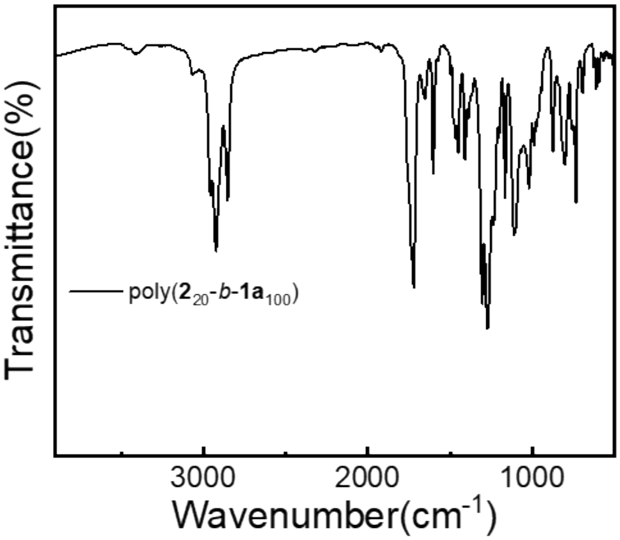


Figure S6. FT-IR spectra of poly($\mathbf{2}_{20}$-*b*-$\mathbf{1a}_{100}$) for stepwise measured at 25 °C using KBr pellets.

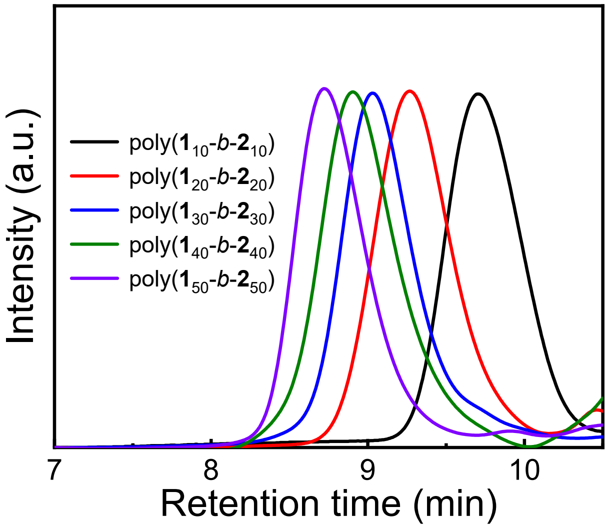


Figure S7. SEC chromatograms of poly(**1a**$_m$-*b*-**2**$_m$) as a function of the initial feed ratios of monomer to catalyst.

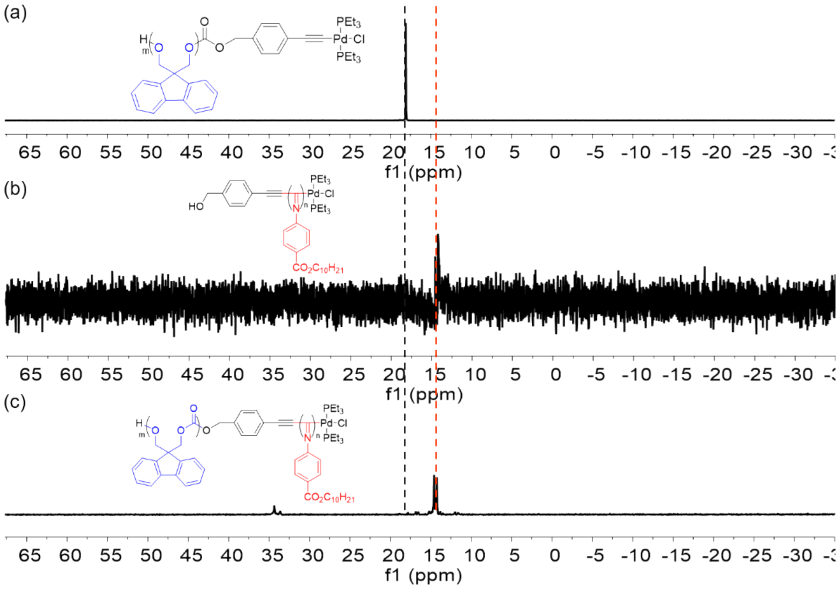


Figure S8. ^{31}P NMR (243 MHz) spectrum of poly-**2**$_m$, poly-**1a**$_m$, and poly(**1a**$_m$-*b*-**2**$_n$) for one-pot measured in CDCl$_3$ at 25 °C.

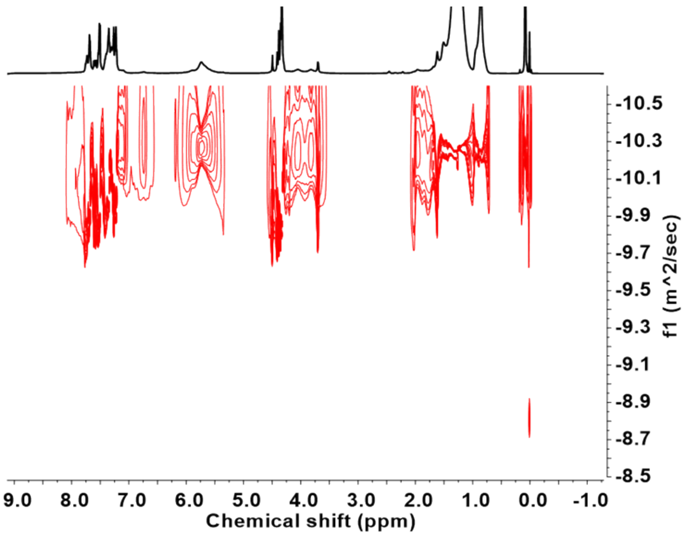


Figure S9. 2D ^{1}H DOSY NMR (600 MHz) spectrum of poly($\mathbf{1a}_m$-*b*-$\mathbf{2}_m$) for one-pot measured in $CDCl_3$ at 25 °C.

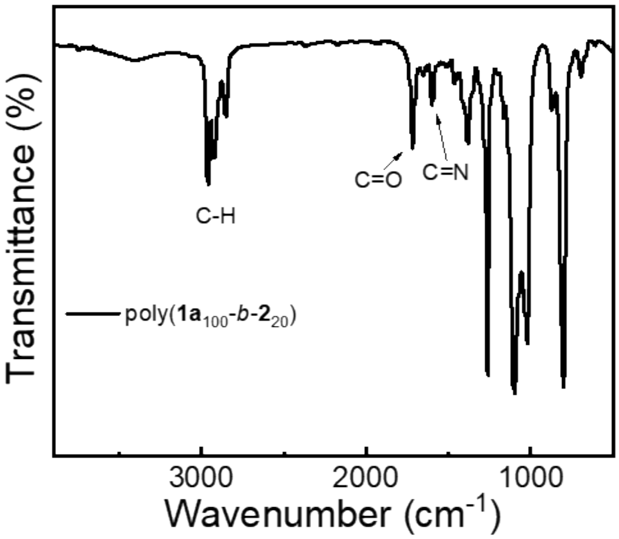


Figure S10. FT-IR spectra of poly($\mathbf{1a}_{100}$-*b*-$\mathbf{2}_{20}$) for one-pot measured at 25 °C using KBr pellets.

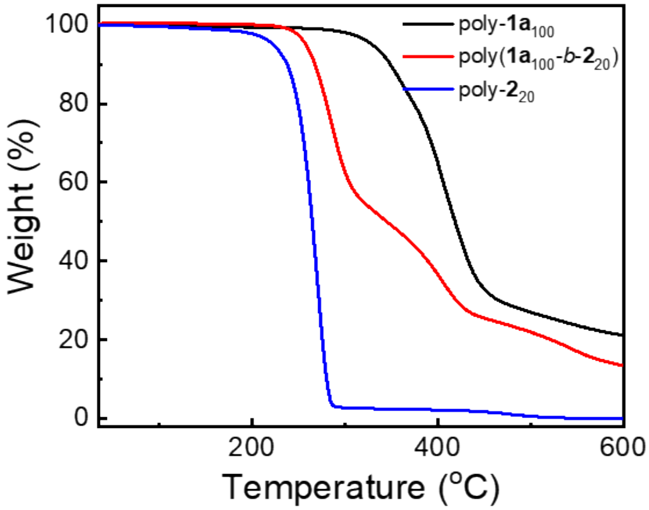


Figure S11. TGA curves of poly-**1a**$_{100}$, poly-**2**$_{20}$, and poly(**1a**$_{100}$-*b*-**2**$_{20}$) performed in N_2 atmosphere at a heating rate of 10 °C/min.

