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ARTICLE

A two step efficient preparation of a renewable dicarboxylic acid monomer 5,5'-[oxybis(methylene)]bis[2-furancarboxylic acid] from D-fructose and application in polyester synthesis

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D-Fructose was converted to the dialdehyde 5, 5'-[oxybis(methylene)]bis[2-furaldehyde] by heating at 110 °C in DMSO with Dowex 50W X8 solid acid catalyst in 76% yield without isolation of the intermediate 5-hydroxymethylfurfural. This dialdehyde was then converted to the dicarboxylic acid monomer, 5,5'-[oxybis(methylene)]bis[2-furancarboxylic acid] using oxygen (1 atm.) and 5% Pt/C catalyst in 1.5M aqueous NaOH at room temperature in 98% yield. The new dicarboxylic acid monomer can be considered as a renewable resources based alternative to terephthalic acid as demonstrated by the preparation of the polyesters with 1,2-ethanediol and 1,4-butanediol in 87-92 % yield.

1. Introduction

The growing interest in renewable resources based feedstock chemicals and polymeric materials has promoted the studies on a number of biomass derived compounds such as triglycerides [1], lactic acid [2, 3], levulinic acid [4, 5, 6], succinic acid [7], 1,3-propanediol [8, 9], 5-hydroxymethylfurfural (HMF) [10, 11, 12], 2,5-furandicarboxylic acid or its derivatives [13, 14], and vanillin [15, 16]. Biomass derived furans, furfural (FF) and 5-hydroxymethylfurfural constitute an important sub-group in these feedstock compounds as most of the abundant C5, C6 monosaccharides can be dehydrated to these furan derivatives under relatively mild acidic conditions using inexpensive acid catalysts. The large scale commercial preparation of FF is a well established process since 1929 due to a relatively easy preparation involving a mineral acid catalyzed aqueous phase process and distillation [17]. Furthermore, furfural is known as one of the earliest renewable monomers; Durite Plastics Inc. started the manufacture of phenol–furfural resins and plastic materials in the 1930's [18]. In contrast, HMF production, is much more problematic due to further transformation to levulinic acid and formic acid via a rehydration reaction as well as polymerizations to humins [19]. Albeit the problems in preparation, isolation and storage of this bifunctional furan, HMF has received considerable attention as its oxidation products, 2,5-furandicarboxaldehyde and 2,5-furandicarboxylic acid (FDCA) are attractive monomers for the synthesis of next generation renewable polymeric materials [20, 21]. The dialdehyde, 2,5-furandicarboxaldehyde has been used in the preparation of resins with urea as well as Schiff base polymers with diamines [22, 23]. However, the diacid is probably the most important derivative of HMF and in recent years FDCA has been used as a monomer in the preparation of polyesters using a range of polymerization techniques including the use of dicarboxylic acid dichloride - diol method, *trans*-esterification, and interfacial poly condensation [24, 25]. The most widely studied diol is 1,2-ethanediol [13, 24, 26], but polyesters have been prepared using other diols like 1,3-propanediol [24], 1,4-butanediol [26], 1,6-hexanediol [26], 1,8-octanediol [26], bis(2,5-hydroxymethyl)-furan [24], bis-(1,4-hydroxymethyl) benzene [24], hydroquinone [24], D-isosorbide [27], D-isoidide [27] and glycerol [28] as well. In addition, FDCA is listed in a 2004 US Department of Energy National Renewable Energy Laboratory (NREL) report as one of the twelve building blocks that can be subsequently converted to a variety of high-value bio-based chemicals and polymeric materials [29].

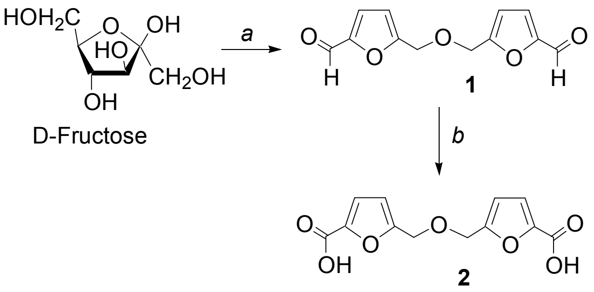

Figure 1. Synthesis of 5,5'-[oxybis(methylene)]bis[2-furancarboxylic acid] (OBFC, **2**) via 5,5'-[oxybis(methylene)]bis[2-furaldehyde] (OBFA, **1**) from D-fructose. *a* = Dowex 50W X8 10% (w/w), DMSO, 110 °C, 24 h, *b* = 5% Pt/C, O_2, 1 atm., 1.5M aqueous NaOH, 23 °C, 48 h.

