

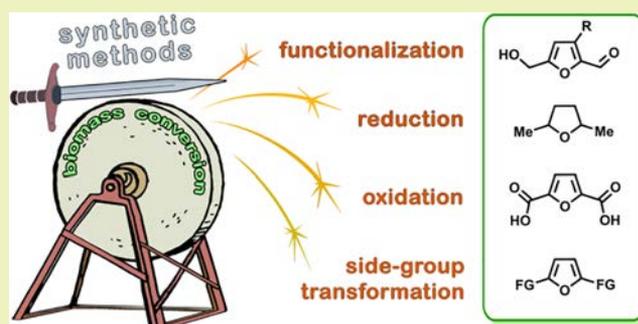
Chemical Transformations of Biomass-Derived C6-Furanic Platform Chemicals for Sustainable Energy Research, Materials Science, and Synthetic Building Blocks

Fedor A. Kucherov, Leonid V. Romashov, Konstantin I. Galkin, and Valentine P. Ananikov*

Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky pr. 47, Moscow 119991, Russia

ABSTRACT: Recent advances in the area of biomass-derived C6-furanic platform chemicals for sustainable biomass processing are analyzed focusing on chemical reactions important for development of practical applications and materials science. Among the chemical processes currently being studied, tuning the amount of oxygen-containing functional groups remains the most active research direction. Production of efficient fuels requires the removal of oxygen atoms (reduction reactions), whereas utilization of biomass-derived furanic derivatives in material science points out the importance of oxidation in order to form dicarboxylic derivatives. Stimulated by this driving force, oxidation and reduction of 5-(hydroxymethyl)furfural (HMF) are nowadays massively studied. Moreover, these fundamental transformations are often used as model reactions to test new catalysts, and HMF transformations guide the development of new catalytic systems. From the viewpoint of organic synthesis, highly diverse chemical reactivity is explored and a number of bioderived synthetic building blocks with different functional groups are now accessible. This Perspective covers the most recent literature (since Jan 2017) to highlight the emerging research trends.

KEYWORDS: Biomass processing, Platform chemicals, HMF, BHMF, DFF, FDCA, Sustainable development, Organic synthesis



1. INTRODUCTION

Extensive utilization of nonrenewable resources and the associated environment pollution are well-recognized problems of paramount importance in modern society.^{1–6} In this regard, usage of renewable resources and development of sustainable technologies are the key directions of ongoing efforts in science and technology.^{7–9} Biomass conversion is a promising way to overcome the dependence of society on fossil hydrocarbons (oil, coal, and gas), especially in fuel production and energy areas. The traditional fossil-based industrial approach has a number of environmental issues at all stages of production and processing; moreover, it shifts the CO₂ level in the atmosphere due to emissions (Figure 1a). The sustainable biomass-based approach converts sunlight energy into the chemical form and the overall process can be balanced in terms of a closed CO₂ cycle (Figure 1b).

Key practical advantages are provided by bioderived furanic platform chemicals, because they are directly accessible from plant biomass (Figure 1b).^{10–13} A sufficiently large scale of annual biosynthesis of cellulose, estimated on the level of 120–150 billion tons per year, can substantially account for the development of sustainable industry.^{14,15} Exciting opportunities of the biomass-based approach have encouraged massive research and development in chemical utilization of 5-(hydroxymethyl)furfural (HMF) and its main derivatives: 2,5-bis(hydroxymethyl)furan (BHMF), 2,5-diformylfuran (DFF), and furan-2,5-dicarboxylic acid (FDCA). Numerous studies on

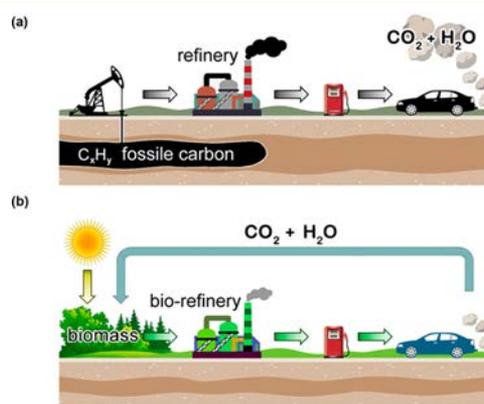


Figure 1. Comparison of traditional fossil-based (a) and sustainable biomass-based (b) approaches to produce fuels and chemicals.

bioderived furanic chemicals have been published recently in a rapidly increased manner and emerged into a very dynamic research field. Several topics have already been summarized in a series of reviews dealing with synthesis,^{16,17} fuel production,^{18–23} chemicals,^{24–28} and polymers.^{29–34}

Received: March 1, 2018

Revised: May 14, 2018

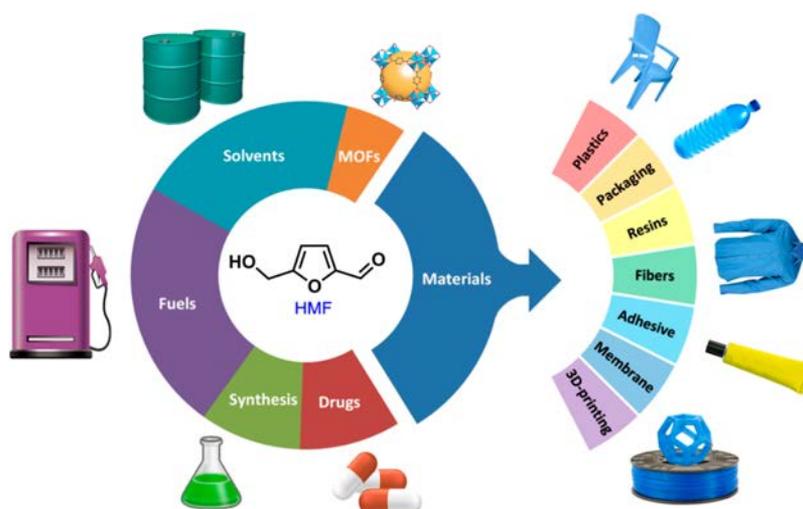


Figure 2. Main areas of practical application of HMF and its derivatives (schematic representation is shown to provide a general overview).

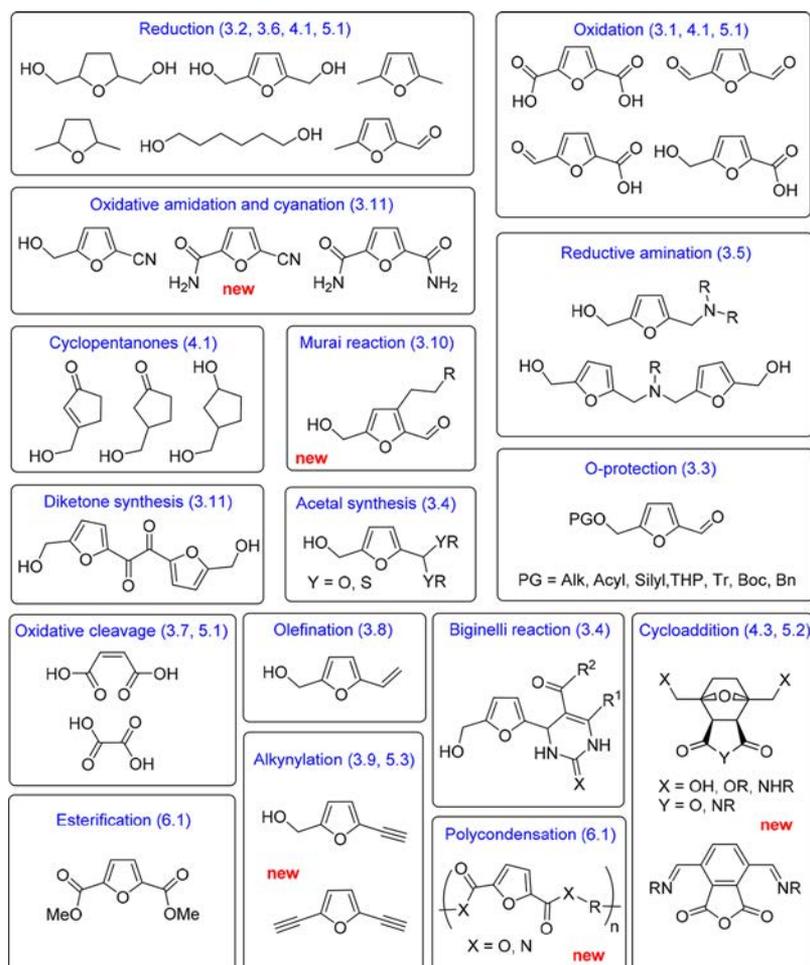


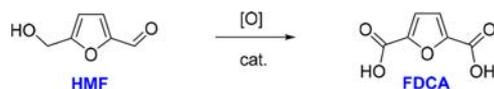
Figure 3. Main pathways of HMF reactivity studied since 2017; the section number is shown after each reaction in parentheses for the discussion of the corresponding product in the present review.

In the present review, we analyze recent advances in the chemistry and applications of the key bioderived furanic chemicals HMF, BHMF, DFF and FDCA. We focus on the most recent studies to highlight the state-of-the-art research directions and to reveal the appealing trends. This review covers the literature starting from January 2017 (both research

articles and patents). Literature references before 2017 were discussed in previous reviews^{35–39} and these discussions will not be repeated here.

We focus on different areas of applications of bioderived furanic chemicals and summarize types of chemical transformations being investigated. A substantial progress in the

Table 1. Oxidation of HMF to FDCA



Entry	Oxidant	Catalyst ^a	Conditions ^{a,b}	Yield ^{a,c} (%)	ref.
1	Oxygen	MnO ₂	1 MPa, water, NaHCO ₃ , 100 °C, 24 h	91	40
2	Oxygen	Pd-Bi-Te/C	water-methanol, KOH, 50 °C, 6 h	95	41,42
3	Oxygen	Pt/CeO ₂	water, NaOH, 70 °C, 12 h	96	43
4	Oxygen	Pt/SiO ₂	1.48 MPa, water/1,4-dioxane, 90 °C, 20 h	91	44
5	Oxygen	MnO _x -CeO ₂	2 MPa, water, KHCO ₃ , 110 °C, 12 h	91	45
6	Oxygen	Au-Pd alloy NPs on poly(ionic liquid)	water, K ₂ CO ₃ , 90 °C, 12 h	99	46
7	Oxygen	Cr ₂ O ₃ /CeO ₂	3 MPa, water, Na ₂ CO ₃ , 150 °C, 12 h	87	47
8	Oxygen	Pt/ZrO ₂	0.4 MPa, water, 100 °C, 12 h	99	48
9	Oxygen	Au-Pd alloy NPs on basic anion-exchange resin	1 MPa, water, Na ₂ CO ₃ , 100 °C, 4 h	93	49
10	Oxygen	Pt-Ni/AC- <i>x</i> ALD	1.0 MPa, water, 100 °C, 15 h	98	50
11	Oxygen	Au/HSAG-N	1.0 MPa, water, NaHCO ₃ , 90 °C, 12 h	75	51
12	Oxygen	AuPd/La-CaMgAl-LDH	0.5 MPa, water, 100 °C, 6 h	86	52
13	Oxygen	Pd/P,N-codoped graphene	0.1 MPa, water, NaOH, 50 °C, 6 h	83	53
14	Oxygen	Pd/CC	0.1 MPa, water, K ₂ CO ₃ , 140 °C, 30 h	85	54
15	Oxygen	Ni-MnO ₂	0.8 MPa, water, NaHCO ₃ , 100 °C, 28 h	94	55
16	Air	Ru/MnCo ₂ O ₄	2.4 MPa, water, 120 °C, 10 h	99	56
17	Air	Pt/C	2.2 MPa, NMP/water, NaOH, 80 °C, 0.5 h	74	57
18	Air	Ni-Pd alloy	water, Na ₂ CO ₃ , 80 °C, 4 h	70	58
19	Air	Au-Pd alloy NPs on basic anion-exchange resin	4 MPa, water, Na ₂ CO ₃ , 100 °C, 4 h	83	49
20	Air	magnetic laccase/TEMPO	water, acetate buffer, 35 °C, 96 h	90	59
21	Air	CoPz/g-C ₃ N ₄	water, illumination, Na ₂ B ₄ O ₇ , 25 °C, 14 h	96	60
22	Air	Co@KIT-6	water, 80 °C, 2 h	100	61
23	Photocatalytic oxidation	Au/TiO ₂	water, illumination, Na ₂ CO ₃ , 30 °C, 40 h	95	62
24	Electrooxidation	Cu-foam-coated electrode	water, KOH, electrolysis	96	63
25	KMnO ₄	None	water, NaOH, 20 °C, 12 h	64	64
26	<i>t</i> -BuOOH	VPO ₄	DMSO, 110 °C, 3 h	53	65

^aThe data corresponding to the best results are provided if a series of experiments was performed. ^bThe pressure is 0.1 MPa (1 atm) if not noted otherwise. ^cThe yield was calculated by multiplying the conversion to selectivity if not provided in the paper.

improvement of known chemical transformations of furanic chemicals and diversification of research activities into the development of novel reactions is outlined.

2. PRACTICAL APPLICATIONS OF BIODERIVED FURANIC COMPOUNDS

The analysis of the recent literature points out the outstanding practical potential of bioderived HMF and its derivatives. The whole spectrum of applications is ranging from fuels and solvents to organic synthesis and preparation of biologically active molecules for pharmaceutical applications (Figure 2). The focus on material science highlights the emerging trends in obtaining plastics (biopolymers) suitable for several important applications (Figure 2).

Traditional manufacturing methods have been recently supplemented with additive technologies, and direct applications of furanic biopolymers in 3D printing have been demonstrated. A series of studies were published to replace dicarboxylic benzoic acids by FDCA, which may further develop into a standalone direction for accessing sustainable metal-organic frameworks (MOFs). Chemical transformations developed in these areas are discussed in the present review in Section 3 (HMF), Section 4 (BHMF), Section 5 (DFF), and Section 6 (FDCA). Conclusions and perspectives are presented in Section 7.

From the synthetic viewpoint, HMF is one of the most intensively studied biomass-derived molecules of the past decade. Main HMF derivatives investigated during the covered

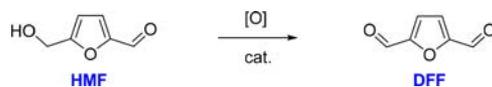
literature period (from January 2017) are summarized in Figure 3. Besides the well-known derivatives, several novel HMF-derived compounds were introduced in 2017 (marked as “new” in Figure 3). Alkynylation, oxidative cyanoamidation and C–H activation via the Murai reaction, as well as the variety of novel polyesters, should be noted.

3. TRANSFORMATIONS OF 5-(HYDROXYMETHYL)FURFURAL (HMF)

In this section, transformations of HMF are grouped by the reaction type. Because the vast majority of HMF reactions are redox transformations, we start this section with oxidation and reduction of the HMF side groups. The experimental data on each transformation are summarized in tables for convenient comparison of conditions, catalysts and product yields.

