

An inexpensive and efficient synthetic method for the preparation of pyromellitic dianhydride promoted by ionic liquid

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Abstract

In this article, pyromellitic dianhydride could be successfully obtained in 76.7% total yield by an aerobic oxidation of 1,4-bis(chloromethyl)-2,5-dimethylbenzene or 1,5-bis(chloromethyl)-2,4-dimethylbenzene catalyzed by VO(acac)₂/Cu(2-Eth)₂/DABCO in [hmim]OTf and a subsequent dehydration of pyromellitic acid upon heating with acetic anhydride. The starting materials including 1,2-bis(chloromethyl)-4,5-dimethylbenzene were prepared by dichloromethylation of their corresponding xylene catalyzed by [C₁₂mim]Br in aqueous media.

Keywords: Pyromellitic dianhydride, ionic liquid, chloromethylation, oxidation, dehydration

Introduction

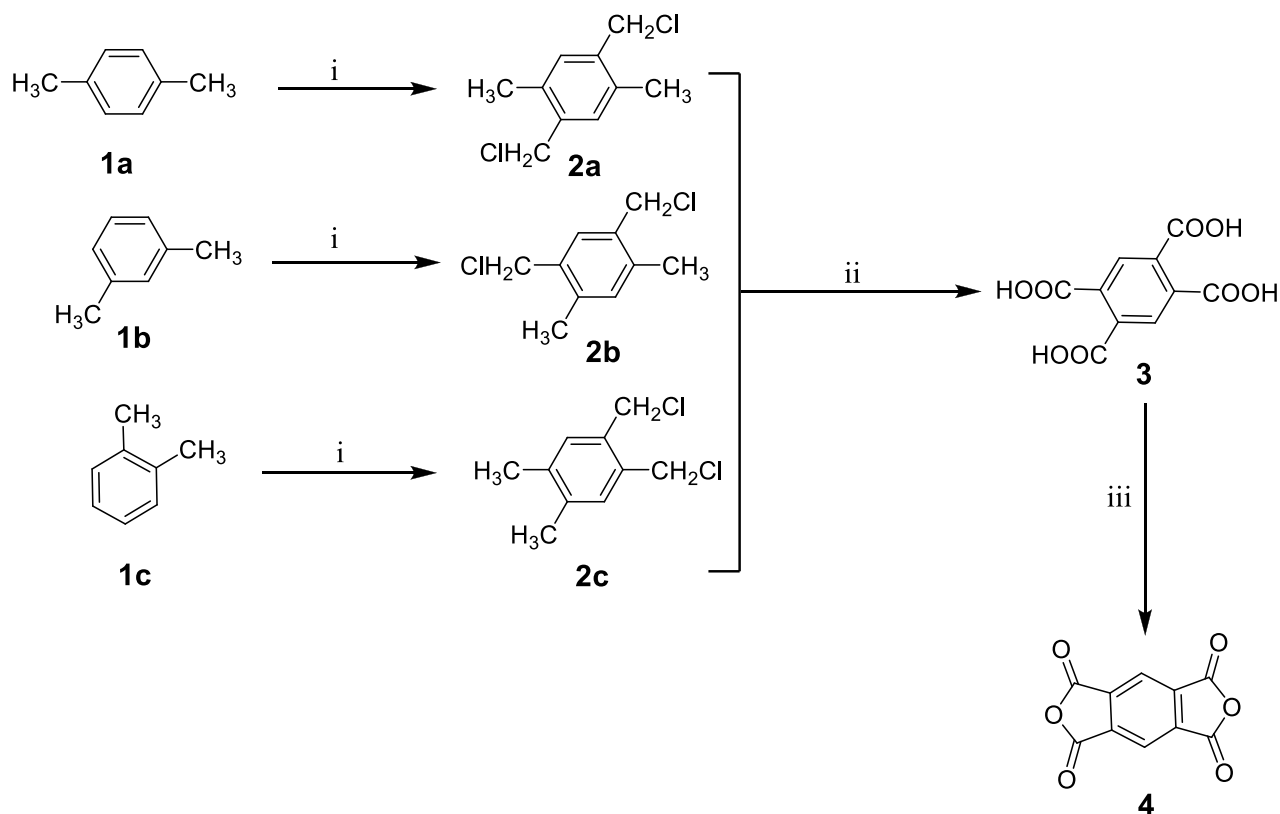
Pyromellitic dianhydride (PMDA) has been used extensively as an important monomer in the preparation of a variety of thermoplastics such as polyesters, polycarbonates, polyethers, plasticizers, epoxy resins, etc. Moreover, it is also useful in the preparation of high performance coatings that have been widely employed in many fields in our daily life because of its excellent thermal, oxidative stability and excellent mechanical properties.¹⁻⁶ Up to now, many publications in the open literature have been found in synthesis or production of pyromellitic dianhydride (PMDA), and the classical method for such a synthesis constitutes the liquid-phase oxidation of 1,2,4,5-tetraalkyl benzene catalyzed by cobalt, manganese, bromine, nitric acid or dichromic acid in the presence of 100-450 psig, and then dehydrating the obtained pyromellitic acid into pyromellitic dianhydride.⁷⁻¹⁰ However, this procedure is invariably associated with certain limitations such as high cost, long reaction time, environmental hazards, special apparatus and drastic reaction conditions. The catalytic vapor-phase oxidation of 1,2,4,5-tetraalkyl benzene

