

Supporting Information

Side-Chain Functionalized Supramolecular Helical Brush

Copolymers

Ru Deng,^a Chengyuan Wang,^a Margarita Milton,^a Danni Tang,^a Andrew D. Hollingsworth,^b and Marcus Weck^{*a}

^aDepartment of Chemistry and Molecular Design Institute, New York University, New York, NY 10003, United States

^bDepartment of Physics and Center for Soft Matter Research, New York University, New York, NY 10003, United States

*Marcus.weck@nyu.edu

Table of Contents

1. Materials and Methods	2
2. Synthetic Procedures	5
2.1. Synthesis of achiral, pyridine functionalized isocyanide monomer (5)	5
2.2. Metal catalyzed controlled isocyanide polymerization	7
2.3. Synthesis of Pd-Pin and Pd-Pin-PS	11
3. Supramolecular Assembly	16
3.1. General procedures	16
3.2. Supramolecular assembly of co-PIC with Pd-Pin small molecule analog	16
3.3. Supramolecular brush copolymer assembly of co-PIC with Pd-Pin-PS	18
4. AFM results	21
5. WAXS results	22
References	23

1. Materials and Methods

All reagents were purchased from Sigma-Aldrich, Acros Organics, TCI Chemical or Alfa Aesar and used without further purification unless otherwise mentioned.

^1H NMR spectra were recorded at 25 °C on Bruker Avance 400 or 600 MHz spectrometers. ^{13}C NMR spectra were recorded on Bruker 150 MHz or 126 MHz spectrometers with complete proton decoupling. Chemical shifts for protons are reported in parts per million (ppm) downfield from tetramethylsilane as reference to the residual proton in the NMR solvent (CHCl_3 : δ 7.26 ppm; CH_2Cl_2 : δ 5.32 ppm). Chemical shifts for carbon are reported in ppm downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (CDCl_3 : δ 77.16 ppm; CH_2Cl_2 : δ 53.84 ppm). All chemical shifts are reported as singlet (s), broad singlet (br s), doublet (d), broad doublet (br d), doublet of doublets (dd), triplet (t), broad triplet (br t), quartet (q) and unresolved multiplet (m).

Quantitative ^{13}C NMR measurements were performed on a Bruker Avance 600 MHz spectrometer with cryo probe, with 36 kHz spectral width, 1024 transients, 2.0 s acquisition time and a 45 s relaxation delay. Spectra were obtained with inverse gated WALTZ-16 proton decoupling. The resulting data were zero filled to 512K and exponentially weighted with 1 Hz line broadening. The measured sample was dissolved in CD_2Cl_2 at 6.0 wt%.

Gel-permeation chromatography (GPC) characterizations were obtained from a Shimadzu pump coupled to Shimadzu UV and RI detectors with dimethylformamide (DMF) with LiCl (0.03 M) as the mobile phase. The injection volume was 50 μL and the flow rate was 1 mL/min on an American Polymer Standards column set (100, 1000, 100,000 Å, linear mixed bed). The GPC instrument were calibrated using poly(styrene) standards (EasiCal, Agilent Technologies, Santa

Clara, CA) and characterizations were carried out at 55 °C. M_w , M_n and \bar{D} represent weight-average molecular weight, number-average molecular weight and polydispersity, respectively.

Viscometry measurements were carried out with a Cannon-Ubbelohde Semi-Micro viscometer (9722-G59) in a 25 °C water bath. Polymer samples were dissolved in chloroform at the initial concentration of 25 g/L and were subject to dissolution by adding chloroform into the viscometer. The viscometer loaded with solution was placed vertically in the water bath and held still for five minutes for temperature equilibrium prior to each measurement. The solution was directed to the measurement bulb by applying suction at the top. Measurement started by allowing the solution to move freely from the measurement bulb to the reservoir, and time required for the solution to pass the top mark and reach the bottom mark of the measurement bulb was recorded. Each measurement was repeated for at least five times.

LCMS results were obtained on an Agilent 6224 TOF LC/MS Mass spectrometer with electrospray ionization (ESI) method.

IR spectra were obtained on a Nicolet 6700 FTIR spectrometer using attenuated total reflectance (ATR) mode. 64 scans from 600 to 4000 cm^{-1} were taken with background absorbance correction.

UV-Vis spectroscopy was performed on a Cary 100 UV-Vis spectrometer from 600 to 180 nm at scanning speed of 100 nm/min, with quartz cells (path length 1 cm) with two polished sides. Samples were dissolved in HPLC/UV grade dichloroethane (DCE) and measured at 25 °C.

Circular dichroism (CD) spectra were collected with a Jasco J-1500 CD spectrometer. The spectra were obtained with a quartz cuvette ($l = 0.2$ cm) in DCE at 25 °C. All homopolymer samples were prepared in DCE at 7.5 μM . Polymer supramolecular assemblies were prepared so that the relative concentration of the helical polymer in solution was equal to 7.5 μM .

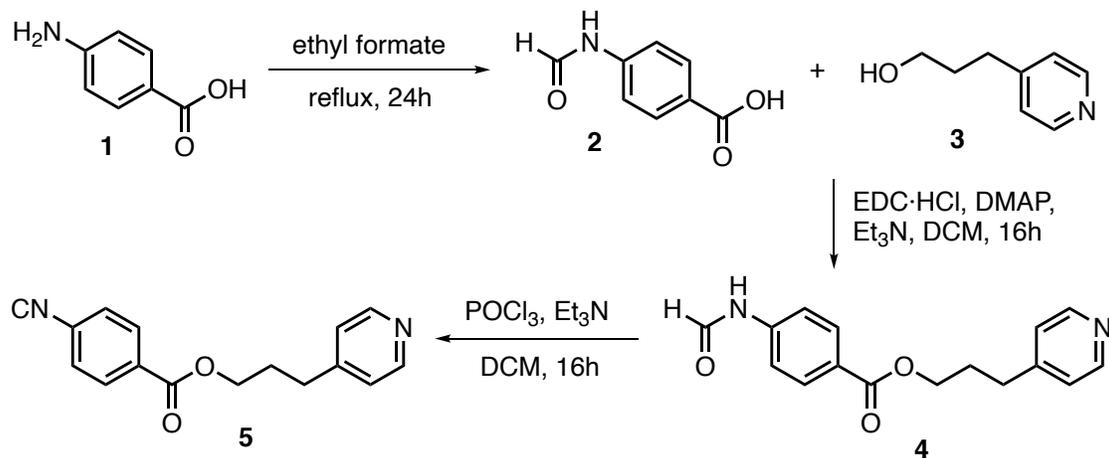
Dynamic light scattering (DLS) studies were performed at 25 °C using an LS spectrometer (goniometer-based, multi-angle static and dynamic light scattering instrument) from LS Instruments, fitted with a 660 nm laser at various scattering angles (140, 90, 40 and 30 degrees). Samples were dissolved in HPLC grade DMSO at concentration of ~5 mg / mL and passed through 0.45 µm syringe filter prior to measurement. Average hydrodynamic diameters were calculated by fitting the DLS correlation function using the CONTIN routine. DLS results for the polystyrene analytical standard ($M_w = 3,680$) were compared to the correlations from published literature.¹

Atomic force microscopy (AFM) measurements were performed with a Bruker Multimode 8 AFM using ScanAsyst-Air-HR probes on silicon nitride cantilevers with a spring constant of 0.4 N/m (rectangular tip, 60 µm length, 20 µm width). All characterizations were done with Bruker ScanAsyst Mode. The polymer samples were dissolved in acetone (0.2 mg/mL) and mounted on silicon wafers that were supported on AFM specimen disks.

X-ray diffraction data was obtained on a Bruker D8 DISCOVER GADDS microdiffractometer equipped with a VANTEC-2000 area detector. X-rays were generated with a sealed Cu tube, monochromated by a graphite crystal, and collimated by a 0.5 mm MONOCAP ($\lambda = 1.54178 \text{ \AA}$). Samples were mounted onto silicon wafers by slow evaporation of polymer solutions (1mg/mL in DCM). Data was collected at room temperature for 30 minutes with $\theta_1 = 11^\circ$, $\theta_2 = 13^\circ$.

2. Synthetic Procedures

2.1. Synthesis of achiral, pyridine functionalized isocyanide monomer (5).



Scheme S1. Synthetic route towards the achiral, pyridine functionalized isocyanide monomer **5**.

4-Formamidobenzoic acid (2) was synthesized according to published records.²

3-(Pyridin-4-yl)propyl 4-formamidobenzoate (4). 1.0 g (7.3 mmol) of **2** and 1.2 g (7.3 mmol) of 3-(pyridin-4-yl)propan-1-ol (**3**) were added to 60 mL dry DCM. The solution was cooled to 0 °C and mixed with 1.34 g (11 mmol) of DMAP. Then, 2.8 g (14.6 mmol) EDC·HCl dissolved in DCM were added into the mixture dropwise. The mixture was warmed to room temperature and stirred for 16 hours, resulting in a bright yellow solution. Subsequent washing (H₂O), drying and solvent evaporation yielded an orange oil. Column chromatography with silica gel and ethyl acetate afforded the product as an off-white powder (1.43 g). The product was used for the next step without further purification.