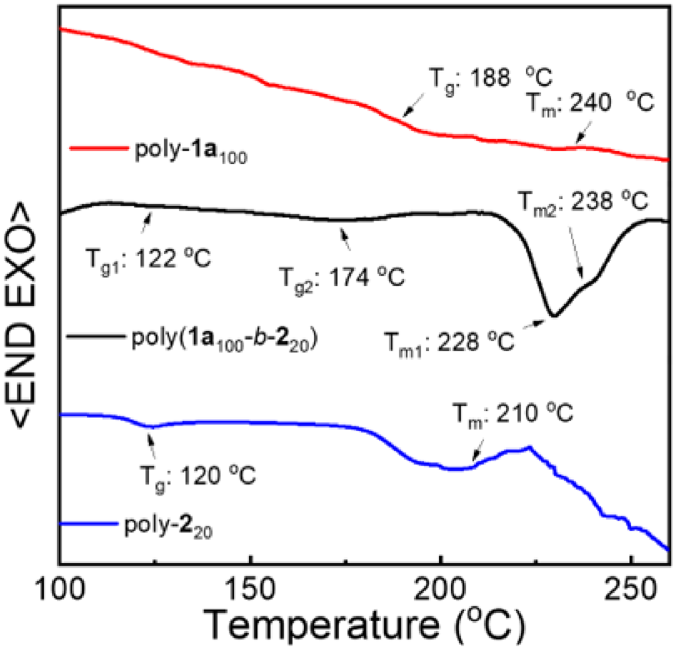


Figure S12. DSC curves of poly-**1a**$_{100}$, poly-**2**$_{20}$, and poly(**1a**$_{100}$-*b*-**2**$_{20}$) recorded under N_2 atmosphere at a heating rate of 10 °C/min.

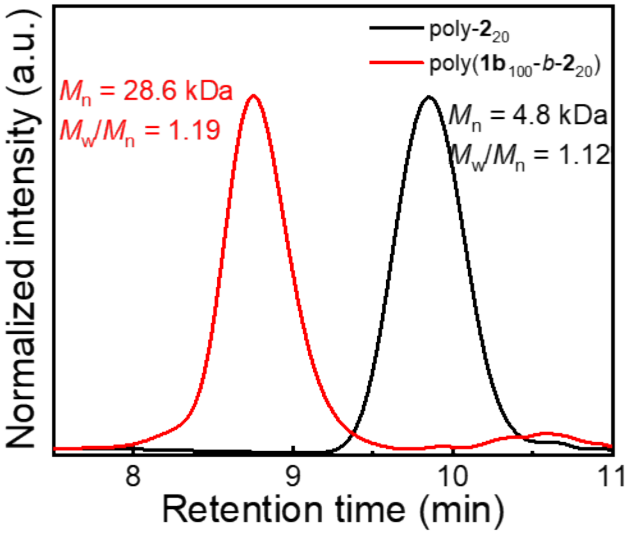


Figure S13. SEC chromatograms of poly-$\mathbf{2}_{20}$, and poly($\mathbf{2}_{20}$-*b*-$\mathbf{1b}_{100}$).

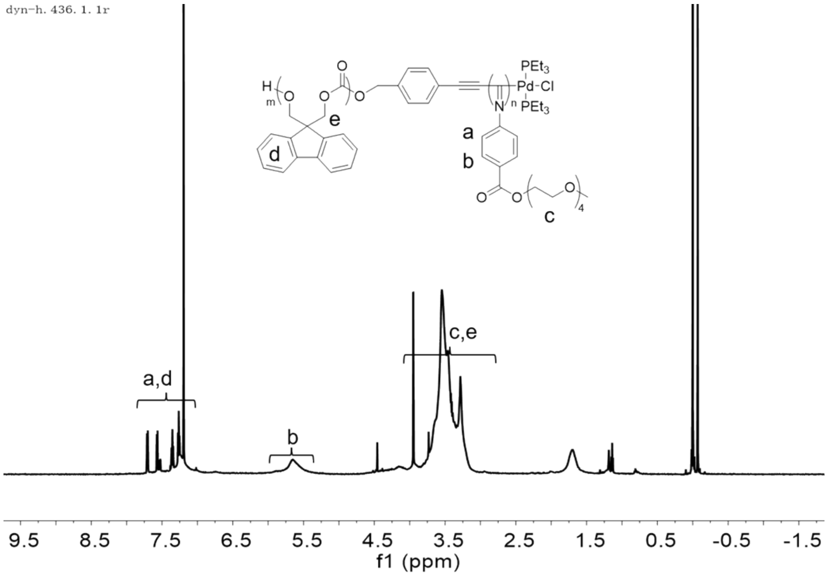


Figure S14. ^{1}H NMR (600 MHz) spectrum of poly($\mathbf{2}_{20}$-*b*-$\mathbf{1b}_{100}$) for stepwise measured in CDCl$_3$ at 25 °C.

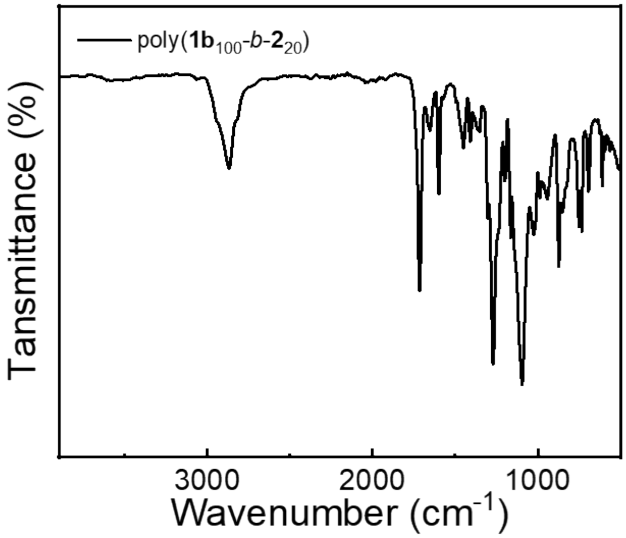


Figure S15. FT-IR spectra of poly($\mathbf{2}_{20}$-*b*-$\mathbf{1b}_{100}$) measured at 25 °C using KBr pellets.

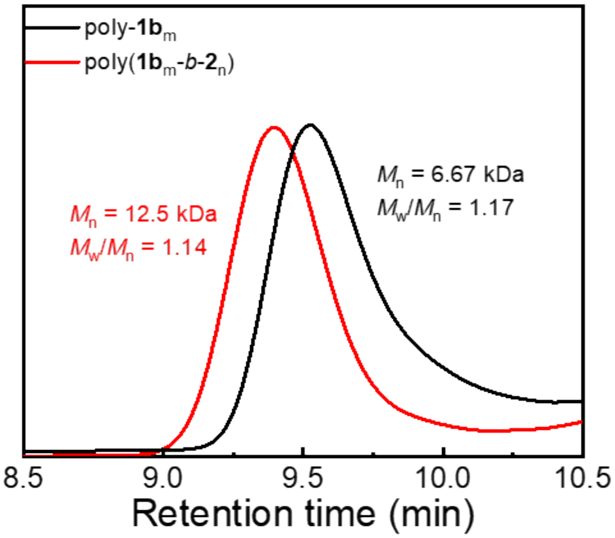


Figure S16. SEC chromatograms of poly-$\mathbf{1b}_{\mathrm{m}}$, and poly($\mathbf{1b}_{\mathrm{m}}$-*b*-$\mathbf{2}_{\mathrm{n}}$).

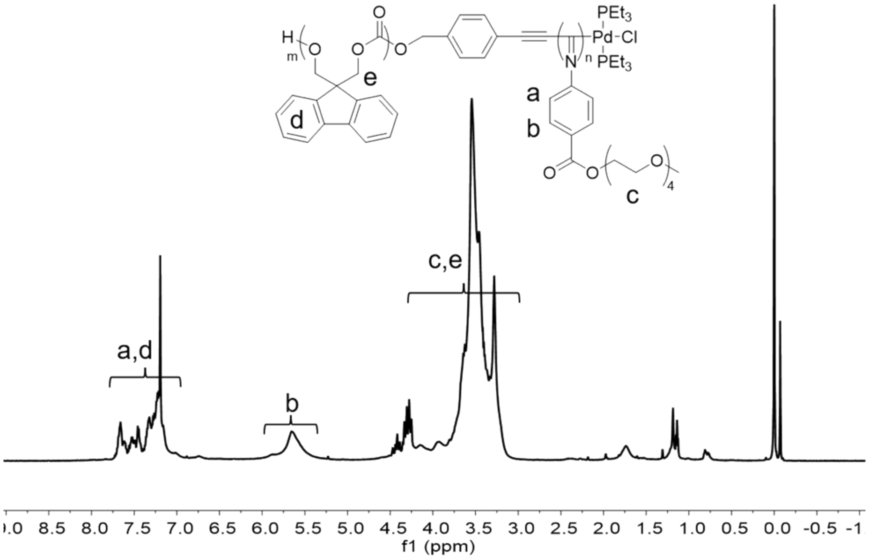


Figure S17. ^{1}H NMR (600 MHz) spectrum of poly($\mathbf{1b}_m$-b-$\mathbf{2}_n$) for stepwise measured in $CDCl_3$ at 25 °C.