under oxygen pressure using a certain catalyst (e.g. V_3O_5 - TiO_2 , WO_2 , V_2O_5 - TiO_2) is another well-known method,¹¹⁻¹⁶ which, however, requires special equipment, low selectivity, use of stoichiometric and even excess amounts of reagents or catalysts, troublesome work-up procedures, etc. Other notable methods to accomplish this conversion include the liquid-phase oxidation of 1,2,4-tetraalkyl benzene,^{17,18} the catalytic vapor-phase oxidation of 1,2,4-tetraalkyl benzene,¹⁹⁻²¹ etc.^{22,23} However, some of these procedures are invariably associated with one or more disadvantages such as high cost, long reaction time, complicated manufactures, special apparatus, etc. Consequently, there is a great need to develop an efficient procedure for the synthesis of pyromellitic dianhydride.

Ionic liquids (ILs) are a class of organic salts with unusually low melting temperatures that have attracted much attention from the scientific community in recent years. As a class of potential greener solvents, ILs exhibit many unique physicochemical properties, such as negligible volatility and nonflammability under ambient conditions, large liquid range, high thermal stability, wide electrochemical window, and strong ability to dissolve many chemicals.^{24,27} Therefore, ILs have found wide applications in chemical synthesis,²⁵⁻²⁷ biocatalytic transformations,^{28,29} electrochemistry,³⁰ and analytical and separation science.^{31,32}

Molecular oxygen may serve as superior oxidant that exhibits lower cost, greater abundance, and improved safety contrast to other oxidizing reagents ($KMnO_4$, MnO_2 , CrO_3 , etc.).³³ Furthermore, the use of molecular oxygen as the primary oxidant may also have the advantage that water is the sole final byproduct. Thus, catalytic aerobic oxidation represents a promising protocol for organic synthesis and industrial applications. Accordingly, there has been concerted effort directed at developing various transition metals (copper, vanadium, palladium, etc.)³⁴⁻³⁷ to catalyze aerobic oxidation. Vanadyl acetylacetonate ($VO(acac)_2$)³⁸⁻⁴⁰ and copper (II) 2-ethylhexanoate ($Cu(2-Eth)_2$)^{41,42} have been extensively used in organic chemistry as reagents in the epoxidation of allylic alcohols, showing to be highly active, stereo- and regioselective catalysts. 1,4-diazabicyclo [2.2.2]octane (DABCO) is a highly efficient ligand and has been extensively applied in various organic reactions, such as Suzuki-Miyaura reaction, Baylis-Hillman reaction, epoxidation reaction, complexing ligand, etc.⁴³⁻⁴⁵

The objectives of the present work are to report an efficient and economic procedure for synthesis of pyromellitic dianhydride by aerobic oxidation reaction of bis(chloromethyl)xylenes **2a**, **2b**, **2c** catalyzed by $VO(acac)_2/Cu(2-Eth)_2/DABCO$ in [hmim]OTf and a subsequent dehydration of pyromellitic acid upon heating with acetic anhydride, and the starting materials were synthesized by chloromethylation of xylene using $[C_{12}mim]Br$ as a catalyst in aqueous media (Scheme 1).



