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Received 00th January 20xx, Accepted 00th January 20xx **diethyl maleate**[†] Yancheng Hu,^a Ning Li,^{*a,b} Guangyi Li,^a Aiqin Wang,^{a,b} Yu Cong,^a Xiaodong Wang^a and Tao Zhang^{*a,b}

Fossil route to PMA

Sustainable production of pyromellitic acid with pinacol and

DOI: 10.1039/x0xx00000x

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Herein, we report an unprecedented and sustainable route to synthesize pyromellitic acid (PMA), a monomer of polyimide, with pinacol and diethyl maleate which can be derived from lignocellulose. Analogously, a sustainable route to trimellitic acid (TMA) was also developed using pinacol and acrylate as the feedstocks.

With the increasing of the social concern about energy and environmental problems, the substitution of fossil resources (such as coal, petroleum and natural gas) with renewable and CO_2 neutral biomass as the feedstock for fuels¹ and chemicals² is drawing more and more attention. Lignocellulose is the main component of agricultural and forestry wastes. Compared with fossil feedstock, lignocellulose is richer in oxygenic groups. Therefore, the selective conversion of lignocellulose and its derivates to high value oxygenates^{3, 4} has great significance.

Polyimide (PI), Kapton for example, has high mechanical strength, unique electrical properties, excellent chemical- and heat-resistance. Thus, it is widely used in many areas, such as engineering plastics, microelectronics, flat panel displays, separation membranes, and aerospace.⁵ Pyromellitic acid (PMA) is a monomer that is used in the production of PI. Nowadays, PMA is usually produced by the oxidation of durene.⁶ However, the approaches towards durene, including separation of durene from C_{10} aromatics, methylation of xylenes or pseudocumene, and disproportionation of pseudocumene, are strongly dependent on non-renewable fossil feedstock (Scheme 1). In this context, the exploration of a sustainable route to synthesize PMA with lignocellulose or its derivates is highly demanded.



Scheme 1 A comparison of fossil and bio route to pyromellitic acid (PMA).

Pinacol is an important vic-diol which can be formed by the metal-mediated coupling⁷ or electrolytic reduction⁸ of acetone from the acetone-butanol-ethanol (ABE) fermentation of lignocellulose.⁹ Besides, a sustainable approach towards pinacol, involving photocatalytic coupling of isopropanol and acetone over heterogeneous catalyst, has been reported.¹⁰ This method is efficient (10.87 mmol $g_{cat}^{-1} h^{-1}$) and feasible because the hydrogen generated during the ABE fermentation can be used to hydrogenate the acetone to isopropanol.⁹ Diethyl maleate is the esterification product of cellulosic ethanol and maleic anhydride (MA), which can be produced by the oxidation of furfural,¹¹ 5-hydroxylmethylfurfural (HMF)¹² or levulinic acid (LA)¹³ from the hydrolysis/dehydration of hemicellulose or cellulose (Scheme 1). Herein, we develop an unprecedented three-step route for the synthesis of renewable PMA with pinacol and diethyl maleate (Scheme 1). In the first step, pinacol and diethyl maleate were directly transformed into diethyl 4,5-dimethylcyclohex-4-ene-1,2-dicarboxylate (i.e. compound 8) by a one-step dehydration/D-A reaction cascade. As reported in the

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 [†]Electronic Supplementary Information (ESI) available: Experimental details and copies of GC chromatograms and NMR spectra. See DOI: 10.1039/x0xx00000x

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literature.¹⁴ pinacol the selective dehvdration to 2.3dimethylbutadiene is very challenging due to the predominance of pinacol rearrangement (a textbook reaction). However, this problem was first solved in this work by employing a choline chloride (ChCl) based deep eutectic solvent (DES) ChCl/HCO₂H. Choline chloride is a non-toxic, cheap, renewable and biodegradable ammonium salt which can be synthesized by the neutralization of choline (a water-soluable vitamin). Formic acid is the side-product in the production of levulinic acid by the hydrolysis/dehydration of cellulose.¹⁵ Thus, the whole reaction system is sustainable and renewable. In the second step, the following dehydrogenation and hydrolysis were successfully integrated into a one-pot reaction, providing 4,5-dimethylphthalic acid (i.e. compound 11) in a high efficiency. Finally, aerobic oxidation under the catalysis of *N*-hydroxyphthalimide (NHPI)/Co(OAc)₂/Mn(OAc)₂ system afforded PMA in an excellent yield.

