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# Crown ether complexes of potassium quinolin-8-olates: synthesis, characterization and catalysis toward the ring-opening polymerization of *rac*-lactide†

Bing-Bing Wu<sup>a</sup> and Zhong-Xia Wang<sup>\*ab</sup>

A series of crown ether complexes of potassium quinolin-8-olates were synthesized and characterized. Catalysis of these complexes towards the ring-opening polymerization of *rac*-lactide was evaluated. The crown ether complexes of potassium quinolin-8-olate and potassium 2-methylquinolin-8-olate exhibited high catalytic activity and good molecular weight control. The 18-crown-6 complex of potassium 5-chloroquinolin-8-olate showed lower catalytic activity and poor molecular weight control; whereas the 18-crown-6 complex of potassium 5,7-dichloroquinolin-8-olate was inactive. Among the complexes, 18-crown-6 complex of potassium quinolin-8-olate showed the best selectivity of isotacticity, the  $P_m$  value achieving 0.75 when the polymerization was performed in toluene at 0 °C.

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## Introduction

Poly(lactides) (PLAs) as biodegradable and biocompatible polymers have found wide applications in medical, agricultural, and other fields. They are also considered as an alternative to petrochemical-derived polyolefin because the monomers can be obtained from annually renewable resources.<sup>1,2</sup> The most efficient method for the production of PLAs is the ring-opening polymerization (ROP) of lactides (LA) catalyzed by metal complexes such as magnesium,<sup>3</sup> calcium,<sup>4</sup> aluminum,<sup>5</sup> zinc,<sup>6</sup> tin,<sup>7</sup> titanium,<sup>8</sup> zirconium<sup>9</sup> and lanthanide complexes,<sup>10</sup> which resulted in PLAs with high and controlled molecular weights, low polydispersity indices (PDIs), and specific stereo-microstructures. In recent years  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  complexes also received considerable attention in catalyzing the ROP of LA because the alkali metal ions are nontoxic, cheap and easily available, and their complexes were often highly catalytically active.<sup>11,12</sup> Various mono-, di-, and tridentate ligands were employed to stabilize the metal ions and tune catalytic properties of the complexes. For example, Cano *et al.* reported catalysis of Li, Na, and K phenoximine complexes toward the ROP of *rac*-LA and demonstrated that the lithium complexes resulted in formation of heterorich-

PLA ( $P_r$  up to 0.75) and the potassium complexes led to atactic PLA.<sup>11b</sup> Lin and Sun respectively reported catalysis of NNO-tridentate Schiff base-sodium complexes in the ROP of L-LA or *rac*-LA.<sup>11p,q</sup> In 2014 Wu and co-workers demonstrated that sodium and potassium complexes supported by a monophenoxy with one xanthenyl group at the *ortho*-position and 18-crown-6 or 15-crown-5 as an auxiliary ligand were highly active and isoselective catalysts for the ROP of *rac*-LA.<sup>12a</sup> Subsequently, several related monophenolato sodium and potassium complexes with crown ethers as auxiliary ligands were tested for the catalysis.<sup>12b-f</sup> In these examples, bulky phenoxy ligands are necessary for the stereoselective polymerization. In view of the work mentioned above, we attempted to study catalysis of crown ether potassium complexes bearing a didentate ligand. A chelate coordination mode will restrict rotation of K–O(quinolin-8-olate) single bond. This is probably helpful to improve the selectivity of the catalytic polymerization of *rac*-LA. For the purpose, we synthesized crown ether complexes of potassium quinolin-8-olates and studied their catalysis towards the ROP of *rac*-LA. Here we report the results.

## Results and discussion

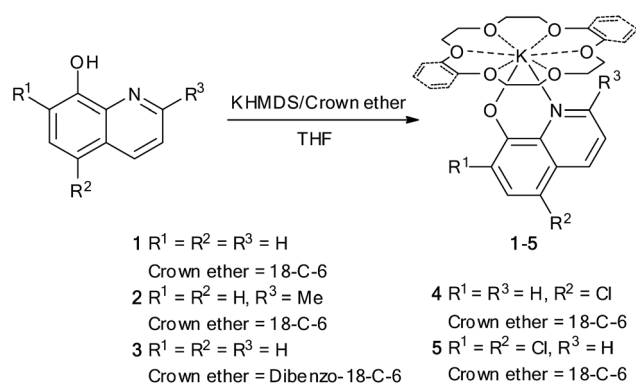
Synthesis of crown ether complexes of potassium quinolin-8-olates is presented in Scheme 1. In the presence of crown ether treatment of 8-hydroxyquinolines with  $\text{KN}(\text{SiMe}_3)_2$  (KHMDs) in THF at room temperature generated corresponding crown ether complexes of potassium quinolin-8-olates 1–5. The complexes are soluble in DMSO, partly soluble in THF and almost insoluble in toluene. Elemental analyses demonstrated that composition of the complexes matched the respective formula of the expected molecules.  $^1\text{H}$  and  $^{13}\text{C}$  NMR

<sup>a</sup>CAS Key Laboratory of Soft Matter Chemistry and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China. E-mail: zxxwang@ustc.edu.cn; Tel: +86 551 63603043

<sup>b</sup>Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, People's Republic of China

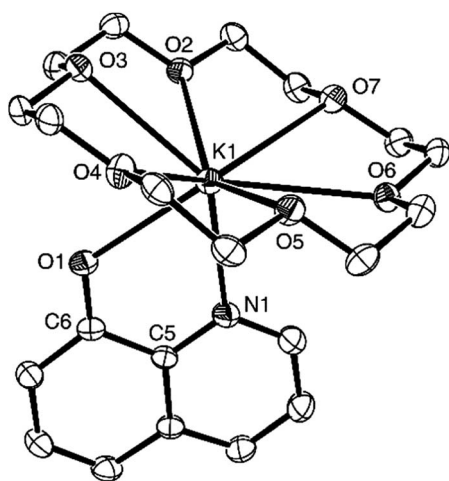
† Electronic supplementary information (ESI) available: MALDI-TOF mass spectrum and  $^1\text{H}$  NMR spectrum of the polymer. CCDC 1509154. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7ra01186e





