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Sustainable production of pyromellitic acid with pinacol and diethyl maleate†

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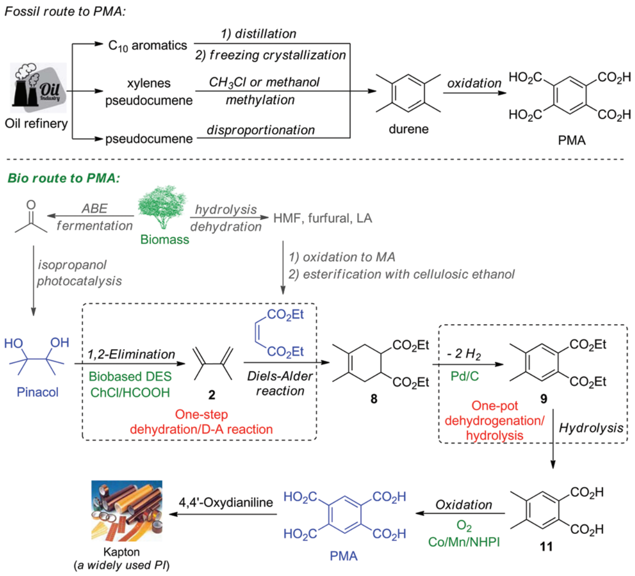
Herein, we report an unprecedented and sustainable route to synthesize pyromellitic acid (PMA), a monomer of polyimide, with pinacol and diethyl maleate which can be derived from lignocellulose. Analogously, a sustainable route to trimellitic acid (TMA) was also developed using pinacol and acrylate as 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 fuels[1] and chemicals[2] 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 derivatives 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 derivatives is highly demanded.

Pinacol is an important *vic*-diol which can be formed by the metal-mediated coupling[7] or electrolytic reduction[8] 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 a 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-dicarboxy-



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

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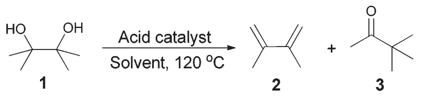
late (*i.e.* compound **8**) by a one-step dehydration/D–A cascade reaction. As reported in the literature,[14] the selective pinacol dehydration to 2,3-dimethylbutadiene is very challenging due to the predominance of pinacol rearrangement (a textbook reaction). However, this problem was first solved in this work by employing a choline chloride (ChCl) based deep eutectic solvent (DES) ChCl/HCO_2H. Choline chloride is a non-toxic, cheap, renewable and biodegradable ammonium salt which can be synthesized by the neutralization of choline (a water-soluble 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 the *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 dehydration 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 conditions or using toluene as the solvent. Only a trace amount of 2,3-dimethylbutadiene (*i.e.* compound **2**) was detected (Fig. S1†). Compound **3** was generated by pinacol rearrangement, which was more preferred than 1,2-elimination of H_2O.[14] It is very interesting to note that evident improvement in the carbon yield of 2,3-dimethylbutadiene 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 beneficial for 1,2-elimination of H_2O. Because both DMSO and NMP are non-renewable, 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).

Table 1 Effect of solvents on the dehydration of pinacol[a]



Entry	Catalyst	Solvent[b]	Carbon yield of **2** (%)	Carbon yield of **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	—	HCOOH	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 °C, 12 h. [b] The ratio in parentheses is the molar ratio of choline chloride (ChCl) to the other components. [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 °C for 12 h.

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 a 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 the DES) is necessary for the excellent performance of ChCl/HCOOH. Moreover, it is noticed that the molar ratio of ChCl and HCOOH in the DES also exerted a great influence on the reaction patterns. With the increasing of the ChCl/HCOOH molar ratio from 1 : 1 to 2 : 1, the carbon yield 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.

The influence of the 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 the ChCl/HCOOH dosage, reached the maximum (78%) when 8.0 g ChCl/HCOOH was used, and then stabilized with further increasing the dosage. In contrast, it is noticed that the dosage of the DES had no evident effect on the carbon yield of compound **3**.