3.1. Oxidation of Side Groups. Oxidation of HMF to FDCA (Table 1) is the most thoroughly studied area of HMF chemistry, because FDCA is often presented as a precursor of biobased polymers (see Section 6 for polymerization). In the majority of works, molecular oxygen is used as stoichiometric oxidant (entries 1–15, Table 1). Ambient air also can be used as oxidant (entries 16–22, Table 1), but for excellent yields, high pressure should be applied. Among the convenient oxidation procedures, photocatalytic oxidation (entry 23, Table 1) should be highlighted. This process occurs via dehydrogenation on an Au/TiO₂ photocatalytic system. It should be noted that in many cases (entries 1–3, 5–7, 9, 11, 13–15, 17–19, 23–25) oxidation proceeds under basic

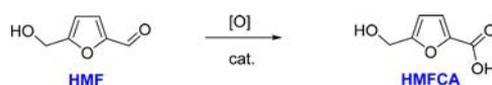
Table 2. Oxidation of HMF to DFF



Entry	Oxidant	Catalyst ^a	Conditions ^{a,b}	Yield ^{a,c} (%)	ref.
1	Oxygen	Cu-doped nanostructured MnO ₂	0.3 MPa, ethanol, 140 °C, 5 h	83	66
2	Oxygen	Fe on N-doped carbon	1 MPa, water, 80 °C, 8 h	40	67
3	Oxygen	MnOOH	1 MPa, water, NaHCO ₃ , 100 °C, 24 h	56	40
4	Oxygen	Pt/C	1.8 MPa, water/DMSO, Na ₂ HPO ₄ , 80 °C, 0.5 h	28	57
5	Oxygen	Pt-Au/SiO ₂	1.48 MPa, water/1,4-dioxane, 90 °C, 20 h	90	44
6	Oxygen	MIL-100(Fe), TEMPO, NaNO ₂	MeCN, 75 °C, 6 h	100	68
7	Oxygen	Pt-Ru, electrogenerative oxidation	0.15 MPa, water, H ₂ SO ₄ , 50 °C, 17 h	40	69
8	Oxygen	MoO ₃ on N-doped carbon	DMSO, 140 °C, 12 h	96	70
9	Oxygen	VO _x -microspheres	3 MPa, water, 130 °C, 1 h	89	71
10	Oxygen	MgO/CeO ₂	0.9 MPa, water, 100 °C, 15 h	96	72
11	Oxygen	Au-Ru/rGO	0.5 MPa, illumination, toluene, 80 °C, 8 h	91	73
12	Air	Mn(NO ₃) ₂ , picolinic acid, TEMPO	acetic acid, 25 °C, 3 h	85	74
13	Air	Mn-doped Co ₃ O ₄	DMF, 130 °C, 4 h	77	75
14	Air	Catalase, galactose oxidase M ₃₋₅ , horse radish peroxidase	water, phosphate buffer, pH = 7, 37 °C, 1 h	91	76
15	Photocatalytic oxidation	Ni/CdS	water, illumination, 24 h	92	77
16	Photoelectro-catalytic oxidation	Pt-loaded nanotube of TiO ₂ on Ti photoanode	water, pH = 5, 25 °C, 0.5 h	40	78
17	MnO ₂	None	toluene, reflux, 6 h	97	64
18	NaNO ₂	None	CF ₃ COOH, 1 h, 25 °C	90	79
19	Iodine	4-acetylamino-2,2,6,6-tetramethyl-1-piperidinyloxy	water/DCM, NaHCO ₃ , collidine, 20 °C, 1 h	93	80
20	<i>t</i> -BuOOH	Fe phthalocyanin	water, 33 °C, 6 min	not given	81
21	<i>t</i> -BuOOH	Co _x O _y on N-doped TiO ₂	water, 80 °C, 5 h	36	82
22	H ₂ O ₂	Cu-Salen/SBA-15	water, 25 °C, 24 h	2	83
23		Rh/C	8 MPa, supercritical CO ₂ , 150 °C, 2 h	99	84

^aThe data corresponding to the best results are provided if a series of experiments was performed. ^bThe pressure is 0.1 MPa (1 atm) if not noted otherwise. ^cThe yield was calculated by multiplying the conversion to selectivity if not provided in the paper.

Table 3. Oxidation of HMF to HMFCA



Entry	Oxidant	Catalyst ^a	Conditions ^{a,b}	Yield ^{a,c} (%)	ref.
1	Oxygen	MnO ₂	1 MPa, water, K ₃ PO ₄ , 100 °C, 24 h	14	40
2	Oxygen	Pt/C	2.2 MPa, water/NMP, NaOH, 80 °C, 0.5 h	18	57
3	Oxygen	Au-Pd alloy NPs on IRA-900	1 MPa, water, Na ₂ CO ₃ , 100 °C, 4 h	36	49
4	Oxygen	Au/HSAG	1.0 MPa, water, NaHCO ₃ , 90 °C, 12 h	93	51
5	H ₂ O ₂	NAD ⁺ /human Hb/horse liver alcohol dehydrogenase	water, phosphate buffer, pH = 7, 30 °C, 24 h	81	85
6	Biocatalytic oxidation	<i>C. testosterone</i> SC1588 cells	water, phosphate buffer, pH = 7, 30 °C, 24 h	90	86

^aThe data corresponding to the best results are provided if a series of experiments was performed. ^bThe pressure is 0.1 MPa (1 atm) if not noted otherwise. ^cThe yield was calculated by multiplying the conversion to selectivity if not provided in the paper.

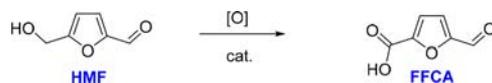
conditions leading to the formation of FDCA in the form of salt rather than the acid itself. Application of stoichiometric chemical oxidants (entries 25 and 26, Table 1) was utilized for laboratory scale syntheses.

Oxidation of HMF to DFF was accomplished by various methods (Table 2). As in the case of DFF, the most popular oxidant for this process is molecular oxygen (entries 1–11, Table 2). Specific oxidation procedures include photocatalysis (entry 15, Table 2), enzymatic oxidation (entry 14, Table 2) and catalytic dehydrogenation on Rh/C in supercritical CO₂ (entry 23, Table 2). Though many highly efficient catalytic processes have been developed, classical oxidations with

stoichiometric oxidants are still popular in laboratory scale synthesis (entries 17–19, Table 2).

Selective oxidation of HMF to HMFCA (Table 3) and FFCA (Table 4) is more complicated because of possible over-oxidation to FDCA. Generally, these compounds serve as intermediates in the synthesis of FDCA, and under optimized conditions, the quantities of HMFCA and FFCA are minimized. As well as in the case of FDCA, synthetic transformations under basic conditions are usually applied (Table 3, entries 1–4; Table 4, entries 2, 4, 5, 8). The best results for selective HMFCA synthesis were obtained using biocatalytic oxidation in whole cells (entry 6, Table 3) and oxidation with molecular oxygen using Au-HSAG catalyst

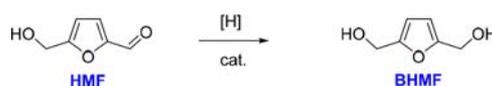
Table 4. Oxidation of HMF to FFCA



Entry	Oxidant	Catalyst ^a	Conditions ^{a,b}	Yield ^{a,c} (%)	ref.
1	Oxygen	MnO ₂	1 MPa, water, 100 °C, 24 h	65	40
2	Oxygen	Pt/C	2.2 MPa, NMP/water, NaOH, 80 °C, 0.5 h	74	57
3	Oxygen	Pt/ZrO ₂	1.48 MPa, water/1,4-dioxane, 90 °C, 20 h	56	44
4	Oxygen	CeO ₂	2 MPa, water, KHCO ₃ , 110 °C, 12 h	31	45
5	Oxygen	Au-Pd/IRA400	1 MPa, water, Na ₂ CO ₃ , 100 °C, 4 h	48	49
6	Oxygen	MgO/CeO ₂	0.9 MPa, water, 130 °C, 9 h	89	72
7	Air	magnetic laccase/TEMPO	water, acetate buffer, 35 °C, 96 h	77	59
8	H ₂ O ₂	Ru/C	water, NaHCO ₃ , 75 °C, 1 h	92	87
9	Photoelectrocatalytic oxidation	Pt-loaded nanotube of TiO ₂ on Ti photoanode	water, illumination, pH = 5, 25 °C, 0.5 h	18	78

^aThe data corresponding to the best results are provided if a series of experiments was performed. ^bThe pressure is 0.1 MPa (1 atm) if not noted otherwise. ^cThe yield was calculated by multiplying the conversion to selectivity if not provided in the paper.

Table 5. Reduction of HMF to BHMF



Entry	Reductant	Catalyst ^a	Conditions ^{a,b}	Yield ^{a,c} (%)	ref.
1	Hydrogen	Cu-Ni/ γ -Al ₂ O ₃	3 MPa, THF, 130 °C, 6 h	62	96
2	Hydrogen	[Ru(2-(ethylthio)-N-[(pyridin-2-yl)methyl]ethan-1-amine)(PPh ₃)Cl ₂]	3 MPa, isopropanol, KO ^t Bu, 80 °C, 1 h	93	97
3	Hydrogen	RANEY Cu	9 MPa, water, 90 °C, 1 h	79	98
4	Hydrogen	Ru/C	0.4 MPa, ethanol, 150 °C, 3 h	95	99
5	Hydrogen	Co _x O _y	2 MPa, methanol, 90 °C, 1 h	93 ^d	100
6	Hydrogen	Cu/SiO ₂	1.5 MPa, 1-butanol, 100 °C, 4 h	93	101
7	Isopropanol	Zr <i>m</i> -xylylenediphosphonate NPs	isopropanol, 120 °C, 2 h	93	102
8	Isopropanol	Ru on N-doped carbon	2 MPa, isopropanol, 160 °C, 8 h	25	103
9	Isopropanol	Zr furan-2,5-dicarboxylate	isopropanol, 140 °C, 8 h	87	104
	Isopropanol	Hf furan-2,5-dicarboxylate	isopropanol, 100 °C, 5 h	95	105
10	Isopropanol	Cp*Ir(pyridinesulfonamide)Cl	isopropanol, 85 °C, 0.5 h	100	106
11	Isopropanol	γ -Fe ₂ O ₃ /hydroxyapatite	1 MPa, isopropanol, 180 °C, 10 h	78	107
12	Isopropanol	ZnO-ZrO ₂ /USY(Si/Al-7)	isopropanol, 180 °C, 2.5 h	91	108
13	Isopropanol	YCl ₃	2 MPa, isopropanol, 150 °C, 1 h	35	109
14	Isopropanol	Al ₇ Zr ₃ @Fe ₃ O ₄	isopropanol, 180 °C, 4 h	71	110
15	Isopropanol	Hf-MOF-808	isopropanol, 100 °C, 1.5 h	92	111
16	NaBH ₄	—	ethanol, 0 °C, 12 h	74	112
17	NaBH ₄	—	water, 24–60 °C, 3 h	99	113
18	NaBH ₄	—	MeOH, 0 °C, 4 h	77	114
19	Glucose	<i>Meyerozyma guilliermondii</i> SC1103	water, phosphate buffer, pH = 7.2, 35 °C, 7 h	89	115

^aThe data corresponding to the best results are provided if a series of experiments was performed. ^bThe pressure is 0.1 MPa (1 atm) if not noted otherwise. ^cThe yield was calculated by multiplying the conversion to selectivity if not provided in the paper. ^dA quantitative yield of 2,5-bis(methoxymethyl)furan was observed if the temperature was increased to 140 °C.

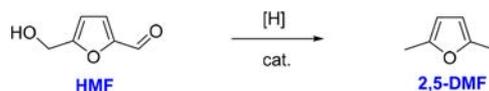
(entry 4, Table 3). Oxidation of HMF to FFCA demands specific conditions to achieve high selectivity. Usually, FFCA is obtained as byproduct in the course of oxidation and can be isolated from the reaction mixture at low conversion. It should be noted that, in spite of close relation to HMF, HMFCFA and FFCA remain hardly available compounds and at the moment cannot be discussed as high potential platform chemicals.

Considering the representative previous studies dedicated to oxidation of HMF, few notes can be mentioned. Aerobic oxidation of HMF using gold nanoparticles produces FDCA with excellent yields according to Table 1, this catalytic system still attracts certain interest.^{88–92} Significant progress in the development of new methods of synthesis of DFF from HMF should be noted (Table 2). Some impactful studies in this area

propose the usage of oxygen and metal/bromide catalysts (Co/Mn/Br, Co/Mn/Zr/Br)⁹³ or catalytic systems based on vanadyl phosphate.^{94,95} Selective synthesis of HMFCFA and FFCA has not been addressed yet; the compounds were reported as byproducts without dedicated targeted procedures.

3.2. Reduction of Side Groups and Furan Ring. Reduction of HMF is another important direction of HMF chemistry, because the reduced products can be used as solvents, fuels and polymer precursors. The main reductants used in these reactions are molecular hydrogen and isopropanol (in the course of the Meerwein–Ponndorf–Verley (MPV) reaction). Varying catalysts and reduction conditions optimized synthetic transformations leading to BHMF (Table 5), 2,5-DMF (Table 6), BHMTHF (Table 7) and DMTHF (Table 8)

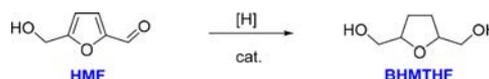
Table 6. Reduction of HMF to 2,5-DMF



Entry	Reductant	Catalyst ^a	Conditions ^{a,b}	Yield ^{a,c} (%)	ref.
1	Hydrogen	Cu/ZrO ₂	1.5 MPa, 1-butanol, 200 °C, 4 h	61	116
2	Hydrogen	Ru-MoO _x /C	1.5 MPa, 1-butanol, 180 °C, 1 h	80	117
3	Hydrogen	Fe on N-doped carbon	4 MPa, 1-butanol, 240 °C, 5 h	86	118
4	Hydrogen	Cu-Co/Al ₂ O ₃	3 MPa, THF, 220 °C, 8 h	78	119
5	Hydrogen	Pd-Zr MOF on sulfonated graphene oxide	1 MPa, THF, 160 °C, 3 h	99	120
6	Hydrogen	Ni/C	0.6 MPa, ethanol, 150 °C, 15 h	90	121
7	Hydrogen	Cu-Co@C	5 MPa, ethanol, 180 °C, 8 h	99	122
8	Hydrogen	Ni-Cu/C	3.3 MPa, 1-propanol, 180 °C, flow reactor	99	123
9	Hydrogen	Ru-NPs/CNT	2 MPa, 1,4-dioxane, 150 °C, 1 h	84	124
10	Hydrogen	NiZnAl	1.5 MPa, 1,4-dioxane, 180 °C, 15 h	94	125
11	Hydrogen	Ni/WO ₃	1 MPa, water, 180 °C, 6 h	95	126
12	Hydrogen	Pd-Au/graphite	1 MPa, THF, 150 °C, 4 h	82	127
13	Methanol	Cu ₃ Al-A	1 MPa, methanol, 240 °C, 1.5 h	97	128
14	Isopropanol	Ru on N-doped carbon	2 MPa, isopropanol, 160 °C, 8 h	55	103
15	Cyclohexanol	Ni-Cu alloy NPs/Al ₂ O ₃	1,4-dioxane, 240 °C	98	129

^aThe data corresponding to the best results are provided if a series of experiments was performed. ^bThe pressure is 0.1 MPa (1 atm) if not noted otherwise. ^cThe yield was calculated by multiplying the conversion to selectivity if not provided in the paper.

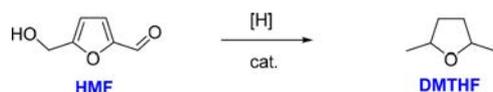
Table 7. Reduction of HMF to BHMTHF



Entry	Reductant	Catalyst ^a	Conditions ^{a,b}	Yield ^{a,c} (%)	ref.
1	Hydrogen	Raney-Ni	5 MPa, methanol, 24 h	62	130
2	Hydrogen	Ru/C	1.5 MPa, 1-butanol, 180 °C, 1 h	10	117
3	Hydrogen	Pd/C	8 MPa, water, 25–180 °C, 6.5 h	96	131
4	Hydrogen	Ru/C	4 MPa, water, 140 °C, 2 h	48	132

^aThe data corresponding to the best results are provided if a series of experiments was performed. ^bThe pressure is 0.1 MPa (1 atm) if not noted otherwise. ^cThe yield was calculated by multiplying the conversion to selectivity if not provided in the paper.

Table 8. Reduction of HMF to DMTHF



Entry	Reductant	Catalyst ^a	Conditions ^{a,b}	Yield ^{a,c} (%)	ref.
1	Hydrogen	Pd/C	1.5 MPa, water, 90 °C	61	116
2	Hydrogen	Pd-Zr MOF on sulfonated graphene oxide	1 MPa, THF, 160 °C, 3 h	68	120

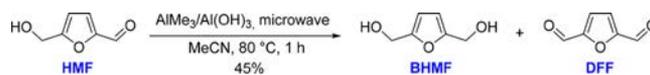
^aThe data corresponding to the best results are provided if a series of experiments was performed. ^bThe pressure is 0.1 MPa (1 atm) if not noted otherwise. ^cThe yield was calculated by multiplying the conversion to selectivity if not provided in the paper.

were carried out. Some interesting reductive protocols should be particularly highlighted: bioreduction of HMF to BHMTHF (entry 19, Table 5) and MPV reduction on FDCA-based Zr- and Hf-MOFs (entries 9, 10 Table 5).