Reagents: (i) $(\text{CH}_2\text{O})_n$, 50% H_2SO_4 , AcOH, $[\text{C}_{12}\text{mim}]\text{Br}$, HCl, 55°C, 12 h. (ii) $\text{VO}(\text{acac})_2$, $\text{Cu}(\text{2-Eth})_2$, DABCO, $[\text{hmim}]\text{OTf}$, O_2 , 120°C, 24 h. (iii) $(\text{CH}_3\text{CO})_2\text{O}$, reflux, 3 h.

Scheme 1. Three-step synthesis of PMDA.

Results and Discussion

The dichloromethylation of *p*-xylene **1a** was initially tested at 55 °C in the presence and absence of 1-dodecyl-3-methylimidazolium bromide ($[\text{C}_{12}\text{mim}]\text{Br}$). As shown in Table 1, in the absence of $[\text{C}_{12}\text{mim}]\text{Br}$, the reaction proceeded very slowly, the yield was only 14% after 24 h (entry 1). Reaction performed with $[\text{C}_{12}\text{mim}]\text{Br}$, it proceeded well, the yield increased to 37% in a shorter time (14 h) when only 0.02 equiv of $[\text{C}_{12}\text{mim}]\text{Br}$ was used (Table 1, entry 2). When the use of 0.09 equiv of the promoter, the desired reaction was efficiently carried out and the yield remarkably increased to 82% in 12 h (Table 1, entry 3). Thus, we can clearly observe that the yield increased with the increase in the amount of $[\text{C}_{12}\text{mim}]\text{Br}$, and it reached maximum (85%) when the 0.10 equiv of the promoter was used (Table 1, entry 4). However, further addition the amount of $[\text{C}_{12}\text{mim}]\text{Br}$, under the same conditions, the yield was not enhanced significantly

(Table 1, entries 5 and 6). These experiments revealed that 12 h and 0.10 equiv of the IL were necessary to complete the reaction. In addition, the IL could be typically recovered and reused with no appreciable decrease in yields and reaction rates (Table 1, entries 7 and 8). Besides [C₁₂mim]Br, we also tried to use another types of ionic liquids such as 1-butyl-3-methylimidazolium bromide ([C₄mim]Br), 1-hexyl-3-methylimidazolium bromide ([C₆mim]Br), 1-methyl-3-octylimidazolium bromide ([C₈mim]Br) and 1-decyl-3-methylimidazolium bromide [C₁₀mim]Br as catalysts in the reaction (Table 1, entries 9-12), it was observed that [C₁₂mim]Br demonstrated the best performance. The experimental facts displayed distinctly the advantage of high efficiency of [C₁₂mim]Br catalysis. A review of the literature⁴⁶ shows that ILs based on 1-alkyl-3-methylimidazolium cation ([C_nmim]⁺) possess inherent amphiphilic character when their alkyl group is a longer hydrocarbon chain, so the role of [C₁₂mim]Br in the reaction probably lies in the fact that it behaves like a classical surfactant and forms aggregates in water at low concentrations and self-assembles to form lyotropic mesophases at higher concentrations. When no surfactant ([C₁₂mim]Br) was used or surfactant concentration was below critical micelle concentration (CMC), the reaction system was a suspension (under stirring) with two phases, and the interface between oil phase and water phase was very small, so the reaction rate was very slow and a low yield was obtained, whilst the concentration was above CMC, the number of micelles increased with the increasing surfactant concentration (i.e. the amount of [C₁₂mim]Br increased), so the rate of chloromethylation speeded up and a higher yield could be obtained. The further increase of the surfactant concentration could induce micelles to expand, which could cause slow increase of oil/water interfacial area. Therefore, at high concentration, the rate increase became gradually slow and the yield did not change significantly.