**Scheme 1** Synthesis of crown ether complexes of potassium quino-8-olates.

spectroscopy were consistent with the respective molecular structure. Single crystal structural analysis of complex **1** (Fig. 1) showed that the central  $K^+$  cation is coordinated by quino-8-olate ligand through N,O-chelate mode and capped by 18-crown-6 through coordination of the six oxygen atoms. The K1–O1 distance of 2.728(2) Å is longer than the C–O distances in the potassium monophenolates reported by Wu *et al.* (2.444(5)–2.6141(14) Å).<sup>12b,c,e</sup> This may be caused by the difference of electron effects of phenyl and quino-8-olate groups. The distances between the potassium atom and the oxygen atoms of the crown ether vary in a range from 2.844(2) to 3.134(2) Å. Among them the K1–O2, K1–O3, and K1–O4 distances [2.8534(19), 2.9581(19) and 2.844(2) Å, respectively] are comparable to those in the crown ether potassium monophenolates reported by Wu *et al.* (2.6695(12)–2.9555(18) Å), whereas K1–O5, K(1)–O(6), and K(1)–O(7) distances (2.980(2), 3.046(2) and 3.134(2) Å, respectively) are longer than the above-mentioned ones.<sup>12b,c,e</sup> The K–N distance of 2.830(2) Å is within the normal range.<sup>13</sup>

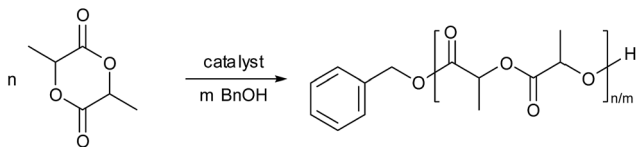


**Fig. 1** ORTEP drawing of complex **1**. Selected bond lengths (Å) and angles (deg): K(1)–O(1) 2.728(2), K(1)–N(1) 2.830(2), K(1)–O(2) 2.8534(19), K(1)–O(3) 2.9581(19), K(1)–O(4) 2.844(2), K(1)–O(5) 2.980(2), K(1)–O(6) 3.046(2), K(1)–O(7) 3.134(2), O(1)–C(6) 1.291(3); O(1)–K(1)–N(1) 59.71(7).

Catalysis of complexes **1–5** towards the ROP of *rac*-LA was evaluated and the results are listed in Table 1. Complexes **1–3** exhibited good catalytic activity in toluene at room temperature. Complexes **1** and **2** can lead to almost complete monomer conversions in 10 min and 5 min, respectively, when using a ratio of 100 : 1 : 1 for  $[LA]_0/[M]_0/[BnOH]_0$  (Table 1, entries 1 and 2). Complex **3** led to 87% monomer conversion in 10 min under the same conditions (Table 1, entry 3). However, complex **4** exhibited lower catalytic activity compared with complexes **1–3**. **4**/BnOH-catalyzed polymerization of *rac*-LA required higher temperature (70 °C) when using a ratio of 100 : 1 : 1 for  $[LA]_0/[M]_0/[BnOH]_0$  and led to 71% monomer conversion in 60 min (Table 1, entry 4). Complex **5** was inactive even at 70 °C. It seems that the electron effects of the ligands markedly affect catalytic activity of the complexes. Electron-rich quino-8-olate ligands are beneficial to increase the catalytic activity of the potassium complexes. 18-Crown-6 complex of potassium quino-8-olate (**1**) exhibited a little higher activity than dibenzo-18-crown-6 complex of potassium quino-8-olate (**3**). But the latter showed better molecular weight control although both led to low PDIs of the polymers (Table 1, entries 1 and 3). The polymer formed by **2**/BnOH catalysis showed a little higher PDI (PDI = 1.47), but the molecular weight determined by GPC approximately matched the calculated value. However, the polymer generated by **4**/BnOH catalysis showed much lower molecular weight than the theoretical value (Table 1, entry 4). This may be due to high reaction temperature and long reaction time which caused side reactions such as transesterification and irreversible chain breaking reactions. The existence of transesterification was supported by the MALDI-TOF mass spectrum of the final polymer. The mass spectrum exhibited two main series of peaks. A series of peaks at  $m/z = 144m + 108 + 39$ , which can be assigned to  $m(C_6H_8O_4) + BnOH + K^+$ . Another series of peaks at  $m/z = 72m + 108 + 39$ , which can be ascribed to  $m(C_3H_4O_2) + BnOH + K^+$  (Fig. S1 in ESI†). The series of peaks separated by  $m/z = 72$  Da is indicative of transesterification occurring in the polymerization process.<sup>14</sup>  $CH_2Cl_2$  and THF were also used as solvents for the polymerization catalyzed by **1**/BnOH. However, they were less effective than toluene. In these solvents the catalyst exhibited lower activity than in toluene and the molecular weight of the polymers obtained in these two solvents were also lower than the theoretical values (Table 1, entries 5 and 6). Catalysis of complex **1** was further tested for the polymerizations of lower and higher ratio of monomer to catalyst at room temperature (Table 1, entries 7–11). Polymerization of 20 equiv. of *rac*-LA was accomplished in 96% conversion within 2 min. When the ratio of monomer to catalyst was higher than 100, the polymerizations required longer time. The molecular weights of the polymers determined by GPC were lower than the calculated values. However, a linear relationship of molecular weights of the polymers to the ratio of monomer to catalyst was still remained (Fig. 2). The PDIs of the polymers were also low, ranging from 1.05 to 1.15. That is to say, the polymerizations are controlled. Complex **1** can also catalyze the immortal ROP of 500 equiv. of *rac*-LA in the presence of 10 equiv. of BnOH, resulting in polymer with controlled molecular weight and a relatively low PDI (Table 1, entry 12).



Table 1 ROP of *rac*-LA catalyzed by complexes 1–4<sup>a</sup>

								
Entry	Cat.	[LA] <sub>0</sub> : [Cat.] <sub>0</sub> : [BnOH] <sub>0</sub>	Time (min)	Conv. <sup>b</sup> (%)	<i>M</i> <sub>n,calc</sub> <sup>c</sup> (g mol <sup>−1</sup> )	<i>M</i> <sub>n,GPC</sub> <sup>d</sup> (g mol <sup>−1</sup> )	PDI	<i>P</i> <sub>m</sub> <sup>e</sup>
1	1	100 : 1 : 1	10	95	13 800	9400	1.07	0.72
2	2	100 : 1 : 1	5	97	14 100	10 100	1.47	0.67
3	3	100 : 1 : 1	10	87	12 600	12 100	1.06	0.70
4 <sup>f</sup>	4	100 : 1 : 1	60	71	10 300	3800	1.14	0.62
5 <sup>g</sup>	1	100 : 1 : 1	60	75	10 900	5700	1.10	0.63
6 <sup>h</sup>	1	100 : 1 : 1	60	34	5000	2000	1.07	0.51
7	1	20 : 1 : 1	2	94	2800	2400	1.11	0.66
8	1	200 : 1 : 1	20	96	27 800	19 900	1.05	0.71
9	1	300 : 1 : 1	40	96	41 600	28 000	1.07	0.72
10	1	400 : 1 : 1	80	95	54 800	31 800	1.13	0.71
11	1	500 : 1 : 1	120	96	69 200	43 100	1.15	0.70
12	1	500 : 1 : 10	7	99	7200	9400	1.25	0.73
13 <sup>i</sup>	1	100 : 1 : 1	90	99	14 400	11 500	1.07	0.75