The MPV-reduction of HMF can be conjugated with the Oppenauer oxidation, which leads to HMF disproportionation to BHMTHF and DFF by using AlMe₃/Al(OH)₃ catalyst under microwave irradiation (Scheme 1).¹³³

In the present Perspective, we focus only on the most recent studies. Considering the representative previous studies on

Scheme 1. Oppenauer Oxidation of HMF



reduction of HMF, it is necessary to mention that supported Pd/C and molecular hydrogen have been the most commonly used catalytic system.^{134,135} More details on the previously studied reductive transformations of HMF are also summarized in the recent review.¹³⁶

3.3. Protection and Functionalization of Hydroxymethyl Group. For a variety of synthetic transformations, the hydroxymethyl group of HMF should be protected. The following common protecting groups were applied: Ac,^{137,138} TBS,¹³⁷ Bn,¹³⁷ Boc,¹³⁸ trityl,¹³⁷ Bz,¹³⁸ Piv,¹³⁹ THP,¹³⁷ and Me.¹³⁸ Esters of HMF with organic¹⁴⁰ and inorganic¹³⁸ acids also were prepared. Ferrier-type glycosylation of HMF was described recently utilizing different glycals.¹⁴¹

The reaction of HMF with alcohols can lead to ethers^{142–144} or acetals^{142,143,145} depending on the reaction conditions. In many cases, ethers are common byproducts in catalytic hydrogenation of HMF in alcoholic media. Particular attention should be paid to the synthesis of the HMF dimer via intermolecular etherification. This compound is a usual byproduct in the HMF synthesis, but selective preparation of the dimer often requires harsh conditions. It was found that the

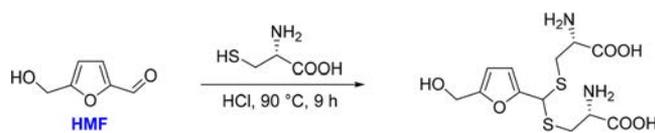
utilization of alumina-supported heteropolyacids as acidic catalysts allows obtaining the dimeric ether in high yield under mild conditions.¹⁴⁶

5-(Chloromethyl)furfural (CMF) is a valuable product of functionalization of the HMF hydroxymethyl group, since CMF can be prepared directly from biomass in high yields and can be discussed as a platform-chemical itself; however, within the scope of this annual review, there are few examples of its application limited to oxidation to DFF¹⁴⁷ and synthesis of imines.¹⁴⁸

3.4. Nucleophilic Addition to Aldehyde Group. The aldehyde group in HMF is active in nucleophilic addition with various nucleophiles. Acetals can be easily prepared from HMF with various alcohols under acidic conditions. The main drawback in the synthesis of acetals is the formation of ethers. It was found that the usage of CePO_4 as a catalyst allowed obtaining acetals in high yield without the formation of ethers.¹⁴⁹

It was shown that dithioacetal obtained from HMF and cysteine was less absorbed by and less toxic against Caco-2 cells than HMF itself (Scheme 2). This is the first report on the

Scheme 2. Synthesis of Dithioacetal of HMF with Cysteine

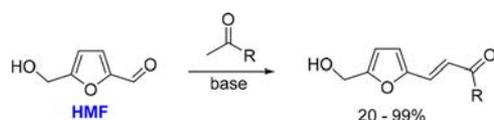


toxicity of an HMF-amino acid adduct, which is of significant importance because such complexes are found in various food products.¹⁵⁰ It was reported that dithioacetals can be prepared under ambient and solvent-free conditions using zeolites as catalysts.¹⁵¹

Various *N*-nucleophiles can be subjected to reaction with HMF leading to imines,¹⁵² oximes, and hydrazones.¹⁵³ Long-chain *N*-hydroxyaminocoumarins were used as LC-MS labels for analysis of HMF.¹⁵⁴

HMF can be used as electrophile in the aldol reaction (Scheme 3). The obtained adducts usually act as substrates for

Scheme 3. Aldol Reaction of HMF

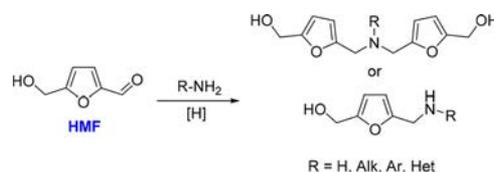


hydrogenolysis in the synthesis of biobased fuels. Simple ketones like acetone, methyl isobutyl ketone (MIBK), cyclopentanone, and cyclohexanone are used as enolate components.¹⁵⁵ The main idea of this process is lengthening the carbon backbone of the molecule to obtain higher hydrocarbons. Various bases like CaO ¹⁵⁶ or piperidine¹⁵⁷ can be applied. A high-yield aldol reaction of HMF with angelica lactone can be carried out by using Mn_2O_3 under solvent-free conditions; it leads to jet fuel range C_9 and C_{10} alkanes.¹⁵⁸ A biologically active aurone derivative was obtained by the aldol reaction with HMF in 20% yield using choline chloride and urea.^{159,160} The Doebner reaction of HMF with malonic acid leads to the corresponding acrylic acid in 95% yield using piperidine as a base.⁶⁴

An interesting example of nucleophilic addition to HMF is a multicomponent Biginelli reaction with 1,3-dicarbonyl compounds and urea-type building blocks leading to the corresponding functionalized dihydropyrimidinones with moderate to good yield up to 86%.¹⁶¹

3.5. Reductive Amination. HMF can be easily introduced into reductive amination with various amines (Scheme 4). Hydrogen¹⁶² as well as carbon monoxide¹⁶³ can be used as reductants.

Scheme 4. Reductive Amination of HMF



An unsubstituted aminomethyl derivative (Table 9) can be obtained with ammonia using heterogeneous catalysts (entries 1 and 2, Table 9), as well as enzymatically via the transamination process (entry 3).

3.6. Reductive Cleavage. Under harsh reductive conditions, HMF can be transformed to acyclic 1-hydroxyhexane-2,5-dione (HHD) (Table 10). In the case of Al_2O_3 as a catalyst support, the obtained HHD can undergo the aldol reaction with subsequent reduction leading to 3-hydroxymethylcyclopentanone (HCPN) ($\text{Cu}/\text{Al}_2\text{O}_3$, 2 MPa H_2 , water, 140 °C, 6 h, yield 79%) or 3-hydroxymethylcyclopentanol (HCPL) ($\text{Co}/\text{Al}_2\text{O}_3$, 2 MPa H_2 , water, 140 °C, 6 h, yield 61%).¹⁶⁶

Using a Pd–Ir–Re catalytic system, it is possible to obtain 1,6-hexanediol directly from HMF (Scheme 5).¹⁷⁰ Besides hexanediol, small amounts of 1,5-hexanediol and *n*-hexane were observed as byproducts in the reaction mixture.

The previously studied reductive ring-opening of HMF leading to the formation of caprolactam has suggested the usage of a Rh–Re/ SiO_2 catalyst.¹⁷¹

3.7. Oxidative Cleavage. It was reported that HMF and furfural can be oxidatively cleaved to maleic acid in high yields using hydrogen peroxide in formic acid (Scheme 6).¹⁷²

Using a Fe catalyst supported on carbon nanotubes, HMF was oxidatively cleaved to oxalic acid with 48% yield (1 MPa O_2 , water, 140 °C, 1.5 h).¹⁷³

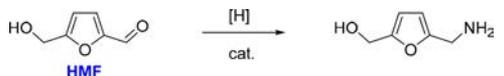
3.8. Olefination of HMF. It was shown that HMF could be introduced into the Wittig reaction without any protecting groups (Scheme 7a).¹⁷⁴ The obtained 2-hydroxymethyl-5-vinylfuran (HMVF) was polymerized giving a polymer with high adhesiveness to steel, copper, aluminum, and glass (Scheme 7b). HMVF has also demonstrated cell-adhesive properties.

3.9. Alkynylation of HMF. It was shown that under mild conditions of the Ohira–Bestmann reaction, HMF and its derivatives could be alkynylated to the corresponding terminal alkynes in nearly quantitative yields (Scheme 8).¹³⁹

The obtained ethynyl derivatives allowed implementing alkyne chemistry for biobased furanic compounds. The Sonogoshira coupling, Glaser oxidation, and [Rh]-catalyzed polymerization of ethynylfurans were performed to illustrate the synthetic value (Scheme 9).¹³⁹

3.10. C–H Activation of HMF. Selective activation of the C(3) position of the HMF furan ring is a challenge. This problem was solved by means of the Murai reaction¹³⁷

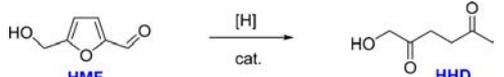
Table 9. Reductive Amination of HMF



Entry	Reductant	Catalyst ^a	Conditions ^{a,b}	Yield ^{a,c} (%)	ref.
1	Hydrogen	Co-MOF	4 MPa, <i>t</i> BuOH, 120 °C, 15 h	89	164
2	Hydrogen	Ru/Nb ₂ O ₅	4 MPa, MeOH, 90 °C, 8 h	96	165
3	Isopropylamine	Transaminase, pyridoxal-5-phosphate	phosphate buffer, 35 °C, pH = 8, 24 h	58	114

^aThe data corresponding to the best results are provided if a series of experiments was performed. ^bThe pressure is 0.1 MPa (1 atm) if not noted otherwise. ^cThe yield was calculated by multiplying the conversion to selectivity if not provided in the paper.

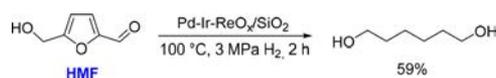
Table 10. Ring-Opening Reduction of HMF to 1-Hydroxyhexane-2,5-dione (HDD)



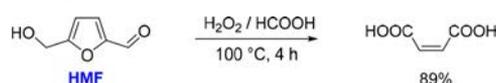
Entry	Reductant	Catalyst ^a	Conditions ^a	Yield ^b (%)	ref.
1	Hydrogen	Pd/Nb ₂ O ₅	4 MPa, water, 140 °C, 8 h	69	132
2	Hydrogen	Al ₂ (SO ₄) ₃ , [(Cp*)Ir(4,4'-dihydroxy-2,2'-bipy)(H ₂ O)][SO ₄]	3 MPa, water, 130 °C, 4 h	74	167
3	Hydrogen	[Cp*Ir(dpa)Cl]Cl	1 MPa, water, 120 °C, 2 h	69	168
4	Hydrogen	[Cp*Ir(dhimp)Cl]Cl	6 MPa, water, phosphate buffer, 140 °C, 1 h	71	169

^aThe pressure is 0.1 MPa (1 atm) if not noted otherwise. ^bThe data corresponding to the best results are provided if a series of experiments was performed.

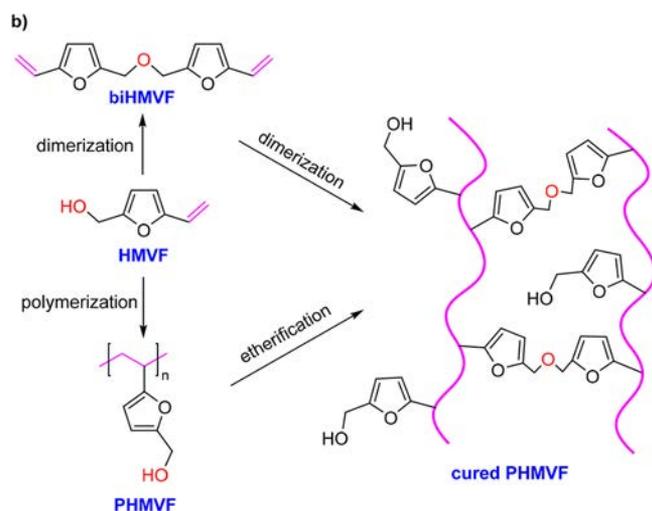
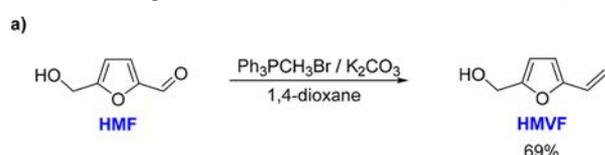
Scheme 5. Reduction of HMF to 1,6-Hexanediol



Scheme 6. Synthesis of Maleic Acid from HMF

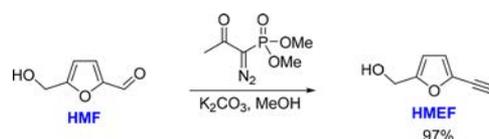


Scheme 7. (a) Wittig Reaction with Unprotected HMF; (b) Cross-Linking Mechanism of HMVF To Form Poly-HMVF

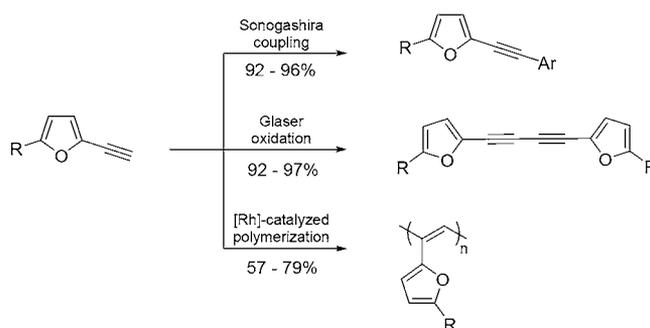


(Scheme 10). Unfortunately, this reaction cannot be performed with HMF itself: its hydroxymethyl group should be protected,

Scheme 8. Alkynylation of HMF



Scheme 9. Reactivity of Ethynylfurans Obtained from HMF



and a directing ethylenediamino-group should be introduced. Nevertheless, this work is a rare example of functionalization of HMF in the third position.

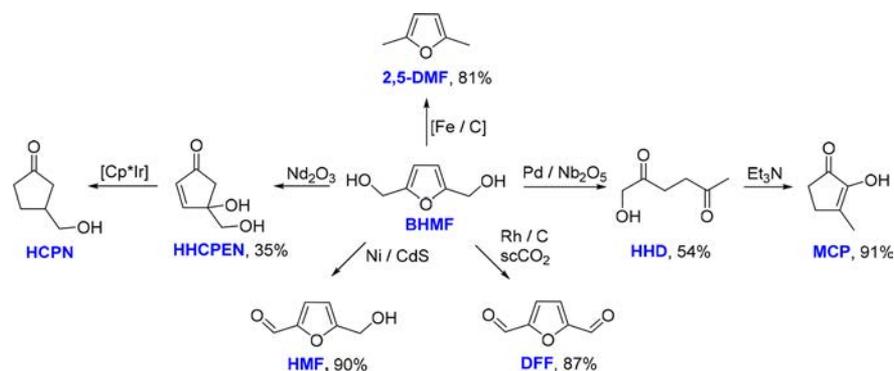
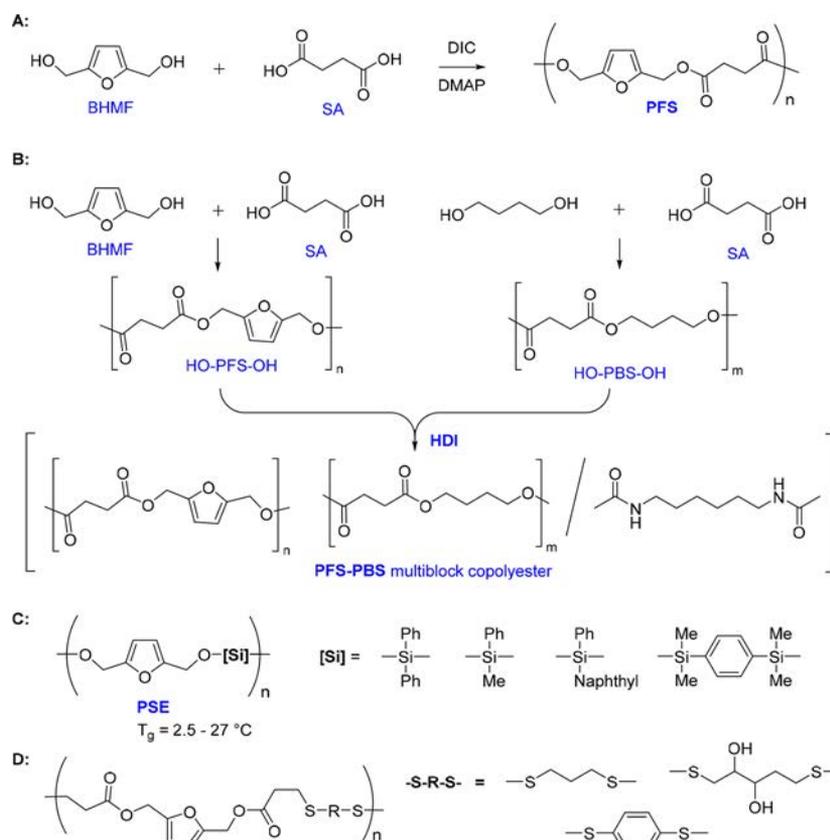
3.11. Other Reactions of HMF. Sharma and co-workers described C–H activation of the indole core utilizing unprotected HMF (Scheme 11).¹⁷⁵ A 2-substituted indole derivative was obtained with a moderate 34% yield.

