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An interchangeable homogeneous ⇔ heterogeneous catalyst system for furfural upgrading†

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Intercalation of benzimidazolium cations $[BI]^+$ into the nanogalleries of Na^+/montmorillonite (MMT) clay leads to generation of recyclable supported precatalysts $[BI]^+$/MMT, which, upon treatment with a base, catalyze furfural self-condensation coupling reaction into furoin in almost constant yields of >96% over the three cycles investigated. This catalyst system combines the best features of both homogeneous and heterogeneous catalyst systems, as it performs the homogeneous molecular catalysis by the discharged N-heterocyclic carbene catalyst in solution and then recovers the catalyst through *in situ* heterogenization after the reaction *via* re-intercalation of the charged precatalyst. The $[^{12,12}BI]^+$/MMT catalyst system carrying two long-chain C_{12} dodecyl substituents on the [BI] nitrogen atoms is particularly effective for achieving both high product yield and catalyst recyclability.

A number of approaches have been developed to bridge homogeneous and heterogeneous catalysis, pursuing the ultimate goal of creating a catalytic system that can combine the best features of both homogeneous catalysis for high activity, efficiency and selectivity enabled by quantitative, discrete molecular catalyst sites and heterogeneous catalysis for ease of product separation and catalyst stability, recovery or recycling.[1] Among which, heterogenization of homogeneous catalysts by supporting a molecular catalyst onto an insoluble inorganic or organic carrier is most common. Such heterogenized molecular catalysts perform catalytic reactions on the surfaces of insoluble carriers, often exhibiting different performances than the original molecular catalysts in a truly homogeneous environment. We hypothesized that a more desirable design would be a supported catalyst system that can release the molecular catalyst into solution for homogeneous catalysis on demand and then recover the catalyst back onto the support through *in situ* heterogenization after the reaction. Such a catalyst release and recapture process can then be repeated for catalyst recyclability.

Along the course of current global efforts in developing technologically and economically feasible routes for converting nonfood lignocellulosic biomass into fuels, chemicals, and materials,[2] furaldehydes (FAs), particularly furfural and 5-hydroxylmethylfurfural (HMF) derived from dehydration of biorefinery carbohydrates, have emerged as two of the most promising value-added biomass building blocks or platform chemicals.[3] However, hydrodeoxygenation of furfural and HMF produces low carbon-number alkanes, unsatisfactory as fuel additives.[4] To produce high-quality liquid fuels, furfural and HMF need to be upgraded into higher energy-density species through chain-extension reactions.[5] As FAs such as HMF cannot undergo self-aldol condensation for chain extension, cross-aldol condensation with acetone has been developed.[4,6] A greener process has been developed for direct self-condensation coupling of HMF[7] by organic N-heterocyclic carbene (NHC) catalysts, which reverse the polarity of the HMF carbonyl (umpolung) and enable coupling of HMF into C_{12} 5,5′-dihydroxymethyl furoin (DHMF) with near quantitative yield and 100% atom-economy.[8,9] This organocatalytic benzoin-condensation-type HMF chain-extension method, which bears the hallmarks of green chemistry (*i.e.*, a solvent-free, metal-free process with 100% atom-economy and quantitative selectivity), also works well for other FAs such as furfural and 5-methylfurfural.[8,10] The proposed mechanism for the NHC-catalyzed self-coupling of FAs into furoins *via* the umpolung condensation[7,8] is analogous to that proposed for the benzoin condensation of benzaldehyde by Breslow.[11]

Homogeneous benzoin condensation of furfural has been extensively investigated,[7,8,10,12] with the best furoin yield (>99%) achieved most recently by the NHC derived from the acetate substituted thiazolium salt.[13] However, from an economic and green chemistry point of view, it is more desirable to develop efficient and reusable heterogeneous NHC catalyst systems for benzoin condensation and FA self-coupling reactions. In this context, polymeric NHCs were developed for benzaldehyde condensation reaction.[9,14] Insoluble polymer