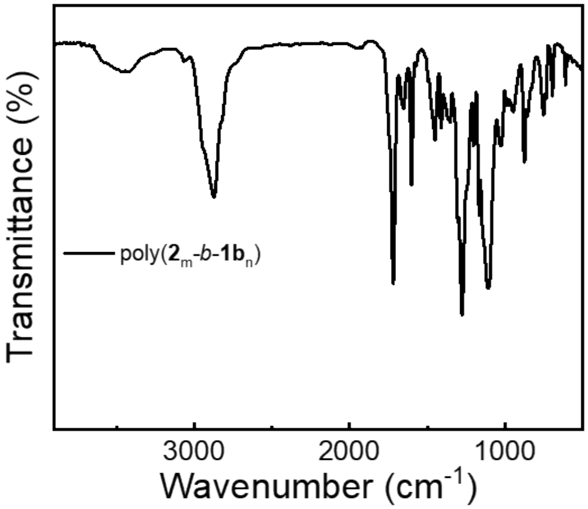


Figure S18. FT-IR spectra of poly($\mathbf{1b}_m$-b-$\mathbf{2}_n$) for stepwise measured at 25 °C using KBr pellets.

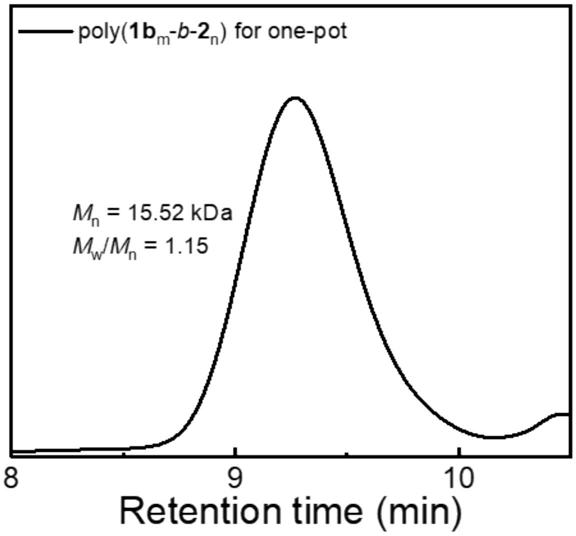


Figure S19. SEC chromatograms of poly(**1b**$_m$-*b*-**2**$_n$) for one-pot.

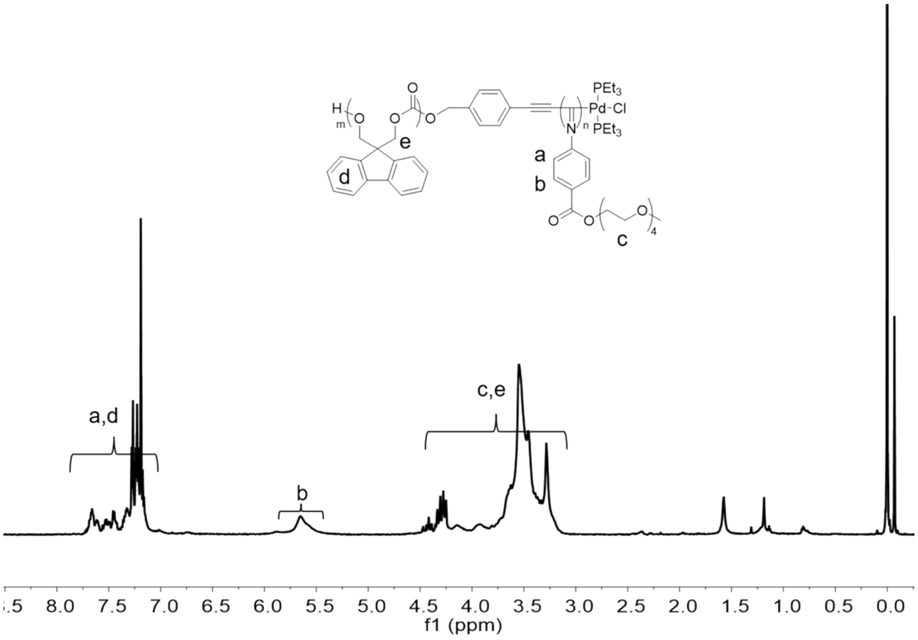


Figure S20. ^{1}H NMR (600 MHz) spectrum of poly(**1b**$_m$-*b*-**2**$_n$) for one-pot measured at 25 °C using KBr pellets.

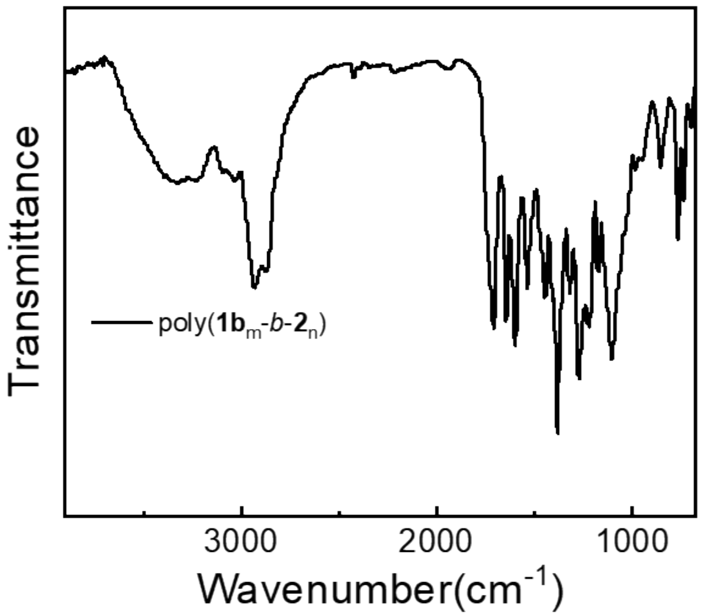


Figure S21. FT-IR spectra of poly($\mathbf{1b}_m$-*b*-$\mathbf{2}_n$) for one-pot measured at 25 °C using KBr. pellets.

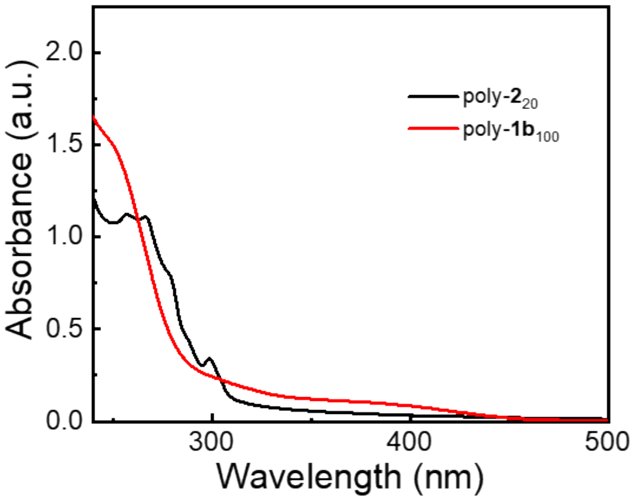


Figure S22. UV-vis spectra of poly-$\mathbf{1b}_{100}$ and poly-$\mathbf{2}_{20}$ in THF (*c* = 0.2 mg/mL).

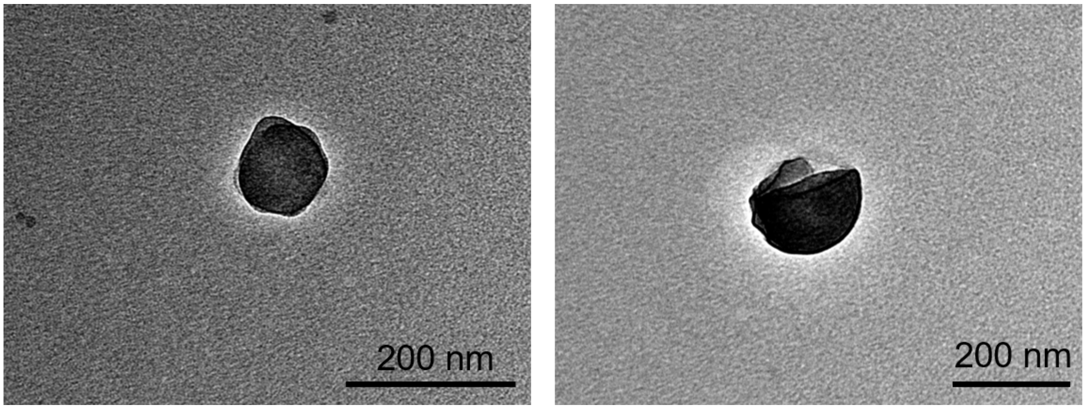


Figure S23. The higher magnification TEM images of poly($\mathbf{1b}_{100}$-*b*-$\mathbf{2}_{20}$) self-assembly in pure MeOH.

