# Self-Supported Rhodium Catalysts Based on a Microporous Metal-Organic Framework for Polymerization of Phenylacetylene and Its Derivatives

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#### **Experimental Section**

#### Materials

 $ZrCl_4$ , 2,2'-bipyridine-5,5'-dimethyl (Me<sub>2</sub>BPY), norbornadiene rhodium(I) chloride dimer ([(nbd)RhCl]<sub>2</sub>), trimethylaluminium (AlMe<sub>3</sub>), triethylaluminium (AlEt<sub>3</sub>), methylaluminoxane (MAO), triethylborane (BEt<sub>3</sub>), dimethylzinc (ZnEt<sub>2</sub>), phenyllithium (LiPh), sodium hydroxide (NaOH), and deuterium generation reagent (DMSO- $d_6$  and CDCl<sub>3</sub>) are purchased from Energy Chemical and used as supplied without further purification. Acetone, phenylacetylene (PA), toluene, dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), tetrahydrofuran (THF), triethylamine (NEt<sub>3</sub>), 2,6-diisopropylaniline (DIPA), ethylenediamine (C<sub>2</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>), N,N-dimethylformamide (DMF), and aniline (C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>) are also purchased from Energy Chemical and purified by vacuum distillation.

# **General information**

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of samples obtained in this paper were recorded on an Avance III HD 400 spectrometer at room temperature. Solid-state <sup>13</sup>C CP-MAS were recorded on an Avance III HD 700 at room temperature. The FTIR spectroscopy were recorded on Thermo IS5. Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) were recorded on Agilent 7700. Powder X-ray diffraction (PXRD) were recorded on an Bruker D8 Advance spectrometer. The thermogravimetric analysis (TGA) spectra were testeyd by DTG-60 spectrometer. Scanning electron microscope (SEM) spectra were recorded on JSM-7500F spectrometer. N<sub>2</sub> adsorption-desorption isotherms were tested by Quantachrome Instruments v3.01. The molecular weights and the molecular weight distributions of the polymer samples were determined at 35 °C by gel permeation chromatography (GPC) on a WATERS 1515 apparatus. THF was employed as the eluent at a flow rate of 1 ml/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd). CD spectra were tested on JASCO Corp J-810. Photoluminescence (PL) were tested by F-7000 FL Spectrophotometer. The dynamic light scattering measurement were tested by Zetasizer Nano. The UV/Vistransmittance and UV absorption were obtained on Ultraviolet spectrophotometer (TU-1901).

#### Synthesis of 2,2'-bipyridine-5,5'-dicarboxylic acid (H<sub>2</sub>BPY)

Compound H<sub>2</sub>BPY were synthesized by previously reported methods.<sup>1</sup> <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  13.54 (s, 2H), 9.20 (s, 2H), 8.57 (d, *J* = 8.1 Hz, 2H), 8.45 (d, *J* = 8.3 Hz, 2H).

#### Synthesis of UiO-67-BPY

The preparation of UiO-67-BPY was based on reported literature.<sup>2-3</sup>  $ZrCl_4$  (23.3 mg, 0.1 mmol), 2,2'bipyridine-5,5'-dicarboxylic acid (H<sub>2</sub>BPY) (24.4 mg, 0.1 mmol) and glacial acetic acid (2 mL) were placed in a 50 mL teflon-capped flask with 20 mL DMF. The mixture was treated with ultrasonification for 2 hours, then heated to 120 °C for 3 days. After cooling, powders were collected and washed with fresh DMF and methanol for 3 times, respectively. After soaking, the powders were evacuation under dynamic vacuum at 100 °C for 10 hours to gain dried white powder solid.

#### Synthesis of UiO-67-BPY-X%Rh

To 20 mLnon-aqueous acetone containing 100 mg UiO-67-BPY,  $[(nbd)RhCl]_2$  (15.3  $\mu$ mol, 30.6  $\mu$ mol, 122.4  $\mu$ mol) was added. The mixture was kept for 12 hours at room temperature (RT), and successively washed with acctone (20 mL × 4). The yellow solids (UiO-67-BPY) were dried under vacuum at 100 °C for 24 hours. Then different loads catalysts were obtained (**c**: UiO-67-BPY-2.76 wt% Rh, **d**: UiO-67-BPY-5.66 wt% Rh, **e**: UiO-67-BPY-11.41 wt% Rh determined by ICP-AES. **c**, **d** and **e** was dissolved in concentrated nitric acid).