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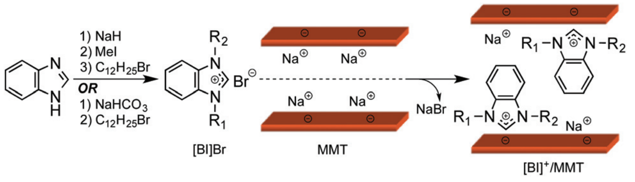
supported thiazolium salts, when combined with a base, produced furoin with under 67% yields in the furfural self-coupling reaction.[15] Likewise, polymer-supported imidazolium salts, when employed for the benzoin condensation of aldehydes in the presence of base, gave the acyloin products under 77% yields.[16]

As can be seen from the above brief overview, highly efficient and recyclable supported catalyst systems for self-coupling of FAs, particularly furfural and HMF, have not yet been achieved. To address this challenge, we have developed a novel interchangeable homogeneous ⇔ heterogeneous catalyst system supported onto Na^+/montmorillonite (MMT) clay and successfully applied it to catalyze highly efficient self-coupling reaction of furfural into furoin, achieving essentially quantitative furoin yields over the three catalyst recovery-reuse cycles performed.

Benzimidazolium $[BI]^+$ salts[17] carrying two different or same alkyl groups on the nitrogen atoms were prepared in high yields from double alkylation of benzimidazolide, derived from deprotonation of benzimidazole with a base (NaH or $NaHCO_3$). More specifically, a stepwise procedure involving the first reaction of benzimidazolide with MeI, followed by the subsequent reaction of the resulting 3-methylbenzimidazole with dodecyl bromide, led to the desired 1-dodecyl-3-methyl benzimidazolium bromide, $[^{1,12}BI]Br$, in 94% overall yield. On the other hand, a simpler one-pot procedure involving the reaction of benzimidazolide with 3 equivalents of dodecyl bromide was employed to prepare 1,3-didodecyl benzimidazolium bromide, $[^{12,12}BI]Br$, in 93% yield. Next, intercalation of the $[BI]^+$ cations into the nanogalleries of MMT proceeded through a cation exchange reaction between the sodium cations of MMT and $[BI]^+$ cations of the [BI]Br salts, affording the MMT-supported $[BI]^+$ precatalysts, $[^{1,12}BI]^+$/MMT and $[^{12,12}BI]^+$/MMT (Scheme 1). The analogous MMT-supported 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium $[TM]^+$ precatalyst, $[TM]^+$/MMT, included here as a comparative example of this study, was prepared in the same manner.

The prepared MMT-supported $[BI]^+$ precatalysts were characterized by powder X-ray diffraction analysis (XRD), Fourier transform infrared (FT-IR) spectroscopy, and thermogravimetric analysis (TGA). The XRD profiles of MMT, $[^{1,12}BI]^+$/MMT, and $[^{12,12}BI]^+$/MMT are overlaid in Fig. 1 for comparison. The basal spacings of these samples were calculated using the Bragg's Equation: $2d \sin\theta = \lambda$, where d is the basal spacing; θ is the Bragg peak angle; and λ is the X-ray wavelength (0.154 nm in the current measurement). The calculated results showed that the basal spacings of MMT, $[^{1,12}BI]^+$/MMT, and $[^{12,12}BI]^+$/MMT were 1.07, 1.63, and 2.35 nm, respectively. It is well known that the basal spacing of the MMT clay treated with a long-chain ammonium salt is largely dependent on the chain length of the ammonium salt.[18] Accordingly, $[^{12,12}BI]^+$/MMT carrying two dodecyl chains on the $[BI]^+$ cation exhibited the largest basal spacing (2.35 nm) of the series, followed by $[^{1,12}BI]^+$/MMT with only one dodecyl chain (1.63 nm) which, nonetheless, had larger basal spacing than the parent MMT with the smallest cation (Na^+) of the series (1.07 nm). This comparative analysis provided this key initial evidence that the $[^{1,12}BI]^+$ and $[^{12,12}BI]^+$ cations were successfully intercalated into the nanogalleries of MMT.