Initially, we investigated the effect of solvents on the dehydation of pinacol using Amberlyst-15 resin (a commercial solid acid which has been used for many dehydration reactions) as the catalyst. As we can see from the entries 1 and 2 of Table 1, pinacolone (i.e. compound 3) was identified as the main product from the dehydration of pinacol under solvent-free condition or using toluene as solvent. Only trace amount of 2,3dimethylbutadiene (i.e. compound 2) was detected (Fig. S1⁺). Compound 3 was generated by pinacol rearrangement, which was more preferred than 1,2-elimination of H₂O.¹⁴ It is very interesting that evident improvement in the carbon yield of 2,3dimethylbutadiene was observed when we used some polar aprotic solvents such as tetrahydrofuran (THF), dimethyl sulfoxide (DMSO) and N-methyl pyrrolidone (NMP) (Table 1, entries 3-5). Notably, the dehydration in DMSO and NMP provided compound 2 as the main product, although pinacol was not completely consumed (Fig. S2⁺). These results indicate that higher solvent polarity is benefical for 1,2-elimination of H₂O. Because both DMSO and NMP are nonrenewable, great efforts were devoted to enhancing the diene selectivity in renewable reaction media. ChCl-based deep eutectic solvents (DESs) are a new class of cheap and biodegradable green solvents which have strong electrostatic force and hydrogen-bond interactions.¹⁶ In view of this fact, we surmised that the dehydration of pinacol in DESs possibly could give better results. As expected, higher carbon yields (66% and 51%) of compound 2 were achieved over Amberlyst-15 resin in neutral DESs which were formed with ChCl and biomass derived polyols (such as ethylene glycol (EG) and glycerol) (Table 1, entries 6 and 7).

To make the system more renewable, we also explored the dehydration in a series of acidic DESs which were formed with ChCl and biomass derived carboxylic acids (at molar ratio of 1:1) according to the method developed by Abbott *et al.*¹⁶ Among the investigated systems, the DES ChCl/HCOOH exhibited the best performance (Table 1, entries 8-15). A high carbon yield (69%) of compound **2** was achieved in this medium. From the blank experiments using HCOOH or ChCl alone (Table 1, entries 16 and 17), no compound **2** was obtained, indicating that the synergism effect of HCOOH and ChCl (or the formation of DES) is necessary for the excellent performance of ChCl/HCOOH. Moreover, it is noticed that the molar ratio of ChCl and HCOOH in DES also exerted a great

influence on the reaction patterns. With the increasing nulf ChCl/HCOOH molar ratio from 1:1 to $2:\mathbb{P}_{\mathcal{O}}$ the learboak of field of compound **2** varied a little, while that of unexpected compound **3** significantly decreased from 22% to 12% (Table 1, entries 8 and 18). This result further proved that the presence of ChCl restrained the pinacol rearrangement. Based on this result, we fixed the ChCl/HCOOH molar ratio in the DES as 2:1 in the following work.

Table 1 Effect of solvents on the dehydration of pinacol.^a

| | | tid catalyst | + | |
|-----------------|--------------|------------------------------|-------------------|-------------------|
| | 1 Sol | vent, 120 °C / \ 2 | 3 | |
| | | | Carbon | Carbon |
| Entry | Catalyst | Solvent ^b | yield of | yield of |
| | | | 2 (%) | 3 (%) |
| 1 | Amberlyst-15 | - | Trace | 88 |
| 2 | Amberlyst-15 | Toluene | Trace | 97 |
| 3 | Amberlyst-15 | THF | 14 | 81 |
| 4 | Amberlyst-15 | DMSO | 31 | 15 |
| 5 | Amberlyst-15 | NMP | 39 | 21 |
| 6 | Amberlyst-15 | ChCl/EG ^c (1:1) | 66 | 20 |
| 7 | Amberlyst-15 | ChCl/glycerol (1:1) | 51 | 33 |
| 8 | - | ChCl/HCOOH (1:1) | 69 | 22 |
| 9 | - | ChCl/HOAc (1:1) | 26 | 4 |
| 10 | - | ChCl/levulinic acid (1:1) | 19 | 4 |
| 11 | - | ChCl/oxalic acid (1:1) | 17 | 35 |
| 12 | - | ChCl/succinic acid (1:1) | 58 | 32 |
| 13 | - | ChCl/adipic acid (1:1) | 44 | 13 |
| 14 | - | ChCl/tartaric acid (1:1) | 43 | 40 |
| 15 | - | ChCl/citric acid (1:1) | 31 | 36 |
| 16 | - | ChCl | N.R. ^d | N.R. ^d |
| 17 | - | нсоон | Trace | 80 |
| 18 | - | ChCl/HCOOH (2:1) | 68 | 12 |
| 19 ^e | - | ChCl/HCOOH (2:1) | 83 | 13 |
| ~ | | | | |

^{*a*}Reaction conditions: pinacol (1.0 g), Amberlyst-15 (100 mg or 0 mg when acidic DESs were used), solvent (4.0 g), 120 ^{*b*}C, 12 h. ^{*b*}The ratio in parenthese is the molar ratio of choline chloride (ChCl) to the other component. ^{*c*}EG = ethylene glycol. ^{*d*}N.R. = no reaction. ^{*e*}The dehydration of pinacol (1.0 g) was carried out in ChCl/HCOOH (2:1, 8 g) at 140 ^{*o*}C for 12 h.

