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Supporting Information

Efficient and Well-Controlled Ring Opening Polymerization of Biobased Ethylene Brassylate by *α*-Diimine $FeCl_3$ Catalysts via a Coordination-Insertion Mechanism

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Table S1. ROP of EB by **L1**-supported late-transition metal complexes.

Entry [a]	Cat.	ROH	[EB]/[ROH]/[Li]/[Cat.]	Yield (%)	M_n [b](10^4 g/mol)	M_w/M_n
1	**Fe^{II}1**	Ph_2CHOH	100:3:3:1	26.0	1.22	1.70
2	**Fe^{III}1**	Ph_2CHOH	100:3:3:1	97.2	3.06	1.52
3	**Co1**	Ph_2CHOH	100:3:3:1	54.4	1.63	1.77
4	**Ni1**	Ph_2CHOH	100:3:3:1	87.4	1.67	1.90
5	**Pd1**	Ph_2CHOH	100:3:3:1	32.1	1.07	1.73

[a] Polymerization conditions: [EB] = 1.5 M, [Cat.] = 9.2 × 10^{-6} mol, in toluene, T = 110 °C, t = 30 min. [b] Determined via GPC against a polystyrene standard, M_w/M_n is polydispersity. Theoretical molecular weight of all polymers are 0.9×10^4 g/mol.

Table S2. ROP of EB by **Fe^{III}1** under different [M]/[Fe] radios.

Entry [a]	**Fe^{III}1**× (10^{-6} mol)	[M]/[Ph_2CHOH]/[Li]/[Fe]	Yield (%)	M_n [b](10^4 g/mol)	M_w/M_n	Theoretical M_n (10^4 g/mol)
1	9.2	100:3:3:1	97.2	3.06	1.52	0.90
2	4.6	200:3:3:1	95.7	2.73	1.88	1.80
3	3.1	300:3:3:1	95.8	3.97	1.90	2.70
4	1.8	500:3:3:1	87.8	3.95	1.90	4.51
5	0.9	1000:3:3:1	62.3	7.32	1.60	9.01

[a] Polymerization conditions: [EB] = 1.5 M, in toluene, T = 110 °C, t = 30 min. [b] Determined via GPC against a polystyrene standard, M_w/M_n is polydispersity.

Table S3. ROP of EB using **Fe^{III}1** under different [$PhCH_2OH$]/[Fe] radios.

Entry [a]	[M]/[$PhCH_2OH$]/[Li]/[Fe]	Yield (%)	M_n [b](10^4 g/mol)	M_w/M_n	Theoretical M_n (10^4 g/mol)
1	100:3:3:1	97.6	1.78	2.08	0.90
2	100:5:3:1	80.1	1.25	1.86	0.54
3	100:10:3:1	88.4	0.57	1.79	0.27
4	100:15:3:1	90.1	0.33	1.71	0.18
5	100:20:3:1	85.8	0.29	1.76	0.13
6	100:25:3:1	82.3	0.25	1.50	0.10
7	100:30:3:1	82.4	0.21	1.47	0.09

[a] Polymerization conditions: [EB] = 1.5 M, [Cat.] = 9.2 × 10^{-6} mol, in toluene, T = 110 °C, t = 30 min. [b] Determined via GPC against a polystyrene standard, M_w/M_n is polydispersity.

Table S4. ROP of EB using **Fe^{III}1** under different [Ph_2CHOH]/[Fe] radios.

Entry ^{a}	[M]/[Ph_2CHOH] /[Li]/[Fe]	Yield (%)	M_n ^{b}(10^4 g/mol)	M_w/M_n	Theoretical M_n (10^4 g/mol)
1	100:3:3:1	97.2	3.06	1.52	0.90
2	100:5:3:1	92.8	1.74	1.68	0.54
3	100:10:3:1	96.5	0.88	1.65	0.27
4	100:15:3:1	88.3	0.52	1.73	0.18
5	100:20:3:1	90.6	0.44	1.61	0.13
6	100:25:3:1	82.5	0.40	1.58	0.10
7	100:30:3:1	88.4	0.37	1.56	0.09

^{a} Polymerization conditions: [EB] = 1.5 M, [Cat.] = 9.2 × 10^{-6} mol, in toluene, T = 110 ^{o}C, t = 30 min. ^{b} Determined via GPC against a polystyrene standard, M_w/M_n is polydispersity.