Scheme 1 Outlined synthesis of $[^{1,12}BI]^+$/MMT and $[^{12,12}BI]^+$/MMT.

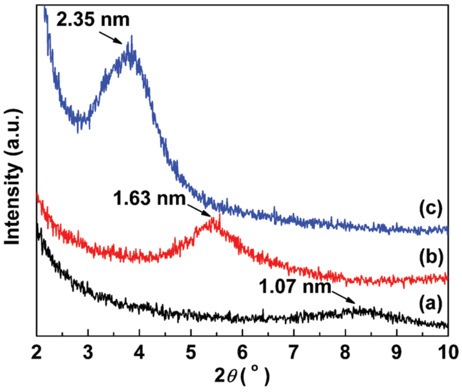


Fig. 1 XRD profiles of MMT (a), $[^{1,12}BI]^+$/MMT (b), and $[^{12,12}BI]^+$/MMT (c).

Additionally, FT-IR was used to further verify the intercalation of the $[BI]^+$ cations into the interlayers of MMT. As can be seen from Fig. 2, FT-IR spectra of $[^{1,12}BI]^+$/MMT and $[^{12,12}BI]^+$/MMT exhibited the characteristic absorption bands at 1472 and 1570 cm^{-1}, which corresponded to C=C and C=N stretching vibrations of the benzimidazole moiety. Additionally, aliphatic C–H stretching vibrations at 2856 and 2930 cm^{-1} were also observed, accounting for the alkyl substituents in the $[^{1,12}BI]^+$ and $[^{12,12}BI]^+$ cations. Hence, these FT-IR results pro-

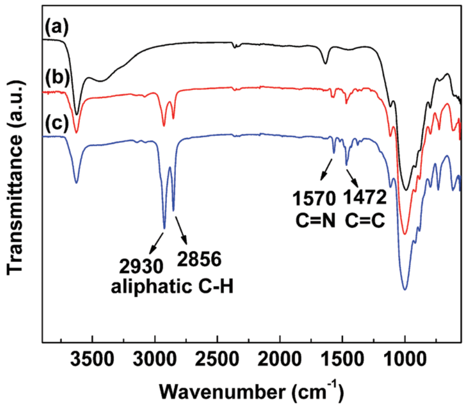
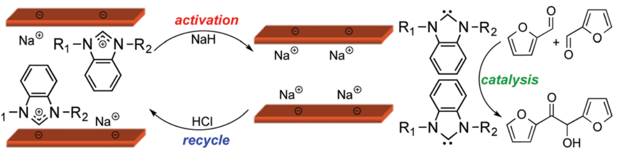


Fig. 2 FT-IR spectra of MMT (a), $[^{1,12}BI]^+$/MMT (b), and $[^{12,12}BI]^+$/MMT (c).

vided additional evidence for the intercalation of the $[BI]^+$ cations into the nanogalleries of MMT.

TGA and elemental analysis (EA) gave comparable results on analyzing the azolium salt content in the inorganic support.[19] In this work, TGA measurements were carried out to determine the contents of the $[BI]^+$ and $[TM]^+$ cations in the resulting MMT-supported precatalysts. The TGA curves of MMT, $[^{1,12}BI]^+$/MMT, $[TM]^+$/MMT, and $[^{12,12}BI]^+$/MMT are shown in Fig. 3, from which the contents of $[^{1,12}BI]^+$ and $[^{12,12}BI]^+$ in the resulting MMT-supported precatalysts were calculated to be 405.8 and 549.9 μmol g^{-1}, respectively. One can note that $[^{12,12}BI]^+$ with two long-chain alkyl substituents was more favorably exchanged into the interlayers of MMT than $[^{1,12}BI]^+$ with only one such long-chain alkyl substituent. The same analysis revealed the content of $[TM]^+$ in the $[TM]^+$/MMT precatalyst to be 647 μmol g^{-1}. These values were used to calculate the loading of the NHC catalyst (which is generated *in situ* upon treatment of the precatalyst with a base, *vide infra*) relative to the furfural substrate.