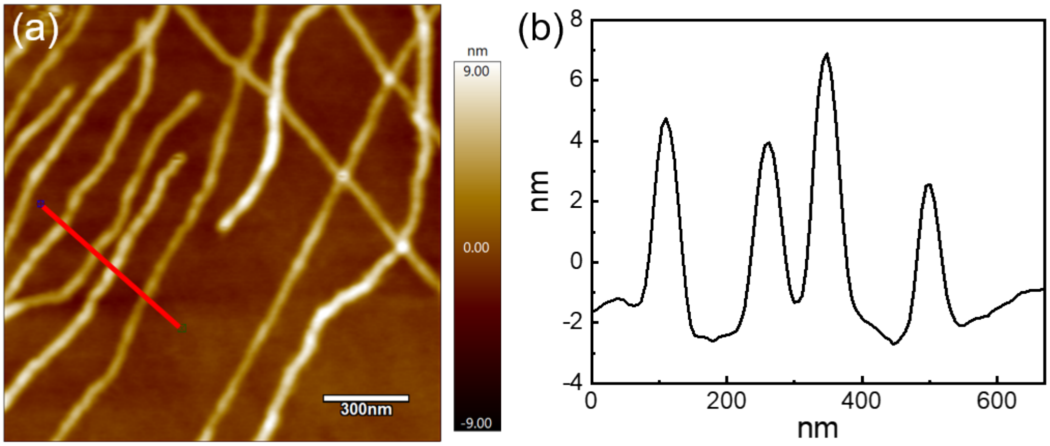


Figure S24. (a) AFM height image of poly($\mathbf{1b}_{100}$-*b*-$\mathbf{2}_{20}$) self-assembly in THF/MeOH (2/8, v/v). (b) The plot shows the AFM height profile along the red line.

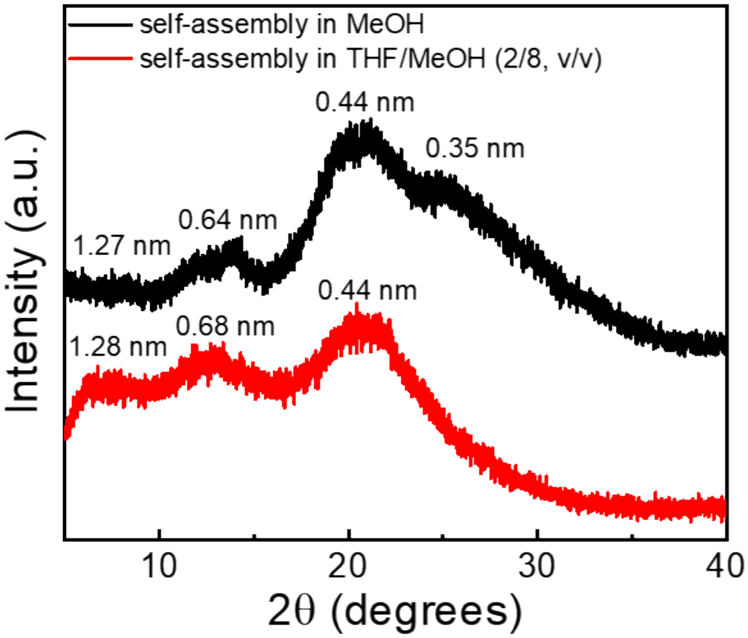


Figure S25. WAXS patterns of poly($\mathbf{1b}_{100}$-*b*-$\mathbf{2}_{20}$) in MeOH and THF/MeOH (2/8, v/v). The thin film samples were prepared by spin-coating the poly($\mathbf{1b}_{100}$-*b*-$\mathbf{2}_{20}$) solution in MeOH and THF/MeOH (2/8, v/v) onto a silicon substrate, respectively.

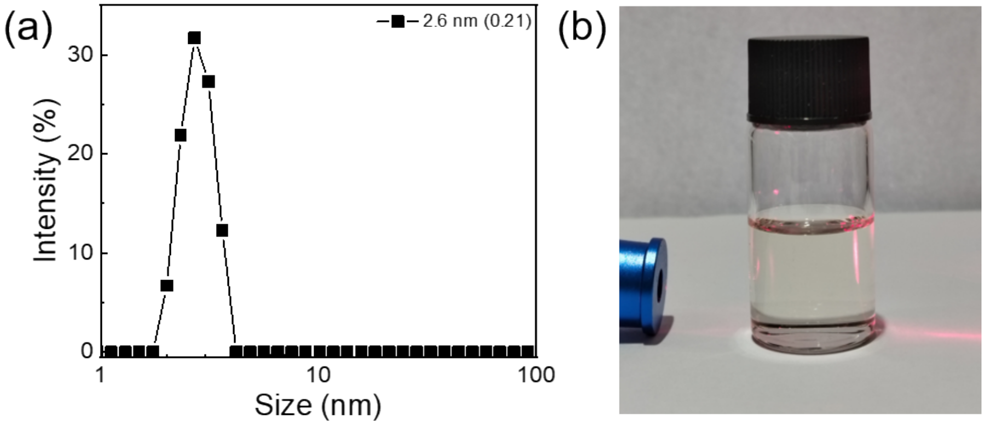


Figure S26. (a) DLS of poly($\mathbf{1b}_{100}$-*b*-$\mathbf{2}_{20}$) and poly-$\mathbf{2}_{20}$ blends in THF solution. (b) Photograph of the poly($\mathbf{1b}_{100}$-*b*-$\mathbf{2}_{20}$) and poly-$\mathbf{2}_{20}$ blends in THF solution targeted with a laser pen.

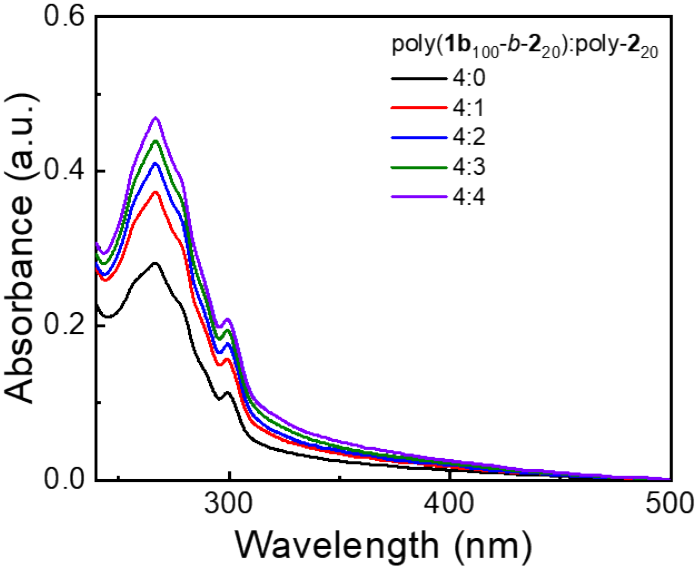


Figure S27. UV-vis poly($\mathbf{1b}_{100}$-*b*-$\mathbf{2}_{20}$) and poly-$\mathbf{2}_{20}$ blends with different mass ration in THF/MeOH (2/8, v/v).

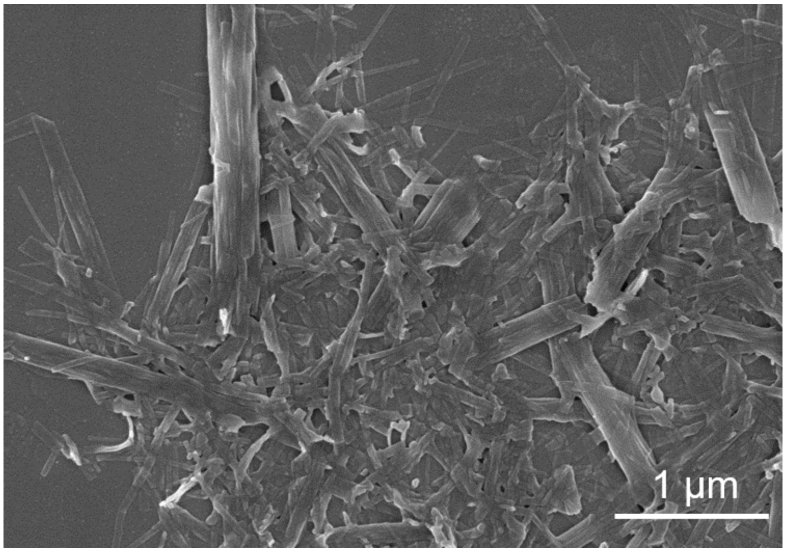


Figure S28. SEM images of 2D nanoribbons self-assembled from poly($\mathbf{1b}_{100}$-*b*-$\mathbf{2}_{20}$)-to-poly-$\mathbf{2}_{20}$ with mass ratios 4:5 in THF/MeOH (v/v = 2/8) solution.