Another example of the reaction involving the aldehyde group of HMF was CO₂-assisted dimerization to α -diketone (Scheme 12).¹⁷⁶

Decarbonylation of HMF could be achieved in compressed CO₂ using an alumina-supported Pd catalyst (Pd/Al₂O₃) yielding furfuryl alcohol.¹⁷⁷

Under oxidizing conditions in the presence of aqueous ammonia, HMF could be transformed into a series of nitrile-amide derivatives (Scheme 13).¹⁷⁸ The course of the catalytic amidation depended on the type of the used MnO₂-catalyst. In

Scheme 14. Synthesis of Derivatives from BHMF

Scheme 15. Synthetic Path to Biobased Copolymers from BHMF^a

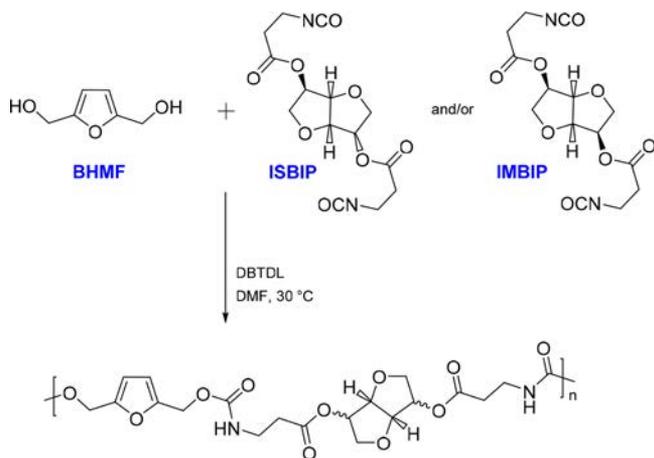
^aA: poly(2,5-furandimethylene succinate), B: multiblock co-polymer, C: poly(silylether)s, D: poly(β -thioether esters).

Functionalization of BHMF by the epoxy-group is a route to furan-based monomers 3–5 with a wide range of applications (Scheme 17). Epoxy 2,5-bis[(2-oxiranylmethoxy)methyl]-furan (BOF) was used as a graphene dispersant for the preparation of new graphene/polymer nanocomposites by the reaction of a BOF/graphene suspension with a bisphenol A epoxy resin in the presence of a curing agent 3,6-*endo*-1,2,3,6-tetrahydrophthalic anhydride and 2-ethyl-4-methylimidazole as a catalyst.¹⁸⁶ A Diels–Alder adduct of BOF with *N*-hexyl maleimide (DA-BOF) was used as a toughening agent in polymerization reaction of BOF. After curing of the mixtures of BOF and DA-BOF contained various ratios of monomers in the presence of isophorone diamine (IPDA), a number of cross-linked networks were formed. Obtained cross-polymers showed increased impact strength and nearly unaffected tensile

properties compared to linear polymer obtained without the use of curing agent.¹⁸⁷

4.3. Other Reactions of BHMF. BHMF and its esters were involved into various cycloaddition reactions. The Diels–Alder reaction of unsubstituted BHMF with maleimide was carried out to give product 1 with high *endo* diastereoselectivity (Scheme 18). Hydrogenation of an unsaturated intermediate afforded bioderived tricyclic compound 2 with nonplanar molecular structure, which could possibly be further functionalized by hydroxyl or imide groups.¹¹³ In accordance with the principles of green chemistry, these transformations were conducted step-by-step or one-pot in water. A recently published review summarizes other results on BHMF synthesis and utilization,¹⁸⁸ and this discussion is not repeated here.

Scheme 16. New BHMF-Based Bioderived Polyurethanes



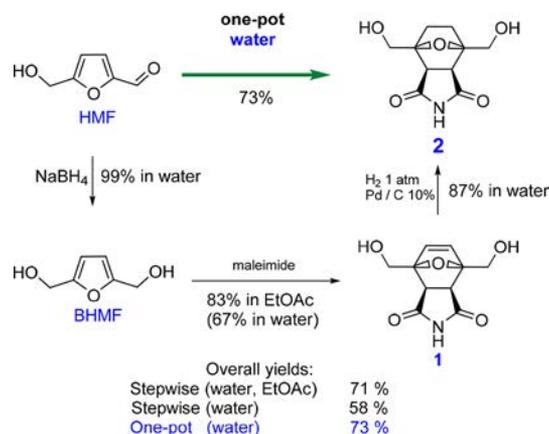
A similar synthetic approach was used for preparation of *O*-functionalized furan-containing compounds **6–9** by one-pot or stage-by-stage Diels–Alder reactions of alkylated or acylated BHMF derivatives **6–9** followed by hydrogenation over Pd/C (Scheme 19).^{113,189}

BHMF was used for preparation of a series of *meso*-oxabenzonorbornadienes OBNDs by the Diels–Alder reaction of BHMF and benzyne followed by functionalization of hydroxyl groups. OBNDs were involved into Rh-catalyzed enantioselective isomerization to 1,2-naphthalene oxides NPOs (Scheme 20), which were obtained with moderate to high yields and *ee* up to 99%.¹⁹⁰

5. TRANSFORMATIONS OF 2,5-DIFORMYLFURAN (DFF)

5.1. Catalytic Reactions of DFF. DFF was thoroughly hydrogenated to the saturated form BHMTFH with 100% conversion and selectivity by a hydroxyapatite-supported Pd catalyst (Pd-HAP) under relatively mild conditions: 40 °C, 1 MPa, and 3 h (Scheme 21).¹⁹¹ Furfurylamines obtained by amination of DFF has diverse applications including the synthesis of furan-containing polymers and design of pharmacologically active compounds. 2,5-Bis(aminomethyl)furan (BAMF) was prepared from DFF with a 70% yield by transaminase-catalyzed amination using α -methylbenzylamines (MBA) as amine donors.¹¹⁴ An efficient and simple system for the conversion of furfurals to maleic acid MA with H₂O₂ as oxidant and formic acid as solvent was reported.¹⁷² 2,5-Dicyanofuran (DCF) could be obtained from DFF via a two-step procedure. DFF was converted to 2,5-diformylfuran dioxime (DFFD) with the subsequent dehydration reaction.¹⁹²

A biocatalytic system based on horse liver alcohol dehydrogenase (HLADH), oxidized nicotinamide adenine dinucleotide (phosphate) cofactors NAD(P)⁺, hemoglobin

Scheme 18. Synthesis of Bis(hydroxymethyl)norcantharimide **2** from HMF or BHMF in Water

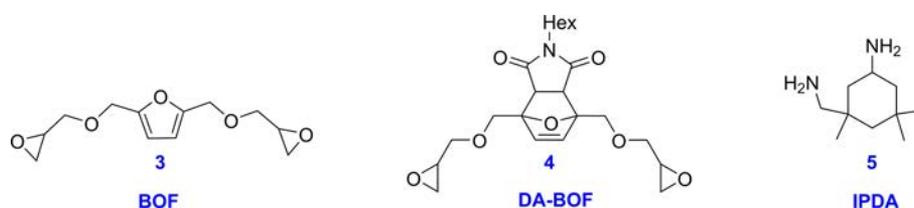
(Hb), and H₂O₂ showed moderate conversion of DFF to FDCA (52% yield was observed after 72 h, Table 11).⁸⁵ Whole-cell biocatalytic selective oxidation of DFF using a newly isolated bacterial strain *Comamonas testosteroni* SC1588 afforded FDCA as the major product, along with the production of minor HMF (61% FDCA was obtained after 48 h).⁸⁶ Oxidation of DFF by a periplasmic aldehyde oxidase (PaoABC) hydrogel combined with immobilized catalase showed 100% selectivity of the FDCA formation over 14 cycles.⁷⁶ An environment-friendly aerobic oxidation of DFF into FDCA using Fe–Zr–O catalyst in an ionic liquid 1-butyl-3-methylimidazolium chloride [BMIM]Cl reaction medium was reported. Aldehyde groups in DFF were quickly converted into the carboxyl groups to give 44.8% yield of FDCA at almost complete conversion attained for 2 h.¹⁹³

5.2. Other Reactions with DFF. A new family of gemini surfactants **10–13** containing the tetrahydrofuran ring and two amphoteric groups (carboxylic acid and tertiary amine) were prepared by selective reduction of *N*-alkyl BAMF derivatives followed by alkylation and debenzoylation processes (Scheme 22). The final compounds demonstrated very low critical micelle concentrations and had a potential as fungicides in crop protection applications.¹⁹⁴

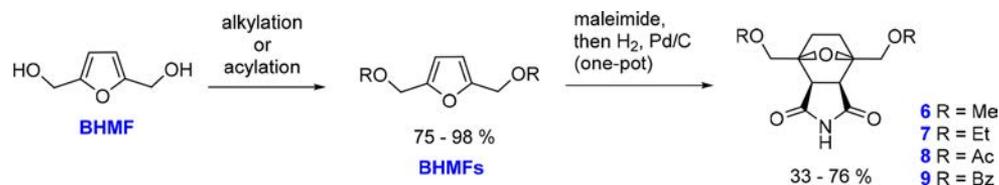
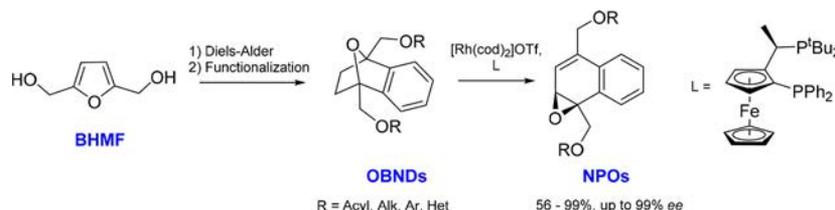
A series of biologically active bis-sulfonamide Schiff bases were synthesized by condensation of DFF with pharmacophoric sulfonamides. The obtained bis-sulfonamide imines showed high activity as inhibitors of four physiologically relevant carbonic anhydrases (CA) isoforms, the cytosolic CA I, CA II and CA VII, as well as the transmembrane tumor-overexpressed CA IX isozyme.¹⁹⁵

In other investigations, BAMF derivatives were used for preparation of new derivatives of naturally occurring bioactive norcantharidinimide by the Diels–Alder reaction of BAMFs

Scheme 17. Examples of BHMF Epoxy Derivatives, Source Material for Epoxy Resins



Scheme 19. Transformation of BHMf to Tricyclic Nonplanar Derivatives

Scheme 20. Synthesis of *meso*-Oxabenzonorbornadienes by DA Reaction from BHMf

Scheme 21. Derivatization of DFF

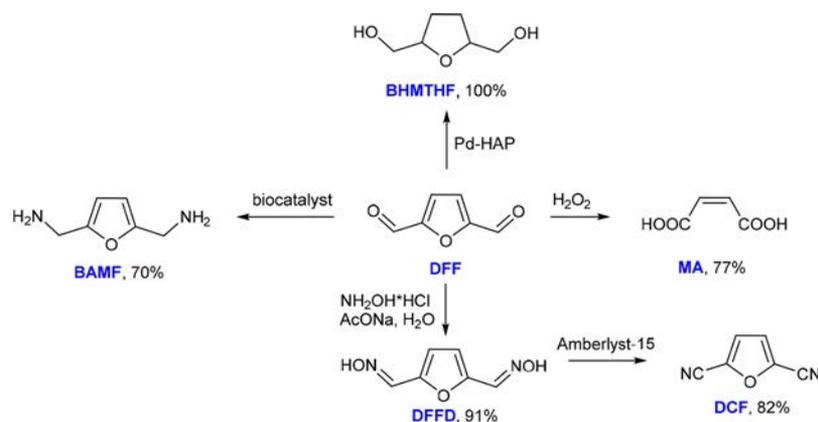


Table 11. Methods of Oxidation of DFF

Entry	Catalyst	Yield (%)	ref.
1	HLADH, NAD(P) ⁺ , Hb, H ₂ O ₂	52	85
2	<i>Comamonas testosteroni</i> SC1588	61	86
3	PaoABC/Catalase	100	76
4	Fe _{0.6} Zr _{0.4} O ₂ , [BMIM]Cl, O ₂	45	193

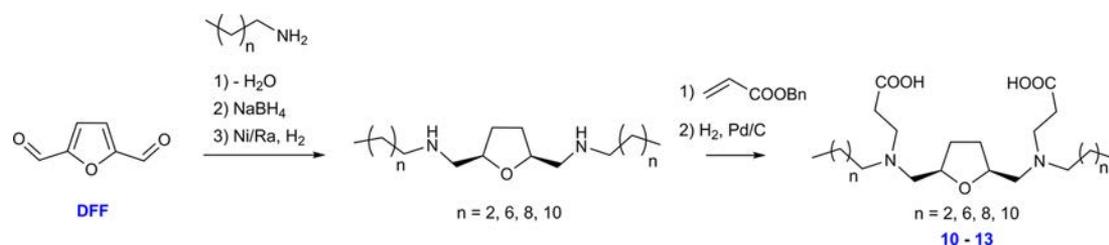
14–17 with maleimide followed by hydrogenation (Scheme 23). Such saturated tricyclic products were obtained predominantly as *endo* diastereomers. It was shown that derivatives containing aminomethyl groups in the side-chains of the

tricyclic core possess increased biological activity compared to unsubstituted analogue (norcantharimide).^{113,189}

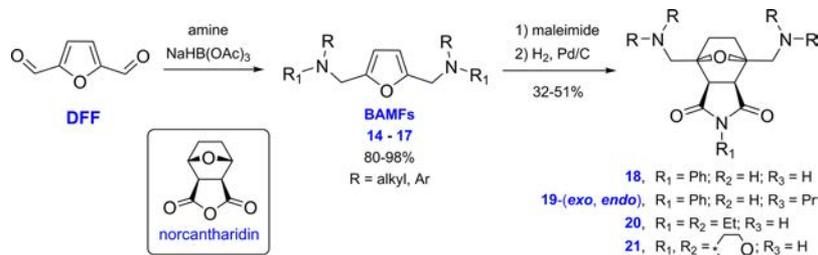
A similar approach was used for synthesis of a series of new aromatic compounds 24–26 using a three-stage methodology starting from DFF (Scheme 24). The Diels–Alder reaction with DFF is unknown, but imines 23 and 24 obtained by the reaction of DFF with oximes were involved in the Diels–Alder reaction with acetylenic ester or maleic anhydride followed by acid-catalyzed dehydration to give targeted aromatic compounds.¹⁹⁶

New furan-containing polyheterocycles from DFF were also investigated (Scheme 25). Oxazole 27 was obtained by the reaction of DFF with tosylmethyl isocyanide with a 47% yield.¹⁹⁷ Dihydropyranoaurone derivative 28 was prepared with a 83% yield using the piperazine-catalyzed aldol reaction of DFF with the appropriate benzofuranone. Evaluation of

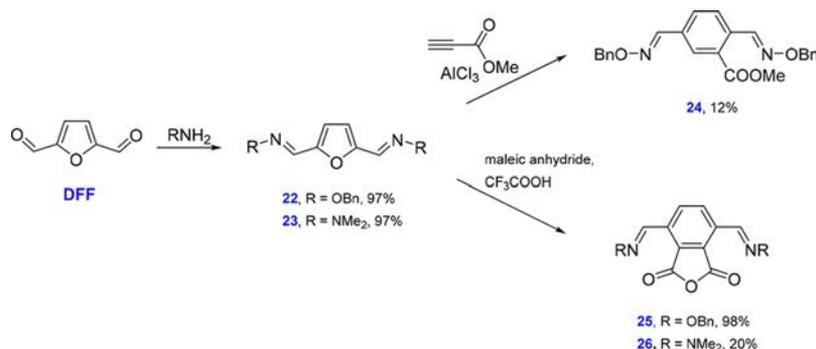
Scheme 22. Synthesis of New Class of Surfactants through the Reductive Amination of DFF