3-(Pyridin-4-yl)propyl 4-isocyanobenzoate (5). Under an Ar atmosphere, formamide **4** (0.64 g, 2.25 mmol) dissolved in 30 mL DCM was added to Et₃N (1.57 mL, 11.25 mmol) and the reaction was cooled to 0 °C. POCl₃ (0.31 mL, 3.38 mmol) was added in one shot. The mixture was stirred for 10 minutes at 0 °C and then stirred overnight at room temperature. The reaction

was quenched by pouring into a large amount of saturated NaHCO₃ (aq.) The mixture was washed with saturated NaHCO₃ (aq.) and brine twice. The organic phase was collected and dried with Na₂SO₄. The crude was obtained by filtration and condensation under vacuum. The product was obtained by silica gel column chromatography as brown crystals. Yield 299.4 mg (50%). The product was mixed with cyclohexane and stored at 0 °C to prevent self-polymerization. ¹H NMR (CD₂Cl₂, 600 MHz) δ (ppm): 8.48 (m, 2H), 8.03 (m, 2H), 7.47 (m, 2H), 7.17 (m, 2H), 4.35 (t, 2H), 2.79 (t, 2H), 2.12 (m, 2H). ¹³C NMR (CD₂Cl₂, 600 MHz) δ (ppm): 167.7, 165.2, 150.6, 150.1, 131.5, 131.1, 126.9, 124.2, 65.0, 32.1, 29.5. HRMS (+ESI): calculated mass for C₁₆H₁₄N₂O₂: 266.1055; found m/z: 267.1123 (M+H)⁺.; difference: 1.85 ppm.

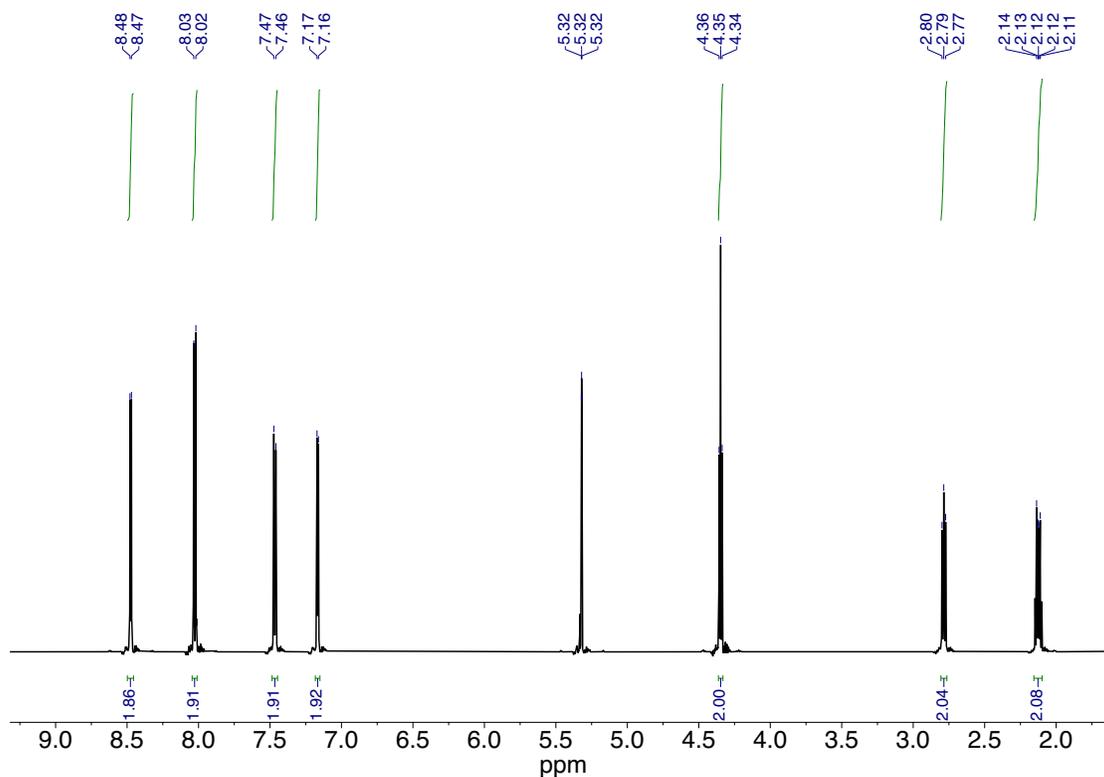


Figure S1. ¹H NMR spectrum of **5** (CD₂Cl₂, 600 MHz).

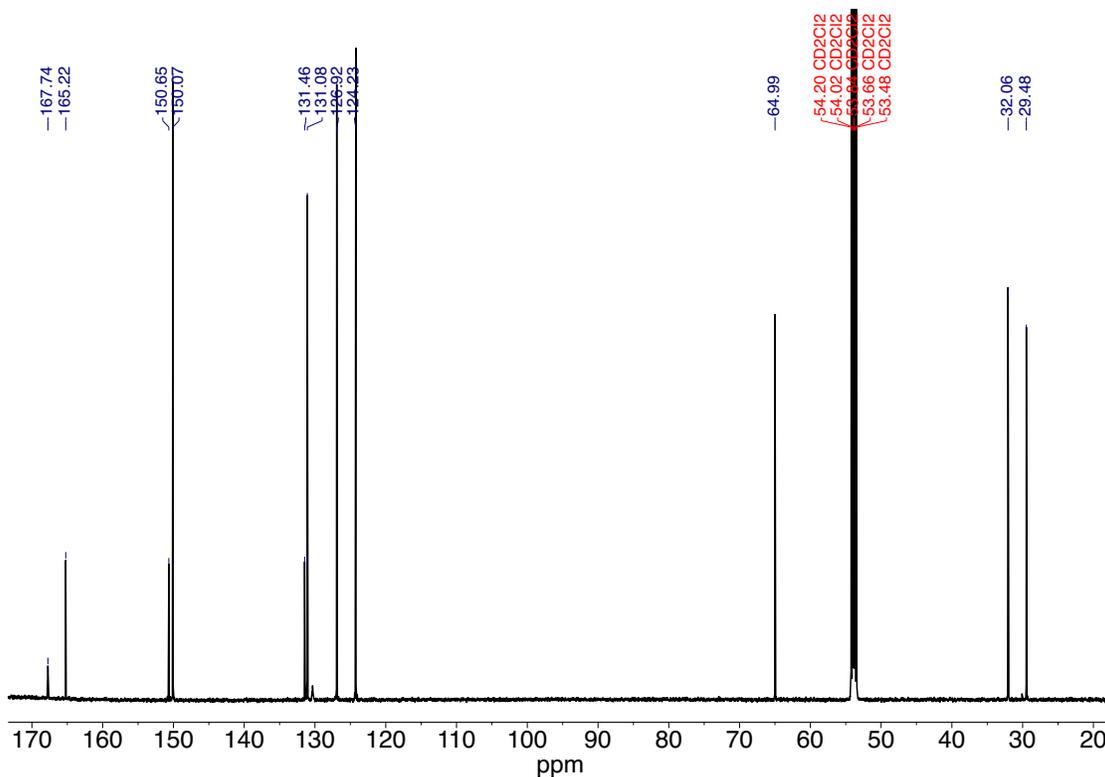
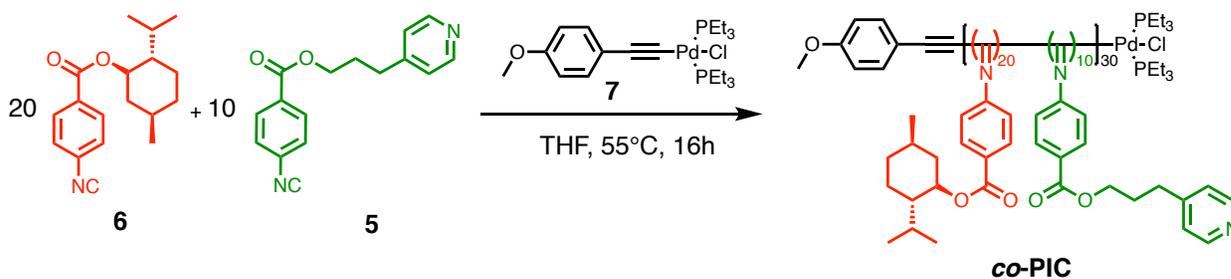


Figure S2. ^{13}C NMR spectrum of **5** (CD_2Cl_2 , 600 MHz).

2.2. Metal catalyzed controlled isocyanide polymerization.



Scheme S2. Synthesis of *co*-PIC via metal catalyzed controlled isocyanide polymerization.

Chiral (1*S*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (**6**) and the palladium anisole initiator (**7**) were prepared according to published protocols.³ **6** was stored as a solution in cyclohexane and was purified by passing through a silica gel plug with hexane/DCM (3:1 v/v) as mobile phase. The monomer was dried under vacuum and polymerized immediately to

prevent unwanted polymerization. 90.3 mg (0.315 mmol) of **6** and 42.0 mg (0.158 mmol) of **5** were dissolved in 1.6 mL anhydrous THF in a Schlenk flask under an Argon flow. The solution was degassed for 20 minutes, followed by the addition of **7** (8.03 mg, 0.0158 mmol) dissolved in a minimum amount of THF. The solution was charged with Ar and heated to 55 °C for 16 hours. Crude polymers were subject to precipitation in an excess amount of cold methanol for at least three times to yield *co*-PIC as a dark brown solid.

