

PAPER

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View Journal | View IssueCite this: *Dalton Trans.*, 2019, **48**, 4887Polynuclear alkoxy–zinc complexes of bowl-shaped macrocycles and their use in the copolymerisation of cyclohexene oxide and CO₂[†]James R. Pankhurst,^a Shyeni Paul,^b Yunqing Zhu,^b Charlotte K. Williams^{*b} and Jason B. Love^{*a}

The reactions between alcohols and the tetranuclear ethyl–Zn complexes of an *ortho*-phenylene-bridged polypyrrole macrocycle, Zn₄Et₄(L¹) **1** and the related anthracenyl-bridged macrocyclic complex, Zn₄Et₄(THF)₄(L²) **2** have been studied. With long-chain alcohols such as *n*-hexanol, the clean formation of the tetranuclear hexoxide complex Zn₄(OC₆H₁₃)₄(L¹) **3** occurs. In contrast, the use of shorter-chain alcohols such as *i*-propanol results in the trinuclear complex Zn₃(μ²-OⁱPr)₂(μ³-OⁱPr)(HL¹) **4** that arises from demetalation; this complex was characterised by X-ray crystallography. The clean formation of these polynuclear zinc clusters allowed a study of their use as catalysts in the ring-opening copolymerisation (ROCOP) reaction between cyclohexene oxide and CO₂. *In situ* reactions involving the pre-catalyst **1** and *n*-hexanol formed the desired polymer with the best selectivity for polycarbonate (90%) at 30 atm CO₂, whilst the activity and performance of pre-catalyst **2** was poor in comparison.

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Introduction

Multidentate macrocycles are attractive as ligands for di- and polynuclear complexes of transition- and f-block metals as they can control both the basic coordination chemistry and the relative spatial positioning of metals within the macrocyclic framework, so providing a pre-organised chemical environment.^{1–4} This ligand design strategy can deliver a diversity of physical and reaction properties in the resulting complexes leading to, for example, clustering and aggregation,^{5–14} catalytic activity,^{15–28} molecular magnetism,²⁹ allosteric constructs,^{30,31} and molecular sensing.^{32–35}

We have been studying macrocycles in which two donor compartments comprising two dipyrromethane and two Schiff-base nitrogen donors (*i.e.* an N₄-donor set) are separated by rigid aryl backbones (*e.g.* L³ and L⁴, Fig. 1).^{36,37} On metalation, the resulting dinuclear complexes adopt Pac-Man structures (*e.g.* **A**, Fig. 1) that promote a diversity of chemistry within the dinuclear molecular cleft, including dioxygen reduction catalysis,^{38–41} halide sensing,⁴² and uranyl reduction

and oxo-group functionalisation.^{43–50} We have also exploited a steric variation of the *meso*-substituent (H instead of alkyl, L¹ and L², Fig. 1) which results in the adoption of bowl-shaped structures on metalation, hinging at the *meso*-carbon instead of the aryl groups.⁵¹ Importantly, using this latter ligand variant allows for the isolation of higher nuclearity complexes such as the tetranuclear zinc alkyl macrocyclic complexes **1**

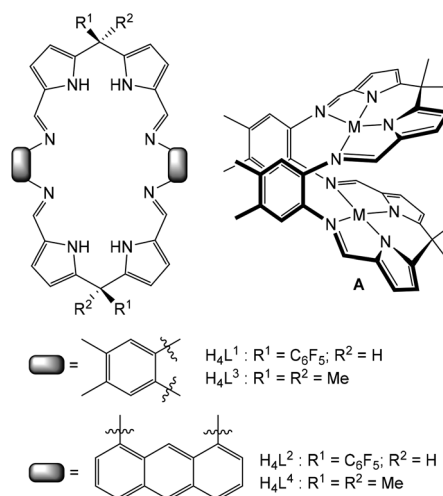


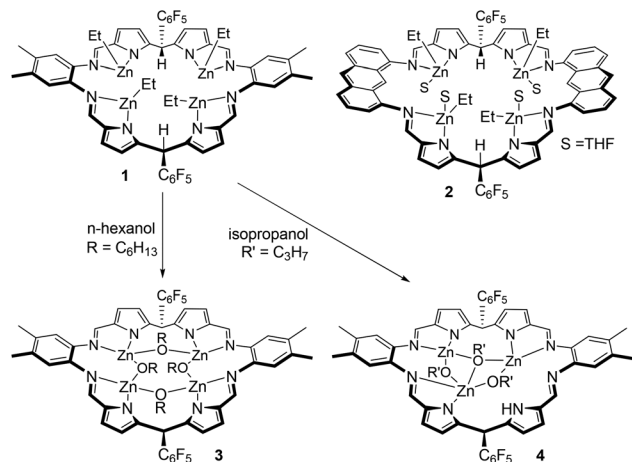
Fig. 1 Schiff-base pyrrole macrocycles with varying *meso*-substituents and aryl linkers and the formation of generic dinuclear complexes of Pac-Man structures.