With the above three MMT-supported $[TM]^+$ and $[BI]^+$ precatalysts in hand, next we investigated their catalytic performances in self-condensation reaction of furfural into furoin. We envisioned that *activation* of the precatalyst through deprotonation of the C2-proton of the azolium salt with a suitable base such as NaH should generate the corresponding NHC catalyst.[20] Then the *in situ* generated neutral NHC catalyst should be discharged into the solution phase as it is a neutral species, while the sodium cations from NaH are intercalated into the interlayers of MMT. Hence, the self-coupling *catalysis* will actually occur in the solution phase behaving much like a homogeneous catalyst, which converts furfural into furoin. The precatalyst *recovery* is accomplished by quenching the reaction with HCl to convert the neutral NHC back to the benzimidazolium salt, which is re-intercalated back into the nanogalleries of MMT through cation exchange (Scheme 2). The recycled MMT-supported $[BI]^+$ precatalyst can then be reused to catalyze the furfural self-coupling reaction. Overall, this novel recyclable supported catalyst concept should combine the best features of homogeneous catalysis for accessing quantitative, selective, discrete molecular catalyst sites and heterogeneous catalysis for ease of product separation and catalyst recovery or recycling.



Scheme 2 Schematic representation of the three processes involved in the self-coupling of furfural by the MMT-supported catalysts.

Guided by this hypothesis, we examined catalytic performances in furfural self-coupling of the MMT-supported precatalysts in combination with NaH. While our initial screening showed that other bases such as Et_3N and 1,8-diaza-bicyclo-[5.4.0]undec-7-ene (DBU) also worked to some certain extent, the best-performing base was determined to be NaH in terms of furoin yield and catalyst recyclability. Hence, subsequent studies were focused on using NaH as the base, the results of which are summarized in Table 1. The blank experiment (Control-1) showed that MMT exhibited no catalytic activity and thus functioned only as a support. In the presence of 10 mol% of $[TM]^+$/MMT and NaH, the self-coupling of furfural in THF at 25 °C produced furoin in 85.8% yield after 5 h (run 1–1). However, the recyclability of this catalyst system was poor, as evidenced by a large reduction in the furoin yield to only 54.1% using the recycled catalyst (run 1–2). The main reason for this phenomenon could be attributed to the high sensitivity of the $[TM]^+$ derived NHC to moisture and oxidation during the quenching process. Switching to the $[BI]^+$ based catalyst and using the current standard conditions (2.0 mmol furfural, 10 mol% of the precatalyst and base relative to furfural, 3 mL THF, 25 °C, 6 h), the furoin yield by $[^{1,12}BI]^+$/MMT + NaH was only moderate (76.0%, run 2). However, the catalyst system based on $[^{12,12}BI]^+$/MMT + NaH gave an excellent furoin yield of 96.6% (run 3–1), and this result was almost identical to that obtained from homogeneous catalysis (Control-2). In

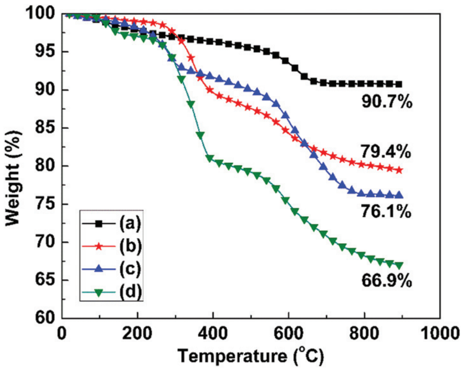


Fig. 3 TGA curves of MMT (a), $[^{1,12}BI]^+$/MMT (b), $[TM]^+$/MMT (c), and $[^{12,12}BI]^+$/MMT (d).