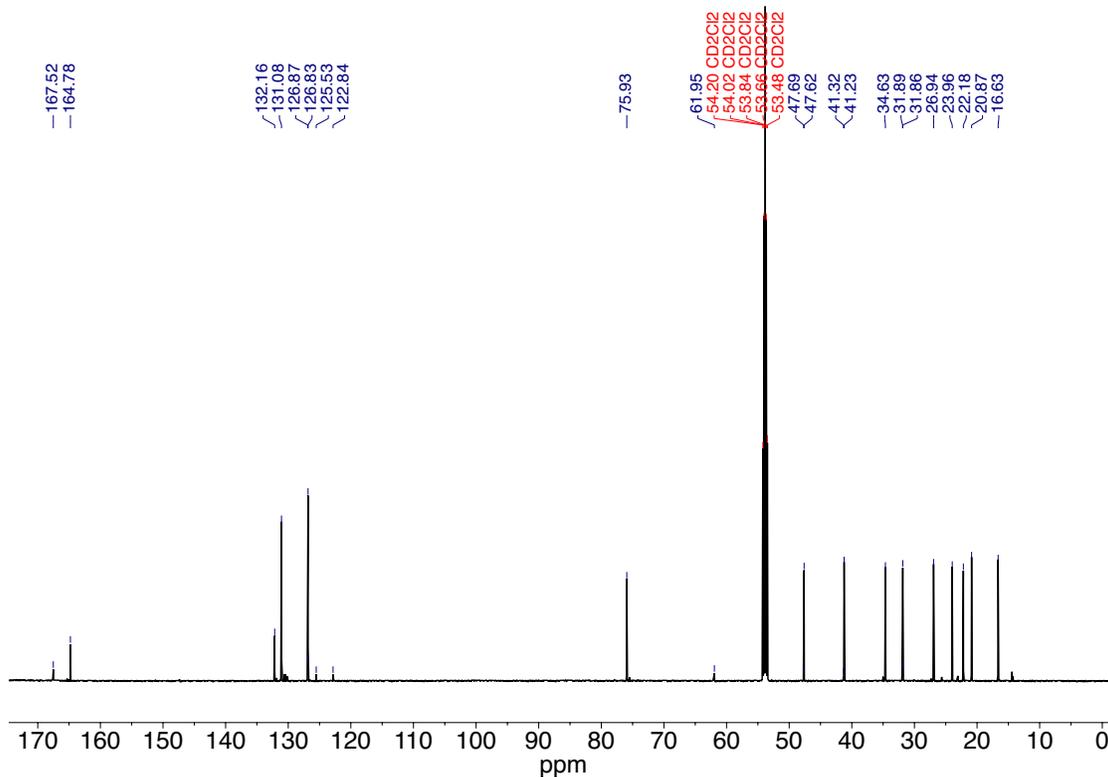


Figure S3. ¹H NMR spectrum of **6** (CD₂Cl₂, 600 MHz).

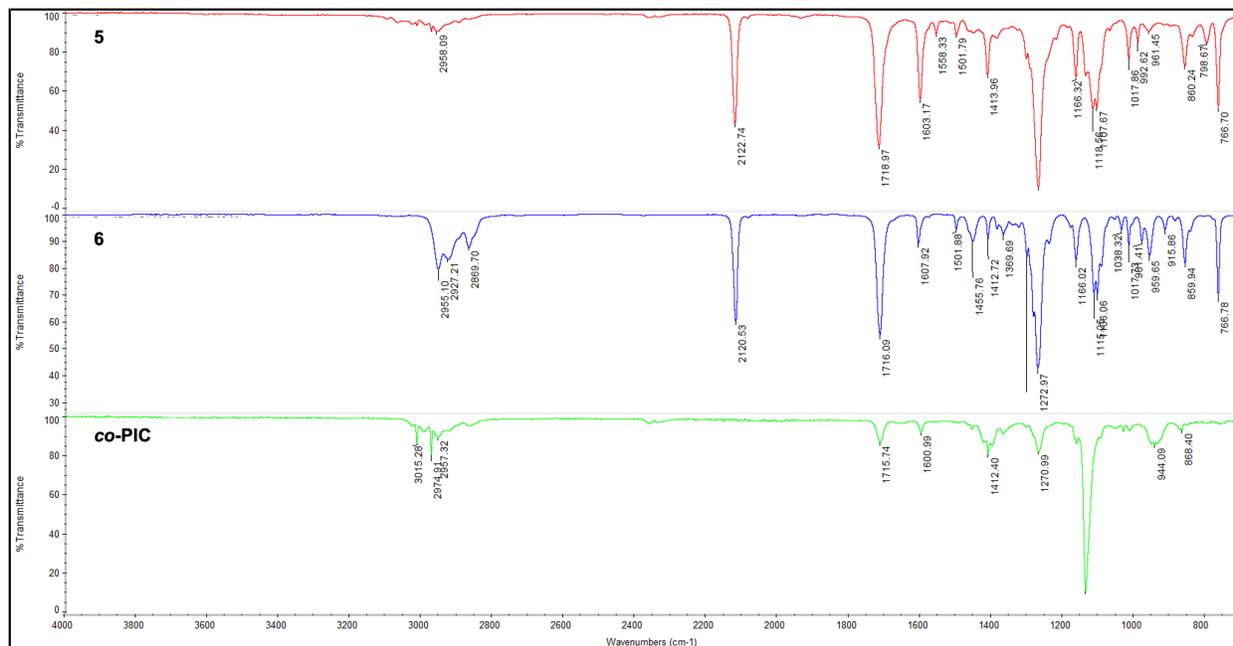


Figure S4. FT-IR spectra of (top to bottom) **5**, **6** and crude *co*-PIC. The disappearance of the isocyanide ν_{CN} band at 2120 cm⁻¹ confirmed complete monomer consumption.

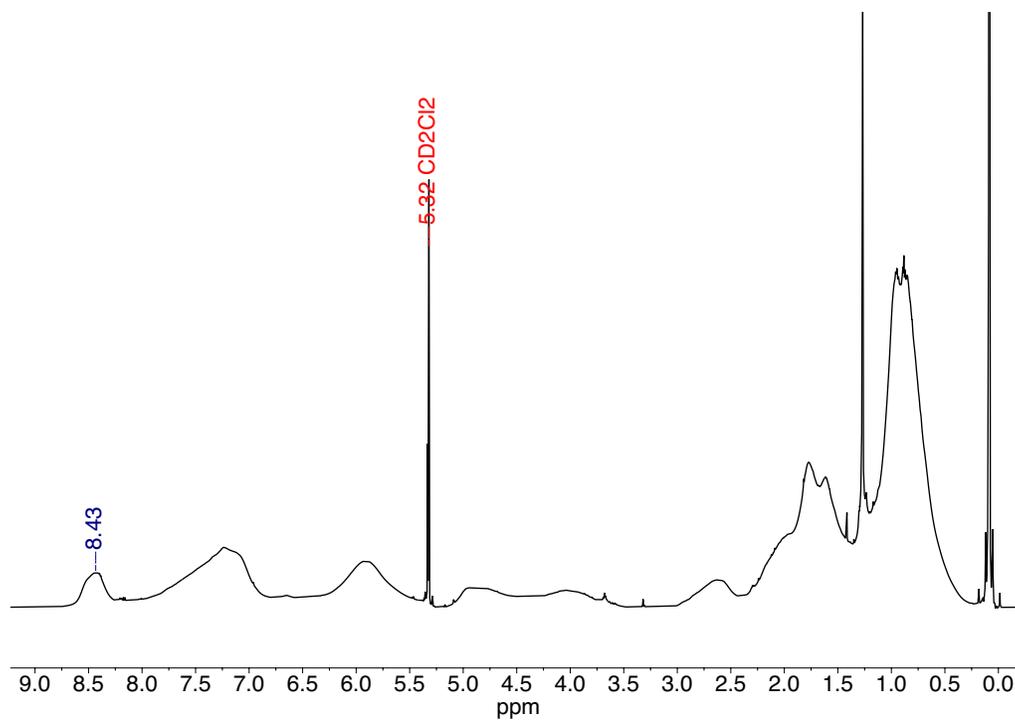


Figure S5. ¹H NMR spectrum of *co*-PIC (CD₂Cl₂, 600 MHz).

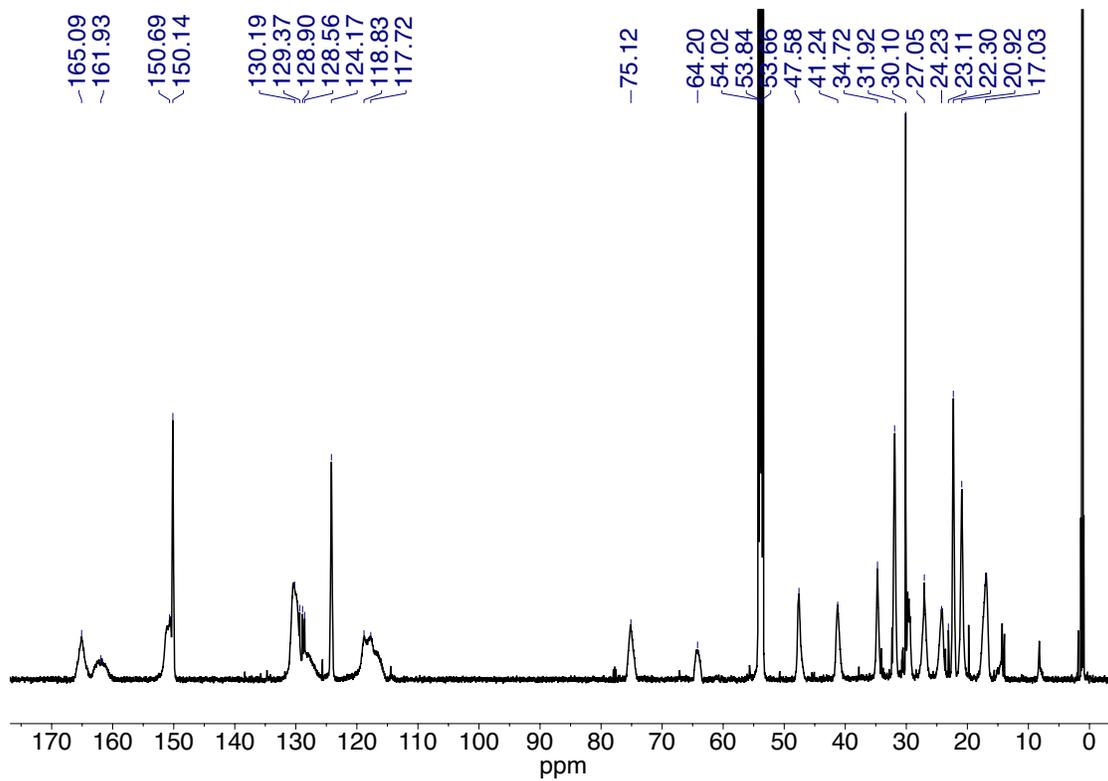


Figure S6. ^{13}C NMR spectrum of *co*-PIC (CD_2Cl_2 , 600 MHz).