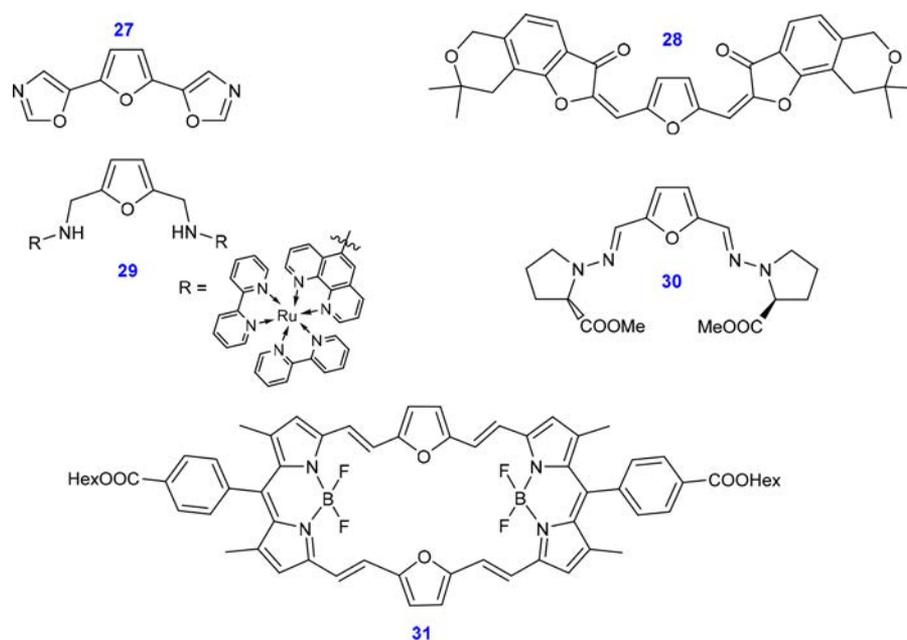
Scheme 23. Synthesis of Bioactive Norcantharidimide Derivatives from DFF



Scheme 24. Synthesis of Six-Membered Aromatic Compounds via DA Reaction of DFF Imines and Oximes



Scheme 25. Structures of New Furan-Containing Polyheterocycles Derived from DFF

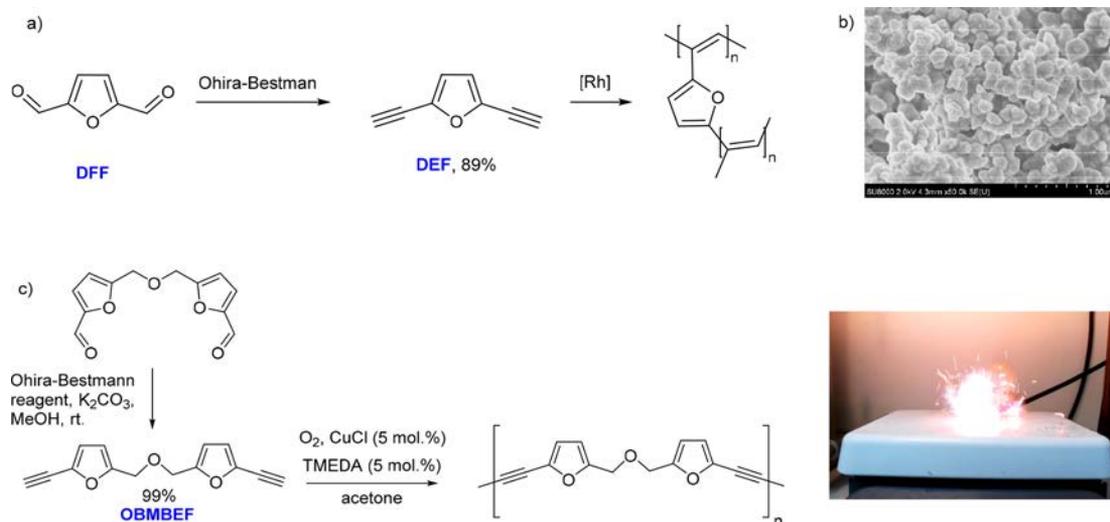


derivative **28** for anti-inflammatory activity showed significant suppression of inducible nitric oxide synthase expression.¹⁹⁸

A furan-containing functionalized polypyridine ligand used for the preparation of a fluorescent anion sensor based on a Ru(II) complex was synthesized by the two-step reductive amination of DFF with 5-amino-1,10-phenanthroline. Unfortunately, the fluorescence intensity of complex **29** has been enhanced only slightly by SCN⁻, F⁻, and H₂SO₃²⁻ anions.¹⁹⁹ Synthetic sample of biologically occurred hydrazinyl Schiff base **30** was prepared by reaction of DFF with *N*-amino-*L*-proline methyl ester in MeOH with 50% yield. Prolineimine **30** was found as a metabolite in Australian marine-derived fungi and represents a rare example of natural compound containing a

hydrazine moiety.²⁰⁰ DFF was used in the synthesis of boron dipyrromethene-based antiaromatic macrocycle **31** via a one-pot Knoevenagel condensation.²⁰¹

5.3. Monomers from DFF. An unstable compound 2,5-diethynylfuran (DEF) was first synthesized with a 89% yield starting from DFF by using the Ohira-Bestman reaction (Scheme 26a).¹³⁹ Rh-catalyzed polymerization of DEF afforded cross-linked polyacetylene. Using scanning electron microscopy (SEM), it was found that the formed polymer had a globular macrostructure (Scheme 26b). Using the same methodology, ether-linked OBMBEF (5,5'-(oxybis(methylene))bis(2-ethynylfuran)) was synthesized in high yield (99%) starting from the corresponding HMF dimer

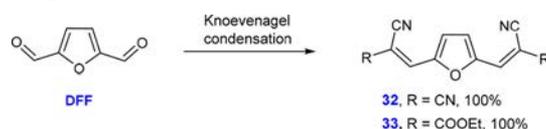
Scheme 26. Alkynylation of Carbonyl Derivatives and Polymerization of the Obtained Alkynes^a

^aReprinted with permission from ref. 139. Copyright 2017 Wiley-VCH Verlag GmbH & Co.

(Scheme 26c). The Glaser coupling of the OBMBEF diyne resulted in the formation of polyacetylenic solids, which underwent explosive decomposition under heating (Scheme 26c). The pathway provided an access to biomass-based high energy materials.

Compounds **32** and **33** with significant potential applications as monomers for new polymeric materials were obtained by the coupling of DFF with methylene-active compounds under mild reaction conditions using the Knoevenagel condensation with malononitrile or ethyl cyanoacetate (Scheme 27).⁶⁸

Scheme 27. Examples of Knoevenagel Condensation Involving DFF



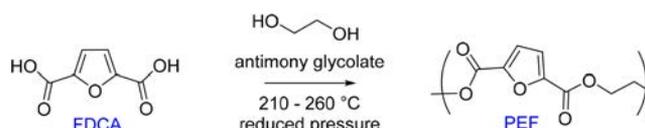
Perspective furan-containing monomers **37–39** were prepared starting from DFF. The Knoevenagel condensation of DFF with malonic acid followed by esterification and hydrogenation of the formed α,β -unsaturated diacid **34** afforded diesters **37–38** with good yields (Scheme 28).¹¹²

6. FURAN-2,5-DICARBOXYLIC ACID (FDCA) AND ITS ESTERS

6.1. Esterification and Polycondensation Reactions of FDCA. Being an important base monomer, 2,5-furandicarboxylic acid (FDCA) was identified as one of 12 priority chemicals.²⁰²

Predominately, FDCA received considerable interest as a potentially renewable replacement for petro-based terephthalic acid in polymer applications. Synthesis of the most common furan-based polyester, polyethylene 2,5-furandicarboxylate (PEF), can be carried out directly from FDCA and ethylene glycol utilizing a standard melt polycondensation procedure with antimony glycolate as catalyst (Scheme 29).²⁰³

Scheme 29. Synthesis of 2,5-Furandicarboxylate (PEF) from 2,5-Furandicarboxylic acid (FDCA)

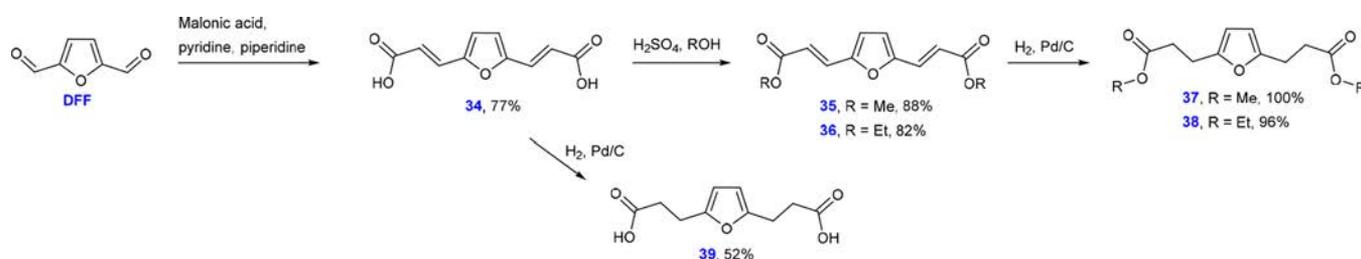


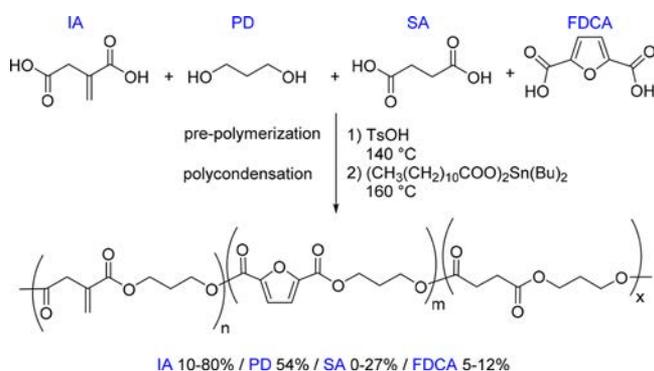
Synthesis of fully bioderived polyesters based on itaconic acid (IA), FDCA, succinic acid (SA), and 1,3-propanediol (PD) via melt polycondensation was described (Scheme 30).²⁰⁴ Such a structure is capable of forming cross-linked networks and cured biopolymers thermally stable up to 330 °C; its T_g is 73.5–141.7 °C.

A highly efficient approach to furan polyesters starting from FDCA was implemented under one-pot conditions (Scheme 31).^{205,206}

The given strategy includes catalytic esterification of FDCA in the presence of alcohol with a homogeneous water-tolerant

Scheme 28. Synthesis of Perspective Furanic Monomers



Scheme 30. Synthesis of Bioderived Unsaturated Polyesters Based on FDCA

Lewis acid catalyst followed by transesterification of an intermediate ester product with glycol catalyzed by the existing catalyst retained in the intermediate ester mixture.

It should be noted that the usage of FDCA in polycondensations is limited. Several issues arise upon using FDCA in melt polymerizations, such as decomposition at the temperatures higher than 200 °C. Such challenges can be resolved by esterifying FDCA.

A practical method of FDCA transformation into esters proceeds through the acid-catalyzed interaction with alcohol (entry 1, Table 12). Over the past year, a number of methods for obtaining alkyl esters of FDCA have been patented. Thus, low-pressure high-temperature esterification processes have been described (entries 2 and 3, Table 12). In those cases, impurities up to 5% of monomethyl ester were observed.

There is an alternative way for esters synthesis, as bis(oxiran-2-yl-methyl)furan-2,5-dicarboxylate was obtained through a one-step reaction of FDCA with epichlorohydrin. Transesterification of FDME with glycidol leads to the same useful synthon.²⁰⁷

Furanic polyesters demonstrate a considerable number of useful properties. Based on the reaction of FDME with diols, a number of homopolymers were synthesized (Scheme 32).

Polyethylene furanoate (PEF) was obtained by conventional melt polycondensation under high vacuum and was successfully utilized as a source material for 3D-printing.²⁰⁸ Poly(trimethylene furandicarboxylate) (PTF) was easily produced from FDME and 1,3-propanediol and was used in fabrication of a gas separation membrane.²¹¹

Because polyfuran dicarboxylates exhibit substantial barrier properties, the development of new gas-impermeable materials is underway. Fully biobased polymer compositions were obtained by the synthesis of poly(butylene 2,5-furan dicarboxylate) (PBF) from FDME and the preparation of a set of blends of polylactic acid (PLA) with PBF (5–30 wt %).²¹² Upon addition of 5 wt % PBF, the elongation at break of the material increases 18.5 times. The gas barrier property of the PLA/PBF blends is also significantly enhanced. In addition, the binary PLA/PBF blends demonstrate stable high reflection properties.

Scheme 31. One-Pot Two-Step Synthesis of PEF from FDCA**Table 12. Conversion of FDCA to 2,5-Amidefuran Dicarboxylic Acid Dimethyl Ester (FDME)**

Entry	reactants/catalysts	conditions	Yield (%)	ref.
1	MeOH, TsOH (cat)	4 h, reflux	83	208
2	HC(OMe) ₃	1 h, 200 °C, pressure vessel	99	209
3	MeOH	0.5 h, 230 °C, pressure vessel	94	210

Thus, objects with shining surface can be prepared easily from the fully biobased polymer. Applicability of additive technologies was also demonstrated.²¹³

A furanic-very-long-aliphatic polyester based on 2,5-furandicarboxylic acid and 1,20-eicosanediol was introduced as a new polymer from renewable resources.²¹⁴ As shown by preliminary experiments, the polymer PE20F is a biodegradable material.

A novel strategy to synthesize FDCA-based polyesters from an asymmetric monomer with terminal methyl ester and hydroxyl groups was proposed (Scheme 33).²¹⁵ This approach allows carrying out faster polycondensation at lower temperature in comparison with conventional methods (180 °C vs 240 °C). A series of polymers with long alkyl chains was obtained.

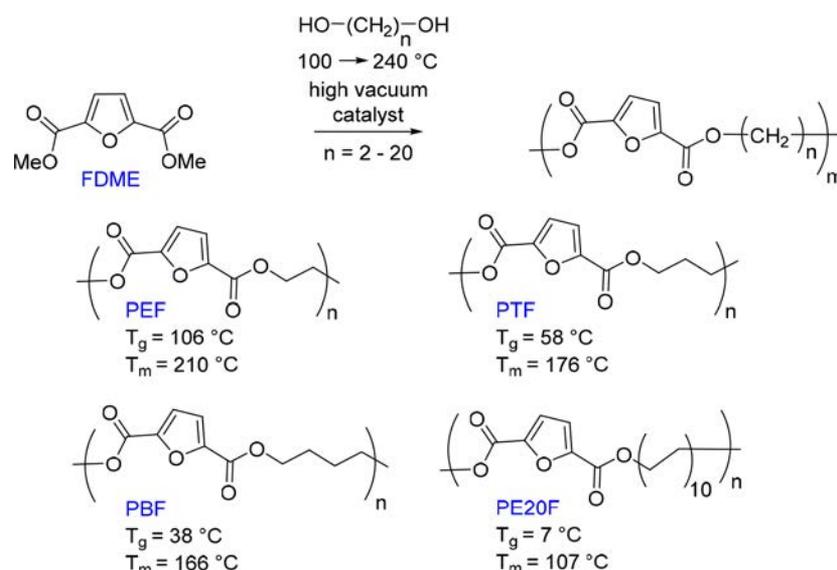
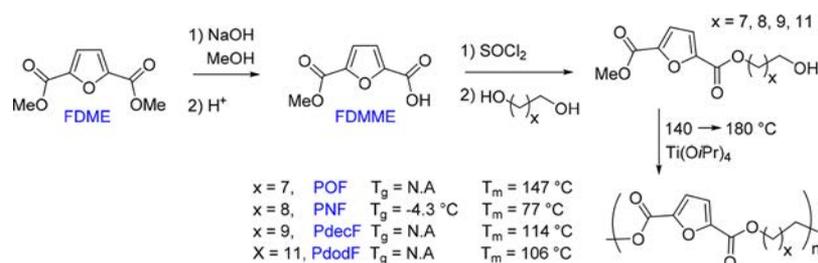
An interesting renewable furan-based cycloaliphatic homopolymer, poly(1,4-cyclohexylene 2,5-furandicarboxylate) (PCdF), was synthesized (Scheme 34).²¹⁶ PCdF exhibits an extremely high glass transition temperature and shows high thermal stability as compared to the methylene spacer-containing PCF.