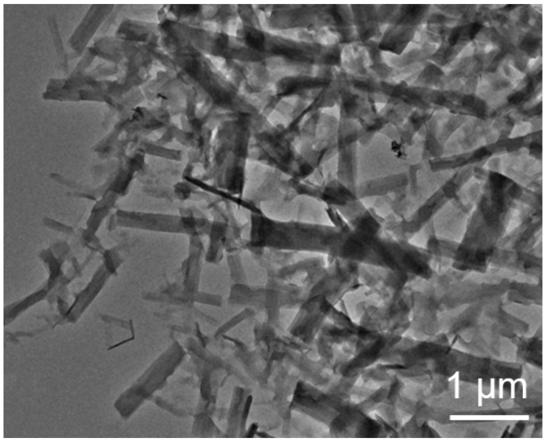


Figure S29. TEM images of the 2D nanoribbon with poly($\mathbf{1b}_{100}$-*b*-$\mathbf{2}_{20}$) and poly-$\mathbf{2}_{20}$ 4 : 4 mass ratio blended solution self-assembly in THF/MeOH (2/8, v/v) (c = 0.2 mg/mL).

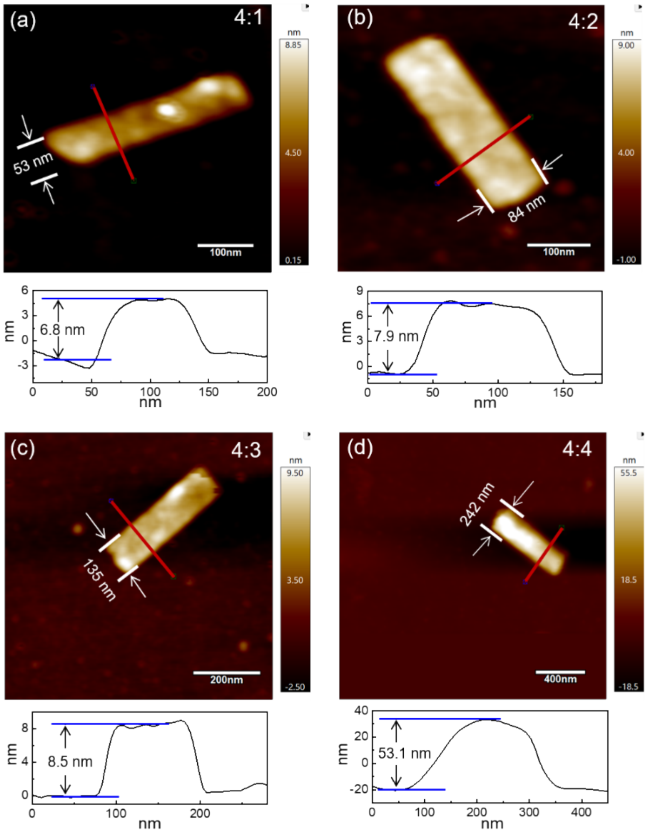


Figure S30. AFM height images and height profile along the red line of 2D nanoribbon with poly($\mathbf{1b}_{100}$-*b*-$\mathbf{2}_{20}$) and poly-$\mathbf{2}_{20}$ mass ratio of 4: 1 (a), 4: 2 (b), 4: 3 (c), and 4: 4 (d).

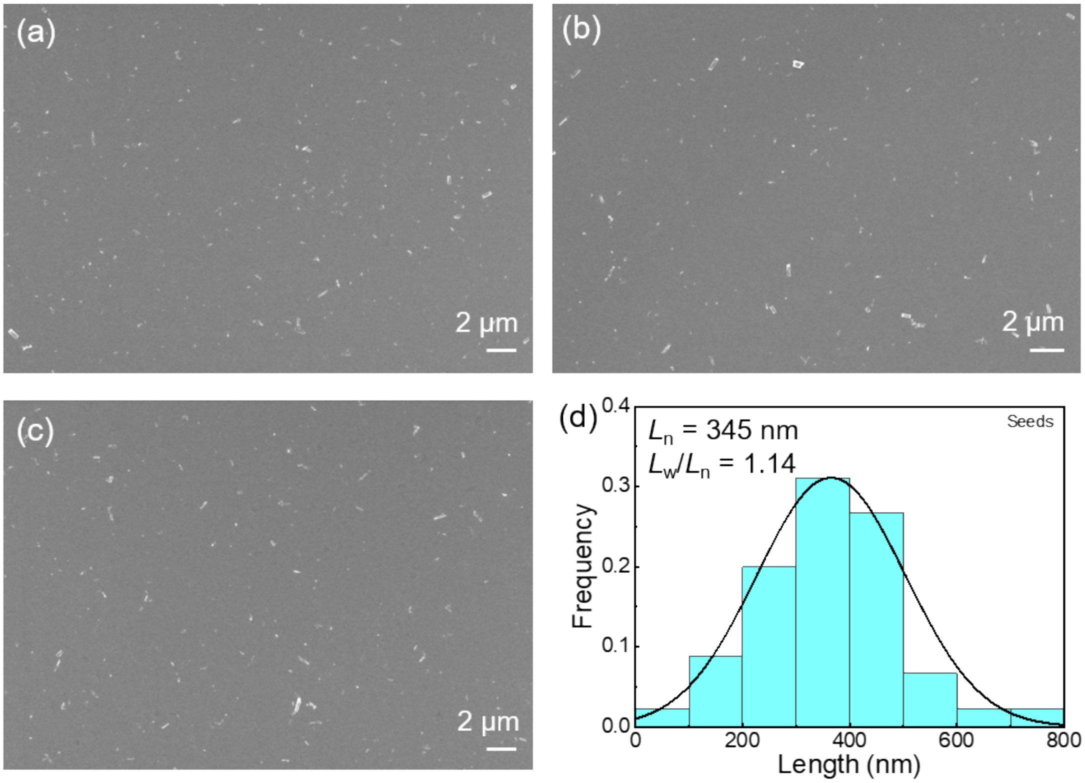


Figure S31. Low-magnified SEM images of seed micelle.

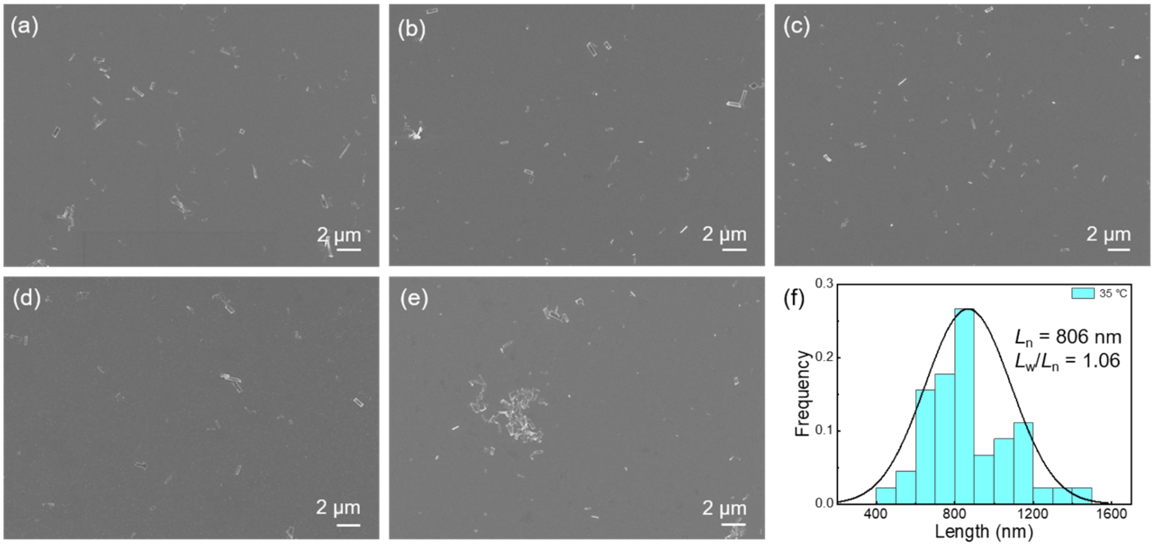


Figure S32. Low-magnified SEM images of self-seeding process by annealing under 35 °C.

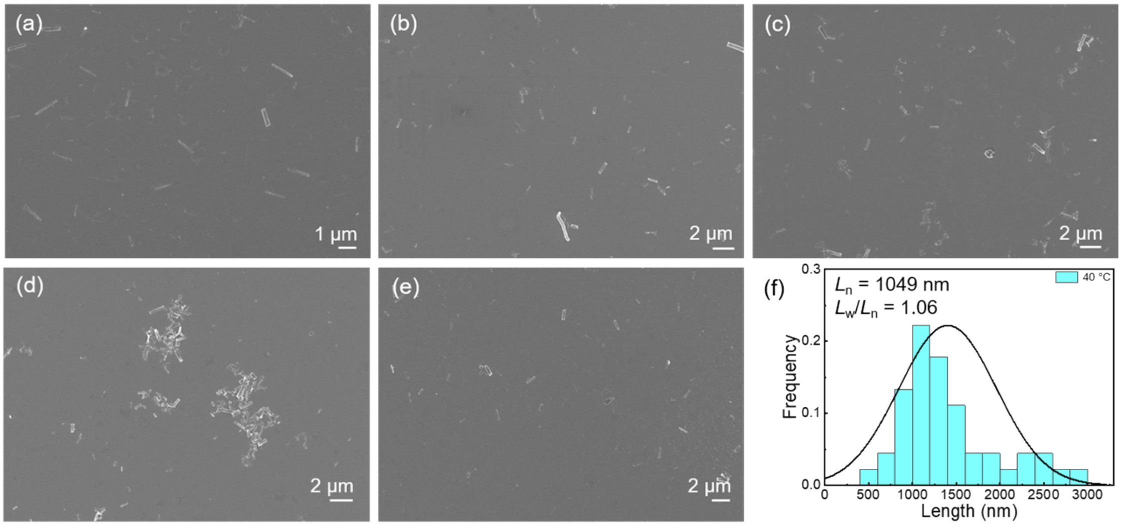


Figure S33. Low-magnified SEM images of self-seeding process by annealing under 40 °C.