<sup>a</sup> [Cat]<sub>0</sub> = 5 mmol L<sup>−1</sup> reactions were conducted in 4 cm<sup>3</sup> of toluene under 25 °C. <sup>b</sup> *rac*-LA conversion was determined by <sup>1</sup>H NMR spectra. <sup>c</sup> *M*<sub>n,calc</sub> = 144.13 × [LA]<sub>0</sub>/[BnOH]<sub>0</sub> × conv. (%) + 108.14. <sup>d</sup> Obtained from GPC analysis and calibrated against the polystyrene standard, multiplied by 0.58.<sup>15</sup> <sup>e</sup> Determined by analysis of all of the tetrad signals in the methine region of the homonuclear-decoupled <sup>1</sup>H NMR spectra. <sup>f</sup> Polymerization reaction was run at 70 °C. <sup>g</sup> Polymerization reaction was carried out in CH<sub>2</sub>Cl<sub>2</sub>. <sup>h</sup> Polymerization reaction was carried out in THF. <sup>i</sup> Polymerization reaction was run at 0 °C.

The polymerizations catalyzed by complexes 1–4 in toluene were stereoselective, the *P*<sub>m</sub> values of the formed polymers ranging from 0.62 to 0.72. Complex 1 led to the best selectivity, the *P*<sub>m</sub> of the polymer achieving 0.72 at room temperature. However, the selectivity of complex 1 catalysis was lower when CH<sub>2</sub>Cl<sub>2</sub> and THF were employed as the polymerization solvents (Table 1, entries 5 and 6). When the ratio of monomer to catalyst was higher than 100, the selectivity

of polymers by complex 1 catalysis was approximately unchanged (Table 1, entries 8–11). In addition, reduction of polymerization temperature led to increase of selectivity. For example, polymerization of 100 equiv. of *rac*-LA catalyzed by

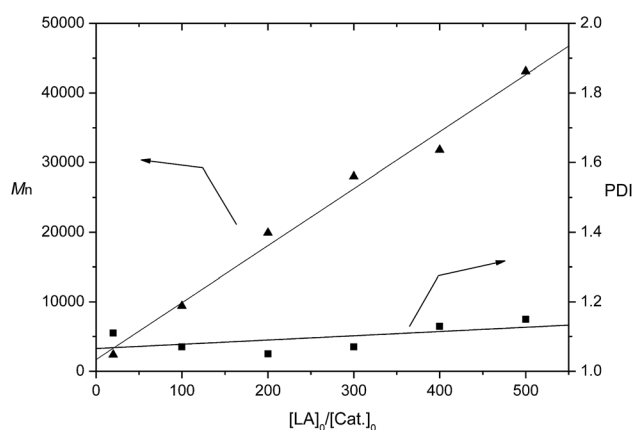


Fig. 2 Polymerization of *rac*-LA catalyzed by 1/BnOH in toluene at room temperature. The relationships between *M*<sub>n</sub> (▲), PDI (■) of the polymer and the initial mole ratios [LA]<sub>0</sub>/[Cat.]<sub>0</sub> is shown (Table 1, entries 3 and 7–11).

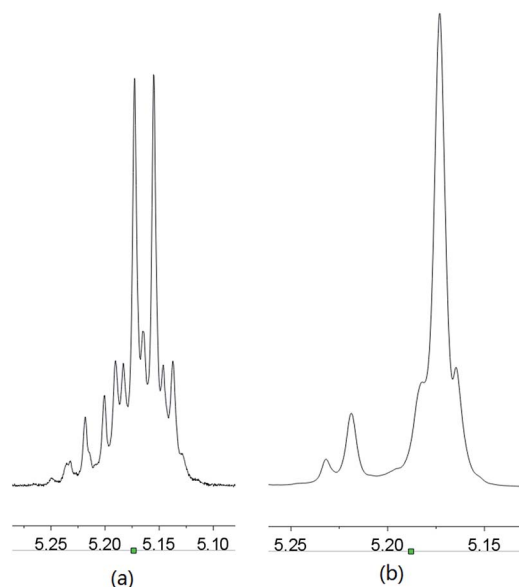
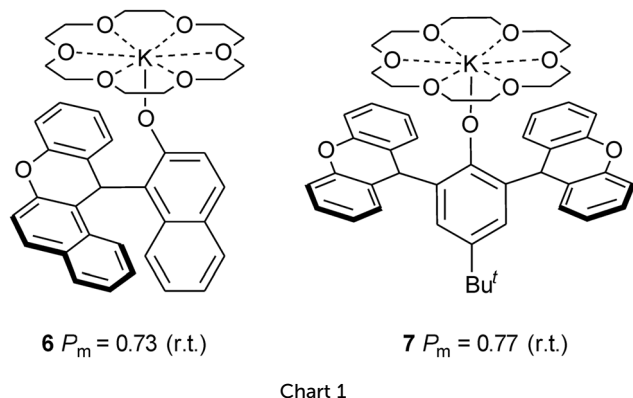
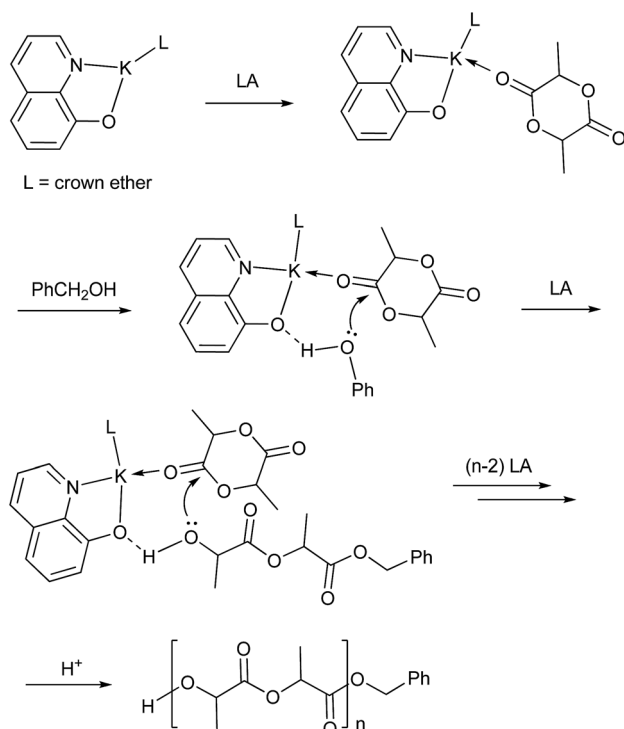