Table S5. Crystallographic data of complex **Fe^{III}1**.

	Fe^{III}1
formula	$C_{54}H_{44}Cl_3FeN_2$
Fw/g mol^{-1}	883.11
crystal System	Monoclinic
space group	$P2_1/c$
a/Å	9.0615(2)
b/Å	18.6688(6)
c/Å	28.0754(6)
α/°	90
β/°	92.536(2)
γ/°	90
V/Å^3	4744.8(2)
Z	4
T/K	300
ρ_{calc}g/cm^3	1.236
μ/mm^{-1}	4.379
F(000)	1836.0
Crystal size/mm^3	0.1 × 0.03 × 0.03
2θ range for data collection/°	5.686 to 153.042
Index ranges	$-11 \le h \le 10, -23 \le k \le 19, -35 \le l \le 33$
Reflections collected	31028
Independent reflections	9435 [R_{int} = 0.0639, R_{sigma} = 0.0610]
Data/restraints/parameters	9435/113/582
Goodness-of-fit on F^2	1.108

Final R indexes [I>=2σ (I)]	R_1 = 0.0909, wR_2 = 0.2760
Final R indexes [all data]	R_1 = 0.1144, wR_2 = 0.2994
Largest diff. peak/hole / e $Å^{-3}$	1.38/-1.76

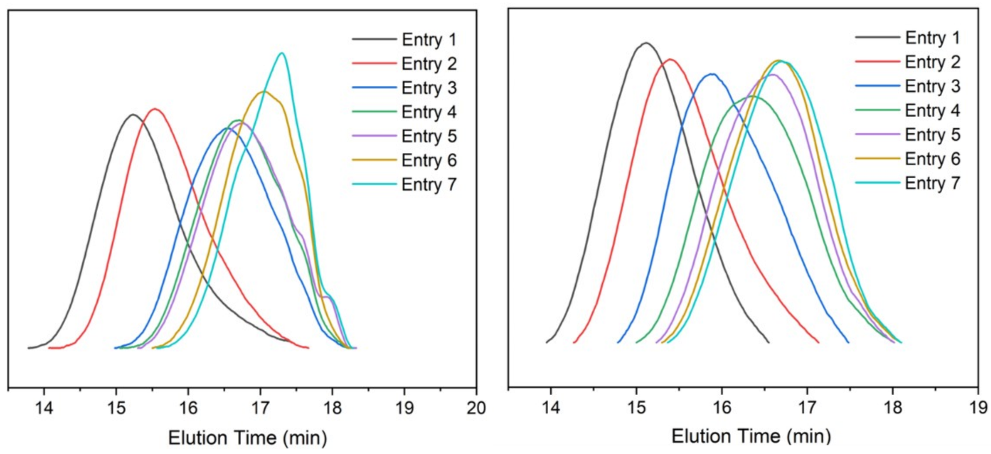

Figure S1. GPC profiles of PEBs obtained from Table S3 (left) and Table S4 (right).