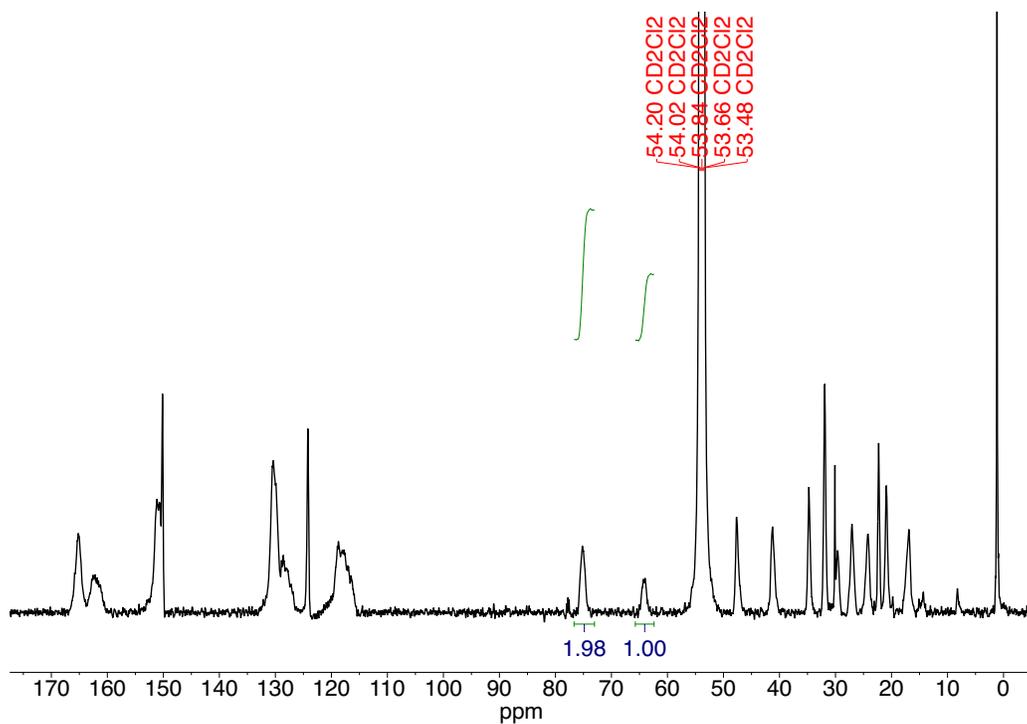
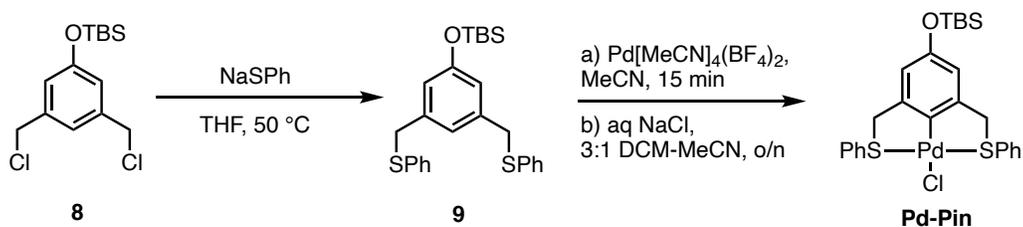


Figure S7. ^{13}C NMR spectrum of *co*-PIC with inverse gated coupling (CD_2Cl_2 , 600 MHz).

2.3.Synthesis of Pd-Pin and Pd-Pin-PS



Scheme S3. Synthetic route towards **Pd-Pin**

Pd-Cl (3,5-bis((phenylthio)methyl)phenoxy)(*tert*-butyl)dimethylsilane (Pd-Pin). **8** was prepared according to reported procedures.⁴ Sodium thiophenolate (8.23 g, 62.5 mmol) was dispersed in anhydrous THF (70 mL) and **8** (4.8 g, 15.8 mmol) dissolved in THF was added to the mixture dropwise at room temperature. The mixture was stirred at 50 °C for 16 hours, followed by THF removal. The suspension was dissolved in DCM and washed with 2M NaOH and H₂O. After solvent removal, crude **9** was isolated as a yellow oil without further purification. Crude ligand **9** (200 mg) dissolved in 12 mL DCM was placed under Argon atmosphere. Pd[MeCN]₄(BF₄)₂ dissolved in 4 mL MeCN was added in one portion to the reaction at room temperature. The solution was stirred for 1 hour followed by pouring into saturated NaCl (50 mL). The mixture was placed at room temperature overnight with vigorous stirring. Then, the Pd-Cl compound was extracted by DCM (50 mL × 3). The combined organic layers were washed with H₂O and dried with Na₂SO₄. Crude product was purified by column chromatography with silica gel and hexane with increasing percentage of ethyl acetate. Resulting Pd-Pin appeared as a yellow solid (64 mg). ¹H NMR (*d*-acetone, 400 MHz) δ (ppm): 7.93 (m, 4H), 7.44 (m, 6H), 6.66 (s, 2H), 4.74 (s, 4H), 0.96 (s, 9H), 0.18 (s, 6H). ¹³C NMR (*d*-acetone, 400 MHz) δ (ppm): 154.1, 151.3, 133.9, 132.9, 132.1, 130.4, 130.3, 115.0, 51.9, 26.0, 18.7, -4.3. HRMS (+ESI): calculated

mass for $C_{26}H_{31}ClOPdS_2Si$: 588.0330; found m/z : 557.0627 (M+H) + (-HCl); compound mass: 588.0334; difference: 0.59 ppm.

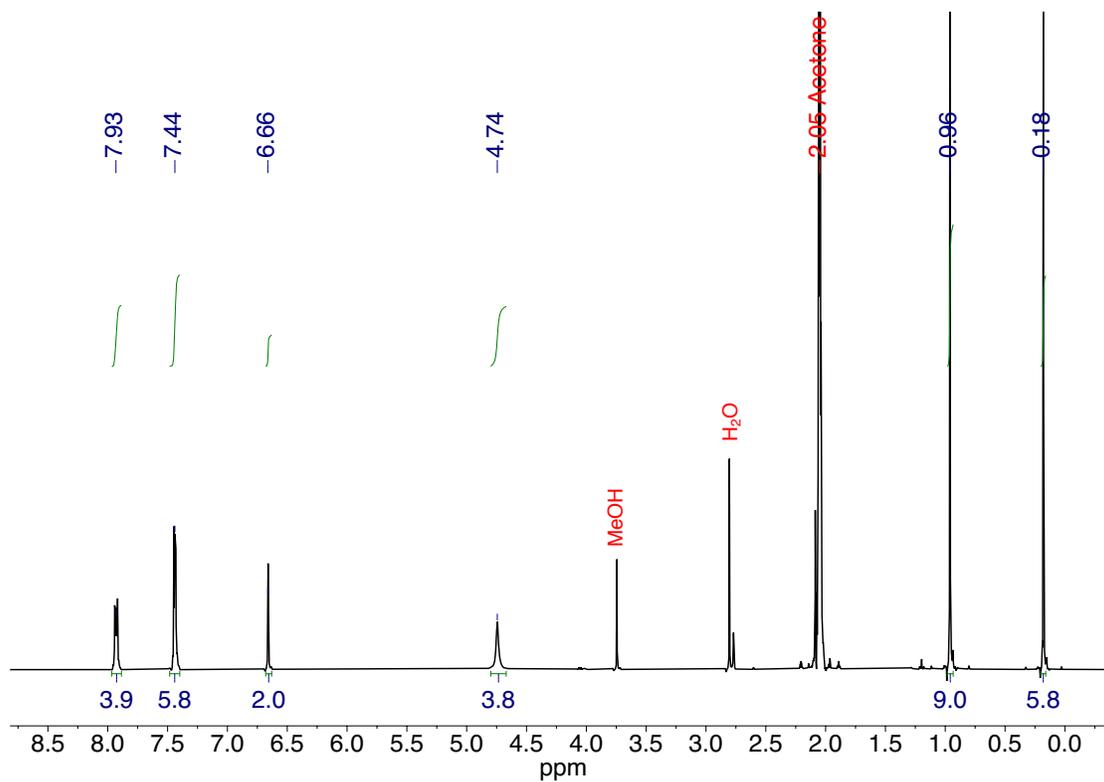


Figure S8. 1H NMR spectrum of Pd-Pin (d -acetone, 400 MHz).