Fig. 3 Methine region of the (a) normal <sup>1</sup>H NMR spectrum and (b) homonuclear decoupled <sup>1</sup>H NMR spectrum of the PLA prepared by complex 1/BnOH catalysis (Table 1, entry 13).





complex **1** at 0 °C gave PLA with a  $P_m$  value of 0.75 (Table 1, entry 13 and Fig. 3). These selectivities are comparable to those of complexes **6** and **7** which involve bulky *ortho*-substituents on the aromatic rings (Chart 1).<sup>12b,c</sup> However, in our catalyst systems bulky substituents on the phenoxy ligands are not necessary. This might be ascribed to rotation hindrance of the K–O bond due to O,N-chelate coordination of the ligand. The end group analysis of the PLA as shown in Fig. S2 (ESI†) proved that the polymer chain was capped with one benzyl ester end and one hydroxyl end, which are consistent with an insertion mechanism of a benzyloxy group into the lactide as supposed for most alkali metal phenoxides (Scheme 2).<sup>12</sup>



Scheme 2 Proposed mechanism for the ROP of LA catalyzed by crown ether complex of potassium quinolin-8-olate.

## Conclusions

We synthesized five crown ether complexes of potassium quinolin-8-olates and demonstrated four of them to be active catalysts for the ROP of *rac*-LA in the presence of BnOH. Electron effects of the quinolin-8-olate ligands strongly affect catalytic activity of the complexes. Electron-withdrawing substituted groups on the quinolyl ring caused reduction of catalytic activity or even inactivation of the complexes. Study using **1**/BnOH in toluene also showed the catalytic polymerizations to be well controlled. Although quinolin-8-olate ligands have small steric hindrance, the complexes still led to stereoselective polymerization in toluene, the  $P_m$  ranging from 0.66 to 0.75 when the catalytic polymerization was carried out at room temperature or 0 °C. The rotation restriction of the O–K bond due to O,N-chelate coordination may play an important role in the selectivity besides the crown ether effect.

## Experimental

All air or moisture sensitive manipulations were performed under dry N<sub>2</sub> using standard Schlenk techniques. Solvents were distilled under nitrogen over sodium (toluene), sodium/benzophenone (tetrahydrofuran), or CaH<sub>2</sub> (dichloromethane) and degassed prior to use. KN(SiMe<sub>3</sub>)<sub>2</sub>, crown ether and 8-hydroxyquinoline and its derivatives were purchased from local chemical companies and used as received. BnOH was distilled from CaO; *rac*-lactide was purchased from Daigang Biomaterial Co. and recrystallized three times from toluene prior to use. DMSO-d<sub>6</sub>, purchased from EMD Millipore Corporation, was degassed, and stored over 4 Å molecular sieves. CDCl<sub>3</sub> was purchased from Cambridge Isotope Laboratories and used as received. NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer at ambient temperature. The chemical shifts of <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were referenced to TMS or internal solvent resonances. Elemental analyses were performed on an Elementar Vario EL III analyzer. Gel permeation chromatography (GPC) was recorded on a Waters 150C instrument equipped with UltraStyragel columns (103, 104, and 105 Å) and a 410 refractive index detector, using monodispersed polystyrene as the calibration standard. THF (HPLC grade) was used as an eluent at a flow rate of 1 cm<sup>3</sup> min<sup>−1</sup>.

### Synthesis of complex **1**

To a stirred solution of 8-hydroxyquinoline (0.14 g, 1.00 mmol) and 18-crown-6 (0.27 g, 1.00 mmol) in THF (10 cm<sup>3</sup>) was slowly added KN(SiMe<sub>3</sub>)<sub>2</sub> (1.1 cm<sup>3</sup>, 1 M solution in THF, 1.1 mmol) at room temperature. Then the mixture was stirred for 10 h and yellow precipitates were formed. The precipitates were collected by filtration, washed with THF, and dried *in vacuo* to give yellow solids (0.22 g, 47%). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 8.33 (dd, *J* = 3.9, 1.6 Hz, 1H), 7.78 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.06 (dd, *J* = 8.2, 4.0 Hz, 1H), 6.97 (t, *J* = 7.8 Hz, 1H), 6.18 (d, *J* = 7.7 Hz, 1H), 6.14 (d, *J* = 8.0 Hz, 1H), 3.54 (s, 24H). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>): δ 170.25, 145.90, 142.54, 134.60, 131.50, 129.27, 119.44, 112.80,





101.44, 69.46. Anal. calcd for  $C_{21}H_{30}KNO_7$ : C 56.36, H 6.76, N 3.13. Found: C 56.24, H 6.67, N 3.34.

Single crystals of complex **1** suitable for X-ray diffraction analysis were obtained from a saturated THF solution.

### Synthesis of complex 2

To a stirred solution of 8-hydroxy-2-methylquinoline (0.16 g, 1.00 mmol) and 18-crown-6 (0.27 g, 1.00 mmol) in THF (10 cm<sup>3</sup>) was slowly added  $KN(SiMe_3)_2$  (1.1 cm<sup>3</sup>, 1 M solution in THF, 1.1 mmol) at room temperature. The resultant mixture was stirred at room temperature for 10 h and yellow precipitates were formed. The precipitates were collected by filtration, washed with THF, and dried *in vacuo* to give yellow solids (0.19 g, 41%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  7.68 (d, *J* = 8.3 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.89 (t, *J* = 7.8 Hz, 1H), 6.13 (d, *J* = 7.6 Hz, 1H), 6.09 (d, *J* = 7.9 Hz, 1H), 3.53 (s, 24H), 2.48 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  169.85, 149.65, 145.06, 135.15, 129.44, 128.29, 119.79, 112.87, 101.34, 69.46, 24.58. Anal. calcd for  $C_{22}H_{32}KNO_7$ : C 57.24, H 6.99, N 3.03. Found: C 57.06, H 6.92, N 3.05.