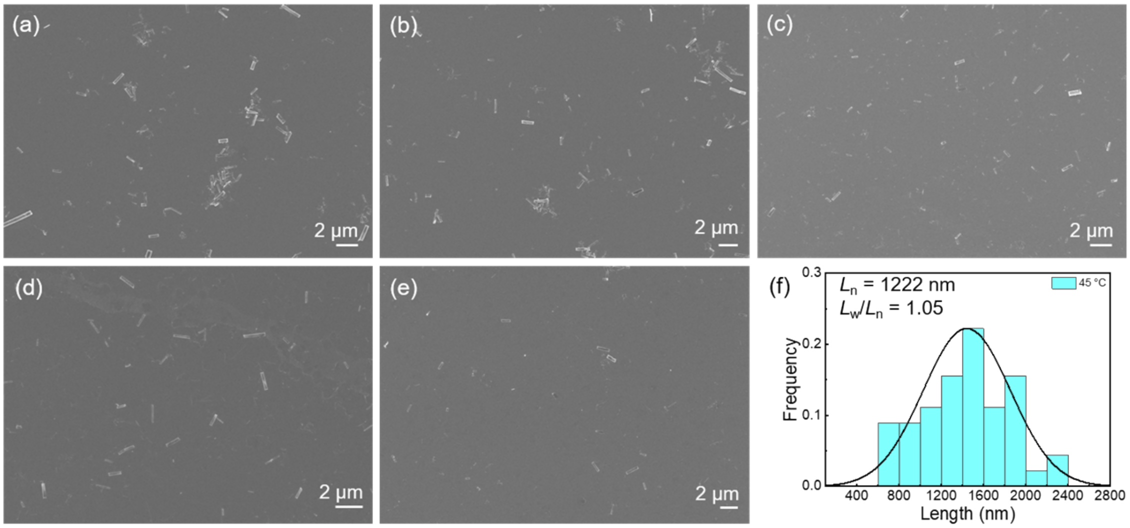


Figure S34. Low-magnified SEM images of self-seeding process by annealing under 45 °C.

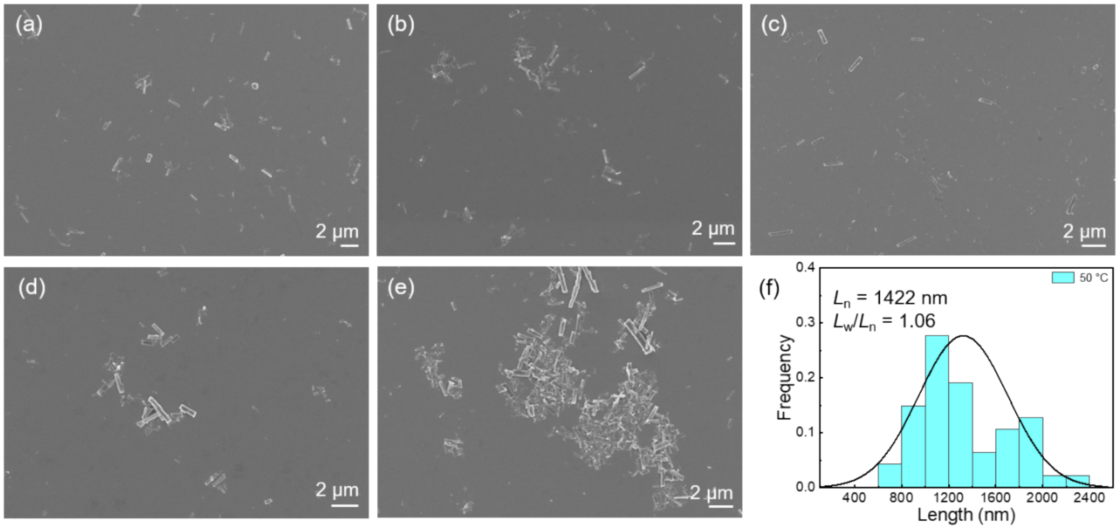


Figure S35. Low-magnified SEM images of self-seeding process by annealing under 50 °C.

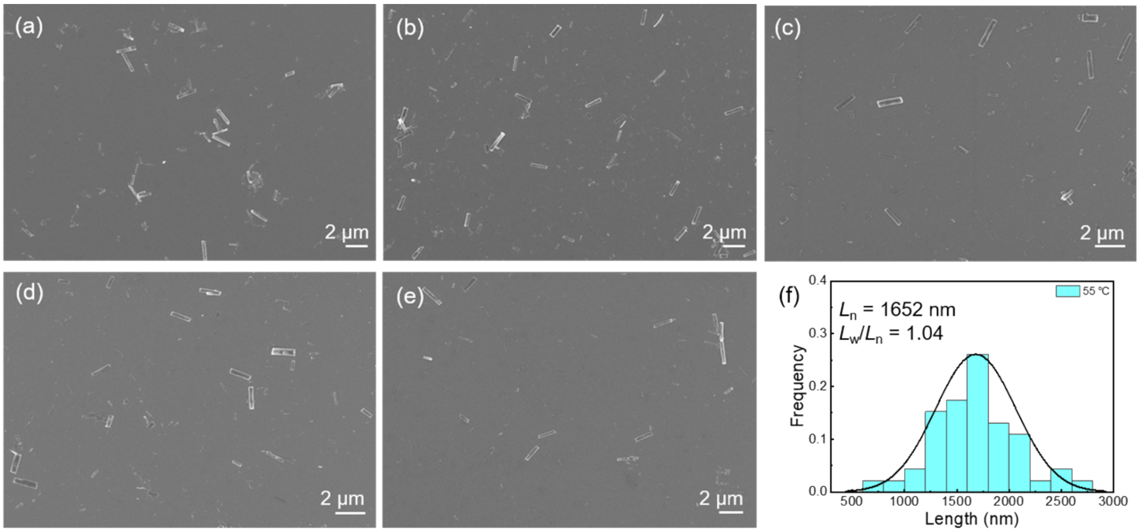


Figure S36. Low-magnified SEM images of self-seeding process by annealing under 55 °C.

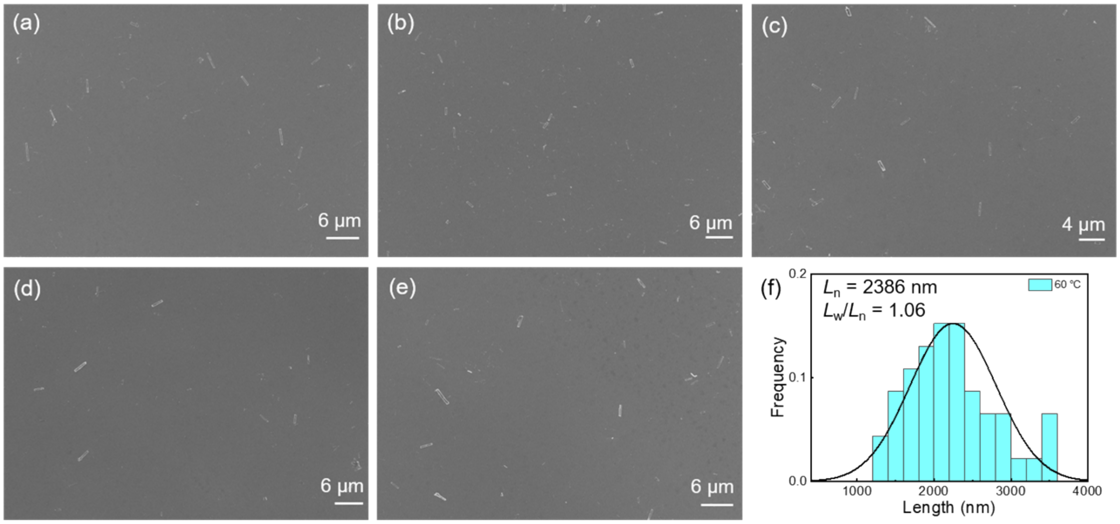


Figure S37. Low-magnified SEM images of self-seeding process by annealing under 60 °C.