Table S1. Rh contents of UiO-67-BPY- Rhs

sample	C	d	е
Rh contents	2.76 wt %	5.66 wt %	11.41 wt %

# Synthesis of (nbd)Rh(Me<sub>2</sub>BPY)Cl

368 mg (2.0 mmol) Me<sub>2</sub>BPY, 461 mg (1.0 mmol,) [(nbd)RhCl]<sub>2</sub> dissolved in 20 mL non-aqueous acctone. The mixture was kept for 12 hours at RT, and successively washed with acctone (20 mL×4). The red solids (nbd)Rh(Me<sub>2</sub>BPY)Cl were dried under vacuum at 50 °C for 24 hours. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.43 (d, *J* = 8.3 Hz, 2H), 8.06 (d, *J* = 8.1 Hz, 2H), 7.75 (s, 2H), 4.15 (d, *J* = 1.9 Hz, 4H), 3.89 (s, 2H), 3.31 (s, 3H), 2.38 (s, 6H), 1.32 (s, 2H).<sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ )  $\delta$  152.47 (s), 149.05 (s), 140.01 (s), 137.03 (s), 122.10 (s), 60.88 (s), 53.45 (d, J = 9.4 Hz), 48.99 (s), 17.79 (s). IR (KBr, v/cm<sup>-1</sup>): 3416 (s), 3053 (w), 3010 (m), 2920 (m), 2358 (w), 2350 (w), 1606 (m), 1578 (m), 1502 (m), 1475 (s), 1411 (m), 1392 (m), 1318 (m), 1311 (m), 1300 (w), 1250 (m), 1230 (m), 1168 (m), 1145 (w), 1108 (w), 1076 (w), 1052 (m), 994 (w), 976 (w), 960 (m), 947 (m), 892 (w), 883 (m), 849 (s), 799 (m), 772 (m), 747 (w), 724 (s), 698 (w), 609 (m).

# Synthesis of monomers (HPA, TPA, TPPA)

The functional monomers were synthesized by previously reported methods.<sup>4-5</sup> HPA, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.47 (s, 2H), 4.67 (d, *J* = 2.9 Hz, 4H), 3.97 – 3.80 (m, 2H), 3.03 (s, 1H), 2.14 (d, *J* = 22.0 Hz, 2H), 1.87 – 1.72 (m, 2H), 1.54 – 1.41 (m, 2H), 1.29 (d, *J* = 20.7 Hz, 17H), 0.88 (t, *J* = 6.7 Hz, 3H). TPA, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.22 (d, *J* = 7.8 Hz, 2H), 7.10 (s, 10H), 7.00 (d, *J* = 8.4 Hz, 8H), 3.03 (s, 1H). TPPA, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.52 (s, 4H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.19 – 7.00 (m, 19H), 3.12 (s, 1H).

# Procedure for polymerization of PA and Its Derivatives.

Under nitrogen atmosphere, the catalyst was dispersed in 3 mL solvent in a round-bottomed flask. Then monomer and cocatalysts were added in the above mixture. The colour of the mixture deepened rapidly. The mixture was stirred vigorously at room temperature and became viscous. The mixture was added to methanol (30 mL) with acetic acid (0.05 mL) in a 100 mL beaker. And then some solids (or powders) were precipitated and filtered to give polymer. The obtained polymer was washed with 50 mL methanol and dried at 40 °C under vacuum overnight. When polymerization solvent was water, the polymerization took place in the air. (For example: Table 2, entry 2. 2 mg c was dispersed in 3 mL toluene, after 10 mins 0.1 mL PA was added in the mixture. After stirring for 1 min, the mixture was added to methanol with acetic acid, which got yellow PPA).

# The formula for calculating the activity of catalyst:

$$A = m_{\text{polymer}} / (n_{\text{Rh}} \cdot \mathbf{t})$$

A: the activity of polymerization (g·mol<sub>Rh</sub><sup>-1</sup>·h<sup>-1</sup>), m<sub>polymer</sub>: the mass of polymer (g), t: the reaction time of polymerization (h), n<sub>Rh</sub>: moles of rhodium in the catalysts (mol)

$$n_{\rm Rh} = m_{\rm catalysts} \cdot \omega_{\rm Rh} / M_{\rm Rh}$$

m <sub>catalysts</sub>: the mass of catalysts (g),  $M_{Rh}$ : the relative molecular weight of rhodium,  $\omega_{Rh}$ : the mass fraction of rhodiumin in the catalysts (determined by ICP-AES).