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Scheme 1 Tetranuclear ethyl-zinc complexes of the Schiff-base pyrrole macrocycles L^1 and L^2 and their reactions with alcohols; complexes **1** and **2** were reported previously.⁵²

and **2** (Scheme 1); these complexes undergo subsequent protonolysis reactions with water to form tetranuclear Zn-oxo and hydroxo clusters.⁵²

The straightforward syntheses of **1** and **2**, and their facile hydrolysis, provides an opportunity to study the ring opening copolymerisation (ROCOP) of carbon dioxide and epoxides to produce aliphatic polycarbonates.^{53–57} ROCOP catalysts are often isolated Lewis-acidic metal-alkoxide complexes or are pre-catalysts that are activated by alcohols to form metal alkoxides *in situ*.^{58–75} Furthermore, homogeneous zinc catalysts are attractive for ROCOP as the metal is redox inert and sustainable. Zinc clusters formed by alcoholysis/hydrolysis of organozinc species act as ROCOP catalysts but have very slow rates.⁷⁶ Highly active zinc β -diketiminate (BDI) catalysts were reported,⁷⁷ with the best forming dimers under the polymerisation conditions.^{78–84} Dinuclear zinc macrocyclic complexes are also highly active and operate under low pressures of carbon dioxide.^{25,84–88} While higher nuclearity zinc catalysts have been reported, it is not yet understood if dinuclear catalysts are optimum.^{89–93} As such, we reasoned that the tetranuclear alkyl-zinc macrocyclic complexes **1** and **2** could be activated by alcoholysis and that the resulting zinc alkoxide complexes could act as catalysts for ROCOP of CO_2 and epoxides.

Results and discussion

Multinuclear Zn^{II} complexes considered for ROCOP catalysis

The two tetranuclear Zn-alkyl complexes $[\text{Zn}_4\text{Et}_4(L)]$, where L is either the *ortho*-phenylene-bridged macrocycle L^1 (**1**) or the anthracenyl-bridged macrocycle L^2 (**2**), were prepared as previously described (Scheme 1).⁵² These complexes are inert towards insertion of CO_2 , but undergo protonolysis reactions with four equivalents of *n*-hexanol to generate Zn-alkoxide complexes. Specifically, the alkoxide complex, $[\text{Zn}_4(\mu^2\text{-OC}_6\text{H}_{13})_4(L^1)]$ (**3**) was isolated, in 84% yield, from the reaction

of **1** with four equivalents of *n*-hexanol in THF (Scheme 1). The reaction proceeds immediately as evident from the ethane gas evolution observed. The ^1H NMR spectrum of **3** implies that it is fully symmetric with a single set of resonances for the macrocycle that are shifted in comparison with **1** (Fig. S1†); in C_6D_6 , the imine protons appear as a single resonance at 8.07 ppm, and the *meso*-protons appear at 6.38 ppm. Importantly, the ethyl resonances, that appear at 1.32 and 0.42 ppm for **1** in C_6D_6 , are absent from the spectrum of **3**. Instead, there are a number of overlapping resonances between 1.89 and 0.57 ppm assigned to the new hexyl alkoxide ligands. Two triplet resonances, at 3.83 and 3.70 ppm, each showing integral values consistent with four protons are assigned to the methylene groups adjacent to the Zn–O bond. The distinct chemical shifts indicate that the alkoxide ligands bridge between two metals, with two alkoxides bridging between imine-donors and the other two bridging between pyrrole donors; the structurally characterised and analogous Zn-hydroxide complex, $[\text{Zn}_4(\mu^2\text{-OH})_4(L^2)]$, also displayed similarly equivalent macrocycle resonances yet two distinct hydroxide environments.⁵² Furthermore, the ^{19}F NMR resonance for the *ortho*-F groups is severely broadened due to restricted rotation of that group; such broadening is typically observed for bowl-shaped tetranuclear complexes.⁵¹ As such, the NMR data support the protonolysis of **1** to form **3** which is a bowl-shaped, tetranuclear Zn-(μ^2 -alkoxide) complex.

Protonolysis reactions between **1** and alcohols other than *n*-hexanol are not straightforward. The reaction of **1** with isopropanol occurs readily, evolving gas from the THF solution, to yield the new trinuclear complex, $[\text{Zn}_3(\mu^2\text{-O}^i\text{Pr})_2(\mu^3\text{-O}^i\text{Pr})(\text{HL}^1)]$ (**4**, Scheme 1). The ^1H NMR spectrum of **4** in d_8 -THF at 300 K shows a number of broad resonances consistent with the formation of a symmetric product and with the successful loss of the ethyl groups from **1** (Fig. S3†). The broad NMR resonances suggests the complex has a fluxional solution structure and so a VT-NMR study was undertaken. At 213 K, the spectrum is sharper and consistent with an asymmetric macrocyclic ligand environment, with each of the four inequivalent imine proton resonances showing signals at 8.86, 8.68, 8.48 and 8.40 ppm (Fig. S4†). Notably, a resonance at 11.98 ppm is only observable at this temperature and is assigned to a single pyrrole N–H proton. In addition, only three iso-propoxyl ligands are seen, with the *ipso*-protons appearing as a single, broad resonance centred at 4.29 ppm, and the six individual methyl groups well resolved between 1.45 and 0.66 ppm. At 330 K, broad, thermally averaged resonances are seen, with the imine protons appearing as a single resonance at 8.36 ppm, whilst the three iso-propoxide *ipso*-protons resonate at 4.11 ppm; the associated methyl protons, with integral values of 18 protons per macrocycle, show a signal at 1.02 ppm.