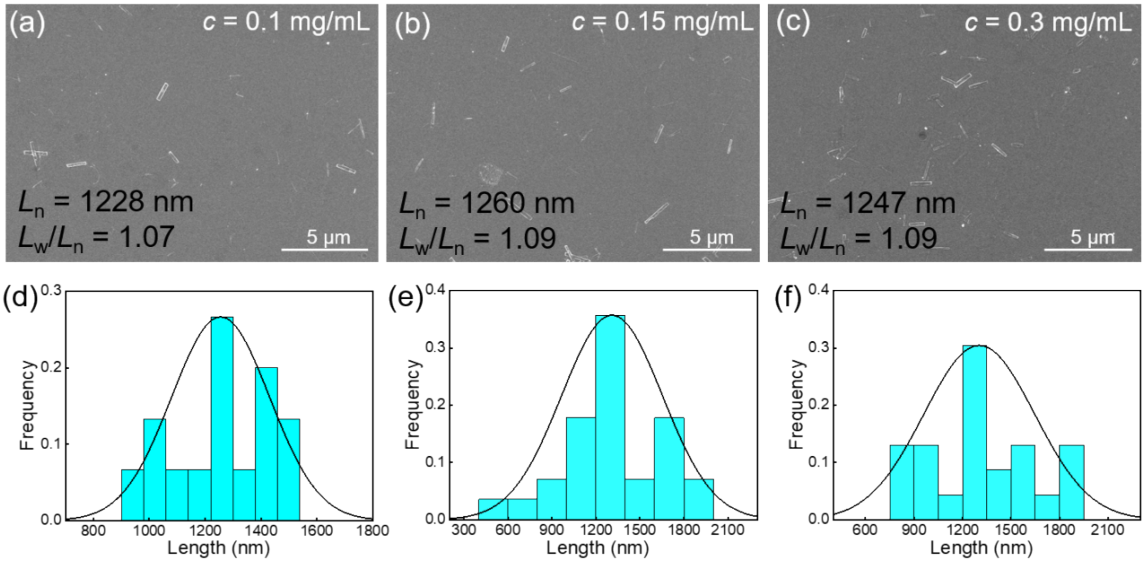


Figure S38. Low-magnified SEM images (a-c) and length distribution histograms (d-f) of self-seeding process with different seed concentrations by annealing under 45 °C.

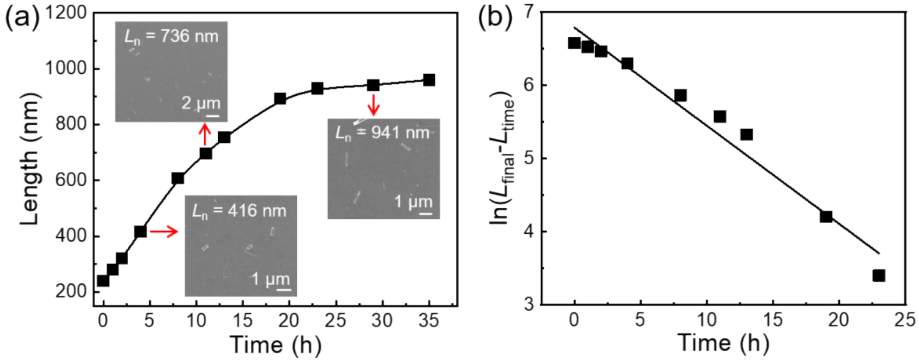


Figure S39. (a) Plots of 2D nanoribbon length over time by self-seeding process under annealing temperature at 40 °C. (b) Polt of ln(L_{final}-L_{time}) versus time from the first-order growth of self-seeding process under annealing temperature at 40 °C.

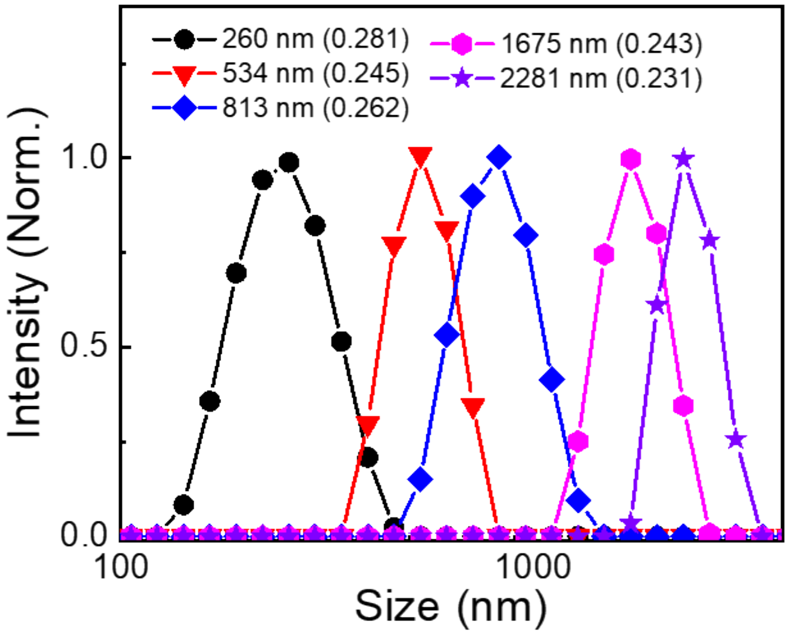


Figure S40. DLS of self-seeding process by different annealing temperature of poly($\mathbf{1b}_{100}$-*b*-$\mathbf{2}_{20}$) and poly-$\mathbf{2}_{20}$ 4 : 4 mass ratio blended solution self-assembly in THF/MeOH (2/8, v/v) (*c* = 0.2 mg/mL).

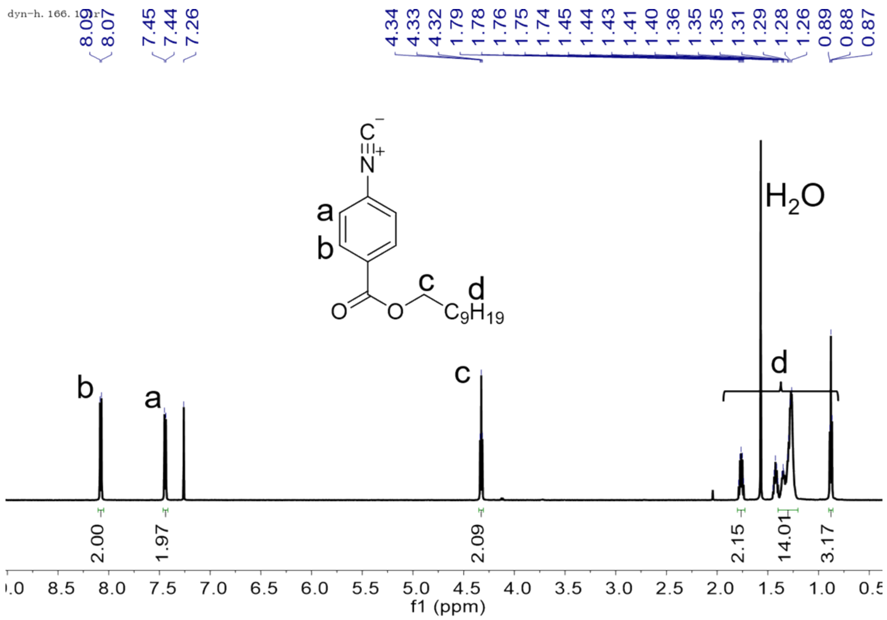


Figure S41. ^{1}H NMR (600 MHz) spectrum of **1a** measured in $CDCl_3$ at 25 °C.

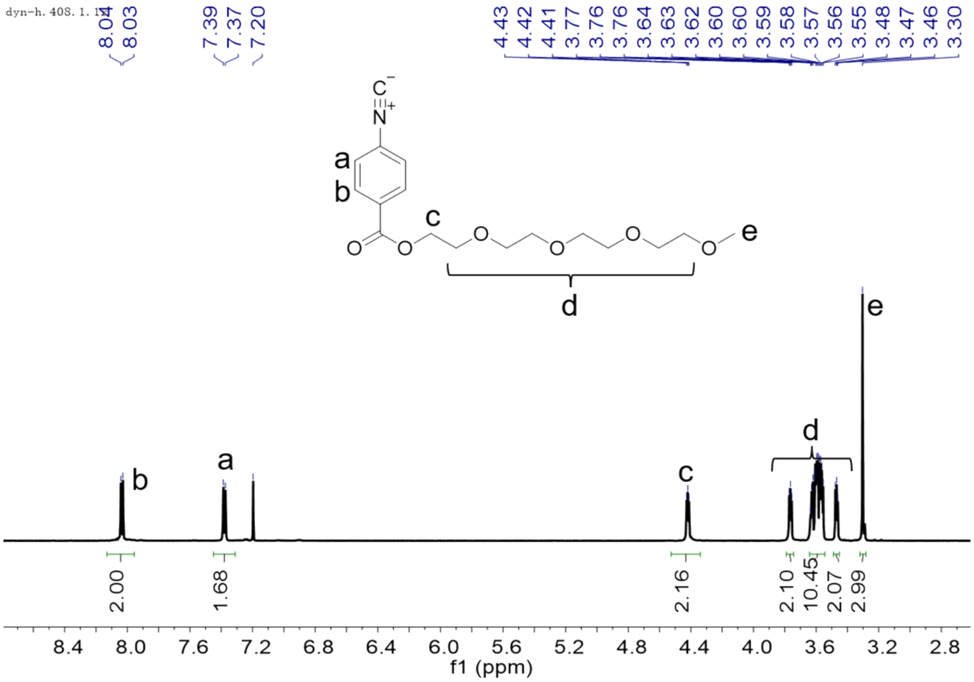


Figure S42. ^{1}H NMR (600 MHz) spectrum of monomer **1b** measured in $CDCl_3$ at 25 °C.