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Furthermore, this aromatic diacid has been considered as a potential replacement and the renewable resources based equivalent of terephthalic acid, which is a monomer in polyethylene terephthalate (PET) plastics [29]. The market for terephthalic acid exceeds 50,000 ktons/year, demonstrating the large potential for FDCA for the preparation of polyethylene furanoate (PEF) as a replacement for PET [30]. In theory the use of FDCA as a substitute for terephthalic acid together with biomass based diols allows the preparation of completely renewable polyesters, leading to a significant reduction of greenhouse gas emissions [30]. In addition, potential applications of FDCA include its use in the manufacture of polyureas, polyamides and polyester-polyols as well [31, 32, 33, 34, 35].

In our efforts to produce new biomass derived monomers via efficient catalytic routes, we have recently found that it is possible to prepare 5,5'-[oxybis(methylene)]bis[2-furancarboxylic acid] (OBFC, **2**) from D-fructose using a two step process as shown in figure 1, and this difuranic-diacid can be considered as a higher molecular weight analog and an alternative to dicarboxylic acid monomer FDCA. In this publication we report an efficient scalable catalytic approach for the preparation of this versatile bio-based diacid monomer and demonstrate the solution polymerization of the acid dichloride with diols to produce polyesters.

2. Experimental

2.1. Materials and Instrumentation

D-Fructose (>99%), Dowex 50W X8 (hydrogen form, 50-100 mesh), platinum 5 wt. % on activated carbon (Aldrich product number 205931), CuO (> 99%), AgO (> 99%), thionyl chloride, pyridine, 1,1,2,2-tetrachloroethane (TCE) and 1,4-butanediol (> 99%) were purchased from Aldrich Chemical Co. ^{1}H NMR spectra were recorded in $CDCl_3$, DMSO-d_6 or CF_3CO_2D on a Varian Mercury plus spectrometer operating at 400MHz and chemical shifts are given in ppm downfield from TMS (δ = 0.00). ^{13}C NMR spectra in $CDCl_3$, DMSO-d_6 or CF_3CO_2D were recorded on the same spectrometer operating at 100MHz; chemical shifts were measured relative to $CDCl_3$, DMSO-d_6 or CF_3CO_2D and converted to δ(TMS) using $\delta(CDCl_3)$ = 77.00, δ(DMSO) = 39.51 and $\delta(CF_3$-) = 116.60 ppm. Attenuated total reflection infrared (ATR-IR) spectra were recorded in the 650–4000 cm^{-1} range on a Smiths IdentifyIR spectrometer with a diamond ATR (Danbury, CT, USA). Thermogravimetric analysis (TGA) was carried out in air using TA instruments TGA 2050 system and platinum crucibles. The TG curves were recorded in the 50-600 °C temperature range using a scanning rate of 10 °C/min. Elemental analysis was performed at QTI laboratories, New Jersey, USA.

*2.2. Preparation of 5,5'-[oxybis(methylene)]bis[2-furaldehyde] (**1**) from D(-)-fructose*

A mixture of D-fructose (9.00 g, 50 mmol) and Dowex 50W X8 (0.90 g) in 20 mL of dimethylsulfoxide was heated in an open boiling tube in an oil bath at 110 °C for 24 h. Then the solution was cooled to room temperature, diluted with 50 mL of $^{t-}$butylmethyl ether and filtered to recover the ion exchange resin. The resin was washed with $^{t-}$butylmethyl ether (3 x 5mL) and the combined filtrate was transferred to a separatory funnel and washed with water (3x 25 mL) to remove DMSO. The $^{t-}$butylmethyl ether layer was concentrated under reduced pressure to give the crude product, which was recrystallized from 50% aqueous ethanol to give 5,5'-[oxybis(methylene)]bis[2-furaldehyde] as tan crystals, 8.89 g, 76 % yield. M.pt. 112-114 °C, Lit. M. pt. 113-115 °C [36].