Large, red, block crystals of **4** were grown from a benzene solution and the solid-state structure was determined by X-ray crystallography. Complex **4** is a trinuclear complex (Fig. 2) and adopts a highly distorted bowl-structure with a bite-angle of 102° between the two N_4 -donor compartments of the macrocycle. This bite-angle is small in comparison with other bowl-



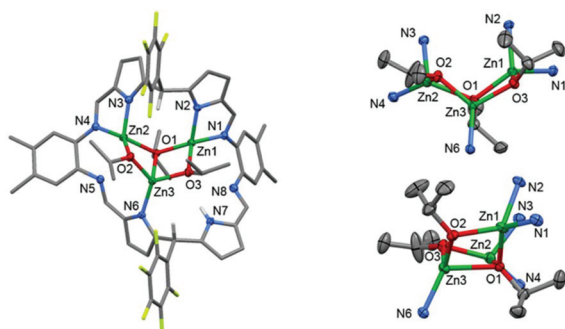


Fig. 2 Solid-state structure of **4** (displacement ellipsoids drawn at 50% probability). For clarity, solvent molecules and all hydrogen atoms except the *meso*- and N–H hydrogen atoms are omitted. Right: Orthogonal views of the $\text{Zn}_3(\text{O}^i\text{Pr})_3$ cluster.

shaped complexes of the same ligand, for example, its Cu^{II} analogue ($\text{Cu}_2(\text{py})_4(\text{L}^1)$, 152°).⁵¹ This small bite-angle is attributed to coordination of the ligand to an L-shaped, trinuclear Zn-iso-propoxide cluster, which resembles a cubane in which two vertices are removed.^{94–96} In this cluster, the Zn centres are bridged by two μ^2 -alkoxide ligands (O2 and O3) and one μ^3 -alkoxide ligand (O1). Each Zn centre is four-coordinate with highly distorted tetrahedral coordination geometries, with bond angles ranging from $81.58(8)^\circ$ to $143.47(9)^\circ$; in order to accommodate this cluster an imine group (N5) from one of the imino-pyrrole chelates is non-coordinating. The inter-metallic distances between nearest neighbours in the cluster are $3.0071(5)$ Å (Zn1–Zn3) and $2.8213(6)$ Å (Zn2–Zn3). The Zn–O bond lengths that describe the edges of the cluster are regular and are in the range $1.920(2)$ Å to $2.143(2)$ Å. However, the cluster is distorted, with inequivalent bond angles in the hinge, of $121.4(1)^\circ$ (Zn2–O1–Zn1) and $111.21(8)^\circ$ (O3–Zn3–O2).

The reaction between **1** and four equivalents of phenol occurs readily and results in the formation of a complex that displays a similar ^1H NMR spectrum to that of **4** (Fig. S5†). A single N–H proton resonance is seen at 11.76 ppm (at 300 K) which indicates that a similar demetalation reaction has occurred to form $[\text{Zn}_3(\text{OPh})_3(\text{HL}^1)]$. In an attempt to introduce a kinetic barrier towards demetalation, the reaction between **1** and 2,6-di-*tert*-butyl-phenol was investigated. No reaction is seen at room temperature, with the ^1H NMR spectrum of **1** unchanged in the presence of the di-substituted phenol. However, after heating at 90°C for 24 h, the ^1H NMR spectrum shows that while partial protonolysis had occurred, no N–H proton is seen, consistent with the reaction avoiding demetalation side-processes (Fig. S6†). Nonetheless, the triplet resonance at 6.91 ppm, assigned to the *para*-proton of phenoxide co-ligands, shows an integral value consistent with there being only two phenoxides per macrocycle. There is also a quartet at 0.55 ppm and its integral is consistent with there being two ethyl ligands per macrocycle. Thus, the product is the tetranuclear complex $[\text{Zn}_4(\text{OC}_6\text{H}_3\text{-}t\text{Bu}_2\text{-}2,6)_2\text{Et}_2(\text{L}^1)]$. Although zinc-phenoxide complexes are able to initiate ROCOP,⁹⁷ this heteroleptic complex was not investigated further as the mixture of

co-ligands would likely complicate initiation processes. Overall, the attempted protonolysis reactions resulted in only **3** as an isolated catalyst suitable for the ROCOP and only *n*-hexanol was considered as an acceptable alcohol for the *in situ* generation of catalytic systems using **1** and **2**.

Demetalation of a tetranuclear Zn-iso-propoxide complex, that presumably forms initially, would yield one equivalent of $\text{Zn}(\text{O}^i\text{Pr})_2$ per equivalent of **4**. The relative instability of the tetranuclear zinc complex suggests that combining **1** or **2** with iso-propanol will not be an effective initiating system as the desired multinuclear zinc alkoxide complex will be contaminated by the homoleptic zinc alkoxide. Indeed, homoleptic zinc alkoxide complexes are known to catalyse the formation of ether linkages in ROCOP reactions.⁹⁸ Demetalation was not observed during the reaction of **1** with *n*-hexanol, which may be a result of the longer-chain alkoxide ligands imparting kinetic stability. The pK_a for *n*-hexanol is predicted at 16.6 in water⁹⁹ and is essentially identical to that of iso-propanol ($\text{pK}_a = 16.5$ in water).¹⁰⁰ Therefore, whilst demetalation occurs through protonolysis of the Zn–pyrrolide bond, the formation of **4** is not attributed to a difference in acidity of the alcohol.