Table 1. Dichloromethylation of *p*-xylene catalyzed by ionic liquids in aqueous media^a

Entry	Ionic liquid	Ionic liquid (equiv.)	Time (h)	Yield (%) ^b
1	[C ₁₂ mim]Br	—	24	14
2	[C ₁₂ mim]Br	0.02	14	37
3	[C ₁₂ mim]Br	0.09	12	82
4	[C ₁₂ mim]Br	0.10	12	85
5	[C ₁₂ mim]Br	0.11	12	85
6	[C ₁₂ mim]Br	0.13	12	85
7	[C ₁₂ mim]Br	0.10	12	85 ^c
8	[C ₁₂ mim]Br	0.10	12	84 ^d
9	[C ₄ mim]Br	0.10	12	37
10	[C ₆ mim]Br	0.10	12	61
11	[C ₈ mim]Br	0.10	12	70
12	[C ₁₀ mim]Br	0.10	12	79

^aReaction conditions: **1a** (0.1 mol), paraformaldehyde (0.3 mol), 50% H₂SO₄ (10 mL), AcOH (5 mL), anhydrous hydrogen chloride gas (60 mL/min), 55 °C. ^bIsolated yield. ^cThe second run. ^dThe third run.

With these results in hand, we subjected *m*-xylene **1b** and *o*-xylene **1c** to the optimized conditions, they were efficiently converted to the corresponding dichloromethyl-substituted products **2b** and **2c**, and the yields were 86% and 65%, respectively (Table 2). The yield of **2c** was merely 65%, because a mixture was obtained from the dichloromethylation of **1c**, the selectivity for **2c** was only 78%, which was confirmed by HPLC.

Table 2. Dichloromethylation of *m*-xylene and *o*-xylene catalyzed by [C₁₂mim]Br in aqueous media^a

Substrate	Catalyst	Yield (%) ^b	Selectivity (%) ^c
<i>m</i> -xylene	[C ₁₂ mim]Br	86	100
<i>o</i> -xylene	[C ₁₂ mim]Br	65	78

^aReaction conditions: **1b** or **1c** (0.1 mol), paraformaldehyde (0.3 mol), 50% H₂SO₄ (10 mL), AcOH (5 mL), [C₁₂mim]Br (0.01 mol), anhydrous hydrogen chloride gas (60 mL/min), 55 °C, 12 h.

^bIsolated yield.

^cIsolated selectivity.

The aerobic oxidation of 1,4-bis(chloromethyl)-2,5-dimethylbenzene **2a** was tested in the presence of DABCO at 120 °C, and the results are summarized in Table 3. No reaction occurred in the absence of VO(acac)₂ (Table 3, entry 1) and very low yield of **3** was obtained (14% yield after 48 h) in the absence of Cu(2-Eth)₂ (Table 3, entry 9). It can be observed that both VO(acac)₂ and Cu(2-Eth)₂ as catalysts are crucial for this reaction. Further efforts were then focused on optimizing the reaction medias for the oxidative process. At first, four types of ionic liquids, 1-hexyl-3-methylimidazolium trifluoromethanesulfonate ([hmim]OTf), 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([bmpyr]NTf₂), 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF₆), and 1-butyl-4-methylpyridinium hexafluorophosphate ([bmpy]PF₆) were tested with VO(acac)₂ and Cu(2-Eth)₂ as the catalysts. It is clear that all the ionic liquids gave comparable isolated yields, and [hmim]OTf showed to be optimal (Table 3, entries 3-6). However, when in the case of entry 2, the reaction did not proceed well, and the yield was only 18% after 48 h. The experimental facts displayed distinctly the advantage of high efficiency of the reaction media [hmim]OTf. ILs are able to dissolve and stabilize the transition-metal catalyst precursors,⁴⁷ thus providing an excellent support and medium for the aerobic oxidation, which may explain why the yields when in the presence of ionic liquids as reaction medias were higher than that of not. The different effects of ILs in the reaction may be attributed to their different abilities of stabilizing and dissolving the transition-metal catalyst precursors and molecular oxygen. Under the same conditions, the IL who stabilizes and dissolves the transition-metal catalyst precursors and molecular oxygen more easily will lead to a larger increase in the effective reactant concentration, which increases the encounter probabilities between **2a** and reactive species, and the higher rate and yield of the reaction is observed. Finally, we also tried to use another types of cocatalysts such as Cu(acac)₂, Cu(OAc)₂ and Pb(OAc)₂ in the reaction, under the same conditions, however, the yields were merely 57%, 72% and 81%, respectively (Table 3, entries 10-12). The best cocatalyst is Cu(2-Eth)₂. Therefore, the optimal reaction conditions were