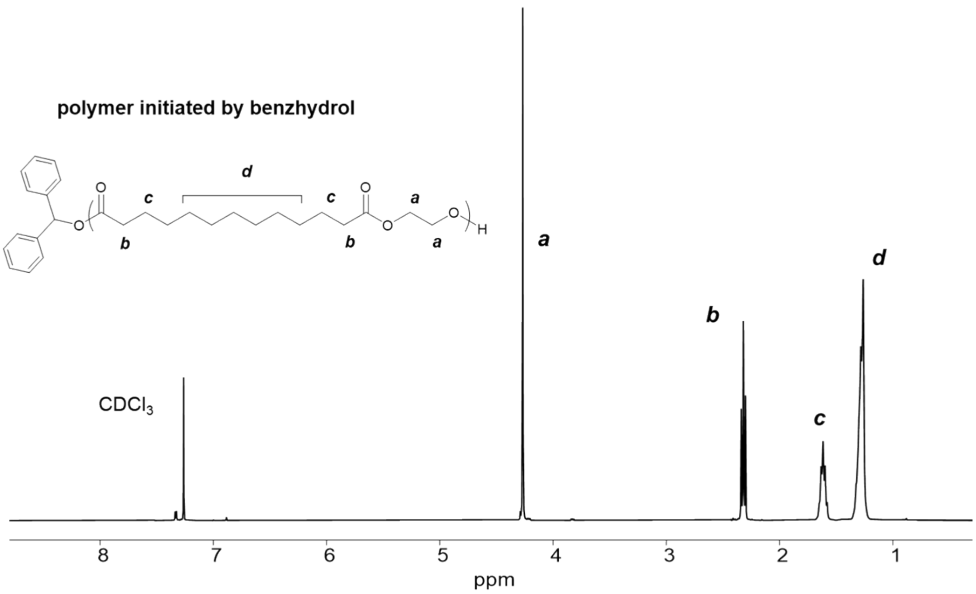

Figure S2. [1]H NMR spectra (in $CDCl_3$) of PEB initiated by Ph_2CHOH (Table 1, Run 2).

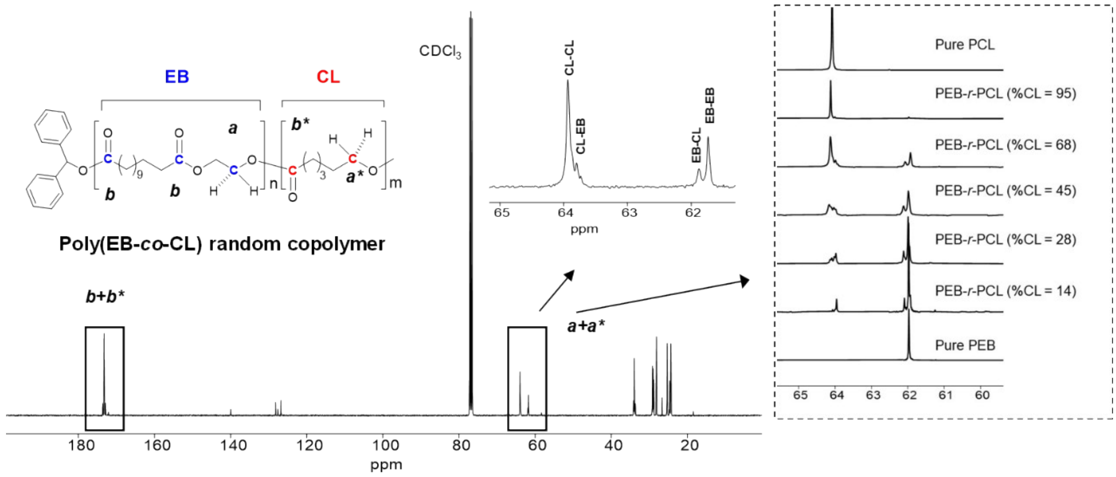

Figure S3. ^{13}C NMR spectra of poly(EB-*co*-CL) random copolymer.

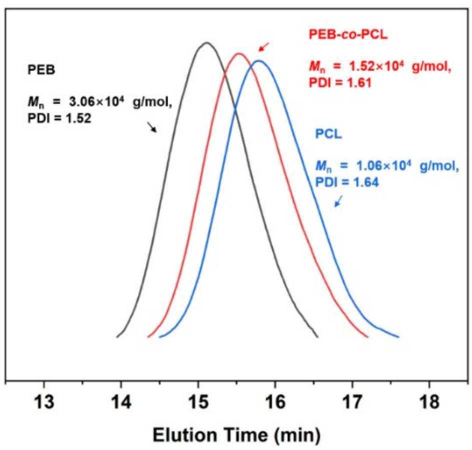

Figure S4. GPC profiles of random PEB-*co*-PCL copolymer and PEB and PCL (Table 2, Run 1, 5 and 8).