Polymerisation catalysis

Ring-opening copolymerisation reactions were conducted using complex **1** reacted *in situ* with four equivalents of *n*-hexanol, with a catalyst loading of 0.1 mol%, in neat cyclohexene oxide (CHO), under 1 bar pressure of CO_2 , at 80°C for 24 h (Table 1, entry 1). Four equivalents of the alcohol (0.4 mol%) were added immediately before the mixture was exposed to carbon dioxide. The catalytic activity was low, with a TOF of 9 h^{-1} . The polymer formed has a low molar mass ($M_n = 4400\text{ g mol}^{-1}$) and broad dispersity ($D = 1.67$). Analysis of the polymer composition using ^1H NMR spectroscopy showed that the majority of linkages are ether, with only 7% carbonate linkages. Complex **1** was also tested, under 1 bar CO_2 , using four equivalents of methanol as the alcohol (Table 1, entry 2). By analogy to the stoichiometric reactions with iso-propanol, it was proposed that a trinuclear Zn-methoxide complex would form and this species shows a low catalytic activity (TOF = 13 h^{-1}). The resulting poly(ether-carbonate) shows a high proportion of ether linkages, moderate molar mass ($M_n = 15\,300\text{ g mol}^{-1}$) and broad dispersity ($D = 2.69$), the latter indicative of slow or multiple initiation reactions.

In order to increase the proportion of carbonate linkages for the catalyst system comprising **1**/*n*-hexanol, the CO_2 pressure was increased (Table 1, entries 3 and 4, Fig. S8†). Using 30 bar pressure of CO_2 , both the activity (TOF = 21 h^{-1}) and the selectivity for carbonate linkages increased (carbonate linkages = 56%). In line with the greater conversion, the resulting polymer shows a higher molar mass ($M_n = 18\,100\text{ g mol}^{-1}$) but the dispersity remains very broad ($D = 3.03$). When the reaction pressure is increased further to 50 bar, the catalyst activity, conversion of epoxide, and carbonate selectivity all decrease. This may be a result of gas expansion which is known to occur under such sub-critical conditions and which effectively dilutes the catalyst concentrations.¹⁰¹



Table 1 Polymerisation catalysis results using pre-catalysts **1** and **2**, and catalyst **3** in the ROCOP of cyclohexene oxide (CHO) and CO₂

Entry	Catalyst	[Epoxide]/M [cat.]/mol%	[CO ₂]/atm	TON ^b	TOF ^c /h ⁻¹	Polycarbonate linkage selectivity ^d /%	M _n , g mol ⁻¹ (<i>D</i>) ^e
1	1	10 (0.1)	1	220	9	7	4400 (1.67)
2 ^a	1	10 (0.1)	1	310	13	6	15 300 (2.69)
3	1	10 (0.1)	30	510	21	56	18 100 (3.03)
4	1	10 (0.1)	50	140	6	29	13 700 (2.97)
5	1	5 (0.2)	30	360	15	90	11 900 (14)
6	1	5 (0.2)	1	0	0	0	—
7	2	10 (0.1)	1	70	3	0	—
8	2	10 (0.1)	50	30	1	68	—
9	2	5 (0.2)	30	10	0.5	88	—
10	3	5 (0.2)	30	250	11	81	7700 (13)

Reactions were conducted for 24 h at 80 °C and when using **1** or **2**, four equivalents of *n*-hexanol (except where stated otherwise) were added immediately prior to the addition of carbon dioxide. Reactions were either conducted in neat epoxide (*i.e.* [CHO] = 10 M) or in toluene ([CHO] = 5 M). ^a Methanol was added instead of *n*-hexanol. ^b TON = (moles epoxide consumed)/(moles catalyst), the conversion was determined by integration of the signals, in the ¹H NMR spectrum for methine protons assigned to CHO (3.14 ppm) and polymer (4.65 ppm). ^c TOF = TON/time (h). ^d Selectivity for carbonate linkages was determined by comparison of the relative integrals in the ¹H NMR spectrum for the signals of polycarbonate (4.65 ppm) and ether linkages (3.43 ppm). ^e The molar mass (*M_n*) and dispersity (*D*) values were determined using size-exclusion chromatography (SEC), in THF, which was calibrated with polystyrene standards.