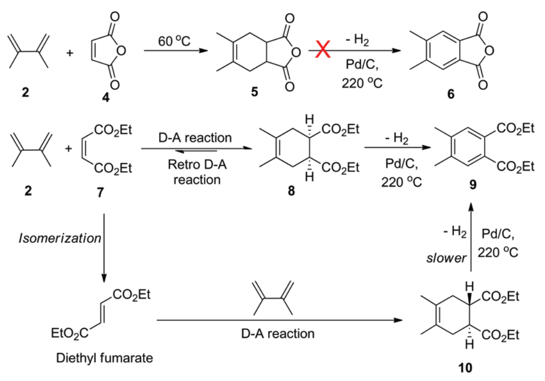
We also investigated the effect of reaction temperature on the carbon yields of compounds **2** and **3**. As shown in Fig. S6,† with the increasing of reaction temperature, the carbon yield of compound **2** slightly increased, reached the maximum (83%) when the pinacol dehydration was performed at 140 °C

(Table 1, entry 19), and then decreased with further increment of the temperature. This can be rationalized because high temperatures 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, and 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 the mixture was submitted 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 results 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 conditions without using any solvents or catalysts (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, an 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.



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

Besides compound **9**, a 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 conditions (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 conditions, lower substrate conversion (87% *vs.* 100%) and carbon yield of compound **9** (66% *vs.* 80%) were achieved from the dehydrogenation 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 economic point of view.

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

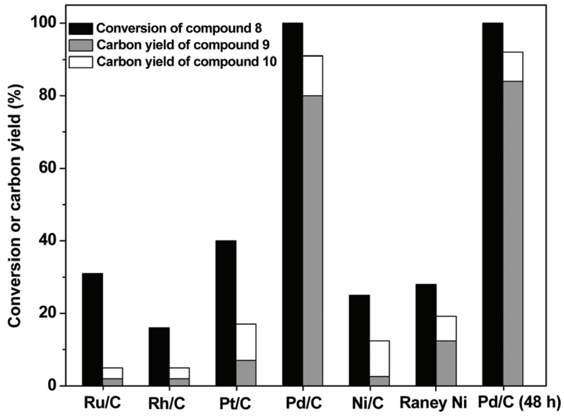
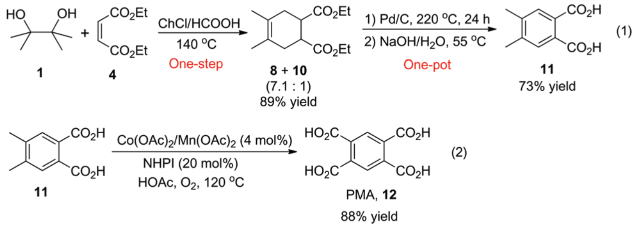


Fig. 1 Conversion of compound **8** and the carbon yields of compounds **9** and **10** over different catalysts. Reaction conditions: compound **8** (10 mmol, 2.5 g), catalyst (250 mg), 220 °C for 24 h.



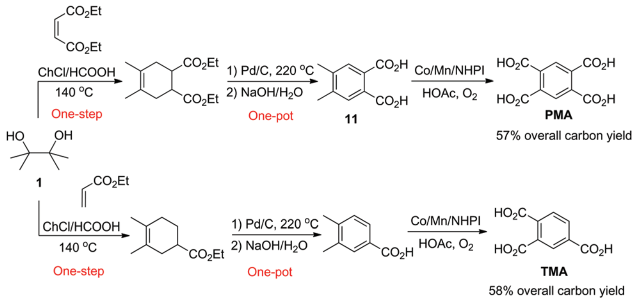
Scheme 3 The conversion of pinacol and diethyl maleate to the PMA precursor (*i.e.* compound **11**) by two cascade reactions, followed by catalytic aerobic oxidation.

similar to 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 the solvent at 120 °C afforded PMA in 88% yield (Scheme 3, eqn (2)).

Based on what we found in this work, a three-step route for the synthesis of renewable PMA with pinacol is 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 the 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 acid[17] 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 detailed information is given in the ESI.† Under the same reaction conditions, a high overall carbon yield of TMA (58%) was achieved.



Scheme 4 The strategies for the synthesis of renewable PMA (or TMA) with pinacol and diethyl maleate (or ethyl acrylate).

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. The 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 the 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

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