### Synthesis of complex 3

To a solution of 8-hydroxyquinoline (0.14 g, 1.00 mmol) and dibenzo-18-crown-6 (0.36 g, 1.00 mmol) in THF (10 cm<sup>3</sup>) was slowly added  $KN(SiMe_3)_2$  (1.1 cm<sup>3</sup>, 1 M solution in THF, 1.1 mmol) at room temperature with stirring. The resultant mixture was stirred at room temperature for 10 h. The yellow orange precipitates were collected by filtration, washed with THF, and dried *in vacuo* to give yellow orange solids (0.28 g, 52%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.33 (dd, *J* = 3.9, 1.5 Hz, 1H), 7.84 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.10 (dd, *J* = 8.2, 4.0 Hz, 1H), 7.05–6.94 (m, 5H), 6.93–6.86 (m, 4H), 6.29 (d, *J* = 7.7 Hz, 1H), 6.27 (d, *J* = 7.9 Hz, 1H), 4.22–4.02 (m, 8H), 3.99–3.78 (m, 8H), 3.64–3.55 (m, THF), 1.80–1.70 (m, THF). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  168.96, 147.26, 145.26, 143.14, 134.82, 131.20, 129.14, 120.84, 119.66, 112.66, 111.85, 103.03, 68.69, 67.14, 67.02, 25.13. Anal. calcd for  $C_{29}H_{30}KNO_7$ : C 64.07, H 5.56, N 2.58. Found: C 63.93, H 5.76, N 2.54.

### Synthesis of complex 4

To a solution of 5-chloro-8-hydroxyquinoline (0.18 g, 1.00 mmol) and 18-crown-6 (0.27 g, 1.00 mmol) in THF (10 cm<sup>3</sup>) was slowly added  $KN(SiMe_3)_2$  (1.1 cm<sup>3</sup>, 1 M solution in THF, 1.1 mmol) at room temperature with stirring. The resultant mixture was stirred at room temperature for 10 h. The yellow precipitates were collected by filtration, washed with THF, and dried *in vacuo* to give yellow solids (0.25 g, 52%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.39 (dd, *J* = 3.9, 1.5 Hz, 1H), 8.03 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.26 (dd, *J* = 8.4, 4.0 Hz, 1H), 7.05 (d, *J* = 8.7 Hz, 1H), 6.08 (d, *J* = 8.7 Hz, 1H), 3.64–3.55 (m, THF), 3.54 (s, 24H), 1.81–1.69 (m, THF). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  169.90, 145.98, 142.87, 130.70, 129.34, 128.00, 120.62, 112.16, 100.65, 69.46, 67.03, 25.14. Anal. calcd for  $C_{21}H_{29}ClKNO_7 \cdot 0.55C_4H_8O$ : C 53.41, H 6.45, N 2.68. Found: C 53.47, H 6.38, N 2.60.

### Synthesis of complex 5

To a stirred solution of 5,7-dichloro-8-hydroxyquinoline (0.21 g, 1.00 mmol) and 18-crown-6 (0.27 g, 1.00 mmol) in THF (10 cm<sup>3</sup>) was slowly added  $KN(SiMe_3)_2$  (1.1 cm<sup>3</sup>, 1 M solution in THF 1.1 mmol) at room temperature. The resultant mixture was stirred at room temperature for 10 h. The yellow precipitates were collected by filtration, washed with THF, and dried *in vacuo* to give yellow solids (0.20 g, 39%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.49 (dd, *J* = 3.9, 1.4 Hz, 1H), 8.07 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.35–7.28 (m, 2H), 3.64–3.56 (m, THF), 3.54 (s, 24H), 1.79–1.71 (m, THF). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  163.61, 145.38, 144.33, 131.11, 128.40, 126.78, 120.76, 114.84, 100.58, 69.45, 67.01, 25.13. Anal. calcd for  $C_{21}H_{28}Cl_2KNO_7$ : C 48.84, H 5.46, N 2.71. Found: C 48.45, H 5.50, N 2.57.

### X-ray crystallography

Single crystal of complex **1** was mounted in Lindemann capillaries under nitrogen. Diffraction data were collected at 298(2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda$  = 0.71073 Å). The structure was solved by direct methods using SHELXS-97 (ref. 16) and refined against  $F^2$  by full-matrix least squares using SHELXL-97.<sup>17</sup> Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determination are listed in Table 2.

### Polymerization of *rac*-LA

A typical polymerization procedure was exemplified using **1**/BnOH as the catalyst. Complex **1** (8.94 mg, 0.02 mmol) and BnOH (0.20 cm<sup>3</sup>, 0.1 M in toluene, 0.02 mmol) were added in sequence to toluene (1.8 cm<sup>3</sup>). The resultant mixture was stirred at room temperature for 10 min and then added to a stirred

Table 2 Details of the X-ray structure determinations of complex **1**

Complex	<b>1</b> ·THF
Empirical formula	$C_{25}H_{38}KNO_8$
fw	519.66
Crystal system	Monoclinic
Space group	$P2_1/n$
<i>a</i> (Å)	15.4725(12)
<i>b</i> (Å)	8.3765(7)
<i>c</i> (Å)	22.2908(19)
$\beta$ (deg)	106.388(2)
<i>V</i> (Å <sup>3</sup> )	2771.6(4)
<i>Z</i>	4
<i>D</i> <sub>calcd</sub> (g cm <sup>−3</sup> )	1.245
<i>F</i> (000)	1112
$\mu$ (mm <sup>−1</sup> )	0.237
$\theta$ range for data collec (deg)	2.61 to 25.02
No. of reflns collected	13 547
No. of indep reflns ( <i>R</i> <sub>int</sub> )	4867 ( <i>R</i> <sub>int</sub> = 0.0584)
Restraints/params	0/316
Goodness of fit on <i>F</i> <sup>2</sup>	1.078
Final <i>R</i> indices <sup>a</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0490, <i>wR</i> <sub>2</sub> = 0.0873
<i>R</i> Indices (all data)	<i>R</i> <sub>1</sub> = 0.1088, <i>wR</i> <sub>2</sub> = 0.0961
Largest diff peak and hole [e Å <sup>−3</sup> ]	0.304 and −0.243

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}.$$



mixture of *rac*-LA (0.2883 g, 2.00 mmol) and toluene (2.0 cm<sup>3</sup>) at the same temperature. The polymerization reaction was terminated after 10 min by adding a drop of water. White precipitates were filtered under reduced pressure and washed with hexane. Drying the wet cake under vacuum gave the polymer as white solid. For GPC analysis, the sample was dissolved in THF, passed through a short neutral aluminum oxide column, precipitated in methanol, and dried under vacuum.