As part of attempts to improve the polymerisation selectivity, polymerisations were conducted in toluene solutions to reduce the overall epoxide concentration and hence slow sequential enchainment reactions (Table 1, entries 5, 6, Fig. S9†). Overall, the absolute catalyst concentration was the same as in the previous reactions conducted in neat epoxide but its relative loading compared to epoxide is increased. Polymerisations conducted in toluene solution at 1 bar CO₂ pressure were unsuccessful (Table 1, entry 6), but at 30 bar pressure polymerisation occurs to form a polymer with significantly increased carbonate linkages (Table 1, entry 5). However, the ROCOP activity is reduced compared to reactions in neat epoxide, for example the TOF decreased from 21 h⁻¹ (10 M) to 15 h⁻¹ (5 M) (Table 1, entries 3 and 5). The polymerisation control is very poor forming a polymer with an exceptionally broad dispersity (*M_n* = 11 000 g mol⁻¹; *D* = 14). To investigate further, the evolution of polycarbonate molar mass *vs.* conversion was analysed (Table S1, Fig. S11†). At low conversions, bimodal molar mass distributions are seen showing a characteristic very high molar mass peak (*M_n* = 194 000 g mol⁻¹; *D* = 1.89) and a lower molar mass peak (*M_n* = 2400; *D* = 3.00). The higher molar mass peak did not increase particularly as polymerisation progressed whereas the lower peak shows a clear increase in molar mass *vs.* conversion. Aliquots were taken and the ¹H NMR spectra show the formation of both carbonate and ether linkages throughout the reaction. It is tentatively proposed that the higher molar mass peak is due to uncontrolled and rapid formation of polyether, whilst the lower molar mass peak arises from ROCOP to form predominantly polycarbonate. Nonetheless, a more detailed analysis is precluded by the very broad molar mass distributions that clearly signal problems with relative initiation rates and number of active sites.

Polymerisations were also conducted under a range of similar conditions using the catalyst system formed from **2** (Table 1, entries 7–9). Under all conditions, its activity is very

low, although the carbonate selectivity could be somewhat increased at higher pressures. The isolated hexyl alkoxide complex **3** shows similar performance to the catalyst system formed using **1** and *n*-hexanol, and is consistent with **3** being the true initiating species formed during alcoholysis of **1**. The polycarbonate product, formed using **3**, shows a similar molecular weight (*M_n* = 7400 g mol⁻¹) and very broad dispersity (*D* > 13) to that formed using the catalyst system of **1**/hexyl alcohol. Finally, ROCOP reactions using propylene oxide and carbon dioxide (50 bar) were unsuccessful with all catalysts. Overall, the activity values for all catalysts are at the lower end in this field and cannot compete with leading catalysts, such as the di-zinc catalysts coordinated by β-diketiminato or macrocyclic ancillary ligands.^{77–88}

Conclusions

The result of reactions between the tetranuclear ethyl zinc complex **1** and alcohols is highly dependent on the alcohol used. While reaction with *n*-hexanol provides the isolable tetranuclear Zn hexyl-alkoxide complex **3**, use of isopropanol results in demetalation and the formation of the trinuclear Zn complex **4**. Reactions between **1** and phenol similarly result in demetalation, while the use of the more sterically hindered alcohol HOC₆H₃-*t*-Bu-2,6 maintains the nuclearity of the complex but limits the protonolysis reaction, with two ethyl groups untouched. Complex **1** showed some activity and selectivity as a catalyst in ring-opening copolymerisation of cyclohexene oxide and carbon dioxide, with optimised conditions of 30 atm pressure of CO₂, 0.1 mol% catalyst loading, 80 °C and in 5 M cyclohexene oxide (diluted in toluene). These conditions enabled the production of polycarbonates with 90% selectivity for carbonate linkages and with a TOF of 15 h⁻¹. However, the polymers produced have very broad molar mass distributions suggesting that multiple catalytic