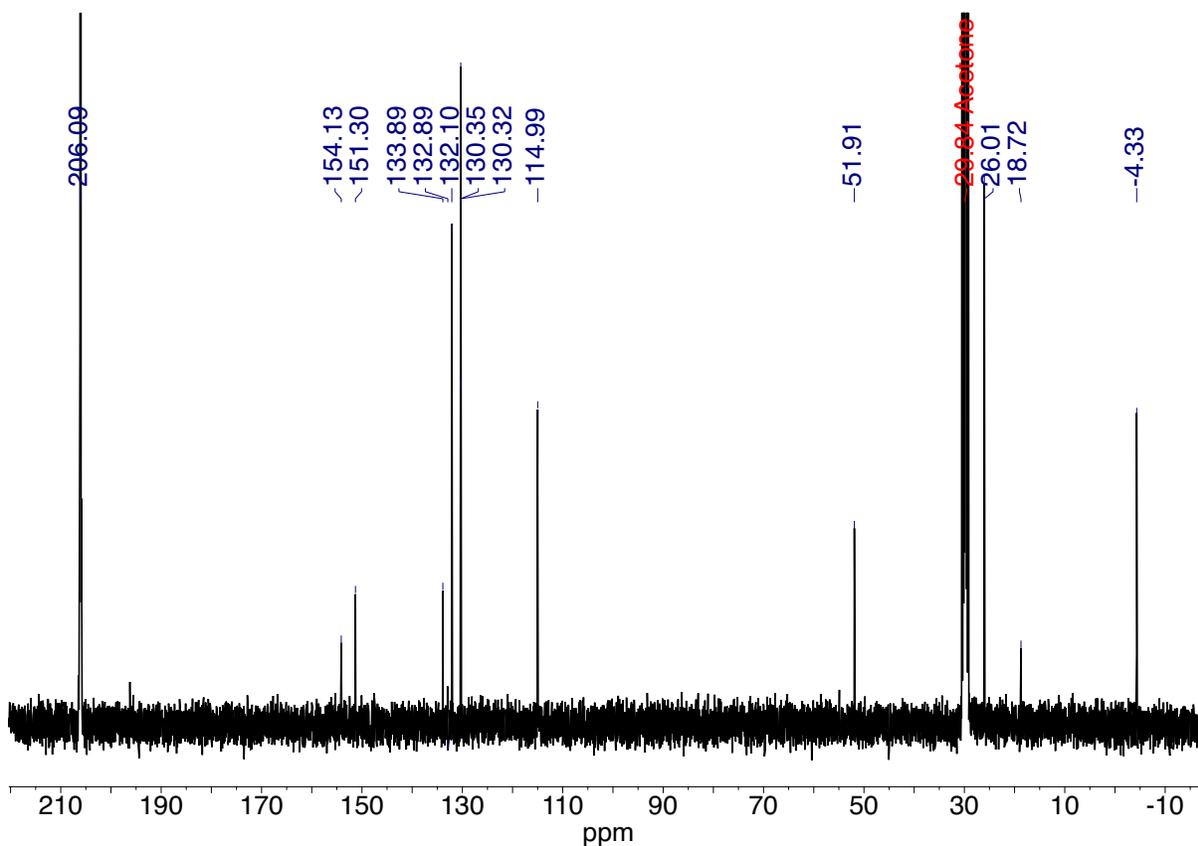
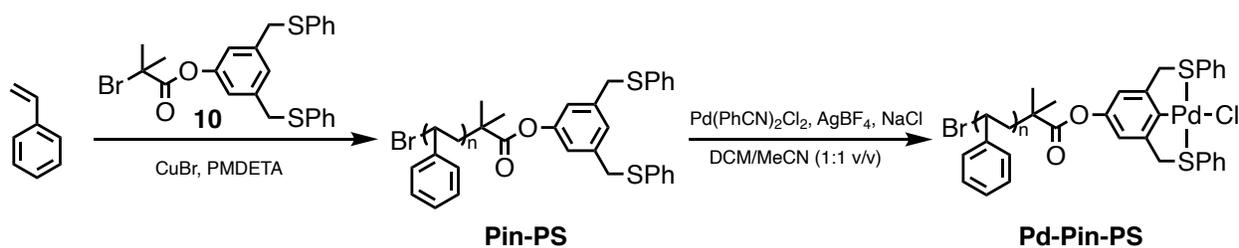


Figure S9. ^{13}C NMR spectrum of **Pd-Pin** (*d*-acetone, 400 MHz).



Scheme S4. Synthesis of **Pd-Pin-PS** via ATRP and post polymerization metalation.

Pin-PS via atom transfer radical polymerization (ATRP). The bromo propionate initiator (**10**) was synthesized according to published procedures.⁵ Degassed styrene (5.00 mL, 43.64 mmol) in a 25 mL Schlenk flask was purged with Ar. CuBr (31.3 mg, 0.22 mmol) and PMDETA (91 μL ,

0.44 mmol) were added into the flask. The flask was degassed by three rounds of freeze-pump-thaw and **10** was added before the last round under an argon flow. The mixture was merged into an oil bath at 90 °C and stirred for 80 minutes before being exposed to air to stop the polymerization. The reaction mixture was diluted with THF and the copper salt was removed by filtering the mixture through a neutral alumina column. The solution was condensed, and the product was obtained through precipitation from methanol, resulting in a white powder (0.77 g).

Pd-Pin-PS. 100 mg of purified **Pin-PS** were dissolved in 20 mL DCM/MeCN (1/1, v/v) under an argon atmosphere at room temperature. 1.5 molar equivalence of Pd(PhCN)₂Cl₂ was added and the mixture was stirred for 30 minutes. A 2.5 molar equivalence of silver tetrafluoroborate (AgBF₄) was added and the solution was stirred for 2 hours prior to pouring into 100 mL saturated NaCl aqueous solution. The mixture was subjected to vigorous stirring overnight. Subsequently, the organic layer was separated and dried over Na₂SO₄. The crude product was purified by precipitation in an excess amount of cold methanol and rinsed with methanol. Vacuum drying afforded a yellow, crispy solid as the final product (quantitative yield). SEC (in DMF): $M_n = 4,000$; $D = 1.23$.

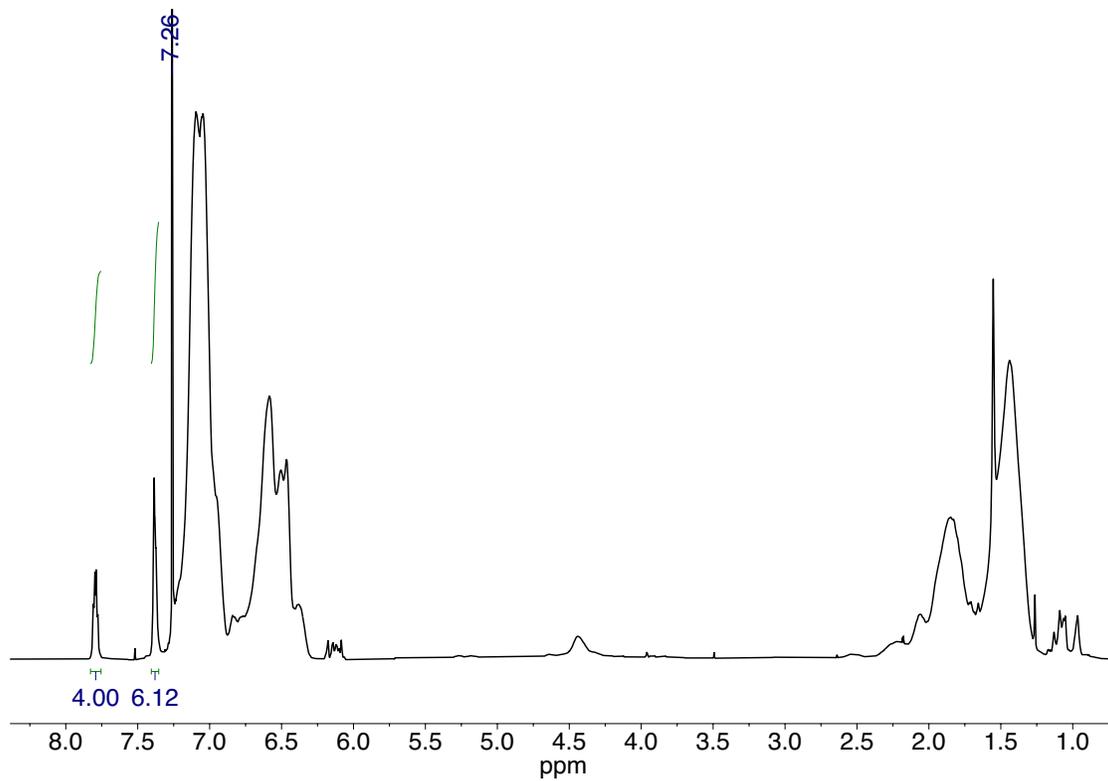


Figure S10. ^1H NMR spectrum of Pd-Pin-PS (CDCl_3 , 400 MHz).