IR (ATR) 730, 828, 947, 1029, 1193, 1268, 1351, 1402, 1447, 1518, 1663, 2845 cm^{-1}

^{1}H NMR ($CDCl_3$) δ 4.63 (4H, s, 2X CH_2-O), 6.57(2H, d, J = 3.6 Hz, Fu - 4,4'), 7.21 (2H, d, J = 3.6 Hz, Fu - 3,3'), 9.62 (2H, 2X CHO), ^{13}C NMR ($CDCl_3$) δ 64.8, 112.1, 122.2, 153.0, 157.4, 177.9.

2.3. Synthesis of 5,5'-[oxybis(methylene)]bis[2-furancarboxylic acid]

A mixture of 5, 5'-[oxybis(methylene)]bis[2-furaldehyde] (234 mg, 1.00 mmol) and platinum 5 wt. % on activated carbon (4.7 mg) in 50 mL of 1.5 M aqueous sodium hydroxide was stirred under 1.0 atmosphere of oxygen for 48 h using an oxygen filled balloon. Then the reaction mixture was centrifuged at 1700 g for 10 min., the recovered catalyst was washed with water (2x5 mL), and the combined aqueous layer was carefully acidified to pH = 2.0 using conc. HCl and the solution was left in a refrigerator overnight to give 5,5'-[oxybis(methylene)]bis[2-furancarboxylic acid] as pale yellow crystals. 260 mg, 98 % yield. M.pt. 207-209 °C, Lit. M. pt. 209-210 °C [37].

IR (ATR) 761, 891, 951, 1029, 1059, 1159, 1208, 1283, 1342, 1424, 1525, 1674, 3128 cm^{-1}

^{1}H NMR (DMSO-d_6) δ 3.38 (2H, bs, 2XCOOH), 4.51 (4H, s, 2X-CH_2O), 6.61 (2H, d, J = 3.6 Hz, C-4,4'), 7.15 (2H, d, J = 3.6 Hz, C-3,3'). ^{13}C NMR (DMSO-d_6) δ 63.8, 112.2, 118.8, 145.3, 155.5, 159.6

*2.4. General procedure for the synthesis of polyester-ethers **3a,b***

A mixture of 5,5'-[oxybis(methylene)]bis[2-furancarboxylic acid] (**2**) (266 mg, 1.0 mmol), thionyl chloride (0.50 mL, 6.9 mmol) and 25μL of DMF were prepared in a round bottom flask connected to an air condenser and heated in an oil bath at 80 °C, for 4 h. Then the mixture was cooled to room temperature and excess $SOCl_2$ and DMF were removed at room temperature under high vacuum connected to a liquid nitrogen cooled trap. The acid chloride formed was dissolved in 0.2 mL of TCE and cooled to 0 °C. Then a mixture of diol (1.0 mmol), 0.2 mL of TCE and 0.3 mL of pyridine was added and stirred under a nitrogen atmosphere, warming to room temperature in about an hour. The reaction mixture was further stirred at room temperature for 6-48 h and a gradual increase in viscosity was observed due to polymerization. At the end of the reaction period 20 mL of methanol was added and allowed to stand at room temperature for 1h to precipitate the polymer, which was separated by decantation. The polymer product was repeatedly washed with methanol (3x5mL) dried under vacuum to give polyester-ethers **3a,b**.

3a, 254 mg, 87% yield.
Anal. Calc. for $C_{14}H_{12}O_7$: C, 57.54; H, 4.14. Found: C, 57.75; H, 4.18.
IR (ATR) 761, 817, 966, 1022, 1077, 1158, 1208, 1294, 1521, 1626, 1719, 2960 cm^{-1}
M_n = 16,800 g/mol and PDI = 1.30 (12 h reaction product)
TGA: T_{onset} = 280 ^{0}C, DTGA: 380, 484 ^{0}C
^{1}H NMR (CF_3CO_2D): 5.66-5.68 (8H, bs), 7.54 (2H, bs), 8.24 (2H, bs) ppm. ^{13}C NMR (CF_3CO_2D): 64.1, 64.3, 113.8, 121.7, 144.3, 155.9, 162.7 ppm.