sites are present which exhibit poor reaction control. The analogous anthracenyl-bridged complex **2** showed even lower activity and a similar lack of polymerisation control. While higher nuclearity macrocyclic zinc complexes have potential as catalysts in ROCOP reactions, the complexes used in this study appear too labile, with facile demetalation occurring under reaction conditions, making them unsuitable as catalysts. This highlights the need for improved ligand design and complex stability towards alcohols to prepare more active and selective catalysts for ROCOP reactions.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- 1 R. J. Hooley, *Inorg. Chem.*, 2018, **57**, 3497–3499.
- 2 Z. Liu, S. K. M. Nalluri and J. F. Stoddart, *Chem. Soc. Rev.*, 2017, **46**, 2459–2478.
- 3 L. F. Lindoy, K.-M. Park and S. S. Lee, *Chem. Soc. Rev.*, 2013, **42**, 1713–1727.
- 4 J. B. Love, *Chem. Commun.*, 2009, 3154–3165.
- 5 T. Ogoshi, T. Kakuta and T.-A. Yamagishi, *Angew. Chem., Int. Ed.*, 2019, **58**, 2197–2206.
- 6 M. T. Chaudhry, F. Lelj and M. J. MacLachlan, *Chem. Commun.*, 2018, **54**, 11869–11872.
- 7 Z. Chen, S. Guieu, N. G. White, F. Lelj and M. J. MacLachlan, *Chem. – Eur. J.*, 2016, **22**, 17657–17672.
- 8 T. Hojo, R. Matsuoka and T. Nabeshima, *Inorg. Chem.*, 2019, **58**, 995–998.
- 9 J. Janczak, D. Prochowicz, J. Lewiński, D. Fairen-Jimenez, T. Bereta and J. Lisowski, *Chem. – Eur. J.*, 2016, **22**, 598–609.
- 10 M. Löffler, J. Gregoliński, M. Korabik, T. Lis and J. Lisowski, *Dalton Trans.*, 2016, **45**, 15586–15594.
- 11 M. A. Minier and S. J. Lippard, *Organometallics*, 2014, **33**, 1462–1466.
- 12 T. Nakamura, Y. Kaneko, E. Nishibori and T. Nabeshima, *Nat. Commun.*, 2017, **8**, 129.
- 13 S. Zhang and L. Zhao, *Acc. Chem. Res.*, 2018, **51**, 2535–2545.
- 14 M. Fondo, A. M. García-Deibe, N. Ocampo, J. Sanmartín and M. R. Bermejo, *Dalton Trans.*, 2004, 2135–2141.
- 15 Y.-M. Zhao, G.-Q. Yu, F.-F. Wang, P.-J. Wei and J.-G. Liu, *Chem. – Eur. J.*, 2019, **25**, 3726–3739.
- 16 M. Biyikal, K. Löhnwitz, P. W. Roesky and S. Blechert, *Synlett*, 2008, 3106–3110.
- 17 A. Gualandi, L. Cerisoli, H. Stoeckli-Evans and D. Savoia, *J. Org. Chem.*, 2011, **76**, 3399–3408.
- 18 R. W. Hogue, O. Schott, G. S. Hanan and S. Brooker, *Chem. – Eur. J.*, 2018, **24**, 9820–9832.
- 19 A. B. Kremer and P. Mehrkhodavandi, *Coord. Chem. Rev.*, 2019, **380**, 35–57.
- 20 P. Mahapatra, S. Ghosh, S. Giri, V. Rane, R. Kadam, M. G. B. Drew and A. Ghosh, *Inorg. Chem.*, 2017, **56**, 5105–5121.
- 21 K. Mase, S. Aoi, K. Ohkubo and S. Fukuzumi, *J. Porphyrins Phthalocyanines*, 2016, **20**, 935–949.
- 22 M. Quernheim, H. Liang, Q. Su, M. Baumgarten, N. Koshino, H. Higashimura and K. Müllen, *Chem. – Eur. J.*, 2014, **20**, 14178–14183.
- 23 C. Redshaw, *Catalysts*, 2017, **7**, 165.
- 24 X. Ribas and M. Devillard, *Chem. – Eur. J.*, 2018, **24**, 1222–1230.
- 25 A. Thevenon, C. Romain, M. S. Bennington, A. J. P. White, H. J. Davidson, S. Brooker and C. K. Williams, *Angew. Chem., Int. Ed.*, 2016, **55**, 8680–8685.
- 26 G. Tseberlidis, D. Intrieri and A. Caselli, *Eur. J. Inorg. Chem.*, 2017, 3589–3603.
- 27 X.-X. Zheng and Z.-X. Wang, *J. Organomet. Chem.*, 2016, **823**, 14–22.
- 28 R. Liu, C. von Malotki, L. Arnold, N. Koshino, H. Higashimura, M. Baumgarten and K. Müllen, *J. Am. Chem. Soc.*, 2011, **133**, 10372–10375.
- 29 S. Dhers, H. L. C. Feltham, M. Rouzières, R. Clérac and S. Brooker, *Dalton Trans.*, 2016, **45**, 18089–18093.
- 30 A. I. d'Aquino, H. F. Cheng, J. Barroso-Flores, Z. S. Kean, J. Mendez-Arroyo, C. M. McGuirk and C. A. Mirkin, *Inorg. Chem.*, 2018, **57**, 3568–3578.
- 31 A. M. Lifschitz, M. S. Rosen, C. M. McGuirk and C. A. Mirkin, *J. Am. Chem. Soc.*, 2015, **137**, 7252–7261.
- 32 J. F. C. Mário and M. P. Sara, *Curr. Org. Synth.*, 2017, **14**, 704–714.
- 33 T. Tanaka and A. Osuka, *Chem. Rev.*, 2017, **117**, 2584–2640.
- 34 S. Saito and A. Osuka, *Angew. Chem., Int. Ed.*, 2011, **50**, 4342–4373.
- 35 B. M. Rambo and J. L. Sessler, *Chem. – Eur. J.*, 2011, **17**, 4946–4959.
- 36 G. Givaja, A. J. Blake, C. Wilson, M. Schroder and J. B. Love, *Chem. Commun.*, 2003, 2508–2509.
- 37 E. Askarizadeh, A. M. J. Devoille, D. M. Boghaei, A. M. Z. Slawin and J. B. Love, *Inorg. Chem.*, 2009, **48**, 7491–7500.
- 38 G. Givaja, M. Volpe, M. A. Edwards, A. J. Blake, C. Wilson, M. Schröder and J. B. Love, *Angew. Chem., Int. Ed.*, 2007, **46**, 584–586.
- 39 M. Volpe, H. Hartnett, J. W. Leeland, K. Wills, M. Ogunshun, B. J. Duncombe, C. Wilson, A. J. Blake, J. McMaster and J. B. Love, *Inorg. Chem.*, 2009, **48**, 5195–5207.