Table 1 Results of furfural self-coupling reaction catalyzed by MMT-supported azolium salts in combination with a base[a]

Run #	Precatalyst	Time (h)	Yield (%)
Control-1	MMT	5	0.0
1–1	$[TM]^+$/MMT	5	85.8
1–2	Recycled	5	54.1
2	$[^{1,12}BI]^+$/MMT	6	76.0
Control-2	$[^{12,12}BI]$Br	6	97.1
3–1	$[^{12,12}BI]^+$/MMT	6	96.6
3–2	Recycled	6	96.1
3–3	Recycled	6	96.1

[a] Furfural, 2.00 mmol for $[BI]^+$ based runs or 3.00 mmol for $[TM]^+$ based runs; MMT supported azolium salt (10 mol%); base (NaH), 10 mol%; THF, 3.0 mL; temperature, 25 °C; reaction time, 6 h for $[BI]^+$ based runs or 5 h for $[TM]^+$ based runs; nitrogen atmosphere.

fact, a model reaction of $[^{12,12}BI]^+$/MMT with NaH confirmed that the majority of *in situ* generated NHC was released from the interlayers of MMT (the TGA result of the recovered MMT-supported catalyst after reacting with NaH was close to that of pristine MMT, Fig. S6†). The observed much superior catalytic performance by the NHC catalyst derived from $[^{12,12}BI]^+$/MMT + NaH, relative to that from $[^{1,12}BI]^+$/MMT + NaH, could be attributed to the Wanzlick equilibrium, which describes the equilibrium of a tetraaminoethylene, formed by dimerization of carbenes, and its corresponding carbene.[17,21] Thus, the $[^{1,12}BI]^+$ derived NHC possessing sterically less demanding substituents may favor the formation of the carbene dimer, verified by ^{1}H NMR (Fig. S7†) of the resulting NHC;[21,22] while the $[^{12,12}BI]^+$ derived NHC bearing sterically demanding substituents facilitates the shift of the equilibrium towards the formation of the catalytically active free carbenes. Furthermore, the long-chain alkyl groups placed in the proximity of the carbene center could also provide a hydrophobic protection pocket for the catalyst to minimize its decomposition or poisoning caused by adventitious protic or oxidative sources.

The recyclability of the best-performing catalyst system $[^{12,12}BI]^+$/MMT + NaH was subsequently investigated. As can be seen from Table 1, the furoin yields for the first three cycles remained at >96%, without notable loss of its catalytic activity. The recovered $[^{12,12}BI]^+$/MMT precatalyst after the first catalytic cycle showed no change in the FT-IR spectrum (Fig. S8†) and recovery of most of the $[^{12,12}BI]^+$ cations by TGA analysis (Fig. S6†). Overall, this catalyst system is both highly efficient and recyclable, achieving a constant, near quantitative yield of furoin from the self-coupling reaction of furfural over the three cycles investigated in this study.

Conclusions

In conclusion, we have developed a novel interchangeable homogeneous ⇔ heterogeneous supported $[BI]^+$/MMT catalyst system for the highly effective self-coupling furfural into furoin. This supported catalyst system combines the best features of homogeneous catalysis for accessing quantitative, discrete molecular catalyst sites and heterogeneous catalysis for ease of product separation and catalyst recovery or recycling. This new concept has been demonstrated by the MMT-supported azolium system that actually performs the furfural upgrading molecular catalysis in the homogeneous, solution phase and then recovers the catalyst through *in situ* heterogenization after the reaction. This concept rests on the nano-galleries of MMT as a charged molecular precatalyst carrier that can discharge the neutral NHC catalyst into the solution phase for catalysis, upon treatment with a base, and recover the catalyst *via* re-intercalation of the charged precatalyst, upon simple quenching the reaction with an acid. Such a system, particularly $[^{12,12}BI]^+$/MMT carrying two long-chain dodecyl substituents on the [BI] nitrogen atoms, when combined with NaH, catalyzes efficient furfural self-coupling to afford furoin in >96% yield, which remained essentially constant over the three catalyst recovery-reuse cycles.