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The influence of ChCl/HCOOH (2:1) dosage on the dehydration of pinacol was studied. According to Fig. S5⁺, the carbon yield of compound **2** increased with the increment of ChCl/HCOOH dosage, reached the maximum (78%) when 8.0 g ChCl/HCOOH was used, then stabilized with further increasing the dosage. In contrast, it is noticed that the dosage of DES had no evident effect on the carbon yield of compound **3**.

We also investigated the effect of reaction temperature on the carbon yields of compounds **2** and **3**. As shown in Fig. S6⁺, with the increasing of reaction temperature, the carbon yield of compound **2** slightly increased, reached the maximum (83%) when the pinacol dehydration was performed at 140 $^{\circ}$ C (Table 1, entry 19), then decreased with further increment of the temperature. This can be rationalized because high temperature led to the self D-A reaction of compound **2** (Fig. S4⁺), which decreased its carbon yield or selectivity.

Another advantage of this DES system is the easier separation of the product. At the beginning, pinacol and ChCl/HCOOH merge together at 140 °C, the reaction system is monophasic (Fig. S7a⁺). After the completion of the reaction, the mixture spontaneously separates into two phases: the upper layer is compound **2** and the lower layer consists of DES and water (Fig. S7b⁺). Remarkably, when submitting the mixture to a low temperature, the DES layer became solid while the upper layer still remained as liquid, thus allowing a facile separation of compound **2** just by decantation (Fig. S7c⁺). In real application, this is highly advantageous.

The reusability of the DES system was also checked. To do this, the ChCl/HCOOH (2:1) was repeatedly used for the pinacol dehydration. After each usage, the upper layer was removed by decantation. The lower layer (*i.e.* the mixture of water and DES system) was recovered by desiccation and reused for the next cycle. From the result shown in Fig. S8⁺, the ChCl/HCOOH system can be conveniently recycled for at least four times without significant decline in the carbon yield of compound **2**. Moreover, we also checked the thermal stability of formic acid under the investigated conditions. According to the blank experiment result illustrated in Fig. S9⁺, the formic acid was stable under the investigated conditions. No decomposition of formic acid was noticed during the reaction.

Subsequently, we explored the synthesis of PMA precursors (i.e. compounds 6 and 9 in Scheme 2) with compound 2 and maleic anhydride (or diethyl maleate) by the D-A reaction and dehydrogenation. It is noticed that the D-A reaction can take place spontaneously under thermal condition without using solvent or catalyst (Fig. S10⁺, S24⁺ and S25⁺). After the reaction was carried out under mild conditions (60 °C for 1.5 h or 120 °C for 6 h), compound 2 and maleic anhydride (or diethyl maleate) were nearly quantitatively converted to the corresponding D-A adducts (i.e. compound 5 or 8). However, evident difference was observed for the following solvent-free dehydrogenation step (Pd/C, 220 °C, 24 h). When compound 5 was used as the substrate, no aromatic compound 6 was detected in the products. In contrast, a high carbon yield (80%) of compound 9 was obtained from the dehydrogenation of compound 8. Based on this result, we can see that the esterification is favorable for the dehydrogenation of D-A adducts.



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Scheme 2 The reaction pathways for the D-A reaction of compound 2 and maleic anhydride (or diethyl maleate), followed by dehydrogenation.



Fig. 1 Conversion of compound **8** and the carbon yields of compounds **9** and **10** over different catalysts. Reaction conditions: compound **8** (10 mmol, 2.5 g), catalyst (250 mg), 220 $^{\circ}$ C for 24 h.

Besides compound **9**, small amount of compound **10** was observed as the main side product in the dehydrogenation step (Fig. S12⁺). As proposed in Scheme 2, compound **10** was generated by a three-step process, including the retro D-A reaction of compound **8**, isomerization of the obtained diethyl maleate to diethyl fumarate, and D-A reaction of compound **2** and diethyl fumarate. This hypothesis was verified by two experimental facts. 1) According to the blank test, diethyl maleate was isomerized to diethyl fumarate over the Pd/C catalyst under the dehydrogenation condition (Fig. S16⁺). 2) The dehydrogenation of compound **10**, which can be easily prepared by the D-A reaction of compound **2** and diethyl fumarate (Fig. S11⁺), was slower than that of compound **8**. Under the same condition, lower substrate conversion (87% vs. 100%) and carbon yield of compound **10** (Fig. S13⁺).