observed in Table 3, entry 2. In addition, the catalytic system could be typically recovered and reused with no appreciable decrease in yields and reaction rates (Table 3, entries 7 and 8). With these results in hand, we subjected **2b** and **2c** to the optimized conditions, and high yields of 92% and 91% were obtained respectively.

Table 3. Aerobic oxidation of 1,4-bis(chloromethyl)-2,5-dimethylbenzene into pyromellitic acid in ionic liquids^a

Entry	Catalyst	Cocatalyst	Ionic liquid	Time (h)	Yield (%) ^b
1	—	Cu(2-Eth) ₂	[hmim]OTf	48	0
2	VO(acac) ₂	Cu(2-Eth) ₂	—	48	18
3	VO(acac) ₂	Cu(2-Eth) ₂	[hmim]OTf	24	93
4	VO(acac) ₂	Cu(2-Eth) ₂	[bmpyr]NTf ₂	48	79
5	VO(acac) ₂	Cu(2-Eth) ₂	[bmim]PF ₆	48	51
6	VO(acac) ₂	Cu(2-Eth) ₂	[bmpy]PF ₆	48	27
7	VO(acac) ₂	Cu(2-Eth) ₂	[hmim]OTf	24	93 ^c
8	VO(acac) ₂	Cu(2-Eth) ₂	[hmim]OTf	24	92 ^d
9	VO(acac) ₂	—	[hmim]OTf	48	14
10	VO(acac) ₂	Cu(acac) ₂	[hmim]OTf	24	57
11	VO(acac) ₂	Cu(OAc) ₂	[hmim]OTf	24	72
12	VO(acac) ₂	Pb(OAc) ₂	[hmim]OTf	24	81

^aReaction conditions: **2a** (0.05 mol), VO(acac)₂ (7 mmol), DABCO (13 mmol), cocatalyst (7 mmol), ionic liquid (0.05 mol), 1 atm O₂, 120 °C.

^bIsolated yield.

^cThe second run.

^dThe third run.

During the process of dehydration, the acetic anhydride had great influences on the reaction, which is shown in Figure 1. No reaction occurred in the absence of acetic anhydride, and the increase in the amount of acetic anhydride (i.e. the ratio increased) enhanced the activity of

dehydration. The yield reached maximum at 15.7 of the ratio. Further addition the amount of acetic anhydride, under the same conditions, the yield was not enhanced significantly.