Two novel polymers, CHD/FDME and BCD/FDME, were synthesized from diols containing rigid cyclic ketal functionalities derived from glycerol and two diketones.²¹⁷ Biomass-derived content in CHD/FDME and BCD/FDME 100% and 50%, respectively. A TGA analysis indicated that both polyesters were thermally stable (decomposition temperature > 300 °C).

Incorporation of a furandicarboxylate moiety into the structure imparts useful properties to the polymer material. Such copolymers exhibit characteristics comparable with those of petroleum-based polymers.

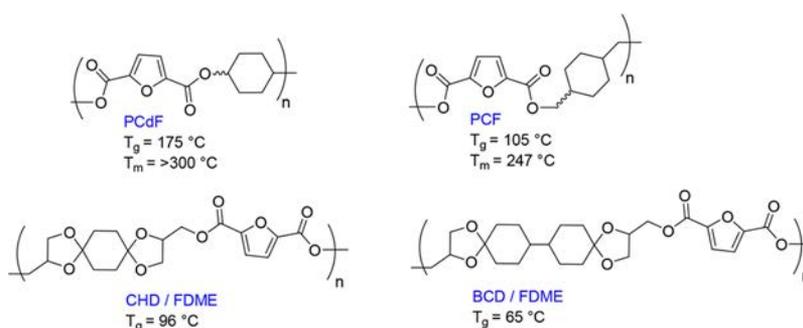
Thus, an addition of 2.25 to 7.5 mol % of the dicarbonylfuran moiety to polyethylene terephthalate (PET) as anticrystallization comonomer enhanced mechanical properties of the resulting polymer.²¹⁸ The usage of bio-PET allows achieving a fully biobased material. A series of poly(ethylene furanoate-co-terephthalate) (PEFT) copolymers with 5–95% of the dicarbonylfuran moiety was synthesized and characterized (Scheme 35).²¹⁹ The structure of polyethylene furanoate (PEF) was modified via copolymerization of FDME with ethylene glycol and 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO). A series of poly(ethylene-co-2,2,4,4-tetramethyl-1,3-cyclobutanediol 2,5-furandicarboxylate)s (PETF) copolyesters

Scheme 32. Synthesis of Homologous Poly-methylenefurandicarboxylates via Conventional Polyesterification Reactions

Scheme 33. Usage of Asymmetric Ester in Synthesis of Poly(alkyl-2,5-furandicarboxylates)^a

^aBecause of fast crystallization behaviors of POF, PdecF and PdodF, no obvious glass transition can be observed in DSC scans.

Scheme 34. FDCA-Based Homopolymers with Cyclohexane Moiety



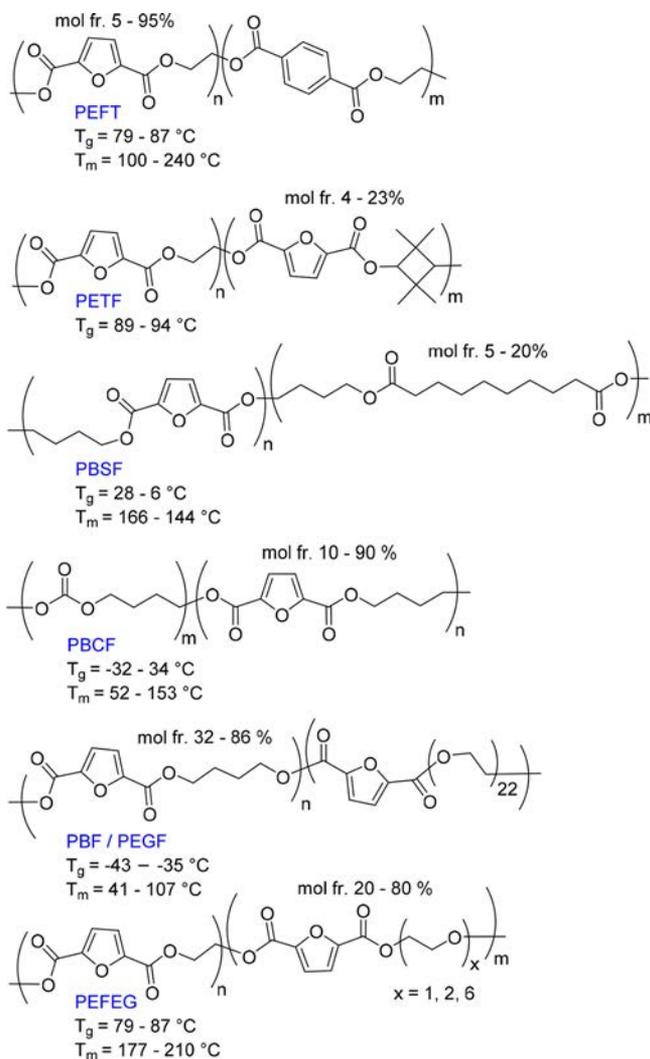
was prepared.²²⁰ Fully biobased poly(butylene sebacate-*co*-butylene furandicarboxylate) (PBSF) copolyesters were synthesized using a two-step melt polycondensation method from FDCA, sebacic acid, and 1,4-butanediol.²²¹ Those copolymers exhibited high thermal stability and excellent elongation at break. Using a similar approach poly(ethylene dodecanedioate-2,5-furandicarboxylate) (PEDF) could be obtained from FDCA, dodecanedioic acid, and ethylene glycol.²²² A series of random copolymers poly(butylene carbonates-*co*-furandicarboxylate) (PBCFs) had been prepared from dimethyl carbonate, 1,4-butanediol, and FDME.²²³ Copolymers based on poly(1,4-butylene 2,5-furandicarboxylate) and poly(ethylene glycol) (PBF/PEGF) with soft and hard segments in the

structure demonstrated lower melting temperature and higher thermal stability (up to 352–380 °C), compared to PBF.²²⁴

A series of multiblock poly(ethylene 2,5-furandicarboxylate)-poly(ethylene glycol) (PEFEGs) copolymers was synthesized from the available biobased ethylene glycol, FDCA, and poly(ethylene glycol) through a two-step melt polycondensation method.²²⁵ In comparison with PEF, the elongation at break of the synthesized PEFEGs was much higher; moreover, the multiblock copolymers exhibited excellent shape memory properties.

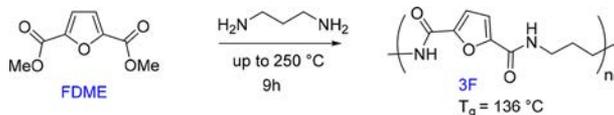
By using a similar synthetic strategy, polyamides can be obtained from FDME and diamines via solid-state polymerization in the temperature range of 60 to 250 °C (Scheme 36).²²⁶ Also polyamides could be synthesized directly from the

Scheme 35. FDCA-Based Copolymers



acid. Thus, a series of FDCA-based copolyamides were obtained utilizing isophthalic acid and 1,6-hexamethylenediamine.²²⁷

Scheme 36. Polyamide Produced from FDME



The synthesis of two series of novel partially biobased polyimides was reported recently, which include 2,5-furandicarboxamide moiety (Scheme 37).²²⁸ PIs possess high glass transition temperatures, high thermal stability with 5% weight loss over 420 °C, and outstanding mechanical properties.

Copolymerization FDCA-derived polymers could also be modified to produce novel composite materials. Thus, biobased PEF was modified by different clays (sepiolite and montmorillonite), and the introduced nanoclays showed a positive molecular weight stabilizing effect.²²⁹

6.2. FDME-Based Epoxy Resins. A biobased heat resistant epoxy resin with high biomass content was produced from FDCA and eugenol (Scheme 38).²³⁰

Methyl hexahydrophthalic anhydride (MHHPA) was used as a curing agent; the glass transition temperature of the resulted resin was as high as 153.4 °C.

6.3. FDCA-Based Metal–Organic Frameworks (MOFs). Metal–organic frameworks (MOFs) typically composed of metal species and organic ligands to generate porous and crystalline polymers have shown potential in a variety of research fields. In 2017, a number of papers describing the production of FDCA-based MOFs with useful optical properties were published.

A range of porous acid–base bifunctional metal–FDCA hybrids (Cr-FDCA, Cu-FDCA, Al-FDCA, Fe-FDCA, Zr-FDCA) was successfully prepared from simple assembly under hydrothermal conditions (Figure 4).¹⁰⁴ In particular, Zr-FDCA-T MOF possessed a microspheric structure, with an average pore diameter of ~4.7 nm, and high thermostability (ca. 400 °C).

A new Zr-based metal–organic framework Zr-CAU-28 [$\text{Zr}_6\text{O}_4(\text{OH})_4(2,5\text{-furandicarboxylate})_4(\text{OH})_4(\text{H}_2\text{O})_4$] was obtained under green synthesis conditions from a mixture of water and acetic acid employing microwave-assisted heating (Figure 5).²³¹ The framework structure adopts a kagome-like topology and hence contains large hexagonal channels with a pore diameter of ~16 Å and small trigonal channels with a size of 3 Å. The synthesized Zr-CAU-28 showed thermal stability up to 270 °C in air.

A FDCA-containing MOF, $(\text{H}_3\text{O})_2[\text{Zn}_4(\text{urotropine})-(\text{H-FDCA})_2(\text{FDCA}^{2-})_4]$, showed high selectivity for Rb^+ and Cs^+ cations and changed its luminescent properties upon the formation of inclusion compounds (Figure 6).²³²

Four novel compounds $[\text{In}(\text{FDCA}^{2-})(\text{FDCA}^-)(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ (In1, Figure 7) and $[\text{Ln}_2(\text{FDCA}^{2-})_2(\text{H}_2\text{O})_{10}] \cdot \text{FDCA}^{2-} \cdot 6\text{H}_2\text{O}$ ($\text{Ln} = \text{Dy}, \text{Eu}, \text{Gd}$) were synthesized hydrothermally by using FDCA as ligand.²³³ These novel materials possessed luminescence sensing and white light emission properties due to the ability of uncoordinated carbonyl groups to encapsulate Dy^{3+} and Eu^{3+} ions into MOF compound.

Two isostructural lanthanide MOFs, $[\text{Ln}_3\text{K}_2(\text{FDCA}^{2-})_4(\text{NO}_3)_3(\text{MeCN})_2]_n$ ($\text{Ln} = \text{Eu}, \text{Tb}$), based on FDCA were successfully synthesized under solvothermal conditions. These MOFs showed strong photoluminescence and excellent fluorescence sensing for small molecules, especially for nitrobenzene (Figure 8).²³⁴

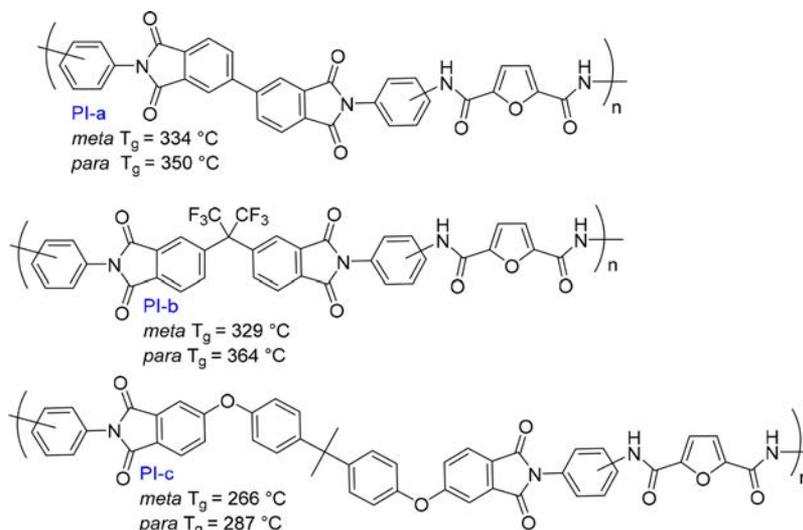
6.4. Other Transformations of FDCA and FDME. The furan core in FDCA can be reduced by molecular hydrogen under pressure utilizing 5% Pd/C to form tetrahydrofuran-2,5-dicarboxylic acid (THFDCA) in quantitative yield.²³⁵ The subsequent ring-opening reaction provides an access to adipic acid (Scheme 39).

The described transformation can be achieved in one step starting directly from FDCA, thus expanding the range of bioderived useful synthons.

A new methodology was developed employing FDCA to produce 2,5-diarylfurans in high yields through palladium-catalyzed double decarboxylative cross-couplings (Scheme 40).²³⁶

Diels–Alder strategy was utilized for access to 1,4-naphthalenedicarboxylate derivatives from FDME via benzene cycloaddition (Scheme 41).²³⁷ Efficient diversification ($\geq 80\%$ yield) into several novel bicyclic compounds was performed.

Scheme 37. Polyimides Produced Using FDME



Scheme 38. Synthesis of Source Material for Epoxy Resin Starting from FDCA and Eugenol

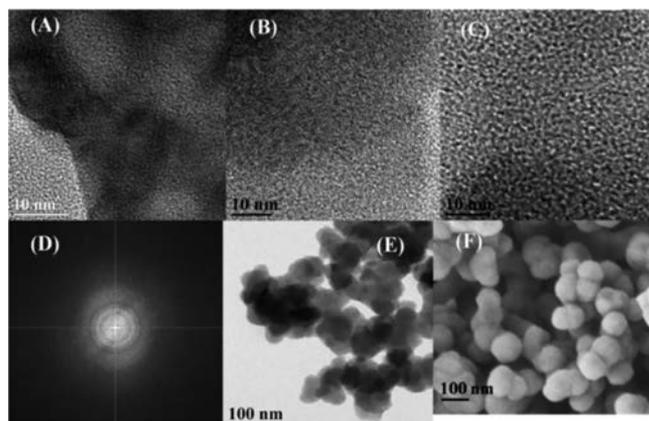
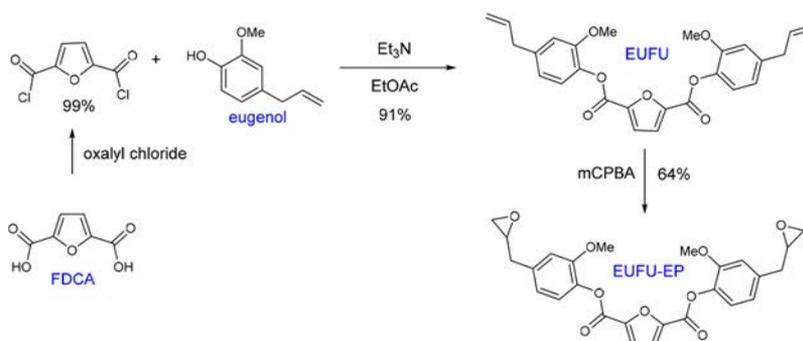


Figure 4. HR-TEM images of ZrO₂ (A), Zr-FDCA (B), and Zr-FDCA-T (C); TEM diffraction pattern of Zr-FDCA-T (D), TEM image of Zr-FDCA-T (E), SEM image of Zr-FDCA-T (F), (T = treated with template). Reprinted with permission from ref. 104. Copyright 2017 Wiley-VCH Verlag GmbH & Co.

7. CONCLUSIONS AND PERSPECTIVES

The analysis of the experimental studies included in the present review expectedly showed that HMF is the most popular starting material in chemical transformations and applications described (Figure 9a). A significant number of studies utilizing

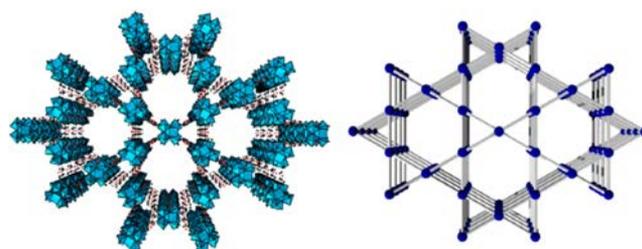


Figure 5. Framework structure of Zr-CAU-28 as seen along the *c*-axis (left) and the underlying kag topology of the simplified framework (right). Reprinted with permission from ref. 231. Copyright 2017 American Chemical Society.