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## Notes and references

- (a) H. Seyednejad, A. H. Ghassemi, C. F. van Nostrum, T. Vermonden and W. E. Hennink, *J. Controlled Release*, 2011, **168**, 152; (b) A. Arbaoui and C. Redshaw, *Polym. Chem.*, 2010, **1**, 801; (c) N. Ajellal, J.-F. Carpentier, C. Guillaume, S. M. Guillaume, M. Helou, V. Poirier, Y. Sarazin and A. Trifonov, *Dalton Trans.*, 2010, **39**, 8363; (d) M. H. Chisholm, *Pure Appl. Chem.*, 2010, **82**, 1647; (e) M. Labet and W. Thielemans, *Chem. Soc. Rev.*, 2009, **38**, 3484; (f) R. H. Platel, L. M. Hodgson and C. K. Williams, *Polym. Rev.*, 2008, **48**, 11; (g) V. R. Sinha, K. Bansal, R. Kaushik, R. Kumria and A. Trehan, *Int. J. Pharm.*, 2004, **278**, 1; (h) D. Mecerreyes, R. Jérôme and P. Dubois, *Adv. Polym. Sci.*, 1999, **147**, 1; (i) B. J. O'Keefe, M. A. Hillmyer and W. B. Tolman, *Dalton Trans.*, 2001, 2215; (j) K. M. Stridsberg, M. Ryner and A.-C. Albertsson, *Adv. Polym. Sci.*, 2002, **157**, 41; (k) E. Chiellini and R. Solaro, *Adv. Mater.*, 1996, **8**, 305.
- (a) M. J.-L. Tschan, E. Brulé, P. Haquette and C. M. Thomas, *Polym. Chem.*, 2012, **3**, 836; (b) J. Wu, T.-L. Yu, C.-T. Chen and C.-C. Lin, *Coord. Chem. Rev.*, 2006, **250**, 602; (c) C. A. Wheaton, P. G. Hayes and B. J. Ireland, *Dalton Trans.*, 2009, 4832.
- (a) H. B. Wang, J. Guo, Y. Yang and H. Ma, *Dalton Trans.*, 2016, **45**, 10942; (b) S. Ghosh, P. K. S. Antharjanam and D. Chakraborty, *Polymer*, 2015, **70**, 38; (c) S. Ghosh, D. Chakraborty and V. Ramkumar, *J. Polym. Sci., Part A: Polym. Chem.*, 2015, **53**, 1474; (d) M. Honrado, A. Otero, J. Fernandez-Baeza, L. F. Sanchez-Barba, A. Garcés, A. Lara-Sánchez, J. Martínez-Ferrer, S. Sobrino and A. M. Rodríguez, *Organometallics*, 2015, **34**, 3196; (e) Y. Sarazin, B. Liu, T. Roisnel, L. Maron and J.-F. Carpentier, *J. Am. Chem. Soc.*, 2011, **133**, 9069; (f) M. H. Chisholm, K. Choojun, J. C. Gallucci and P. M. Wambua, *Chem. Sci.*, 2012, **3**, 3445; (g) C.-Y. Sung, C.-Y. Li, J.-K. Su, T.-Y. Chen, C.-H. Lin and B.-T. Ko, *Dalton Trans.*, 2012, **41**, 953; (h) S. Song, H. Ma and Y. Yang, *Dalton Trans.*, 2013, **42**, 14200; (i) R. A. Collins, J. Unruangsri and P. Mountford, *Dalton Trans.*, 2013, **42**, 759; (j) Y. Huang, W. Wang, C.-C. Lin, M. P. Blake, L. Clark, A. D. Schwarz and P. Mountford, *Dalton Trans.*, 2013, **42**, 9313; (k) Y. Gao, Z.-G. Dai, J.-J. Zhang, X.-X. Ma, N. Tang and J.-C. Wu, *Inorg. Chem.*, 2014, **53**, 716; (l) B. Gao, D.-H. Zhao, X. Li, Y. Cui, R.-L. Duan and X. Pang, *RSC Adv.*, 2015, **5**, 440; (m) T. J. J. Whitehorne, B. Vabre and F. Schaper, *Dalton Trans.*, 2014, **43**, 6339.
- (a) D. J. Darensbourg, W. Choi, O. Karroonnirun and N. Bhuvanesh, *Macromolecules*, 2008, **41**, 3493; (b) M.-W. Hsiao and C.-C. Lin, *Dalton Trans.*, 2013, **42**, 2041; (c) M. G. Cushion and P. Mountford, *Chem. Commun.*, 2011, **47**, 2276; (d) J. P. Davin, J. C. Buffet, T. P. Spaniol and J. Okuda, *Dalton Trans.*, 2012, **41**, 12612.
- (a) P. McKeown, M. G. Davidson, G. Kociok-Köhnb and M. D. Jones, *Chem. Commun.*, 2016, **52**, 10431; (b) Z. Sun, R. Duan, J. Yang, H. Zhang, S. Li, X. Pang, W. Chen and X. Chen, *RSC Adv.*, 2016, **6**, 17531; (c) A. Pilone, N. D. Maio, K. Press, V. Venditto, D. Pappalardo, M. Mazzeo, C. Pellicchia, M. Kol and M. Lamberti, *Dalton Trans.*, 2015, **44**, 2157; (d) Y.-L. Hsieh, N. Huang, G.-H. Lee and C.-H. Peng, *Polymer*, 2015, **72**, 281; (e) H. Z. Du, A. H. Velders, P. J. Dijkstra, Z. Y. Zhong, X. S. Chen and J. Feijen, *Macromolecules*, 2009, **42**, 1058; (f) H.-L. Chen, S. Dutta, P.-Y. Huang and C.-C. Lin, *Organometallics*, 2012, **31**, 2016; (g) B. Gao, X. Li, R. L. Duan, Q. Duan, Y. H. Li, X. Pang, H. J. Zhuang and X.-S. Chen, *RSC Adv.*, 2015, **5**, 29412; (h) A. Pilone, K. Press, I. Goldberg, M. Kol, M. Mazzeo and M. Lamberti, *J. Am. Chem. Soc.*, 2014, **136**, 2940; (i) Y. Cui, D. Li, B. Gao, Y. Zhou, L. Chen, B. Qiu, Y. Li, Q. Duan and N. Hu, *J. Coord. Chem.*, 2016, **69**, 4; (j) B. Gao, D. Li, X. Li, R. Duan, X. Pang, Y. Cui, Q. Duan and X. Chen, *Catal. Sci. Technol.*, 2015, **5**, 4644; (k) B. Gao, R. Duan, X. Pang, X. Li, Z. Qu, Z. Tang, X. Zhuang and X. Chen, *Organometallics*, 2013, **32**, 5435.
- (a) H. Wang, Y. Yang and H. Ma, *Inorg. Chem.*, 2016, **55**, 7356; (b) M. J. Walton, S. J. Lancaster, J. A. Wright, M. R. J. Elsegood and C. Redshaw, *Dalton Trans.*, 2014, **43**, 18001; (c) M. Honrado, A. Otero, J. Fernández-Baeza, L. F. Sánchez-Barba, A. Garcés, A. Lara-Sánchez and A. M. Rodríguez, *Dalton Trans.*, 2014, **43**, 17090; (d) W.-A. Ma and Z.-X. Wang, *Organometallics*, 2011, **30**, 4364; (e) C. A. Wheaton and P. G. Hayes, *Chem. Commun.*, 2010, **46**, 8404; (f) P. L. Arnold, I. J. Casely, Z. R. Turner, R. Bellabarba and R. B. Tooze, *Dalton Trans.*, 2009, 7236; (g) Y.-H. Tsai, C.-H. Lin, C.-C. Lin and B.-T. Ko, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 4927; (h) C. K. Williams, L. E. Breyfogle, S. K. Choi, W. Nam, V. G. Young Jr, M. A. Hillmyer and W. B. Tolman, *J. Am. Chem. Soc.*, 2003, **125**, 11350; (i) M. Cheng, A. B. Attygalle, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 1999, **121**, 11583; (j) B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2001, **123**, 3229.
- (a) A. P. Dove, V. C. Gibson, E. L. Marshall, A. J. P. White and D. J. Williams, *Chem. Commun.*, 2001, 283; (b) N. Nimitsiriwat, V. C. Gibson, E. L. Marshall and M. R. J. Elsegood, *Inorg. Chem.*, 2008, **47**, 5417; (c) H. Y. Chen, H. J. Fang, Y. J. Chen, S. C. N. Hsu, Y. C. Lai, H. W. Ou, W. T. Peng, Y. J. Chang, Y. C. Tsou, T. Y. Wu,