# The formula for calculating the *cis*-selective of polyphenylacetylene (PPA):

The diverse somer contents of PPA were calculated from the <sup>1</sup>H NMR spectra.<sup>6-7</sup>

$$\% cis = (6 I_{H1}/I_{total}) \times 100$$

 $I_{H1}$  in eq 1 means the integrate area of one alkynyl proton of PA unit at 5.84 ppm,  $I_{total}$  is the total integrate area of aryl protons of the benzene ring unit at 6.94 ppm, 6.78 ppm (trans), and 6.63 ppm and alkynyl proton of PA unit at 5.84 ppm in the <sup>1</sup>H NMR spectrum.

# **Recycling Tests of Catalyst**

The recycling polymerization test was carried out with recycled catalyst by centrifugation (5 min) using the same conditions like the first run. The recovered catalyst just washed by THF three times and reused for the next polymerization. With the increase of cycle times, the color of supernatant becomes lighter and lighter, while the color of catalyst of **c** changed from beige to brown (Figure S13). A new portion of cocatalyst AlMe<sub>3</sub> and PA was then added and the polymerization was carried out in the usual method.

Cycle	Cat	Coast	Cal	Y	Act. <sup>b</sup>	<i>Cis</i> -Sel. <sup>c</sup>	M <sub>n</sub>	ha ina d
times	times Cat. Cocat	Cocal.	501.	(%)	(10 <sup>6</sup> )	(%)	$(10^4)^d$	IVI <sub>w</sub> /IVI <sub>n</sub>
1	С	AlMe <sub>3</sub>	THF	100	10.6	93	2.4	2.21
5	С	AlMe <sub>3</sub>	THF	85	9.0	94	4.1	2.13
10	С	AlMe <sub>3</sub>	THF	15	1.6	99	5.1	1.69
1	С	-	H <sub>2</sub> O	86	9.2	96	2.8	1.94
5	С	-	H <sub>2</sub> O	75	8.0	96	4.2	2.80
10	С	-	H <sub>2</sub> O	13	1.4	97	5.0	2.71

Table S2	. Recycling	experiments	of PA po	lymerization	by c
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<sup>*a*</sup>Conditions: [MOF-Rh] = 2 mg, UiO-67-BPY-2.76 wt% Rh (c) = 0.54  $\mu$ mol Rh, AlMe<sub>3</sub>/[Cat.] =1, [Mon.] = 918  $\mu$ mol, 3 mL solvent, 1 min. <sup>*b*</sup>Activity: g·mol<sub>Rh</sub><sup>-1</sup>·h<sup>-1</sup>. <sup>*c*</sup>Determined by <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> at 25 °C. <sup>*d*</sup>Determined by GPC in THF at 35 °C on the basis of a polystyrene calibration.



**Figure S1.** <sup>1</sup>H NMR spectra of 2, 2'-bipyridine-5,5'-dicarboxylic acid ( $H_2BPY$ ) in DMSO- $d_6$ .



**Figure S2.** <sup>1</sup>H NMR spectra of (nbd)Rh(Me<sub>2</sub>BPY)Cl (**b**) in DMSO- $d_6$ .





**Figure S4.** FTIR spectra of Rh catalysts: (a) [(nbd)RhCl]<sub>2</sub>; (b) (nbd)Rh(Me<sub>2</sub>BPY)Cl; (c) UiO-67-BPY; (d) UiO-67-BPY-2.76 wt% Rh.



Figure S5. Solid-state <sup>13</sup>C CP-MAS of (a) UiO-67-BPY-11.41 wt% Rh and (b) UiO-67-BPY.