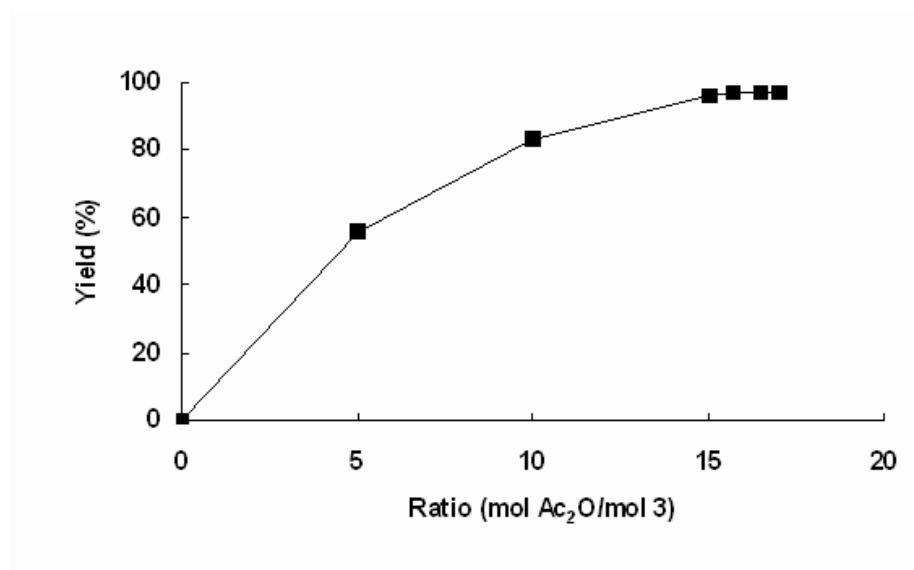


Figure 1. Influences of the amount of acetic anhydride on the dehydration. Reaction conditions: pyromellitic acid (0.05 mol), reflux, 3 h.

Conclusions

In conclusion, we have developed an efficient synthetic pathway for the preparation of pyromellitic dianhydride starting from commercially available *p*-xylene or *m*-xylene in three steps. Compared to the synthetic methods reported in previous literature,⁷⁻²³ not only was the yield of product greatly improved, but also the operating units were easy workup. One of the noticeable points in our paper was that the catalysts are easy to handle and could be recycled and reused without any significant loss of catalytic activity, and another glittery point was that the facile manipulations in the isolation of the products. Judging from the conditions employed, this method showed has great prospects in industrial applications.

Experimental Section

General. All the used chemicals were from commercial sources without any pretreatment. All reagents were of analytical grade. The ionic liquids were synthesized according to the literature

procedures.⁴⁸⁻⁵⁰ The required substrates **2-4** were prepared according to the related methods.^{42,51,52} The target substrates were characterized by Elemental analysis, ¹H NMR, ¹³C NMR or compared with their authentic samples. Melting points were determined on an electrothermal (Prolabo 9200) apparatus and are uncorrected. NMR spectra were recorded on a Bruker 400-MHz spectrometer. High performance liquid chromatography (HPLC) experiments were performed on a liquid chromatograph (Dionex Softron GmbH, America), consisting of a pump (P680) and ultraviolet-visible light detector (UVD) system (170U). The experiments were performed on Diacore C18 column, ϕ 4.6 \times 250 mm. IR spectra were recorded on a Perkin Elmer PE-983 infrared spectrometer, as KBr pellets with absorption in cm^{-1} . Elemental analysis were performed on a Vario EL III instrument (Elementar Analysensysteme GmbH, Germany).

Preparation of bis(chloromethyl)xylene (**2a**, **2b**, **2c**) using *p*-xylene as an example

A mixture of compound **1a** (10.6 g, 0.1 mol), paraformaldehyde (9.0 g, 0.3 mol), aqueous H₂SO₄ (50%, 10 mL), AcOH 5 mL and [C₁₂mim]Br (3.34 g, 0.01 mol) were added in a 100 mL round flask equipped with reflux condenser and oil-bath. Anhydrous hydrogen chloride gas was bubbled into the flask at the flow rate of 60 mL/min. The reaction mixture was stirred for 12 h at 55 °C, the reaction progress was monitored by HPLC. After the reaction, the mixture was cooled and filtered and extracted with methylene chloride (3 \times 20 mL). The organic phases were combined and rinsed with NaHCO₃ solution (20%, 3 \times 20 mL) and water (3 \times 20 mL), then dried over anhydrous Na₂SO₄. The solvent was evaporated and the crude product was recrystallized from hexane and methylene chloride afforded a white powder.

2a. 17.3 g, yield 85%; m.p. 102-104 °C; IR (KBr, cm^{-1}): 2976 (s), 2865 (m), 1637 (m), 1506 (s), 1454 (s), 1382 (m), 895 (s), 806 (s), 656 (vs); ¹H NMR (400MHz, δ in ppm from TMS in CDCl₃): 2.34 (s, 3H, CH₃), 4.67 (s, 2H, CH₂), 7.16 (s, 2H, Ar-H); ¹³C NMR (400MHz, δ in ppm from TMS in CDCl₃): 17.8 (q), 40.7 (t), 131.2 (d), 133.7 (s), 138.3 (s). Anal. Calcd for C₁₀H₁₂Cl₂: C, 59.03; H, 5.98; Cl, 34.97. Found: C, 59.13; H, 5.96; Cl, 34.91.