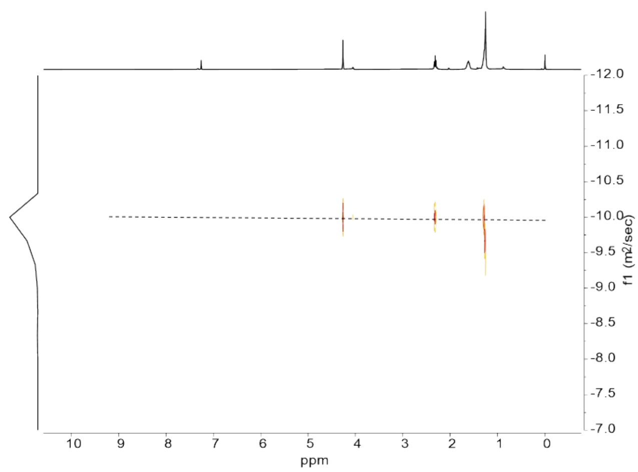

Figure S5. The 2D DOSY NMR spectrum (in $CDCl_3$) of PEB-*co*-PCL (Table 2, Run 2)

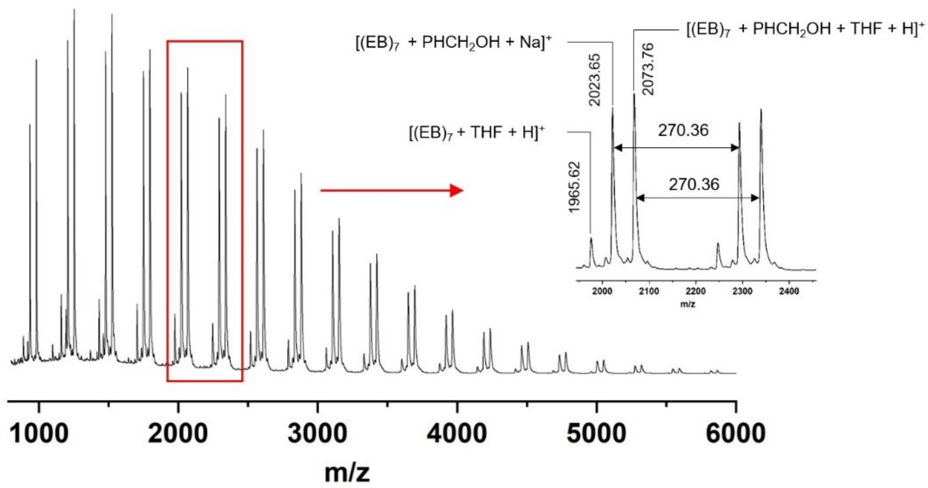

Figure S6. MALDI-TOF MS analysis of PEB obtained from **Fe^{III}1**/$PhCH_2OH$/$TMSCH_2Li$ (table S3 entry 3)

Experimental

Materials and methods

All operations involving water-oxygen sensitive complexes are performed in the glove box in a dry nitrogen atmosphere. The solvents in the experiment, including toluene, dichloromethane, tetrahydrofuran and hexane were stirred on sodium filament and benzophenone or CaH_2 for reflux distillation overnight at atmospheric pressure to use. Monomer, EB were dried on the CaH_2 overnight and distilled under reduced pressure, with degassed by three freeze–pump–thaw cycles prior to use. Ph_3COH and Ph_2CHOH were dried under vacuum before use. $PhCH_2OH$ was distilled under reduced pressure in the presence of CaH_2. (Trimethylsilyl)methyllithium were synthesized in previous work. The FTIR spectra of complexes were determined by Fourier transform infrared spectrometer through KBr was pressed. The weight-average molecular weight (M_n) and molecular weight distribution (PDI) values of the polymers were determined by GPC in THF according to PS standards. Differential scanning calorimetry (DSC) analyses of the polymeric samples were conducted under a nitrogen atmosphere by a PerkinElmer DSC 204F1 at a heating/cooling rate of 10 °C min^{-1}. Single crystals were obtained via recrystallization from saturated dichloromethane solutions. Single crystal grains obtained by solution diffusion were coated with liquid butadiene and placed on a Rigaku HyPix X-ray single crystal diffractometer. CCD detector, Cu-Kα ray as light source, wavelength 1.54184 Å. CCDC number for the ferric complex is 2246579.

Synthesis of complexes Fe^{III}1–Fe^{III}8

General procedure. A typical procedure was shown in the following: into a flask was loaded a mixture of anhydrous $FeCl_3$ (0.25 mmol), ligand (0.25 mmol) and 20 mL of DCM, the resultant reaction mixture was stirred for 24 h at room temperature. Part of the solvent was removed under vacuum and the complex was precipitated by addition of hexane. The precipitate was collected by filtration and washed with hexane three times (3 × 10 mL) to afford a dark black solid.