**Figure S6.** <sup>1</sup>H NMR spectra of the decomposition reaction of UiO-67-BPY-11.41 wt% Rh (e) in hydrofluoric acid (HF) inDMSO- $d_6$ : (a) H<sub>2</sub>BPY ligand; (b) (nbd)Rh(Me<sub>2</sub>BPY)Cl; (c) UiO-67-BPY-11.41wt% Rh in HF; (d) mixture of UiO-67-BPY and [(nbd)RhCl]<sub>2</sub> (0.5 eq) in HF; (e) UiO-67-BPY in HF; (f) [(nbd)RhCl]<sub>2</sub> in HF; (g) [(nbd)RhCl]<sub>2</sub>; (h) nbd. (In comparison with these spectra, the peaks assigned to the free nbd ligand and the chelated nbd ligand of [(nbd)RhCl]<sub>2</sub> couldn't be observed in the spectrum of (c). However, three peaks d', e', and f' in the spectrum of (c) were similar to those in the spectra of (b) and (d), which might beassigned to nbd ligand of (nbd)Rh(H<sub>2</sub>BPY)Cl. Such (nbd)Rh(H<sub>2</sub>BPY)Cl should be released from the anchored Rh catalysts.)



**Figure S7.** (a) PXRD patterns in literature (simulated UiO-67-BPY (black), pristine UiO-67-BPY (red), fresh Zn-UiO-67-BPY (blue), Zn-UiO-67-BPY recovered from hydroamination after one cycle (purple) and after five cycles (green)). (The successful synthesis of UiO-67-BPY was proved by comparing the diagrams of Figure 1 for the new synthesized UiO-67-BPY and Figure S7a for the known UiO-67-BPY in the literature since all of the characteristic peaks appeared at the same positions.)) (b) PXRD patterns of UiO-67-BPY-2.76 wt% Rh soaked in different solvents such as dichloromethane ( $CH_2CI_2$ ), toluene, THF, water ( $H_2O$ ) and AlMe<sub>3</sub>. (These results show very good stability of UiO-67-BPY-2.76 wt% Rh in different solvents)



**Figure S8.** TGA curves of UiO-67-BPY(black), UiO-67-BPY-2.76 wt % Rh (red). UiO-67-BPY-5.56 wt % Rh (blue). UiO-67BPY-11.41 wt % Rh (green).



**Figure S9.** EDS elemental mappings of UiO-67-BPY-11.41 wt% Rh. (scale bar: 2.5  $\mu$ m) (Show that Rh and were well dispersed on the UiO-67-BPY matrix similar to other atoms)



**Figure S10.** Verify photos of heterogeneous systems of PA polymerization catalysed by **c**: (a) Photo of **c** dispersed in THF 10 mins; (b) After centrifugal; (c) The clear supernatant (up) and the precipitation dispersed in THF (down); (c) The clear supernatant no reaction (the color doesn't change) (up) and the precipitation catalyze the polymerization of PA (The reaction turns yellow) (down).



**Figure S11.** Photo of the facile precipitation of **c** by centrifugation from the polymerization reaction mixture after recycling 5 times in THF.



**Figure S12.** *In-situ* <sup>1</sup>H NMR spectra of PA polymerization catalyzed by (nbd)Rh(Me<sub>2</sub>BPY)Cl in water in DMSO $d_6$ . (As evidenced by the <sup>1</sup>H NMR spectra, the structure of (nbd)Rh(Me<sub>2</sub>BPY)Cl remains stable during PA polymerization in water.)



**Figure S13.** Photos of polymerization of PA catalyzed by **c** in THF after different recycling times. (a) after recycling 1 time; (b) after recycling 5 times; (c) after recycling 10 times. (ICP displayed that the loss of Rh from the catalysts **c** in (b) and (c) were less than 5.0 mg/kg.)



**Figure S14.** PXRD images of UiO-67-BPY-2.76 wt% Rh (red) after recycling 5 times in water (blue), 10 times in water (green), 5 times in THF (brown), and 10 times in THF (pink). (PXRD confirmed that the skeleton of recycled **c** was not destroyed in the whole recycling process.)



**Figure S15.** <sup>1</sup>H NMR spectra of PPA in Table 2, entry 2 in CDCl<sub>3</sub>. A small amount of solvent is left in the polymer because it will be hard to dissolve when fully dried.(*cis*-PPA has one alkynyl proton of PA unitat 5.84 ppm, while trans-PPA has acharacteristic broad signal at about 7 ppm (around 6.95 ppm, 6.78 ppm, and 6.63 ppm).<sup>7-8</sup>

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Figure S16. <sup>1</sup>H NMR spectra of PPAs in Table 2, entries 2-16.