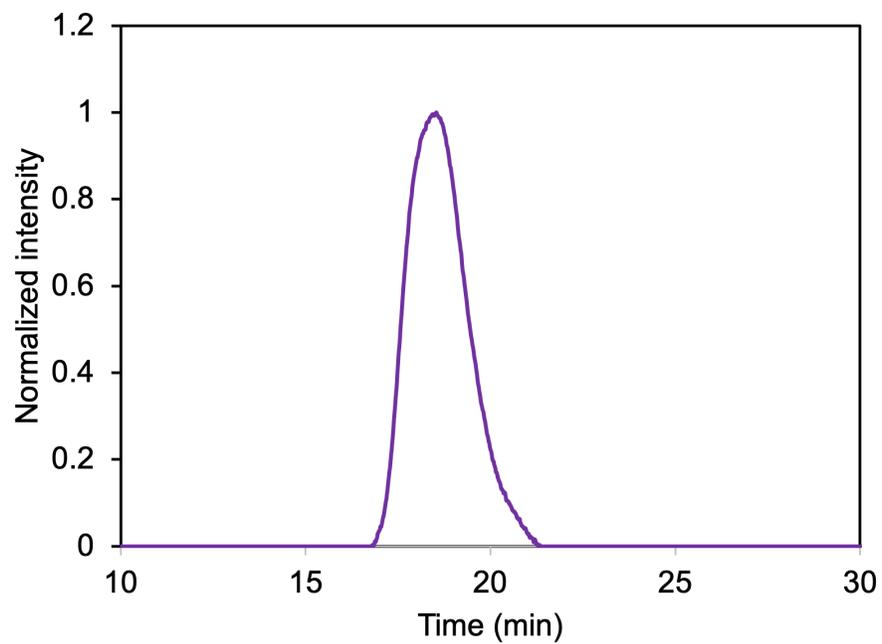


Figure S11. SEC trace of Pd-Pin-PS (DMF).

3. Supramolecular Assembly

3.1. General procedures

The pyridine-pincer metal coordination was performed in various solvents. In general, **co-PIC** and Pd^{II}-pincer containing moieties were dissolved in the desired solvents so that the molar ratio of **co-PIC** and Pd^{II}-pincer is 1:10 ([pyridine]:[Pd^{II}-pincer] = 1:1). For the model assembly test, equal molar of pyridine and **Pd-Pin** were dissolved in DCE. Then, pre-weighed AgBF₄ was added into the solution in one portion. The solutions turned turbid immediately. The mixture was put on a shaker for at least 30 minutes. The turbid mixture was passed through a 0.45 μm syringe filter, resulting in a clear solution.

3.2. Supramolecular assembly of **co-PIC** with **Pd-Pin** small molecule analog

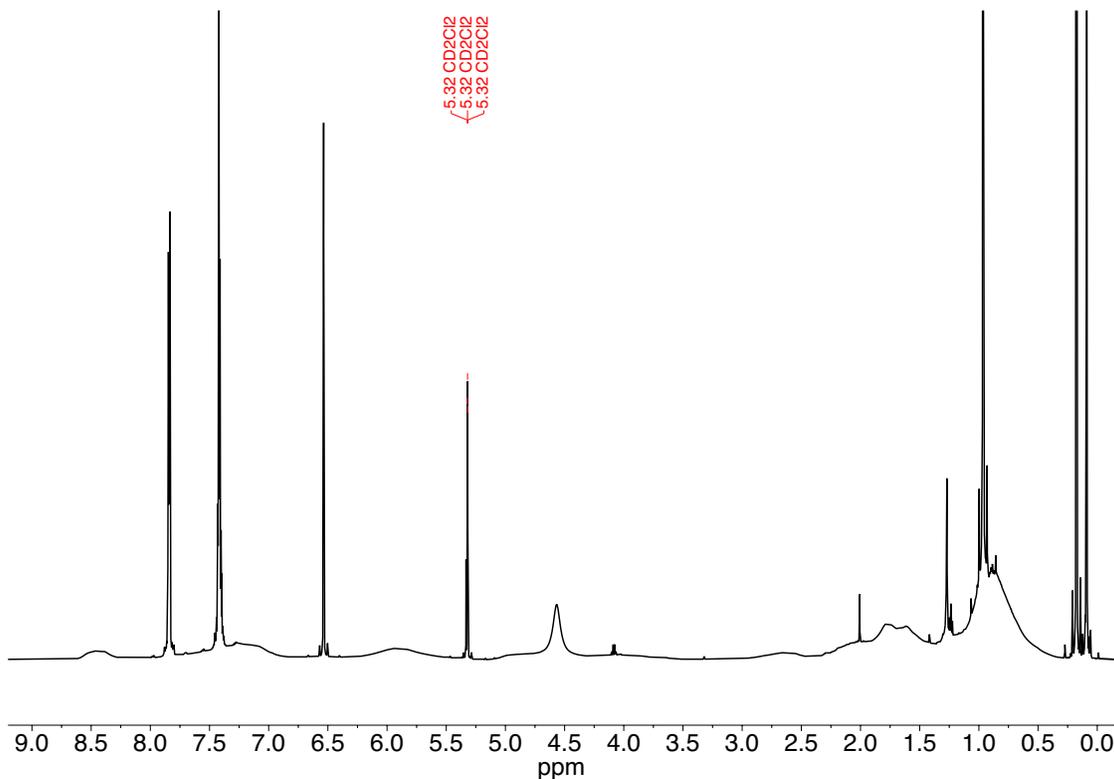


Figure S12. ¹H NMR spectrum of physical mixture of **co-PIC** and **Pd-Pin** (CD₂Cl₂, 600 MHz).

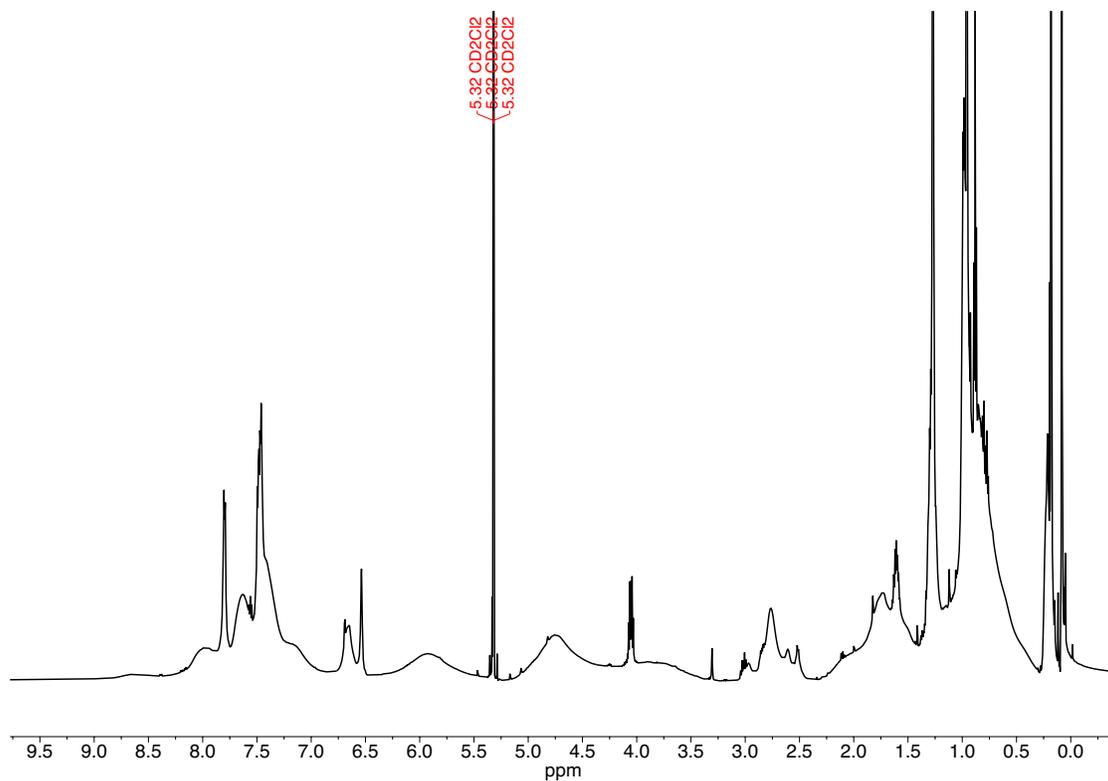


Figure S13. ^1H NMR spectrum of *co*-PIC and Pd-Pin after AgBF_4 addition (CD_2Cl_2 , 600 MHz).

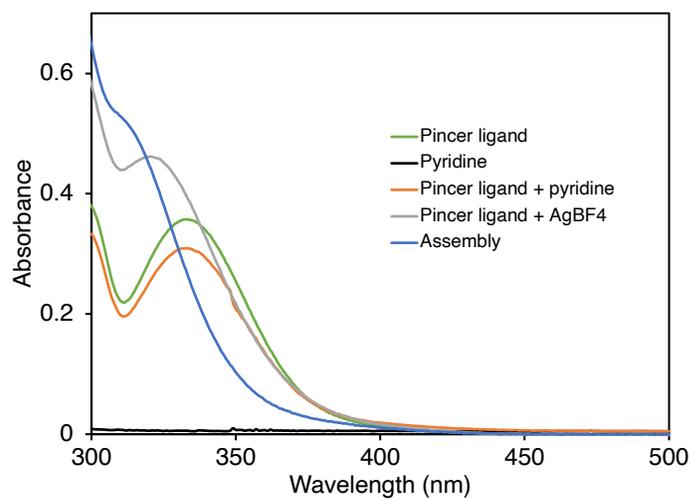


Figure S14. UV-Vis spectrum of supramolecular assembly of pyridine and Pd-Pin.