Complex Fe^{III}1. Yield: 64.9%. FT-IR (KBr, cm^{-1}): 3059 (w), 3022 (w), 2918 (w), 1626 (w), 1585 (m), 1492 (m), 1446 (m), 1290 (w), 1032 (w), 859 (w), 833 (w), 775 (m), 741 (m), 701 (s), 629 (w), 534 (w). ESI-MS (m/z): calcd. for: $C_{54}H_{44}Cl_3FeN_2$: 881.19, found 721.35 $[M - FeCl_3 + H]^+$. Anal. Calcd. for $C_{54}H_{44}Cl_3FeN_2$: C, 73.44; H, 5.02; N, 3.17. Found: C, 73.24; H, 5.16; N, 3.19.

Complex Fe^{III}2. Yield: 67.4%. FT-IR (KBr, cm^{-1}): 3058 (w), 3023 (w), 1732 (w), 1650 (w), 1602 (m), 1489 (s), 1447 (s), 1277 (w), 1072 (w), 1030 (m), 1032 (s), 909 (w), 827 (w), 768 (m), 746 (m), 700 (s), 605 (m), 558 (w). ESI-MS (m/z): calcd. for: $C_{78}H_{60}Cl_3FeN_2$: 1185.31, found 1025.48 $[M - FeCl_3 + H]^+$. Anal. Calcd. for $C_{78}H_{60}Cl_3FeN_2$: C, 78.89; H, 5.09; N, 2.36. Found: C, 78.98; H, 5.23; N, 2.49.

Complex Fe^{III}3. Yield: 91.3%. FT-IR (KBr, cm^{-1}): 2999 (w), 2833 (w), 1606 (m), 1580 (m), 1511 (s), 1458 (m), 1303 (w), 1252 (s), 1177 (s), 1111 (w), 1032 (s), 833 (m), 777 (w), 581 (w). ESI-MS (m/z): calcd. for: $C_{86}H_{76}Cl_3FeN_2O_8$: 1425.40, found 1265.55 $[M - FeCl_3 + H]^+$. Anal. Calcd. for $C_{86}H_{76}Cl_3FeN_2O_8$: C, 72.35; H, 5.37; N, 1.96. Found: C, 72.46; H, 5.27; N, 2.08.

Complex Fe^{III}4. Yield: 83.4%. FT-IR (KBr, cm^{-1}): 3059 (w), 3025 (w), 1657 (m), 1632 (m), 1601 (m), 1580 (m), 1493 (s), 1450(s), 1293 (w), 1219 (w), 1174 (w), 1077 (w), 1028 (w), 891 (w), 830 (w), 766 (m), 739 (m), 699 (s), 602 (m), 554 (w). ESI-MS (m/z): calcd. for: $C_{78}H_{52}Cl_3F_8FeN_2$: 1329.24, found 1169.41 $[M - FeCl_3 + H]^+$. Anal. Calcd. for $C_{78}H_{52}Cl_3F_8FeN_2$: C, 70.36; H, 3.94; N, 2.10. Found: C, 70.49; H, 3.83; N, 2.18.

Complex Fe^{III}5. Yield: 53.9%. FT-IR (KBr, cm^{-1}): 3060 (w), 3027 (w), 2959 (m), 2866 (w), 1630 (m), 1596 (m), 1493 (m), 1446 (m), 1364 (w), 1184 (w), 1077 (w), 1029 (w), 761 (m), 735 (m), 699 (s), 605 (m) 475 (w). ESI-MS (m/z): calcd. for $C_{84}H_{72}Cl_3FeN_2$: 1269.41, found 1109.58 [M – $FeCl_3$ + H] $^+$. Anal. Calcd. for $C_{84}H_{72}Cl_3FeN_2$: C, 79.34; H, 5.71; N, 2.20. Found: C, 79.43; H, 5.60; N, 2.11.

Complex Fe^{III}6. Yield: 59.5%. FT-IR (KBr, cm^{-1}): 3021 (w), 2959 (m), 2920 (w), 2866 (w), 1626 (m), 1585 (s), 1509 (s), 1447 (m), 1418 (w), 1361 (w), 1275 (w), 1187 (m), 1111 (m), 1018 (m), 816 (s), 772 (s), 725 (w), 665 (w), 575 (m), 484 (w). ESI-MS (m/z): calcd. for:$C_{92}H_{88}Cl_3FeN_2$: 1381.53, found 1221.70 [M – $FeCl_3$ + H] $^+$. Anal. Calcd. for $C_{92}H_{88}Cl_3FeN_2$: C, 79.85; H, 6.41; N, 2.02. Found: C, 79.80; H, 6.33; N, 2.10.