- 40 E. Askarizadeh, S. B. Yaghoob, D. M. Boghaei, A. M. Z. Slawin and J. B. Love, *Chem. Commun.*, 2010, **46**, 710–712.
- 41 A. M. J. Devoille and J. B. Love, *Dalton Trans.*, 2012, **41**, 65–72.
- 42 A. M. J. Devoille, P. Richardson, N. L. Bill, J. L. Sessler and J. B. Love, *Inorg. Chem.*, 2011, **50**, 3116–3126.
- 43 P. L. Arnold, M. S. Dutkiewicz, M. Zegke, O. Walter, C. Apostolidis, E. Hollis, A.-F. Pécharman, N. Magnani, J.-C. Griveau, E. Colineau, R. Caciuffo, X. Zhang, G. Schreckenbach and J. B. Love, *Angew. Chem., Int. Ed.*, 2016, **55**, 12797–12801.
- 44 P. L. Arnold, E. Hollis, G. S. Nichol, J. B. Love, J.-C. Griveau, R. Caciuffo, N. Magnani, L. Maron, L. Castro, A. Yahia, S. O. Odoh and G. Schreckenbach, *J. Am. Chem. Soc.*, 2013, **135**, 3841–3854.
- 45 P. L. Arnold, G. M. Jones, S. O. Odoh, G. Schreckenbach, N. Magnani and J. B. Love, *Nat. Chem.*, 2012, **4**, 221.
- 46 P. L. Arnold, D. Patel, A. J. Blake, C. Wilson and J. B. Love, *J. Am. Chem. Soc.*, 2006, **128**, 9610–9611.
- 47 P. L. Arnold, D. Patel, C. Wilson and J. B. Love, *Nature*, 2008, **451**, 315.
- 48 P. L. Arnold, A.-F. Pécharman, E. Hollis, A. Yahia, L. Maron, S. Parsons and J. B. Love, *Nat. Chem.*, 2010, **2**, 1056.
- 49 B. E. Cowie, G. S. Nichol, J. B. Love and P. L. Arnold, *Chem. Commun.*, 2018, **54**, 3839–3842.
- 50 P. L. Arnold, A.-F. Pécharman, R. M. Lord, G. M. Jones, E. Hollis, G. S. Nichol, L. Maron, J. Fang, T. Davin and J. B. Love, *Inorg. Chem.*, 2015, **54**, 3702–3710.
- 51 J. R. Pankhurst, T. Cadenbach, D. Betz, C. Finn and J. B. Love, *Dalton Trans.*, 2015, **44**, 2066–2070.
- 52 T. Cadenbach, J. R. Pankhurst, T. A. Hofmann, M. Curcio, P. L. Arnold and J. B. Love, *Organometallics*, 2015, **34**, 2608–2613.
- 53 Z. Qin, C. M. Thomas, S. Lee and G. W. Coates, *Angew. Chem., Int. Ed.*, 2003, **42**, 5484–5487.
- 54 D. J. Darensbourg, P. Rainey and J. Yarbrough, *Inorg. Chem.*, 2001, **40**, 986–993.
- 55 C. K. Williams and M. A. Hillmyer, *Polym. Rev.*, 2008, **48**, 1–10.
- 56 A. M. Chapman, C. Keyworth, M. R. Kember, A. J. J. Lennox and C. K. Williams, *ACS Catal.*, 2015, **5**, 1581–1588.
- 57 S. Paul, Y. Zhu, C. Romain, R. Brooks, P. K. Saini and C. K. Williams, *Chem. Commun.*, 2015, **51**, 6459–6479.
- 58 A. Thevenon, A. Cyriac, D. Myers, A. J. P. White, C. B. Durr and C. K. Williams, *J. Am. Chem. Soc.*, 2018, **140**, 6893–6903.
- 59 M. R. Kember and C. K. Williams, *J. Am. Chem. Soc.*, 2012, **134**, 15676–15679.
- 60 D. J. Darensbourg, R. M. Mackiewicz, A. L. Phelps and D. R. Billodeaux, *Acc. Chem. Res.*, 2004, **37**, 836–844.
- 61 D. J. Darensbourg and J. C. Yarbrough, *J. Am. Chem. Soc.*, 2002, **124**, 6335–6342.
- 62 D. J. Darensbourg, R. M. Mackiewicz, J. L. Rodgers and A. L. Phelps, *Inorg. Chem.*, 2004, **43**, 1831–1833.
- 63 A. Buchard, M. R. Kember, K. G. Sandeman and C. K. Williams, *Chem. Commun.*, 2011, **47**, 212–214.
- 64 E. K. Noh, S. J. Na, S. S. S.-W. Kim and B. Y. Lee, *J. Am. Chem. Soc.*, 2007, **129**, 8082–8083.
- 65 X.-B. Lu and Y. Wang, *Angew. Chem., Int. Ed.*, 2004, **43**, 3574–3577.
- 66 X.-B. Lu, L. Shi, Y.-M. Wang, R. Zhang, Y.-J. Zhang, X.-J. Peng, Z.-C. Zhang and B. Li, *J. Am. Chem. Soc.*, 2006, **128**, 1664–1674.
- 67 H. Sugimoto and K. Kuroda, *Macromolecules*, 2008, **41**, 312–317.
- 68 C.-H. Li, H.-J. Chuang, C.-Y. Li, B.-T. Ko and C.-H. Lin, *Polym. Chem.*, 2014, **5**, 4875–4878.
- 69 C.-Y. Tsai, F.-Y. Cheng, K.-Y. Lu, J.-T. Wu, B.-H. Huang, W.-A. Chen, C.-C. Lin and B.-T. Ko, *Inorg. Chem.*, 2016, **55**, 7843–7851.
- 70 C.-Y. Tsai, B.-H. Huang, M.-W. Hsiao, C.-C. Lin and B.-T. Ko, *Inorg. Chem.*, 2014, **53**, 5109–5116.
- 71 R. Eberhardt, M. Allmendinger, G. A. Luinstra and B. Rieger, *Organometallics*, 2003, **22**, 211–214.
- 72 D. J. Darensbourg and M. W. Holtcamp, *Macromolecules*, 1995, **28**, 7577–7579.
- 73 D. J. Darensbourg, M. W. Holtcamp, G. E. Struck, M. S. Zimmer, S. A. Niezgoda, P. Rainey, J. B. Robertson, J. D. Draper and J. H. Reibenspies, *J. Am. Chem. Soc.*, 1999, **121**, 107–116.
- 74 H. Sugimoto, H. Ohtsuka and S. Inoue, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 4172–4186.
- 75 T. Aida, M. Ishikawa and S. Inoue, *Macromolecules*, 1986, **19**, 8–13.
- 76 S. Inoue, H. Koinuma and T. Tsuruta, *J. Polym. Sci., Part B: Polym. Lett.*, 1969, **7**, 287–292.
- 77 D. R. Moore, M. Cheng, E. B. Lobkovsky and G. W. Coates, *Angew. Chem., Int. Ed.*, 2002, **41**, 2599.
- 78 D. R. Moore, M. Cheng, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2003, **125**, 11911–11924.
- 79 B. Y. Lee, H. Y. Kwon, S. Y. Lee, S. J. Na, S.-i. Han, H. Yun, H. Lee and Y.-W. Park, *J. Am. Chem. Soc.*, 2005, **127**, 3031–3037.
- 80 S. Kissling, P. T. Altenbuchner, M. W. Lehenmeier, E. Herdtweck, P. Deglmann, U. B. Seemann and B. Rieger, *Chem. – Eur. J.*, 2015, **21**, 8148–8157.
- 81 M. W. Lehenmeier, S. Kissling, P. T. Altenbuchner, C. Bruckmeier, P. Deglmann, A.-K. Brym and B. Rieger, *Angew. Chem., Int. Ed.*, 2013, **52**, 9821–9826.
- 82 S. Klaus, S. I. Vagin, M. W. Lehenmeier, P. Deglmann, A. K. Brym and B. Rieger, *Macromolecules*, 2011, **44**, 9508–9516.
- 83 K. Nakano, S. Hashimoto and K. Nozaki, *Chem. Sci.*, 2010, **1**, 369–373.
- 84 C. Romain, M. S. Bennington, A. J. P. White, C. K. Williams and S. Brooker, *Inorg. Chem.*, 2015, **54**, 11842–11851.
- 85 M. R. Kember, P. D. Knight, P. T. R. Reung and C. K. Williams, *Angew. Chem., Int. Ed.*, 2009, **48**, 931–933.