FDCA should also be mentioned, whereas the usage of DFF and BHMF is rarer (Figure 9a).

The reduction of bioderived furanic chemicals is the most massively studied chemical transformation (Figure 9b), because the removal of the extra oxygen is required to access high-performance fuels. The transformation of HMF to FDCA and the building of longer polymeric chains target on material science applications and provide the driving force for oxidation and polymerization studies (Figure 9b).

For synthetic purposes, a number of different functionalization processes were studied, including aldol reaction, nucleophilic additions, OH group modifications, reductive amination, ring transformations, C–H activation, preparation of MOFs and others (Figure 9b).

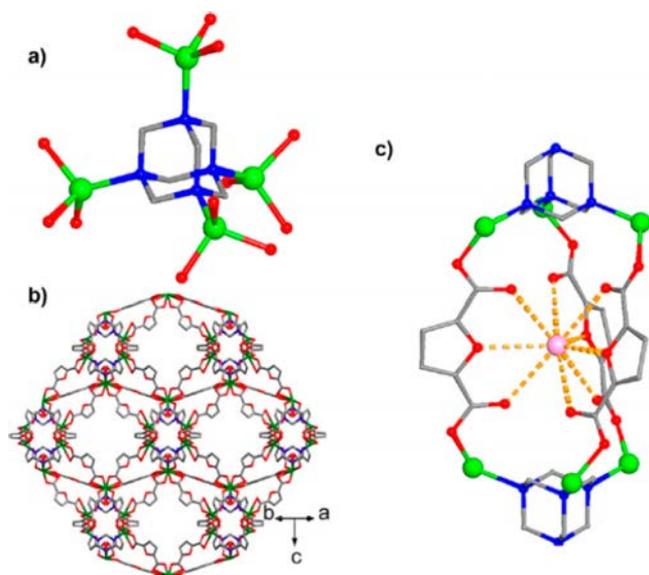


Figure 6. Views of the structure of $(\text{H}_3\text{O})_2[\text{Zn}_4(\text{urotropine})-(\text{H-FDCA})_2(\text{FDCA}^{2-})_4]$: (a) tetrahedral secondary building unit (Zn atoms are green, N - blue, O - red, C - gray, and H is omitted for clarity); (b) framework structure; (c) anionic cavity with hydroxonium counteraction shown in pink with electrostatic contacts shown as orange lines. Reprinted with permission from ref. 232. Copyright 2017 Wiley-VCH Verlag GmbH & Co.

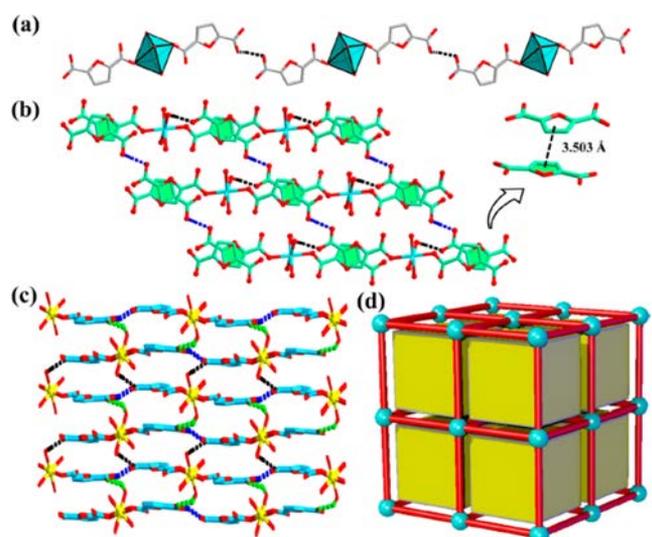


Figure 7. Compound In1 showing (a) 1D chain through O–H...O interactions; (b) 2D layers through O–H...O interactions; (c) 3D supramolecular framework of In1; and (d) topological representation of 3D structure. Reprinted with permission from ref. 233. Copyright 2017 ACS Publications.

A noticeable increase in the number of publications over the years can be clearly seen in the case of HMF, as well as BHMF, DFF and FDCA (Figure 10b). For FDCA, the most rapid trend should be mentioned: the number of publications increased 6-fold from 2011 to 2017, whereas a 2-fold increase for HMF was observed over the same time period (Figure 10a). The other two derivatives, DFF and BHMF, are also synthons of interest, and the data on them are increasing steadily.

Redox reactions are in the central focus in the chemistry of HMF and the corresponding derivatives (>50% of overall amount of studies; Figure 10b). The global aim is to develop

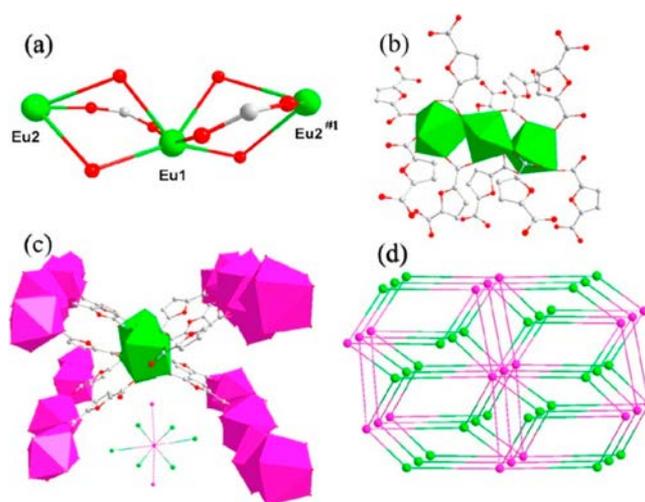
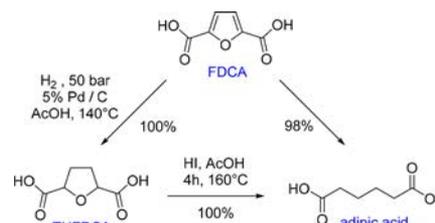
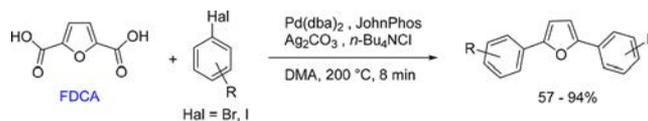


Figure 8. (a) Trinuclear Eu_3 secondary building units; (b) trinuclear surrounded by ten FDA^{2-} ligands; (c) 8-connected node; (d) schematic view of the topology excluding K^+ ions. Reprinted with permission from ref. 234. Copyright 2017 Elsevier.

Scheme 39. Reduction of FDCA



Scheme 40. Aryl Cross-Coupling Reaction with FDCA



reliable industrial technologies to access fuels (reduction reactions) and dicarboxylic acid monomers (oxidation reactions). Several excellent catalytic systems have been developed to accomplish the goal. However, further optimizations are required in order to reach cost-efficiency and sustainability levels required for commercialization.

In spite of the defined practical targets, several studies employ experimental conditions with significant waste outcome (i.e., 2 equiv of MnO_2 for oxidation, etc.) or low catalytic efficiency (poorly recyclable catalysts, large amount of noble metals, etc.). Such studies may contribute to the fundamental development of the area; however, their large-scale practical application is hardly possible. Despite considerable progress and a bunch of synthetic procedures available, the field still demands the development of cost-efficient recyclable catalysts stable against leaching and utilizing convenient and cheap oxidants (O_2 , H_2O_2 , regenerable oxidants, etc.) and reductants (H_2 , regenerable reductants, etc.). An interesting direction would be to explore entrapped/supported molecular catalysts, which, for example, showed a good performance in the selective and clean alcohol oxidation.^{2,59}

A recent trend has shown that HMF is often used as a challenging substrate to test new catalysts developed for reduction or oxidation processes. Indeed, biomass processing

Scheme 41. Benzyne Diels–Alder Cycloaddition to FDME

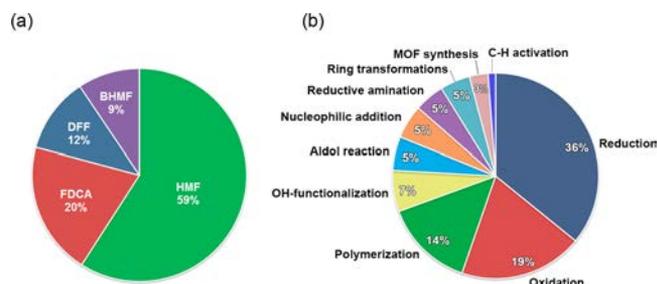
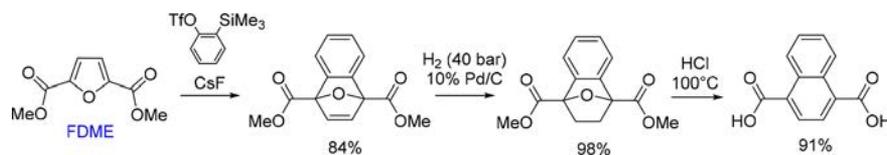


Figure 9. Distribution of publications covered in this review according to the type of the starting material (a) and type of the chemical transformation (b).²³⁸

provides a strong driving force and acts as a “grindstone” for sharpening new catalytic systems. The outcome can substantially influence the area of redox reactions in organic synthesis and stimulate the further progress.

Using HMF, BHMF, DFF, and FDCA as starting materials for synthetic applications is a highly promising and catchy direction. Various synthetic transformations have been already developed and many more are anticipated in the nearest future. Furan derivatives can be readily prepared for obtaining biologically active molecules, drugs, and useful organic synthones, among many others.

At the same time, apart from the significant progress in HMF chemistry, several challenges should be mentioned. The functionalization of positions 3 and 4 of the furan ring in HMF remains mostly undeveloped. Next, studies on methods of recyclization of HMF into other heterocycles should pave the way into a vast field of derivatives. The low stability of HMF and some of its derivatives in solution, as well as aging and oligomerization, introduce shortcomings in terms of lower yields and side-reactions.²⁴⁰ Mechanistic studies can involve

rather complicated networking and nanostructured systems in a liquid phase.²⁴¹

An amazing development has been achieved in the area of material science, where FDCA-based polymers (i.e., PEF and similar) are evaluated as a possible replacement for polyethylene terephthalate (PET) based on oil-derived terephthalic acid. Currently, PET occupies a huge market worldwide and is produced in amounts of 56 million tons per year.²⁴² The practical usage of PET includes plastic bottles, fibers, and several other products. A considerable interest to employing biobased PEF as a coadditive or replacement of PET is inevitable and stimulates cutting-edge studies. A combination of bioderived PEF and a waste-free 3D-printing technology expands the biomass approach to carbon-neutral production of plastic objects.²⁰⁸

Overall, the chemistry of biomass-derived furanic chemicals is an extremely rapidly developing field, which has passed its initial stage and now should actively contribute to both academic and industrial sectors.

AUTHOR INFORMATION

Corresponding Author

*V. P. Ananikov. E-mail: val@ioc.ac.ru.

ORCID

Valentine P. Ananikov: 0000-0002-6447-557X

Notes

The authors declare no competing financial interest.

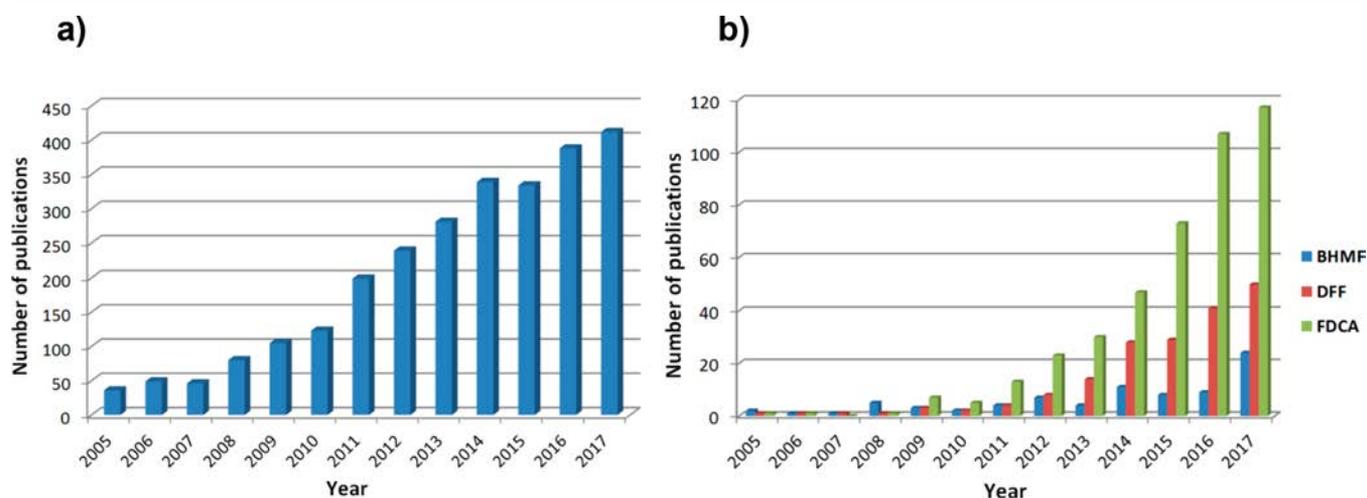


Figure 10. Number of publications mentioning HMF (a) and BHMF, DFF, or FDCA (b) per year, according to the databases and structural search.

Biographies



Fedor Kucherov received his doctoral degree from Zelinsky Institute of Organic Chemistry (Moscow) in 2004. In 2006 he joined the Chemical Diversity Institute, as senior researcher at medicinal chemistry lab. In 2015 he moved back to his *alma mater* to continue research work. His scientific interests include the organic chemistry, selective drug delivery, green chemistry and biomass conversion.



Leonid Romashov received his B.Sc. in Chemistry from the Higher Chemical College of Russian Academy of Sciences in 2012 and joined the Prof. Ananikov research group in Zelinsky Institute of Organic Chemistry as a graduate student where he investigated biomass conversion and the chemistry of biomass derived compounds, receiving his Ph.D. in 2017. His current studies are focused on chemical transformations of HMF and organic synthesis.



Konstantin Galkin is a research fellow of the Laboratory of Transition Metal and Nanoparticle Catalysis at the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences. His research areas

of interest include biomass conversion, ionic liquids chemistry and organocatalysis.



Valentine Ananikov received his M.Sc degree in 1996 (Biochemistry), Ph.D. degree in 1999 (Organic Chemistry and Catalysis), Habilitation in 2003, and in 2005 he was appointed professor and laboratory head of the Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences. In 2008 he was elected as a member of the Russian Academy of Sciences. In 2012 he became professor of the Chemistry Department of Moscow State University. He was a recipient of the Russian State Prize for Outstanding Achievements in Science and Technology (2004), an Award of the Science Support Foundation (2005), a Medal of the Russian Academy of Sciences (2000), Liebig Lecturer by German Chemical Society (2010), and Balandin Prize for outstanding achievements in the field of catalysis (2010), Organometallics Distinguished Author Award Lectureship by American Chemical Society (2016), Hitachi High-Technologies Award In Appreciation for Novel Approach and Outstanding Contribution to Setting New Standards for Electron Microscopy Applications in Chemistry (2016). His research interests are focused on mechanistic studies, catalysis, sustainable development and molecular complexity.

■ ACKNOWLEDGMENTS

This study was supported by the Russian Science Foundation (RSF Grant 17-13-01176).