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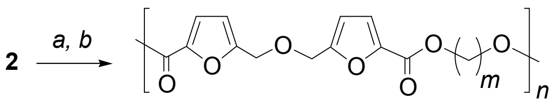
3b, 294 mg, 92% yield.
Anal. Calc. for $C_{16}H_{16}O_7$: C, 60.00; H, 5.04. Found: C, 60.28; H, 5.15.
IR (ATR) 760, 816, 966, 1022, 1077, 1158, 1208, 1294, 1522, 1712, 2964, 3118 cm^{-1}
M_n = 17,600 g/mol and PDI = 1.45 (12 h reaction product),
TGA: T_{onset} = 272 ^{0}C, DTGA: 371, 492 ^{0}C
^{1}H and ^{13}C NMR spectra of polyester-ether **3** are shown in figure 3.



3a,b

Figure 2. Solution polymerization of OBFC (**2**) via diacid dichloride to give polyesters **3a** (*m* = 2) and **3b** (*m* = 4).
a = $SOCl_2$, DMF, 80 °C, 4 h; *b* = 1,2-ethanediol or 1,4-butanediol, pyridine, 1,1,2,2-tetrachloroethane, 0-23 °C, 12 h.

3. Results and discussion

*3.1. Synthesis and characterization of 5,5'-[oxybis(methylene)]bis[2-furancarboxylic acid] (**2**)*

The dialdehyde 5,5'-[oxybis(methylene)]bis[2-furaldehyde] (**1**) can be prepared in good yields by heating D-fructose in DMSO at 110 °C for 24 h in an open container and using Dowex- 50W X8 (10% w/w) catalyst as shown in figure 1. During the initial experiments, shorter reaction times and lower catalyst loadings produced higher yields of HMF, however longer reaction times with at least 10% (w/w) solid acid catalyst caused the dimerization of the initially formed HMF to OBFA as shown in table 1. This technique avoids the isolation of the unstable HMF and allows in situ conversion to the stable symmetrical dimer OBFA. In addition, the bis aldehyde is a larger hydrophobic molecule than HMF; more soluble in organic phase and the favourable partition coefficient makes it easier to isolate by solvent extraction than HMF. Further oxidation of OBFA to OBFC is simpler, as only aldehyde groups are oxidized to carboxylic acid groups; whereas in HMF one aldehyde group and one alcohol group needs to be oxidized to COOH functions.

Table 1. Percentage yields of HMF and OBFA (**1**) produced by heating D-fructose in DMSO using Dowex 50W X8 catalyst under different reaction conditions. 9.0 g of D-fructose in 20 mL of DMSO was used in all experiments

Entry	Dowex 50 catalyst loading (%, w/w)	Reaction conditions Temperature, Time	Yield (%)	
			HMF	OBFA
1	2	80 °C, 4 h	32	0
2	5	110 °C, 4 h	54	6
3	10	110 °C, 12 h	20	54
4	10	110 °C, 24 h	0	76
5	10	110 °C, 48 h	0	72

At the end of the reaction period Dowex 50W X8 solid acid catalyst was filtered and the dialdehyde **1** was isolated by solvent extraction method. The catalyst recovered by filtration could be reused for four catalytic cycles without appreciable loss in the catalytic activity. The yields obtained in reusing the catalyst from entry 4 in table 1 for three more catalysis cycles is shown in table 2.

Table 2. The percentage yields of OBFA (**1**) produced from D-fructose in reusing of Dowex 50W X8 catalyst. 9.0 g of D-fructose in 20 mL of DMSO, Dowex 50W X8 10% (w/w), 110 °C, 24 h, was used in all experiments

Trial	Yield (%)
1	76
2	74
3	71
4	73

The OBFA was further purified by recrystallization from aqueous ethanol and then both aldehyde groups were oxidized to produce the dicarboxylic acid monomer OBFC (**2**) as shown in figure 1. In the initial screening experiments to develop a catalytic oxidation method four different metal catalysts were tested for the oxidation of OBFA to OBFC as shown in Table 3.