- 86 J. A. Garden, P. K. Saini and C. K. Williams, *J. Am. Chem. Soc.*, 2015, **137**, 15078–15081.
- 87 F. Jutz, A. Buchard, M. R. Kember, S. B. Fredriksen and C. K. Williams, *J. Am. Chem. Soc.*, 2011, **133**, 17395–17405.
- 88 C. Romain, J. A. Garden, G. Trott, A. Buchard, A. J. P. White and C. K. Williams, *Chem. – Eur. J.*, 2017, **23**, 7367–7376.
- 89 D. J. Darensbourg, J. R. Wildeson and J. C. Yarbrough, *Inorg. Chem.*, 2002, **41**, 973–980.
- 90 M. B. Dinger and M. J. Scott, *Inorg. Chem.*, 2001, **40**, 1029–1036.
- 91 K. L. Orchard, J. E. Harris, A. J. P. White, M. S. P. Shaffer and C. K. Williams, *Organometallics*, 2011, **30**, 2223–2229.
- 92 R. Duchateau, W. J. van Meerendonk, S. Huijser, B. B. P. Staal, M. A. van Schilt, G. Gerritsen, A. Meetsma, C. E. Koning, M. F. Kemmere and J. T. F. Keurentjes, *Organometallics*, 2007, **26**, 4204–4211.
- 93 M. R. Kember, A. J. P. White and C. K. Williams, *Inorg. Chem.*, 2009, **48**, 9535–9542.
- 94 J. W. Leeland, F. J. White and J. B. Love, *J. Am. Chem. Soc.*, 2011, **133**, 7320–7323.
- 95 P. E. Eaton and T. W. Cole, *J. Am. Chem. Soc.*, 1964, **86**, 3157–3158.
- 96 D. Schroder, H. Schwarz, S. Polarz and M. Driess, *Phys. Chem. Chem. Phys.*, 2005, **7**, 1049–1053.
- 97 D. J. Darensbourg, J. R. Wildeson, J. C. Yarbrough and J. H. Reibenspies, *J. Am. Chem. Soc.*, 2000, **122**, 12487–12496.
- 98 M. H. Chisholm, J. C. Huffman and K. Phomphrai, *J. Chem. Soc., Dalton Trans.*, 2001, 222–224.
- 99 M. J. Citra, *Chemosphere*, 1999, **38**, 191–206.
- 100 W. Reeve, C. M. Erikson and P. F. Aluotto, *Can. J. Chem.*, 1979, **57**, 2747–2754.
- 101 S. Mang, A. I. Cooper, M. E. Colclough, N. Chauhan and A. B. Holmes, *Macromolecules*, 2000, **33**, 303–308.