Complex Fe^{III}7. Yield: 77.2%. FT-IR (KBr, cm^{-1}): 3059 (w), 3023 (w), 2835 (w), 1598 (s), 1494 (s), 1453 (s), 1302 (m), 1222 (w), 1193 (m), 1135 (m), 1051 (m), 955 (w), 857 (w), 827 (w), 767 (m), 740 (m), 699 (s), 600 (m), 575 (w), 530 (w). ESI-MS (m/z): calcd. for: $C_{78}H_{60}Cl_3FeN_2O_2$: 1217.30, found 1057.47 [M – $FeCl_3$ + H] $^+$. Anal. Calcd. for $C_{78}H_{60}Cl_3FeN_2O_2$: C, 76.82; H, 4.96; N, 2.30. Found: C, 76.72; H, 5.08; N, 2.21.

Complex Fe^{III}8. Yield: 71.4%. FT-IR (KBr, cm^{-1}): 3020 (w), 2918 (w), 2863 (w), 1632 (m), 1884 (m), 1512 (s), 1426 (m), 1275 (w), 1216 (w), 1182 (m), 1110 (m), 1018 (m), 954 (w), 904 (m), 815 (s), 775 (s), 721 (m), 661 (w), 573 (m), 487 (m). ESI-MS (m/z): calcd. for: $C_{84}H_{70}Cl_5FeN_2$: 1340.59, found 1179.50 [M – $FeCl_3$ + H] $^+$. Anal. Calcd. for $C_{84}H_{70}Cl_5FeN_2$: C, 75.26; H, 5.26; N, 2.09. Found: C, 75.35; H, 5.21; N, 2.18.

Synthesis of complexes Fe^{II}1, Co1, Ni1 and Pd1

General procedure. L1 ligand (0.25 mmol) were mixed with anhydrous $FeCl_2$ (0.25 mmol) and anhydrous $NiCl_2$ (0.25 mmol) in 20 mL of THF and DCM, respectively, the resultant reaction mixture was stirred for 48 h and 24 h at room temperature. Part of the solvent was removed under vacuum and the complex was precipitated by addition of hexane. The precipitate was collected by filtration and washed with hexane three times (3 × 10 mL) to afford a dark solid. **Co1** and **Pd1** were synthesized according to the literature procedures. [1, 2]

Typical procedure for EB polymerization

In a typical homopolymerization, ROH, $TMSCH_2Li$ and required amount of toluene were added into the 20 ml vial in a ratio of 3:3, and the reaction system was shaken for a couple of minutes until the white precipitate appeared, indicating the formation of lithium alkoxide species. Afterwards, the ferrous precatalyst and EB monomer were to added sequentially, and the reaction system was left to be stirring for a given time at 110 ^{o}C. The reaction was quenched by excessive ethanol, and the resulting mixture was washed repeatedly with ethanol until white powder was obtained. Then the white powder was collected and dried under vacuum.

In a typical random copolymerization reaction, ROH, $TMSCH_2Li$ and required amount of toluene were added into the 20 ml vial in a ratio of 3:3, and the reaction system was shaken for a couple of minutes until the white precipitate appeared, indicating the formation of lithium alkoxide species. Afterwards, the ferrous precatalyst and EB/CL mixed monomer were to added sequentially, and the reaction system was left to be stirring for a given time at 110 ^{o}C. The reaction was quenched by excessive ethanol, and the resulting mixture was washed repeatedly with ethanol until white powder was obtained. Then the white powder was collected and dried under vacuum. The conversion of two components in a mixture was determined from ^{13}C NMR analysis in $CDCl_3$.

References

1. L. Liu, F. Wang, C. Zhang, H. Liu, G. Wu and X. Zhang, *Molecular Catalysis*, 2022, **517**, 112044.
2. J. S. Ouyang, Y. F. Li, D. S. Shen, Z. Ke and F. S. Liu, *Dalton Trans*, 2016, **45**, 14919-14927.