Table 3. The percent yield of OBFC (**2**) produced in the oxidation of OBFA (**1**) using oxygen and different metal catalysts

Entry	Catalyst	Percent yield of OBFC (%)
1	CuO	0
2	AgO	24
3	5% Pd/C	0
4	5% Pt/C	98

1 mmol of OBFA, 50 mL of 1.5M aqueous NaOH, O_2, 1 atm., 23 °C, 48 h, 2% (w/w) catalyst used in all experiments

Four catalysts, CuO, AgO, 5% Pd/C, and 5% Pt/C were tested for the oxidation of OBFA to OBFC; only AgO and 5% Pt/C showed catalytic activity and 5% Pt/C resulted nearly complete oxidation reaction after 48 h. The initial screening using air as the oxygen source resulted very slow reactions, therefore O_2 gas was used in later experiments. The catalyst could be recovered by centrifugation of the solution at 1700 g for 10 min, and then solution was acidified to pH = 2.0 by careful addition of concentrated HCl, the precipitate formed was filtered and recrystallized from aqueous ethanol to give OBFC as a pale yellow solid. The possibility of reusing the catalyst was also tested and the 5% Pt/C catalyst recovered in the entry 4 of table 3 was reused in three more catalysis cycles with negligible loss in the catalytic activity as shown in table 4.

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Table 4. The percentage yields of OBFC produced from OBFA in reusing of 5% Pt/C catalyst. 1 mmol of OBFA, 50 mL of 1.5M aqueous NaOH, 1 atm. O_2, 23 °C, 48 h, 2% (w/w) catalyst used in all experiments

Trial	Yield (%)
1	98
2	96
3	97
4	95

We have prepared the FDCA related dimer 5,5'-[oxybis(methylene)]bis[2-furancarboxylic acid] (OBFC, **2**) from D-fructose in 74 % overall yield from D-fructose via the dialdehyde 5, 5'-[oxybis(methylene)]bis[2-furaldehyde] (OBFA, **1**) as shown in figure 1 [38] . This is much higher overall yield from a carbohydrate in comparison with the typical yield in the production of FDCA from monosaccharides; obviously higher yield in this new approach is due to in situ dimerization of unstable HMF to the stable dialdehyde OBFA [39, 40]. The diacid OBFC is known as far back as 1933, as Iseki and Sugiura reported the isolation of this diacid from the urine after feeding the dialdehyde OBFA to animals [41, 37]. Then later Chundury and Szmant reported the preparation of OBFC by chemical oxidation of the OBFA by using stoichiometric quantities of oxidants, $KMnO_4$ as well as AgO in 50 and 90% yields respectively [42].

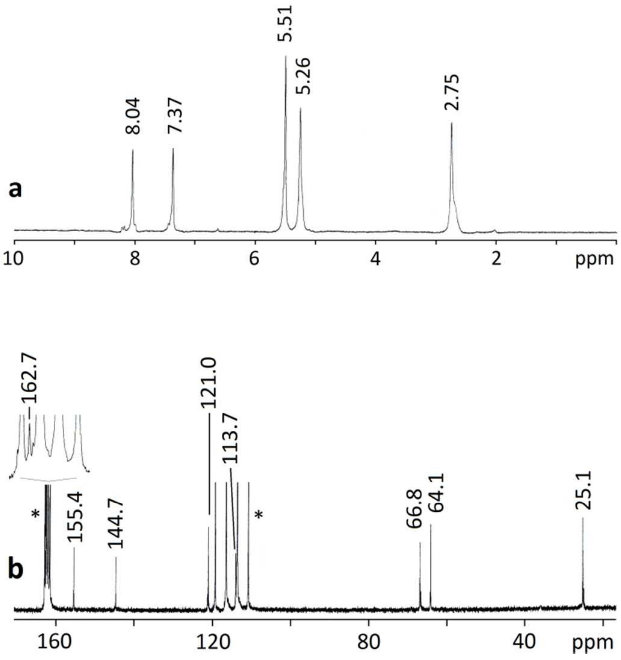

Figure 3. ^1H (a) and ^{13}C (b) NMR spectra of polyester-ether **3b** in CF_3CO_2D, * solvent