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**Figure S17.** <sup>1</sup>H NMR spectra of PPAs in Table 2, entries 17-31.

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Figure S18. <sup>1</sup>H NMR spectra of PPAs in Table 2, entries 32-46.



**Figure S19.** <sup>1</sup>H NMR spectra of the resulting PPAs catalyzed by **c** in THF and water after different recycling times. Solvent: CDCl<sub>3</sub>. The *cis* selectivity of PPAs increases with the number of cycles proved the channel confinement effect in the polymerization of PA.



Figure S20. FTIR spectra of PA (black) and PPA(red).



Figure S21. GPC profiles of the PPA in Table 2, entry 2.



Figure S22. GPC profiles of the PPA in Table 2, entry 3.



Figure S23. GPC profiles of the PPA in Table 2, entry 4.



Figure S24. GPC profiles of the PPA in Table 2, entry 5.



Figure S25. GPC profiles of the PPA in Table 2, entry 6.



Figure S26. GPC profiles of the PPA by in Table 2, entry 7.



Figure S27. GPC profiles of the PPA in Table 2, entry 8.



Figure S28. GPC profiles of the PPA in Table 2, entry 9.



Figure S29. GPC profiles of the PPA in Table 2, entry 10.



Figure S30. GPC profiles of the PPA in Table 2, entry 11.







Figure S32. GPC profiles of the PPA in Table 2, entry 13



Figure S33. GPC profiles of the PPA in Table 2, entry 14



Figure S34. GPC profiles of the PPA in Table 2, entry 15.



Figure S35. GPC profiles of the PPA in Table 2, entry 16.



Figure S36. GPC profiles of the PPA in Table 2, entry 17.



Figure S39. GPC profiles of the PPA in Table 2, entry 20



Figure S40. GPC profiles of the PPA in Table 2, entry 21



Figure S41. GPC profiles of the PPA in Table 2, entry 22



Figure S42. GPC profiles of the PPA in Table 2, entry 23



Figure S43. GPC profiles of the PPA in Table 2, entry 24



Figure S44. GPC profiles of the PPA in Table 2, entry 25



Figure S45. GPC profiles of the PPA in Table 2, entry 26



Figure S46. GPC profiles of the PPA in Table 2, entry 27



Figure S47. GPC profiles of the PPA in Table 2, entry 28



Figure S48. GPC profiles of the PPA in Table 2, entry 29



Figure S49. GPC profiles of the PPA in Table 2, entry 30



Figure S50. GPC profiles of the PPA in Table 2, entry 31



Figure S51. GPC profiles of the PPA in Table 2, entry 32



Figure S52. GPC profiles of the PPA in Table 2, entry 33



Figure S53. GPC profiles of the PPA in Table 2, entry 34



Figure S54. GPC profiles of the PPA in Table 2, entry 35



Figure S55. GPC profiles of the PPA in Table 2, entry 36



Figure S56. GPC profiles of the PPA in Table 2, entry 37



Figure S57. GPC profiles of the PPA in Table 2, entry 38







Figure S59. GPC profiles of the PPA in Table 2, entry 40



Figure S60. GPC profiles of the PPA in Table 2, entry 41



Figure S61. GPC profiles of the PPA in Table 2, entry 42



Figure S62. GPC profiles of the PPA in Table 2, entry 43



Figure S63. GPC profiles of the PPA in Table 2, entry 44



Figure S64. GPC profiles of the PPA in Table 2, entry 45



Figure S65. GPC profiles of the PPA in Table 2, entry 46



**Figure S66.** GPC profiles of the PPA catalyzed by **c** after recycling 5 times in THF (Mn =  $4.14 \times 10^4$  g·mol<sup>-1</sup> M<sub>w</sub>/M<sub>n</sub> = 2.13 ).



**Figure S67.** GPC profiles of the PPA catalyzed by **c** after recycling 10 times in THF (Mn =  $5.08 \times 10^4$  g·mol<sup>-1</sup> M<sub>w</sub>/M<sub>n</sub> = 1.69 ).