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References

1 C. Li and Y. Liu, *Bridging Heterogeneous and Homogeneous Catalysis: Concepts, Strategies, and Applications*, Wiley-VCH, Weinheim, Germany, 2014.

2 Selective reviews: (*a*) D. Liu and E. Y.-X. Chen, *Green Chem.*, 2014, **16**, 964; (*b*) D. M. Alonso, S. G. Wettstein and J. A. Dumesic, *Green Chem.*, 2013, **15**, 584; (*c*) P. Gallezot, *Chem. Soc. Rev.*, 2012, **41**, 1538; (*d*) D. M. Alonso, J. Q. Bond and J. A. Dumesic, *Green Chem.*, 2010, **12**, 1493; (*e*) A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411; (*f*) A. Corma and G. W. Huber, *Angew. Chem., Int. Ed.*, 2007, **46**, 7184; (*g*) G. W. Huber, S. Iborra and A. Corma, *Chem. Rev.*, 2006, **106**, 4044.

3 Selected reviews: (*a*) T. Wang, M. W. Nolte and B. H. Shanks, *Green Chem.*, 2014, **16**, 548; (*b*) B. Saha and M. M. Abu-Omar, *Green Chem.*, 2014, **16**, 24; (*c*) S. P. Teong, G. Yi and Y. Zhang, *Green Chem.*, 2014, **16**, 2015; (*d*) R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres and J. G. de Vries, *Chem. Rev.*, 2013, **113**, 1499; (*e*) J.-P. Lange, E. van der Heide, J. van Buijtenen and R. Price, *ChemSusChem*, 2012, **5**, 150; (*f*) A. A. Rosatella, S. P. Simeonov, R. F. M. Frade and C. A. M. Afonso, *Green Chem.*, 2011, **13**, 754; (*g*) M. E. Zakrzewska, E. Bogel-Łukasik and R. Bogel-Łukasik, *Chem. Rev.*, 2011, **111**, 397; (*h*) T. Ståhlberg, W. Fu, J. M. Woodley and A. Riisager, *ChemSusChem*, 2011, **4**, 451; (*i*) O. O. James, S. Maity, L. A. Usman, K. O. Ajanaku, O. O. Ajani, T. O. Siyanbola, S. Sahu and R. Chaubey, *Energy Environ. Sci.*, 2010, **3**, 1833; (*j*) J. J. Bozell and G. R. Petersen, *Green Chem.*, 2010, **12**, 539; (*k*) T. Werpy and G. Petersen, Top Value Added Chemicals from Biomass, U.S. Department of Energy (DOE) report: DOE/GO-102004-1992, 2004.

4 (*a*) A. E. King, T. J. Brooks, Y.-H. Tian, E. R. Batista and A. D. Sutton, *ACS Catal.*, 2015, **5**, 1223; (*b*) A. D. Sutton, F. D. Waldie, R. Wu, M. Schlaf, L. A. Silks and J. C. Gordon, *Nat. Chem.*, 2013, **5**, 428.

5 (*a*) B. L. Wegenhart, S. Liu, M. Thom, D. Stanley and M. M. Abu-Omar, *ACS Catal.*, 2012, **2**, 2524; (*b*) M. Balakrishnan, E. R. Sacia and A. T. Bell, *Green Chem.*, 2012, **14**, 1626; (*c*) A. Corma, O. de la Torre and M. Renz, *Energy Environ. Sci.*, 2012, **5**, 6328; (*d*) A. Corma, O. de la Torre, M. Renz and N. Villandier, *Angew. Chem., Int. Ed.*, 2011, **50**, 2375.