3.3. Supramolecular brush copolymer assembly of *co*-PIC with Pd-Pin-PS

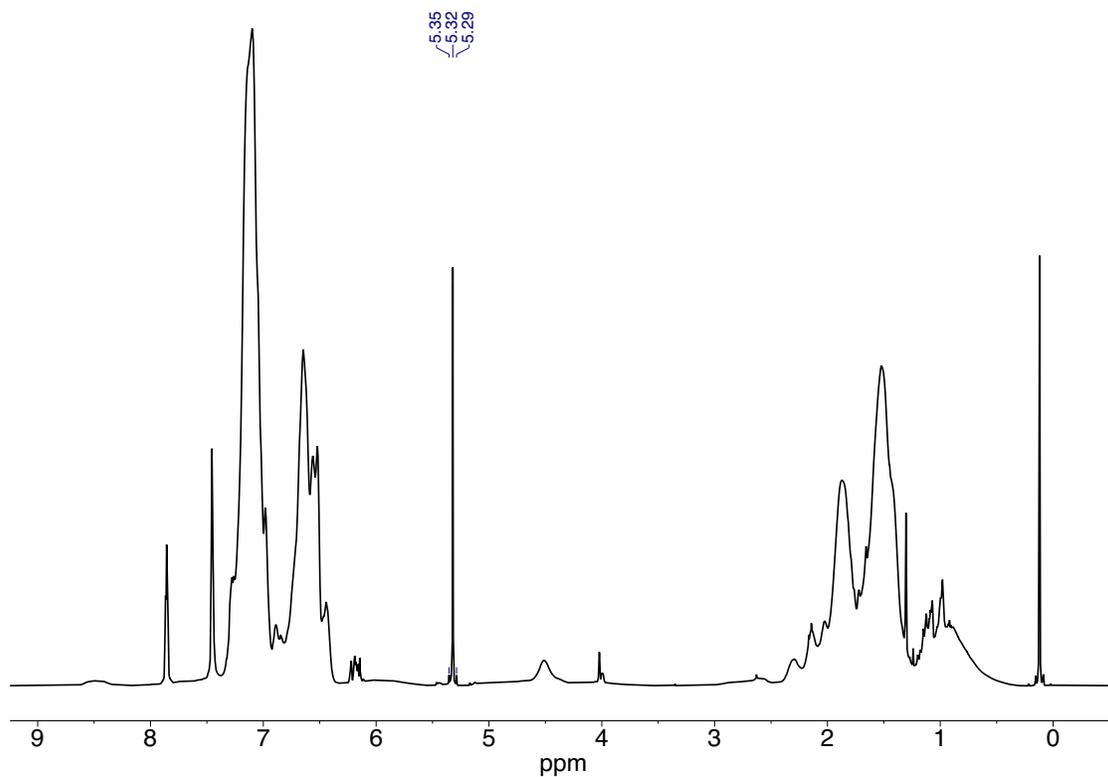


Figure S15. ¹H NMR spectrum of physical mixture of *co*-PIC and Pd-Pin-PS (CD₂Cl₂, 600 MHz).

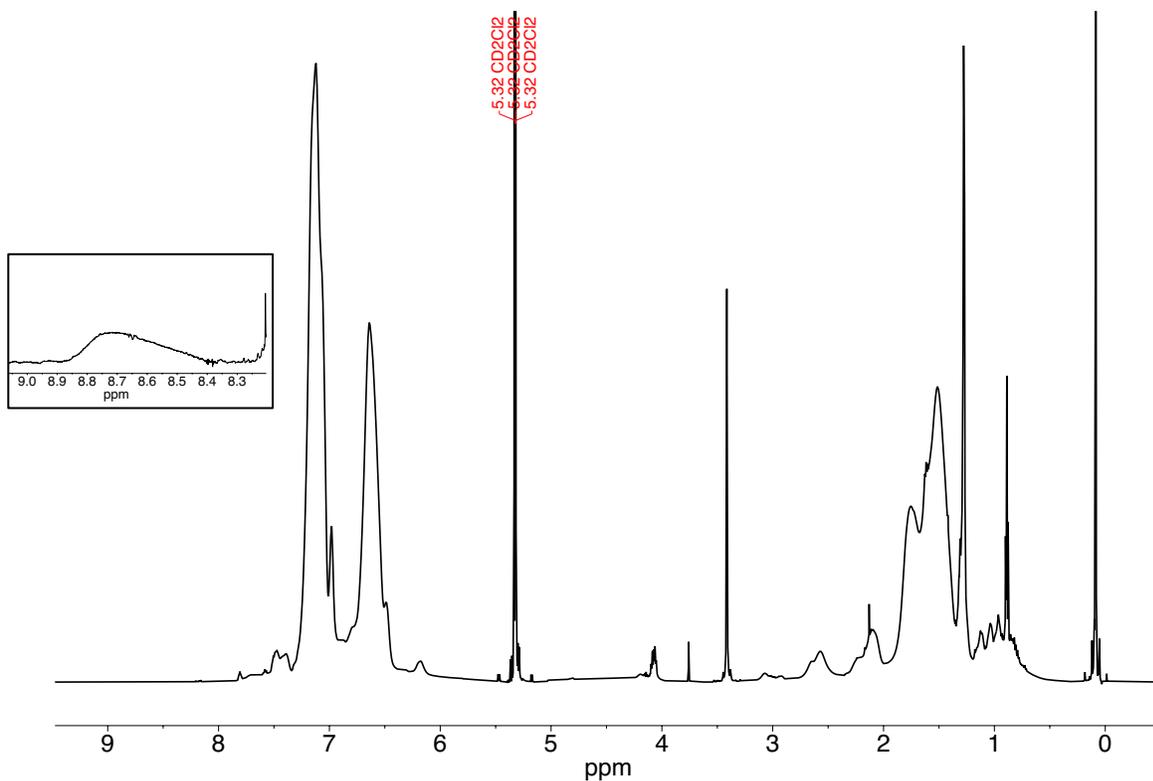


Figure S16. ^1H NMR spectrum of *co*-PIC and Pd-Pin-PS after AgBF₄ addition (CD₂Cl₂, 600 MHz). (insert) Partial zoomed spectrum from 8.2 to 9.0 ppm.

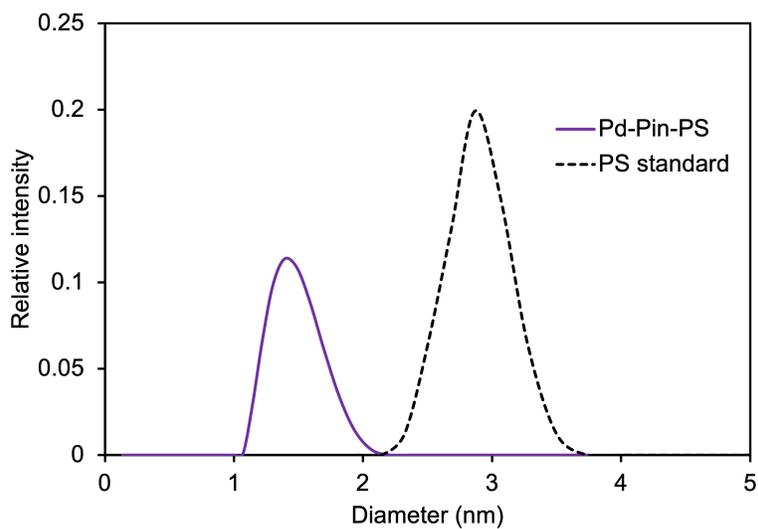


Figure S17. Size distributions of (purple) Pd-Pin-PS, (black, dashed) poly(styrene) standard sample with MW = 3,680.

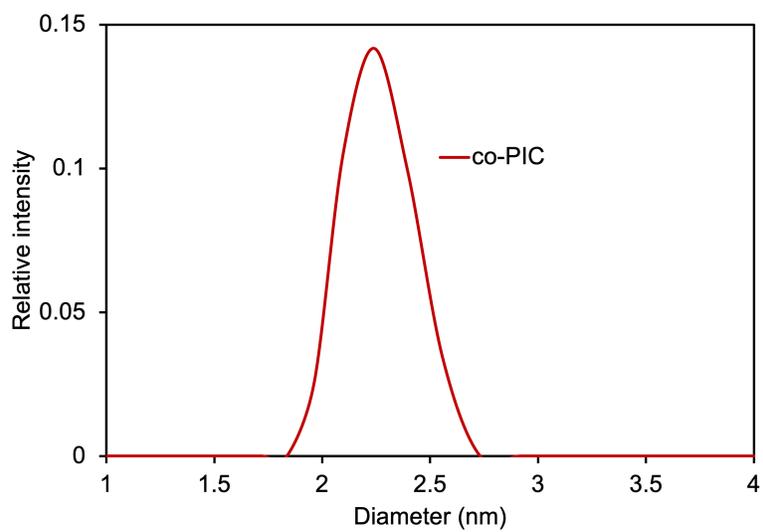


Figure S18. Size distribution of *co-PIC*.