- H. Chung, Y. Chen, T. C. Huang and B. S. Wu, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 3286; (d) P. Degee, P. Dubois, S. Jacobsen, H. G. Fritz and R. Jerome, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, **37**, 2413; (e) M. Moller, R. Kange and J. L. Hedrick, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 2067; (f) S. J. Moravek, J. M. Messman and R. F. Storey, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 797; (g) X. C. Zhang, D. A. Macdonald, M. F. A. Goosen and K. B. McAuley, *J. Polym. Sci., Part A: Polym. Chem.*, 1994, **32**, 2965; (h) A. P. Dove, V. C. Gibson, E. L. Marshall, H. S. Rzepa, A. J. P. White and D. J. Williams, *J. Am. Chem. Soc.*, 2006, **128**, 9834; (i) N. Nimitsiriwat, E. L. Marshall, V. C. Gibson, M. R. J. Elsegood and S. H. Dale, *J. Am. Chem. Soc.*, 2004, **126**, 13598; (j) K. B. Aubrecht, M. A. Hillmyer and W. B. Tolman, *Macromolecules*, 2002, **35**, 644; (k) M. Lahcini, P. M. Castro, M. Kalmi, M. Leskela and T. Repo, *Organometallics*, 2004, **23**, 4547; (l) V. Poirier, T. Roisnel, S. Sinbandhit, M. Bochmann, J. F. Carpentier and Y. Sarazin, *Chem.-Eur. J.*, 2012, **18**, 2998.
- 8 (a) A. Sauer, A. Kapelski, C. Flidel, S. Dagorne, M. Kol and J. Okuda, *Dalton Trans.*, 2013, **42**, 9007; (b) B. Gao, X. Li, R. L. Duan and X. Pang, *New J. Chem.*, 2015, **39**, 2404; (c) B. Gao, Q. Duan, Y. H. Li, D. N. Li, L. Q. Zhang, Y. Cui, N. H. Hu and X. Pang, *RSC Adv.*, 2015, **5**, 13437.
- 9 (a) M. D. Jones, S. L. Hancock, P. McKeown, P. M. Schäfer, A. Buchard, L. H. Thomas, M. F. Mahon and J. P. Lowe, *Chem. Commun.*, 2014, **50**, 15967; (b) A. Stopper, J. Okuda and M. Kol, *Macromolecules*, 2012, **45**, 698.
- 10 (a) M. Zhang, X. Ni and Z. Shen, *Organometallics*, 2014, **33**, 6861; (b) L. Clark, M. G. Cushion, H. E. Dyer, A. D. Schwarz, R. Duchateau and P. Mountford, *Chem. Commun.*, 2010, **46**, 273; (c) L. Clark, G. B. Deacon, C. M. Forsyth, P. C. Junk, P. Mountford, J. P. Townley and J. Wang, *Dalton Trans.*, 2013, **42**, 9294; (d) H. E. Dyer, S. Huijser, N. Susperregui, F. Bonnet, A. D. Schwarz, R. Duchateau, L. Maron and P. Mountford, *Organometallics*, 2010, **29**, 3602; (e) S. Yang, K. Nie, Y. Zhang, M.-Q. Xue, Y.-M. Yao and Q. Shen, *Inorg. Chem.*, 2014, **53**, 105; (f) J.-S. Qiu, M. Lu, Y.-M. Yao, Y. Zhang, Y.-R. Wang and Q. Shen, *Dalton Trans.*, 2013, **42**, 10179; (g) X.-D. Shen, M.-Q. Xue, R. Jiao, Y. Ma, Y. Zhang and Q. Shen, *Organometallics*, 2012, **31**, 6222; (h) W.-J. Zhang, S.-F. Liu, W.-H. Yang, X. Hao, R. Glaser and W.-H. Sun, *Organometallics*, 2012, **31**, 8178; (i) W.-J. Zhang, S.-F. Liu, W.-H. Sun, X. Hao and C. Redshaw, *New J. Chem.*, 2012, **36**, 2392; (j) M. Bouyahyi, N. Ajellal, E. Kirillov, C. M. Thomas and J. F. Carpentier, *Chem.-Eur. J.*, 2011, **17**, 1872; (k) E. Grunova, E. Kirillov, T. Roisnel and J. F. Carpentier, *Dalton Trans.*, 2010, **39**, 6739; (l) J. C. Buffet, A. Kapelski and J. Okuda, *Macromolecules*, 2010, **43**, 10201; (m) T. Cao, A. Buchard, X. F. Le Goff and C. K. Williams, *Inorg. Chem.*, 2012, **51**, 2157; (n) C. Bakewell, T. Cao, N. Long, X. F. Le Goff, A. Auffrant and C. K. Williams, *J. Am. Chem. Soc.*, 2012, **134**, 20577; (o) S. Sun, K. Nie, Y. F. Tan, B. Zhao, Y. Zhang, Q. Shen and Y.-M. Yao, *Dalton Trans.*, 2013, **42**, 2870; (p) Y. Cui, W. Gu, Y. Wang, B. Zhao, Y. Yao and Q. Shen, *Catal. Sci. Technol.*, 2015, **5**, 3302; (q) Y.-L. Duan, J.-X. He, W. Wang, J.-J. Zhou, Y. Huang and Y. Yang, *Dalton Trans.*, 2016, **45**, 10807.