2b. 17.5 g, yield 86%; m.p. 88-90 °C; IR (KBr, cm^{-1}): 2963 (s), 2869 (m), 1615 (m), 1512 (s), 1468 (s), 1384 (m), 902 (s), 808 (s), 658 (vs); ¹H NMR (400MHz, δ in ppm from TMS in CDCl₃): 2.37 (s, 3H, CH₃), 4.69 (s, 2H, CH₂), 7.04 (s, 1H, Ar-H), 7.25 (s, 1H, Ar-H); ¹³C NMR (400MHz, δ in ppm from TMS in CDCl₃): 17.5 (q), 40.5 (t), 129.2 (d), 131.2 (d), 134.5 (s), 136.8 (s). Analysis Calcd for C₁₀H₁₂Cl₂: C, 59.09; H, 5.97; Cl, 34.94. Found: C, 59.13; H, 5.96; Cl, 34.91.

2c. 13.2 g, yield 65%; m.p. 103-105 °C; IR (KBr, cm^{-1}): 2972 (s), 2871 (m), 1628 (m), 1510 (s), 1457 (s), 1381 (m), 910 (s), 807 (s), 661 (vs); ¹H NMR (400MHz, δ in ppm from TMS in CDCl₃): 2.36 (s, 3H, CH₃), 4.70 (s, 2H, CH₂), 7.14 (s, 2H, Ar-H); ¹³C NMR (400MHz, δ in ppm from TMS in CDCl₃): 18.5 (q), 40.7 (t), 131.2 (d), 134.1 (s), 138.1 (s). Analysis Calcd for C₁₀H₁₂Cl₂: C, 59.07; H, 6.01; Cl, 34.92. Found: C, 59.13; H, 5.96; Cl, 34.91.

Preparation of pyromellitic acid (**3**) using compound **2a** as an example

A mixture of compound **2a** (10.1 g, 0.05 mol), VO(acac)₂ (1.86 g, 7mmol), Cu(2-Eth)₂ (2.45 g, 7 mmol), DABCO (1.45 g, 13 mmol), and [hmim]OTf (15.8 g, 0.05 mol) were added in a 100

mL round flask equipped with reflux condenser and oil-bath. The round flask was capped with a rubber septum, and the reaction mixture was vigorously stirred at 120 °C under 1 atm O₂ for 24 h, the reaction progress was monitored by HPLC. After the reaction, the mixture was extracted with methylene chloride (3×20 mL). The combined organic phases was concentrated in vacuo. The residue was recrystallized from distilled water afforded a white powder 11.8 g, yield 93%. m.p. 272-274 °C; ¹H NMR (400MHz, δ in ppm from TMS in DMSO-*d*₆): 7.83 (s, 2H, Ar-H), 12.2-13.3 (br s, 4H, COOH); ¹³C NMR (400MHz, δ in ppm from TMS in DMSO-*d*₆): 129.4 (d), 136.7 (s), 167.9 (s). Analysis Calcd for C₁₀H₆O₈: C, 47.31; H, 2.40; O, 50.32. Found: C, 47.26; H, 2.38; O, 50.36.

Preparation of PMDA (4)

In a 250 mL round flask, compound **3** (12.7 g, 0.05 mol) was added to the stirred solution containing acetic anhydride (80 mL, 0.784 mol). The suspension was gradually heated to reflux for 3 h, the reaction progress was monitored by HPLC. After the reaction, the mixture was cooled, the precipitate was filtered off, dried in vacuum, afford a white powder 10.6 g, yield 97%. m.p. 283-285 °C (lit.¹⁷ m.p. 281-284 °C); ¹H NMR (400MHz, δ in ppm from TMS in DMSO-*d*₆): 8.72 (s, 2H, Ar-H); ¹³C NMR (400MHz, δ in ppm from TMS in DMSO-*d*₆): 124.2 (d), 137.3 (s), 162.7 (s). Analysis Calcd for C₁₀H₂O₆: C, 55.07; H, 0.89; O, 44.03. Found: C, 55.06; H, 0.92; O, 44.01.

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