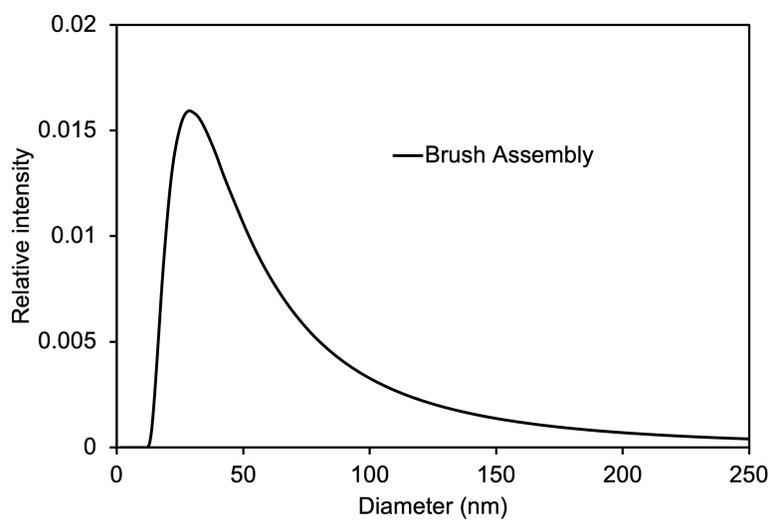


Figure S19. Size distribution of *co-PIC-brush-Pd-Pin-PS*.

4. AFM results

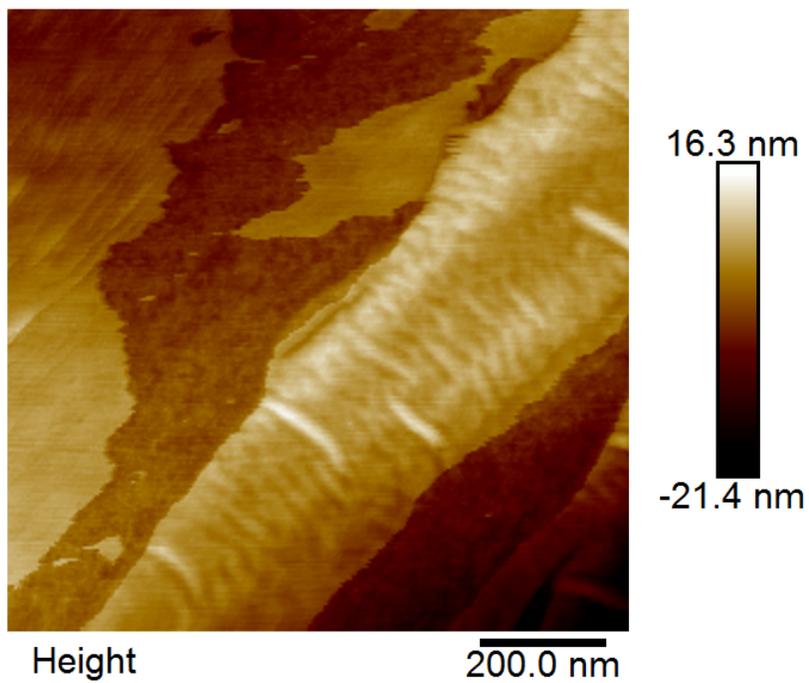


Figure S20. AFM surface image (phase and height) of *co-PIC-brush-Pd-Pin-PS*. The alternating bright and dark bands indicates periodical height changes, suggesting a lamellar structure.

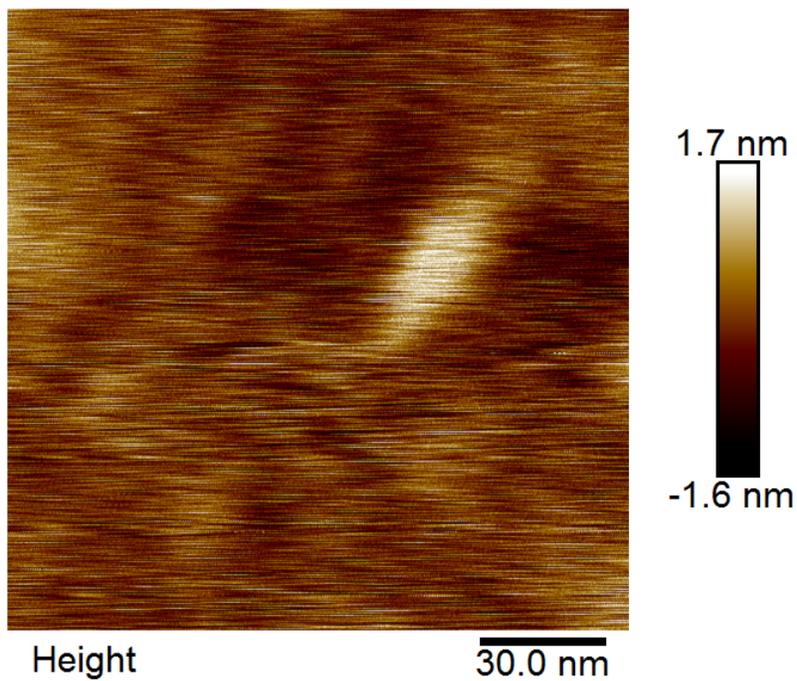


Figure S21. AFM surface image (phase and height) of **Pd-Pin-PS**.

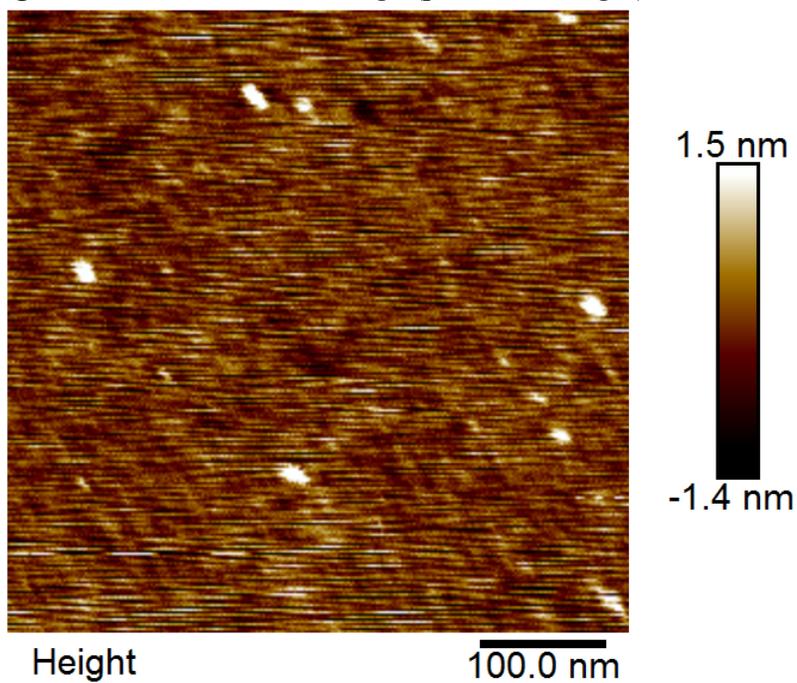


Figure S22. AFM surface image (phase and height) of *co*-PIC.

5. WAXS results

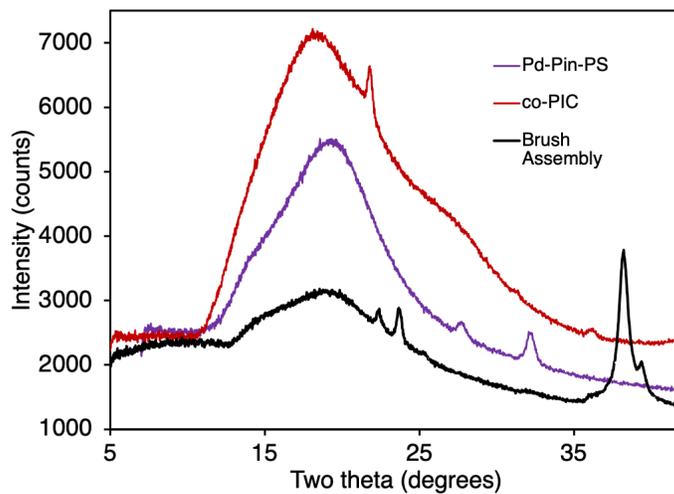


Figure S23. WAXS diffractograms corresponding to *co*-PIC, **Pd-Pin-PS** and the metallosupramolecular brush copolymer.

References

- 1 S. Kawaguchi, G. Imai, J. Suzuki, A. Miyahara, T. Kitano and K. Ito, Aqueous solution properties of oligo- and poly(ethylene oxide) by static light scattering and intrinsic viscosity, *Polymer*, 1997, **38**, 2885–2891.
- 2 A. Xu, G. Hu, Y. Hu, X. Zhang, K. Liu, G. Kuang and A. Zhang, Remarkable Structure Effects on Chiroptical Properties of Polyisocyanides Carrying Proline Pendants, *Chem. - Asian J.*, 2013, **8**, 2003–2014.
- 3 Y.-X. Xue, J.-L. Chen, Z.-Q. Jiang, Z. Yu, N. Liu, J. Yin, Y.-Y. Zhu and Z.-Q. Wu, Living polymerization of arylisocyanide initiated by the phenylethynyl palladium(II) complex, *Polym. Chem.*, 2014, **5**, 6435–6438.
- 4 J. M. Pollino and M. Weck, Supramolecular Side-Chain Functionalized Polymers: Synthesis and Self-Assembly Behavior of Polynorbornenes Bearing Pd^{II} SCS Pincer Complexes, *Synthesis*, **2002**, 1277–1285.
- 5 D. S. Lye, Y. Xia, M. Z. Wong, Y. Wang, M.-P. Nieh and M. Weck, ABC Supramolecular Triblock Copolymer by ROMP and ATRP, *Macromolecules*, 2017, **50**, 4244–4255.