- 11 (a) A. K. Sutar, T. Maharana, S. Dutta, C.-T. Chen and C.-C. Lin, *Chem. Soc. Rev.*, 2010, **39**, 1724; (b) F. M. García-Valle, R. Estivill, C. Gallegos, T. Cuenca, M. E. G. Mosquera, V. Tabernero and J. Cano, *Organometallics*, 2015, **34**, 477; (c) E. Kober, R. Petrus, P. Kociecka, Z. Janas and P. Sobota, *Polyhedron*, 2015, **85**, 814; (d) Y. Huang, Y.-H. Tsai, W.-C. Hung, C.-S. Lin, W. Wang, J.-H. Huang, S. Dutta and C.-C. Lin, *Inorg. Chem.*, 2010, **49**, 9416; (e) L. Wang, X. Pan, L. Yao, N. Tang and J. Wu, *Eur. J. Inorg. Chem.*, 2011, 632; (f) B. Calvo, M. G. Davidson and D. García-Vivó, *Inorg. Chem.*, 2011, **50**, 3589; (g) W.-Y. Lu, M.-W. Hsiao, S. C. N. Hsu, W.-T. Peng, Y.-J. Chang, Y.-C. Tsou, T.-Y. Wu, Y.-C. Lai, Y. Chen and H.-Y. Chen, *Dalton Trans.*, 2012, **41**, 3659; (h) J. Zhang, C. Jian, Y. Gao, L. Wang, N. Tang and J. Wu, *Inorg. Chem.*, 2012, **51**, 13380; (i) H.-Y. Chen, L. Mialon, K. A. Abboud and S. A. Miller, *Organometallics*, 2012, **31**, 5252; (j) R. K. Dean, A. M. Reckling, H. Chen, L. N. Dawe, C. M. Schneider and C. M. Kozak, *Dalton Trans.*, 2013, **42**, 3504; (k) S.-C. Roşca, D.-A. Roşca, V. Dorcet, C. M. Kozak, F. M. Kerton, J.-F. Carpentier and Y. Sarazin, *Dalton Trans.*, 2013, **42**, 9361; (l) C. Thomas, A. Milet, F. Peruch and B. Bibal, *Polym. Chem.*, 2013, **4**, 3491; (m) D. Alhashmialameer, N. Ikpo, J. Collins, L. N. Dawe, K. Hattenhauera and F. M. Kerton, *Dalton Trans.*, 2015, **44**, 20216; (n) C. Gallegos, V. Tabernero, M. E. G. Mosquera, T. Cuenca and J. Cano, *Eur. J. Inorg. Chem.*, 2015, 5124; (o) F. M. García-Valle, R. Estivill, C. Gallegos, T. Cuenca, M. E. G. Mosquera, V. Tabernero and J. Cano, *Organometallics*, 2015, **34**, 477; (p) H.-W. Ou, K.-H. Lo, W.-T. Du, W.-Y. Lu, W.-J. Chuang, B.-H. Huang, H.-Y. Chen and C.-C. Lin, *Inorg. Chem.*, 2016, **55**, 1423; (q) Q. Zhang, W. Zhang, S. Wang, G. A. Solan, T. Liang, N. M. Rajendrana and W.-H. Sun, *Inorg. Chem. Front.*, 2016, **3**, 1178; (r) W.-J. Chuang, Y.-T. Huang, Y.-H. Chen, Y.-S. Lin, W.-Y. Lu, Y.-C. Lai, M. Y. Chiang, S. C. N. Hsu and H.-Y. Chen, *RSC Adv.*, 2016, **6**, 33014.
- 12 (a) J.-J. Zhang, J. Xiong, Y.-Y. Sun, N. Tang and J.-C. Wu, *Macromolecules*, 2014, **47**, 7789; (b) J. Xiong, J.-J. Zhang, Y.-Y. Sun, Z.-R. Dai, X.-B. Pan and J.-C. Wu, *Inorg. Chem.*, 2015, **54**, 1737; (c) Z.-R. Dai, Y.-Y. Sun, J. Xiong, X.-B. Pan and J.-C. Wu, *ACS Macro Lett.*, 2015, **4**, 556; (d) Z. R. Dai, Y.-Y. Sun, J. Xiong, X.-B. Pan, N. Tang and J.-C. Wu, *Catal. Sci. Technol.*, 2016, **6**, 515; (e) Y.-Y. Sun, J. Xiong, Z.-R. Dai, X.-B. Pan, N. Tang and J.-C. Wu, *Inorg. Chem.*, 2016, **55**, 136; (f) Y.-Q. Cui, C.-J. Chen, Y.-Y. Sun, J.-C. Wu and X.-B. Pan, *Inorg. Chem. Front.*, DOI: 10.1039/c6qi00449k; (g) Y.-G. Li, H.-W. Zhao, X.-Y. Mao, X.-B. Pan and J.-C. Wu, *Dalton Trans.*, 2016, **45**, 9636; (h) C.-J. Chen, Y.-Q. Cui, X.-Y. Mao, X.-B. Pan and J.-C. Wu, *Macromolecules*, 2017, **50**, 83.
- 13 (a) D. L. Hughes and M. R. Truter, *J. Chem. Soc., Dalton Trans.*, 1979, 520; (b) P. B. Hitchcock, M. F. Lappert and D.-S. Liu, *J. Organomet. Chem.*, 1995, **488**, 241; (c) A. R. Kennedy, R. E. Mulvey, R. I. Urquhart and



- S. D. Robertson, *Dalton Trans.*, 2014, **43**, 14265; (d) R. Travieso-Puente, M.-C. Chang and E. Otten, *Dalton Trans.*, 2014, **43**, 18035.
- 14 L. N. Saunders, L. N. Dawe and C. M. Kozak, *J. Organomet. Chem.*, 2014, **749**, 34.
- 15 M. Save, M. Schappacher and A. Soum, *Macromol. Chem. Phys.*, 2002, **203**, 889.
- 16 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, 467.
- 17 G. M. Sheldrick, *SHELXL97: Programs for Structure Refinement*, Universität Göttingen, Göttingen, Germany, 1997.