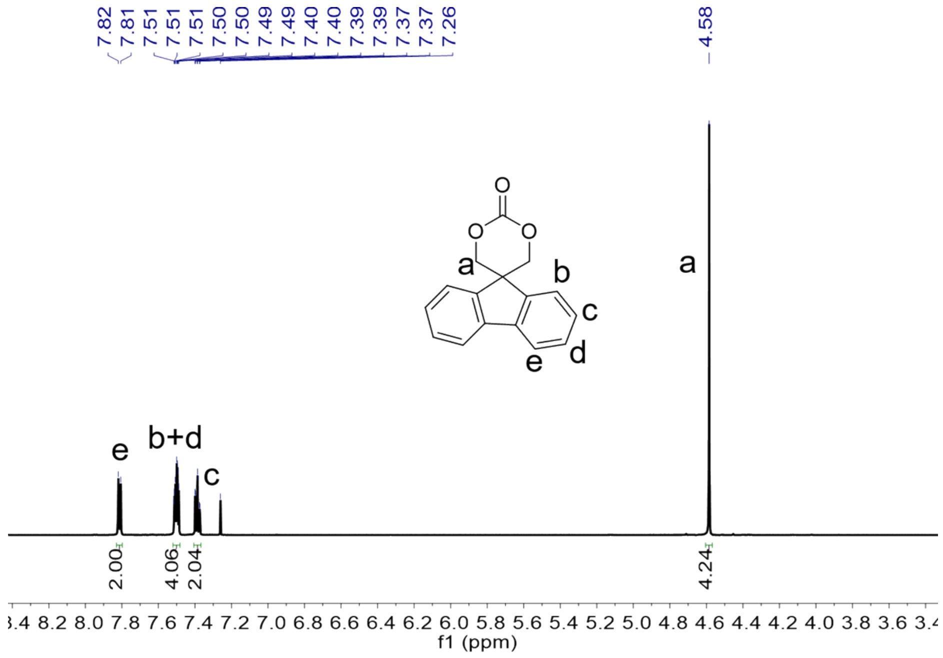


Figure S43. ^{1}H NMR (600 MHz) spectrum of **2** measured in $CDCl_3$ at 25 °C.

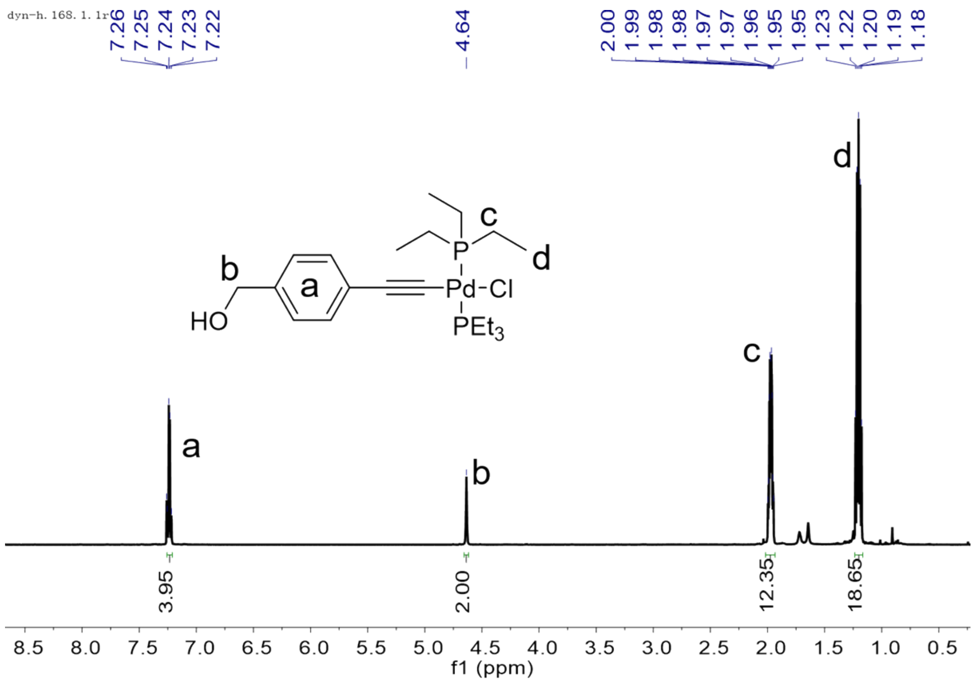


Figure S44. ^{1}H NMR (600 MHz) spectrum of Pd(II)-OH measured in $CDCl_3$ at 25 °C.

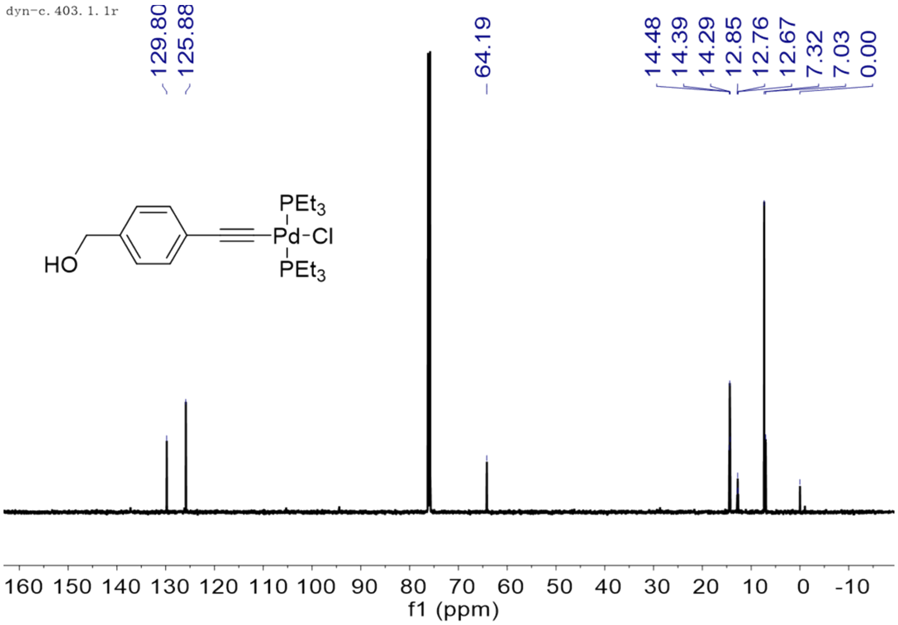


Figure S45. ^{13}C NMR (150 MHz) spectrum of Pd(II)-OH measured in $CDCl_3$ at 25 °C.

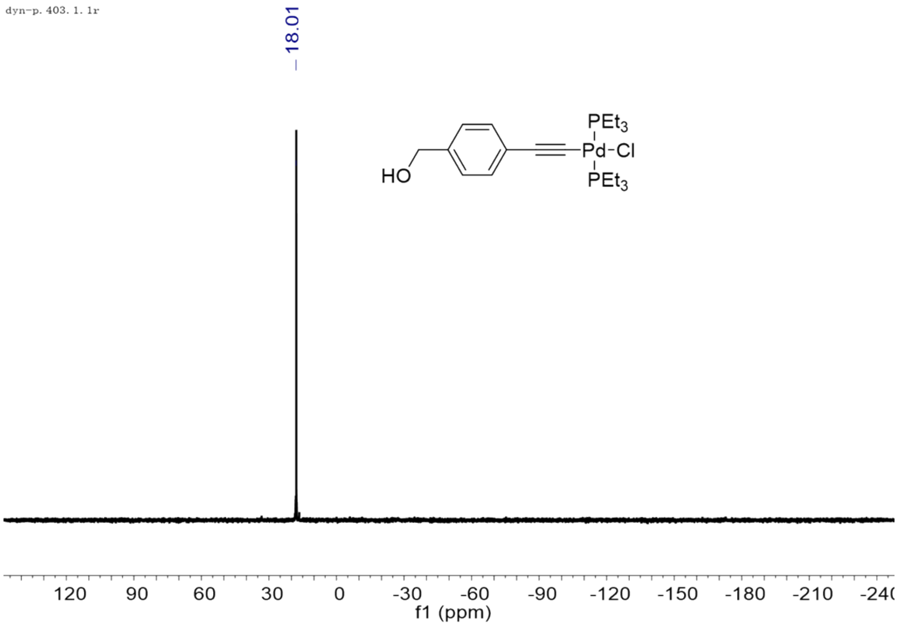


Figure S46. ^{31}P NMR (243 MHz) spectrum of Pd(II)-OH measured in $CDCl_3$ at 25 °C.

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