6 G. W. Huber, J. N. Chheda, C. J. Barrett and J. A. Dumesic, *Science*, 2005, **308**, 1446.

7 D. Liu, Y. Zhang and E. Y.-X. Chen, *Green Chem.*, 2012, **14**, 2738.

8 D. Liu and E. Y.-X. Chen, *ChemSusChem*, 2013, **6**, 2236.

9 D. Liu and E. Y. X. Chen, *ACS Catal.*, 2014, **4**, 1302.

10 B. L. Wegenhart, L. Yang, S. C. Kwan, R. Harris, H. I. Kenttaemaa and M. M. Abu-Omar, *ChemSusChem*, 2014, **7**, 2742.

11 (*a*) R. Kluger and K. Tittmann, *Chem. Rev.*, 2008, **108**, 1797; (*b*) R. Breslow, *J. Am. Chem. Soc.*, 1958, **80**, 3719; (*c*) R. Breslow, *J. Am. Chem. Soc.*, 1957, **79**, 1762.

12 (*a*) A. Kabro, E. C. Escudero-Adán, V. V. Grushin and P. W. N. M. van Leeuwen, *Org. Lett.*, 2012, **14**, 4014; (*b*) Y. Shimakawa, T. Morikawa and S. Sakaguchi, *Tetrahedron Lett.*, 2010, **51**, 1786; (*c*) A. S. K. Hashmi, M. Wölfle, J. H. Teles and W. Frey, *Synlett*, 2007, 1747; (*d*) D. Enders and U. Kallfass, *Angew. Chem., Int. Ed.*, 2002, **41**, 1743; (*e*) C. K. Lee, M. S. Kim, J. S. Gong and I.-S. H. Lee, *J. Heterocycl. Chem.*, 1992, **29**, 149; (*f*) H. Stetter, R. Y. Raemsch and H. Kuhlmann, *Synthesis*, 1976, 733.

13 H. Zang and E. Y. X. Chen, *Int. J. Mol. Sci.*, 2015, **16**, 7143.

14 (*a*) U. R. Seo and Y. K. Chung, *RSC Adv.*, 2014, **4**, 32371; (*b*) P. Coupillaud, J. Pinaud, N. Guidolin, J. Vignolle, M. Fevre, E. Veaudecrenne, D. Mecerreyes and D. Taton, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 4530; (*c*) J. Pinaud, J. Vignolle, Y. Gnanou and D. Taton, *Macromolecules*, 2011, **44**, 1900; (*d*) A. B. Powell, Y. Suzuki, M. Ueda, C. W. Bielawski and A. H. Cowley, *J. Am. Chem. Soc.*, 2011, **133**, 5218.

15 J. Castells, E. Dunach, F. Geijo, G. Pujol and P. M. Segura, *Isr. J. Chem.*, 1978, **17**, 278.

16 J. M. D. Storey and C. Williamson, *Tetrahedron Lett.*, 2005, **46**, 7337.

17 K.-i. Iwamoto, M. Hamaya, N. Hashimoto, H. Kimura, Y. Suzuki and M. Sato, *Tetrahedron Lett.*, 2006, **47**, 7175.

18 (*a*) Z.-M. Liang, J. Yin and H.-J. Xu, *Polymer*, 2003, **44**, 1391; (*b*) E. P. Giannelis, R. Krishnamoorti and E. Manias, *Adv. Polym. Sci.*, 1999, **138**, 107.

19 L. Han, S.-W. Park and D.-W. Park, *Energy Environ. Sci.*, 2009, **2**, 1286.

20 (*a*) M. N. Hopkinson, C. Richter, M. Schedler and F. Glorius, *Nature*, 2014, **510**, 485; (*b*) L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Laponnaz and V. Cesar, *Chem. Rev.*, 2011, **111**, 2705; (*c*) P. de Fremont, N. Marion and S. P. Nolan, *Coord. Chem. Rev.*, 2009, **253**, 862.

21 V. P. W. Bohm and W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2000, **39**, 4036.

22 Y. F. Liu, P. E. Lindner and D. M. Lemal, *J. Am. Chem. Soc.*, 1999, **121**, 10626.