**Figure S68.** GPC profiles of the PPA catalyzed by **c** after recycling 5 times in  $H_2O$  (Mn = 5.02 ×10<sup>4</sup> g·mol<sup>-1</sup>  $M_w/M_n = 2.80$ )



**Figure S69.** GPC profiles of the PPA a catalyzed by **c** after recycling 10 times in H<sub>2</sub>O (Mn =  $4.20 \times 10^4 \text{ g} \cdot \text{mol}^{-1}$  M<sub>w</sub>/M<sub>n</sub> = 2.71)



**Figure S71.** <sup>1</sup>H NMR spectra of PHPA in  $CDCl_3$ . A small amount of solvent is left in the polymer because it will be hard to dissolve when fully dried.



**Figure S73.** <sup>1</sup>H NMR spectra of PTPA in CDCl<sub>3</sub>. A small amount of solvent is left in the polymer because it will be hard to dissolve when fully dried.







**Figure S75.** <sup>1</sup>H NMR spectra of PTPPA in CDCl<sub>3</sub>. A small amount of solvent is left in the polymer because it will be hard to dissolve when fully dried.



Figure S76. FTIR spectra of HPA (black) and PHPA (red).



Figure S77. FTIR spectra of TPA (black) and PTPA (red).



Figure S78. FTIR spectra of TPPA (black) and PTPPA (red).



Figure S79. GPC profiles of the PHPA in Table 3, entry 1



Figure S80. GPC profiles of the PTPA in Table 3, entry 2



Figure S81. GPC profiles of the PTPPA in Table 3, entry 3



Figure S82.GPC profiles of the PHPA in Table 3, entry 4



Figure S83. GPC profiles of the PHPA in Table 3, entry 5



Figure S84. GPC profiles of the PTPA in Table 3, entry 6







Figure S86. GPC profiles of the PHPA in Table 3, entry 11



Figure S87. GPC profiles of the PTPA in Table 3, entry 12



Figure S88. GPC profiles of the PTPPA in Table 3, entry 13



**Figure S89.** Photos of Photoluminescence (PL) spectra of TPA and TPPA in THF/H<sub>2</sub>O mixtures with different water fractions. (concentration:  $1 \times 10^{-5}$  M, excitation wavelength: 365 nm)



**Figure S90.** The UV/Vis transmittance spectra of (a) TPA and (b) PTPA (Table 3, entry 6) with the water fraction in the THF/water mixture ranging from 0 to 99%.



**Figure S91.** UV absorption spectra of (a) TPA and (b) PTPA (Table 3, entry 6) with the water fraction in the THF/water mixture ranging from 0 to 99%.



**Figure S92.** The dynamic light scattering measurement of (a) TPA and (b) PTPA (Table 3, entry 6) at 80% water fraction in the THF–water mixture.



**Figure S93.** The UV/Vis transmittance spectra of (a) TPPA and (b) PTPPA (Table 3, entry 7) with the water fraction in the THF/water mixture ranging from 0 to 99%



**Figure S94.** UV absorption spectra of (a) TPPA and (b) PTPPA (Table 3, entry 7) with the water fraction in the THF/water mixture ranging from 0 to 99%.



**Figure S95.** The dynamic light scattering measurement of (a) TPPA and (b) PTPPA (Table 3, entry 7) at 80% water fraction in the THF–water mixture.





**Figure S96.** High resolution ESI-MS spectra of oligomer obtained from PA polymerization by use of homogeneous Rh complex **b** under the PA: **3b** molar ratio 5: 1 in toluene.

The PA monomer can serve as termination agent in the PA coordinative polymerization without other chain transfer agent and the termination reaction between Rh-polymer and C-H of terminal alkyne of PA monomer can occur to give a new Rh-C≡C-Ph active species and a polymer chain. High resolution ESI-MS spectra of oligomer obtained from PA polymerization by use of the homogeneous Rh complex **b** under the

PA: **2** molar ratio 5: 1 confirmed the formation of a series of peaks at 431.2127 and 447.2245 m/z, which were attributed to  $C_6H_5$ -C=C-[HC=C(Ph)]<sub>3</sub>-H + Na<sup>+</sup>,  $C_6H_5$ -C=C-[HC=C(Ph)]<sub>3</sub>-H + K<sup>+</sup>, respectively, demonstrated that phenylethynyl ( $C_6H_5$ -C=C) and hydrogen (H) can serve as the end groups of polymer chains

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