3.2. Polyester synthesis using OBFC

Polyester preparations using difuran diacid monomers are reported in the literature, for example Gandini and co-workers have used the acid dichloride and diesters of 5,5'-(1-methylethylidene)bis[2-furancarboxylic acid] for the preparation of polyesters [43, 44, 45, 46]. In these examples, the methylene bridged difuran diacid has been used in the synthesis of a variety of polyesters with aliphatic and aromatic diols. In the present work we have prepared similar polyesters using the new ether bridged difuran diacid 5,5'-[oxybis(methylene)]bis[2-furancarboxylic acid] (**2**) and two common aliphatic diols as shown in figure 2. We have chosen the solution polyesterfication technique similar to the one used by Gandini et al. in the preparation of the polyesters from 2,5-furandicarboxylic acid. The 1,2-ethandiol and 1,4-butanediol used in the polyester synthesis can also be prepared from renewable resources, making all renewable carbon based polymers [47, 48, 49]. The poly condensations of the diacid dichloride were tested for different reaction times 6, 12, and 24 h at room temperature. A small increase in molecular weights were observed from 6 h to 12 h, however, further increase in reaction time to 24 h failed to yield improvements in the molecular weight. Polyester-ethers **3a** and **b** are insoluble in common organic solvents: dichloromethane, chloroform, hexane, ethanol and methanol, but slightly soluble in 1,1,2,2-tetrachloroethane, DMF and CF_3CO_2D.

The polyester-ethers were characterized by FT-IR, ^1H and ^{13}C NMR spectroscopy. FT-IR spectra of the polymers **3a** and **3b** showed strong ester carbonyl absorptions at 1719 and 1712 cm^{-1} respectively. These values are comparable to similar C=O absorptions reported for polyesters prepared from FDCA [24]. The ^1H NMR of polyester **3a** showed a broad peak at 5.60 - 5.68 ppm, representing eight protons of four $-OCH_2-$ groups, and two absorptions at 7.54 and 8.24 ppm for furan ring protons. The ^{13}C NMR of **3a** showed seven peaks, including ester $\underline{C}$=O peak at 162.7 ppm, further confirming the repeating unit of the polyester-ether.

The representative NMR spectra of OBFC - 1,4-butanediol polyester (**3b)** are shown in figure 3. ^1H NMR of **3b** showed five peaks and the four 1,4-butane diol derived methylene groups were seen as two broad peaks at 2.75 and 5.26 ppm. ^1H-^1H COSY spectrum further confirmed the coupling of these pairs of methylene groups. The peak at 5.51 ppm was assigned to methylene groups in the ether bridge. The furan protons were observed as two 2H peaks at 7.37 and 8.04 ppm and ^1H-^1H COSY spectrum showed a cross peak confirming the coupling of these peaks as well. ^{13}C NMR of the polyester-ether **3b** showed eight peaks. The 1,4-butane diol derived methylene carbons were observed as two peaks at 25.1 and 64.1 ppm, whereas the methylene ether carbons were observed at 66.8 ppm. The four peaks at 113.7, 121.0, 144.7 and 155.4 ppm were assigned to furan ring carbons. The ester carbonyl carbon was observed at 162.7 ppm and this value is comparable to the reported ester $\underline{C}$=O absorption at 161.0 ppm for PFF in CF_3CO_2D [13].

Thermogravimetric analysis (TGA) of polyesters **3a** and **3b** showed decomposition onset temperatures at 280 and 272 °C. These are comparable to T_{onstet} values of similar difuranic polyesters reported in the literature, prepared by polymerization of 5,5'-(1-methylethylidene)*bis*[2-furancarboxylic acid] with 1,2-ethanediol and 1,4-butane diol [46]. The polyester **3a** decomposed in two steps with DTGA peaks at 380, 484 °C; whereas the DTGA curve of **3b** showed two similar peaks 371 and 492 °C.

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4. Conclusion

In conclusion, we have shown that renewable resources based monomer 5,5'-[oxybis(methylene)]bis[2-furancarboxylic acid] can be prepared in 74 % overall yield from D-fructose via the stable dialdehyde 5,5'-[oxybis(methylene)]bis[2-furaldehyde] without isolation of the unstable HMF. This is a significant improvement in overall yield from a carbohydrate in comparison with the typical yield for the production of the terephthalic acid equivalent FDCA from monosaccharides. This two step catalytic process is scalable for industrial production of the dicarboxylic acid monomer as catalysts are efficiently reusable in both catalytic steps. The new renewable dicarboxylic acid monomer can be used to prepare renewable resources based polymers, as demonstrated by the preparation of the polyesters with 1,2-ethanediol and 1,4-butanediol in 87-92 % yield.

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