The catalytic performances of Raney Ni and a series of active carbon loaded metal catalysts in the dehydrogenation step were compared. As shown in Fig. 1, the Pd/C exhibited evidently higher activity than those of other catalysts such as Raney Ni, Ni/C, Pt/C, Rh/C and Ru/C. After prolonging the reaction time to 48 h, 84% carbon yield of compound **9** was obtained. However, we still think 24 h is better from the point view of economic.

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Scheme 3 The conversion of pinacol and diethyl maleate to PMA precursor (*i.e.* compound **11**) by two cascade reactions, followed by catalytic aerobic oxidation.

We also tried to combine the pinacol dehydration and the following D-A reaction into one-step. Gratifyingly, submitting pinacol and diethyl maleate to the DES ChCl/HCOOH at 140 °C could directly produce the D-A adduct in 89% yield (the molar ratio of compounds 8 and 10 is 7.1:1), which was similar as the one obtained by the two-step method (Scheme 3, eqn 1). The product can also be isolated by a simple decantation. Besides, we were delighted to find that the subsequent dehydrogenation and hydrolysis can also be conducted in a one-pot fashion, affording 4,5-dimethylphthalic acid 11 in 73% yield (Scheme 3, eqn 1). These two cascade reactions avoid the isolation of intermediates (*i.e.* compounds 2 and 9), thus rendering the whole process shorter and simpler.

Finally, the oxidation of compound **11** with oxygen (1 atm) in the presence of a catalytic amount of $Co(OAc)_2$ (4 mol%), $Mn(OAc)_2$ (4 mol%), and *N*-hydroxyphthalimide (NHPI, 20 mol%) using acetic acid as solvent at 120 °C afforded PMA in 88% yield (Scheme 3, eqn





Based on what we found in this work, a three-step route for the synthesis of renewable PMA with pinacol was proposed in Scheme 4. In the first step, the one-step selective pinacol dehydration and D-A reaction with diethyl maleate occurred. A renewable and recyclable DES ChCl/HCOOH was highly selective for this reaction. In the second step, 4,5-dimethylphthalic acid **11** was formed by a one-pot dehydrogenation/hydrolysis cascade. Finally, the aerobic oxidation of compound **11** catalyzed by NHPI/Co(OAc)₂/Mn(OAc)₂ system efficiently afforded pyromellitic acid (PMA). The overall carbon yield of PMA of the whole process was estimated as 57%.

Ethyl acrylate is the esterification product of cellulosic ethanol and acrylic acid which can be produced by the dehydration of lactic acid¹⁷ from the catalytic conversion of carbohydrates.^{4, 18} Analogously, we also developed a route for the synthesis of renewable trimellitic acid (TMA) with pinacol and ethyl acrylate (Scheme 4). The detail information was given in ESI⁺. Under the same reaction conditions, a high overall carbon yield of TMA (58%) was achieved. DOI: 10.1039/C6GC03576K

Conclusions

In summary, we have developed an unprecedented three-step route for the synthesis of PMA with pinacol and diethyl maleate which can be derived from lignocellulose. Noteworthy features of our protocol include a renewable and recyclable DES ChCl/HCOOH for the one-step selective pinacol dehydration and D-A reaction with diethyl maleate. an integrated one-pot dehydrogenation/hydrolysis cascade, and aerobic oxidation catalyzed by NHPI/Co(OAc)₂/Mn(OAc)₂ system. An analogous route to renewable TMA was also developed using pinacol and acrylate as the feedstocks. This work paves a new way for the synthesis of renewable polyimide with lignocellulosic platform compounds. Meanwhile, this work also offers a practical and sustainable approach towards 2,3-dimethylbutadiene, which is an important precursor in organic synthesis and polymer science.¹⁹

Acknowledgements

This work was supported by the National Natural Science Foundation of China (no. 21690082; 21690084; 21506213; 21476229; 21277140), Dalian Science Foundation for Distinguished Young Scholars (no. 2015R005), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB17020100), Department of Science and Technology of Liaoning Province (under contract of 2015020086-101). Dr. Hu appreciates the Postdoctoral Science Foundation of China (2015M581365) and the dedicated grant for methanol conversion from DICP for funding this work.

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Published on 22 February 2017. Downloaded by University of California - San Diego on 22/02/2017 19:34:28.

Published on 22 February 2017. Downloaded by University of California - San Diego on 22/02/2017 19:34:28.

View Article Online DOI: 10.1039/C6GC03576K

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Sustainable production of pyromellitic acid with pinacol and diethyl maleate

Yancheng Hu, Ning Li,* Guangyi Li, Aiqin Wang, Yu Cong, Xiaodong Wang and Tao Zhang*

An unprecedented and sustainable route to synthesize pyromellitic acid (PMA), a monomer of polyimide, with bio-derived pinacol and diethyl maleate was developed.