■ ABBREVIATIONS

2,5-DMF	2,5-dimethylfuran
3F	poly(1,3-propdiyl furan-2,5-dicarboxylamide)
BAMF	bis(aminomethyl)furan
BHMF	2,5-bishydroxymethylfuran
BHMTHF	(tetrahydrofuran-2,5-diyl)dimethanol
BOF	2,5-bis[(2-oxiranylmethoxy)methyl]-furan
BTO	1,2,4-benzenetriol
DBTDL	dibutyltin dilaurate
DCF	2,5-dicyanofuran
DEF	2,5-diethynylfuran
DFE	furan-2,5-dicarbaldehyde
DFFD	2,5-diformylfuran dioxime
DIC	<i>N,N'</i> -diisopropylcarbodiimide
DMAP	<i>N,N</i> -dimethyl-4-aminopyridine
DMTHF	2,5-dimethyltetrahydrofuran
FDCA	furan-2,5-dicarboxylic acid
FDME	dimethyl furan-2,5-dicarboxylate
FDMME	5-(methoxycarbonyl)furan-2-carboxylic acid
FFCA	5-formylfuran-2-carboxylic acid
FFME	methyl 5-formylfuran-2-carboxylate
HCPN	3-hydroxymethylcyclopentanone

HDI	1,6-hexamethylene diisocyanate
HHCPEN	4-hydroxy-4-(hydroxymethyl)cyclopent-2-en-1-one
HHD	1-hydroxyhexane-2,5-dione
HMEF	(5-ethynylfuran-2-yl)methanol
HMF	5-(hydroxymethyl)furan-2-carbaldehyde
HMFCFA	5-(hydroxymethyl)furan-2-carboxylic acid
HMFME	methyl 5-(hydroxymethyl)furan-2-carboxylate
HMVF	2-hydroxymethyl-5-vinylfuran
HO-PBS-OH	poly(butylene succinate)
HO-PFS-OH	poly(2,5-furandimethylene succinate)
IA	itaconic acid
IMBIP	isomannide bis(3-isocyanatopropanoate)
IPDA	isophorone diamine
ISBIP	isosorbide bis(3-isocyanatopropanoate)
LA	levulinic acid
MA	maleic acid
MCP	2-hydroxy-3-methyl-2-cyclopenten-1-one
MF	5-methylfuran-2-carbaldehyde
MFME	(5-methylfuran-2-yl)methanol
NPOs	1,2-naphthalene oxides
OBMBEF	(5,5'-(oxybis(methylene))bis(2-ethynylfuran)
OBNDs	meso-oxabenzonorbornadienes
PBCF	poly(butylene carbonate-co-furandicarboxylate)
PBF	poly(butylene 2,5-furan dicarboxylate)
PBSF	poly(butylene sebacate-co-butylene furandicarboxylate)
PCdF	poly(1,4-cyclohexylene 2,5-furandicarboxylate)
PCF	poly(cyclohexane-1,4-diylbis(methylene) 2,5-furandicarboxylate)
PD	1,3-propanediol
PdecF	poly(1,10-decadiyl 2,5-furandicarboxylate)
PdodF	poly(1,12-dodecadiyl 2,5-furandicarboxylate)
PE20F	poly(1,20-eicosandiyl 2,5-furandicarboxylate)
PEDF	poly(ethylene dodecanedioate-2,5-furandicarboxylate)
PEF	poly(ethylene 2,5-furandicarboxylate)
PEFEG	multiblock poly(ethylene 2,5-furandicarboxylate)-poly(ethylene glycol) copolymers
PEFT	poly(ethylene furanoate-co-terephthalate)
PETF	poly(ethylene-co-2,2,4,4-tetramethyl-1,3-cyclobutanediol 2,5-furandicarboxylate)
PFS	poly(2,5-furandimethylene succinate)
PFS-PBS	poly(2,5-furandimethylene succinate)-b-poly(butylene succinate)
PHMVF	poly(2-hydroxymethyl-5-vinylfuran)
PLA	polylactic acid
PNF	poly(1,9-nondiyl 2,5-furandicarboxylate)
POF	poly(1,8-octadiyl 2,5-furandicarboxylate)
PTF	poly(trimethylene furandicarboxylate)
SA	succinic acid
THFDCA	tetrahydrofuran-2,5-dicarboxylic acid

REFERENCES

- (1) Tollefson, J. Reality check for fossil-fuel divestment. *Nature* **2015**, *521* (7550), 16–7.
- (2) Fabian, N. Economics: support low-carbon investment. *Nature* **2015**, *519* (7541), 27–29.
- (3) Gentner, D. R.; Jathar, S. H.; Gordon, T. D.; Bahreini, R.; Day, D. A.; El Haddad, I.; Hayes, P. L.; Pieber, S. M.; Platt, S. M.; de Gouw, J.; Goldstein, A. H.; Harley, R. A.; Jimenez, J. L.; Prévôt, A. S. H.; Robinson, A. L. Review of Urban Secondary Organic Aerosol Formation from Gasoline and Diesel Motor Vehicle Emissions. *Environ. Sci. Technol.* **2017**, *51* (3), 1074–1093.
- (4) Tollefson, J. Can the world kick its fossil-fuel addiction fast enough? *Nature* **2018**, *556* (7702), 422–425.
- (5) Gies, E., The real cost of energy. *Nature* **2017**, *551* (7682), DOI DOI: 10.1038/d41586-017-07510-3.
- (6) Di, Q.; Wang, Y.; Zanobetti, A.; Wang, Y.; Koutrakis, P.; Choirat, C.; Dominici, F.; Schwartz, J. D. Air Pollution and Mortality in the Medicare Population. *N. Engl. J. Med.* **2017**, *376* (26), 2513–2522.
- (7) García-Olivares, A. Substitutability of Electricity and Renewable Materials for Fossil Fuels in a Post-Carbon Economy. *Energies* **2015**, *8* (12), 13308.
- (8) Zhu, H.; Luo, W.; Ciesielski, P. N.; Fang, Z.; Zhu, J. Y.; Henriksson, G.; Himmel, M. E.; Hu, L. Wood-Derived Materials for Green Electronics, Biological Devices, and Energy Applications. *Chem. Rev.* **2016**, *116* (16), 9305–9374.
- (9) Spevacek, J. A change is gonna come. *Nat. Rev. Chem.* **2017**, *1*, 0008.
- (10) Sheldon, R. A.; Arends, I. W. C. E.; Hanefeld, U., Chemicals from Renewable Raw Materials. In *Green Chemistry and Catalysis*; Wiley-VCH Verlag GmbH & Co. KGaA: 2007; pp 329–387.
- (11) Bozell, J. J.; Petersen, G. R. Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy's "Top 10" revisited. *Green Chem.* **2010**, *12* (4), 539–554.
- (12) Mika, L. T.; Cséfalvay, E.; Németh, Á. Catalytic Conversion of Carbohydrates to Initial Platform Chemicals: Chemistry and Sustainability. *Chem. Rev.* **2018**, *118* (2), 505–613.
- (13) Mascal, M.; Dutta, S., Chemical-Catalytic Approaches to the Production of Furfurals and Levulinates from Biomass. In *Selective Catalysis for Renewable Feedstocks and Chemicals*, Nicholas, K. M., Ed. Springer International Publishing: Cham, 2014; pp 41–83.
- (14) Rajoka, M. I.; Malik, K. A. Cellulase production by *Cellulomonas biazotea* cultured in media containing different cellulosic substrates. *Bioresour. Technol.* **1997**, *59* (1), 21–27.
- (15) Field, C. B.; Behrenfeld, M. J.; Randerson, J. T.; Falkowski, P. Primary Production of the Biosphere: Integrating Terrestrial and Oceanic Components. *Science* **1998**, *281* (5374), 237–240.
- (16) Liu, B.; Zhang, Z. H. One-Pot Conversion of Carbohydrates into Furan Derivatives via Furfural and 5-Hydroxymethylfurfural as Intermediates. *ChemSusChem* **2016**, *9* (16), 2015–2036.
- (17) Dumeignil, F.; Capron, M.; Katryniok, B.; Wojcieszak, R.; Lofberg, A.; Girardon, J. S.; Desset, S.; Araque-Marin, M.; Jalowiecki-Duhamel, L.; Paul, S. Biomass-derived Platform Molecules Upgrading through Catalytic Processes: Yielding Chemicals and Fuels. *Jpn. Pet. Inst.* **2015**, *58* (5), 257–273.
- (18) Bhanja, P.; Bhaumik, A. Porous nanomaterials as green catalyst for the conversion of biomass to bioenergy. *Fuel* **2016**, *185*, 432–441.
- (19) Bhaumik, P.; Dhepe, P. L. Solid acid catalyzed synthesis of furans from carbohydrates. *Catal. Rev.: Sci. Eng.* **2016**, *58* (1), 36–112.
- (20) Patel, A.; Arora, N.; Sartaj, K.; Pruthi, V.; Pruthi, P. A. Sustainable biodiesel production from oleaginous yeasts utilizing hydrolysates of various non-edible lignocellulosic biomasses. *Renewable Sustainable Energy Rev.* **2016**, *62*, 836–855.
- (21) Alipour, S.; Omidvarborna, H.; Kim, D. S. A review on synthesis of alkoxyethyl furfural, a biofuel candidate. *Renewable Sustainable Energy Rev.* **2017**, *71*, 908–926.
- (22) Hu, L.; Lin, L.; Liu, S. J. Chemoselective Hydrogenation of Biomass-Derived 5-Hydroxymethylfurfural into the Liquid Biofuel 2,5-Dimethylfuran. *Ind. Eng. Chem. Res.* **2014**, *53* (24), 9969–9978.
- (23) Zang, H.; Wang, K.; Zhang, M.; Xie, R.; Wang, L.; Chen, E. Y. X. Catalytic coupling of biomass-derived aldehydes into intermediates for biofuels and materials. *Catal. Sci. Technol.* **2018**, *8* (7), 1777–1798.
- (24) Sheldon, R. A. Green and sustainable manufacture of chemicals from biomass: state of the art. *Green Chem.* **2014**, *16* (3), 950–963.
- (25) Rout, P. K.; Nannaware, A. D.; Prakash, O.; Kalra, A.; Rajasekharan, R. Synthesis of hydroxymethylfurfural from cellulose using green processes: A promising biochemical and biofuel feedstock. *Chem. Eng. Sci.* **2016**, *142*, 318–346.

- (26) Zhang, H.; Pan, H.; Yang, S. Upgrading of Cellulose to Biofuels and Chemicals with Acidic Nanocatalysts. *Curr. Nanosci.* **2017**, *13* (5), 513–527.
- (27) Tang, X.; Wei, J.; Ding, N.; Sun, Y.; Zeng, X.; Hu, L.; Liu, S.; Lei, T.; Lin, L. Chemoselective hydrogenation of biomass derived 5-hydroxymethylfurfural to diols: Key intermediates for sustainable chemicals, materials and fuels. *Renewable Sustainable Energy Rev.* **2017**, *77*, 287–296.
- (28) Verrier, C.; Moebis-Sanchez, S.; Queneau, Y.; Popowycz, F. The Piancatelli reaction and its variants: recent applications to high added-value chemicals and biomass valorization. *Org. Biomol. Chem.* **2018**, *16* (5), 676–687.
- (29) Chernyshev, V. M.; Kravchenko, O. A.; Ananikov, V. P. Conversion of plant biomass to furan derivatives and sustainable access to the new generation of polymers, functional materials and fuels. *Russ. Chem. Rev.* **2017**, *86* (5), 357–387.
- (30) Papageorgiou, G. Z.; Papageorgiou, D. G.; Terzopoulou, Z.; Bikiaris, D. N. Production of bio-based 2,5-furan dicarboxylate polyesters: Recent progress and critical aspects in their synthesis and thermal properties. *Eur. Polym. J.* **2016**, *83*, 202–229.
- (31) Zhang, D. H.; Dumont, M. J. Advances in Polymer Precursors and Bio-Based Polymers Synthesized from 5-Hydroxymethylfurfural. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55* (9), 1478–1492.
- (32) Zhang, J. H.; Li, J. K.; Tang, Y. J.; Lin, L.; Long, M. N. Advances in catalytic production of bio-based polyester monomer 2,5-furandicarboxylic acid derived from lignocellulosic biomass. *Carbohydr. Polym.* **2015**, *130*, 420–428.
- (33) Shaghaleh, H.; Xu, X.; Wang, S. Current progress in production of biopolymeric materials based on cellulose, cellulose nanofibers, and cellulose derivatives. *RSC Adv.* **2018**, *8* (2), 825–842.
- (34) Nguyen, H. T. H.; Qi, P.; Rostagno, M.; Feteha, A.; Miller, S. A. The quest for high glass transition temperature bioplastics. *J. Mater. Chem. A* **2018**, DOI: 10.1039/C8TA00377G.
- (35) van Putten, R.-J.; van der Waal, J. C.; de Jong, E.; Rasrendra, C. B.; Heeres, H. J.; de Vries, J. G. Hydroxymethylfurfural, A Versatile Platform Chemical Made from Renewable Resources. *Chem. Rev.* **2013**, *113* (3), 1499–1597.
- (36) de Vries, J. G., Chapter Eight - Green Syntheses of Heterocycles of Industrial Importance. 5-Hydroxymethylfurfural as a Platform Chemical. In *Adv. Heterocycl. Chem.*, Scriven, E. F. V.; Ramsden, C. A., Eds. Academic Press: 2017; Vol. 121, pp 247–293.
- (37) Besson, M.; Gallezot, P.; Pinel, C. Conversion of biomass into chemicals over metal catalysts. *Chem. Rev.* **2014**, *114* (3), 1827–70.
- (38) Rosatella, A. A.; Simeonov, S. P.; Frade, R. F. M.; Afonso, C. A. M. 5-Hydroxymethylfurfural (HMF) as a building block platform: Biological properties, synthesis and synthetic applications. *Green Chem.* **2011**, *13* (4), 754–793.
- (39) Vries, A. C. G. d. Catalytic Conversion of Renewable Resources into Bulk and Fine Chemicals. *Chem. Rec.* **2016**, *16* (6), 2787–2800.
- (40) Hayashi, E.; Komanoya, T.; Kamata, K.; Hara, M. Heterogeneously-Catalyzed Aerobic Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid with MnO₂. *ChemSusChem* **2017**, *10* (4), 654–658.
- (41) Stahl, S. S.; Powell, A. B.; Root, T. W.; Mannel, D. S.; Ahmed, M. S. Conversion Of Alcohols To Alkyl Esters And Carboxylic Acids Using Heterogeneous Palladium-Based Catalysts. US20170137362A1, 2017.
- (42) Ahmed, M. S.; Mannel, D. S.; Root, T. W.; Stahl, S. S. Aerobic Oxidation of Diverse Primary Alcohols to Carboxylic Acids with a Heterogeneous Pd–Bi–Te/C (PBT/C) Catalyst. *Org. Process Res. Dev.* **2017**, *21* (9), 1388–1393.
- (43) Gong, W.; Zheng, K.; Ji, P. Platinum deposited on cerium coordination polymer for catalytic oxidation of hydroxymethylfurfural producing 2,5-furandicarboxylic acid. *RSC Adv.* **2017**, *7* (55), 34776–34782.
- (44) Sokolovskii, V.; Murphy, V. J.; Boussie, T. R.; Diamond, G. M.; Dias, E. L.; Zhu, G.; Longmire, J. M.; Herrmann, S.; Torssell, S.; Lavrenko, M. Processes for the preparation of 2,5-furandicarboxylic acid and intermediates and derivatives thereof. US20170197930, 2017.
- (45) Han, X.; Li, C.; Liu, X.; Xia, Q.; Wang, Y. Selective oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid over MnO_x-CeO₂ composite catalysts. *Green Chem.* **2017**, *19* (4), 996–1004.
- (46) Wang, Q.; Hou, W.; Li, S.; Xie, J.; Li, J.; Zhou, Y.; Wang, J. Hydrophilic mesoporous poly(ionic liquid)-supported Au-Pd alloy nanoparticles towards aerobic oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid under mild conditions. *Green Chem.* **2017**, *19* (16), 3820–3830.
- (47) Yanqin, W.; Chaoqun, L.; Xuewang, H.; Xiaohui, L.; Qineng, X. Method for preparing 2, 5-furandicarboxylic acid by conducting catalytic oxidation on 5-hydroxymethylfurfural. CN106565647, 2017.
- (48) Jie, F.; Jinshan, S.; Hao, C.; Xiuyang, L.; Pingkai, O. Method using 5-hydroxymethylfurfural to prepare 2,5-furandicarboxylic acid. CN106749130, 2017.
- (49) Antonyraj, C. A.; Huynh, N. T. T.; Park, S.-K.; Shin, S.; Kim, Y. J.; Kim, S.; Lee, K.-Y.; Cho, J. K. Basic anion-exchange resin (AER)-supported Au-Pd alloy nanoparticles for the oxidation of 5-hydroxymethyl-2-furfural (HMF) into 2,5-furan dicarboxylic acid (FDCA). *Appl. Catal., A* **2017**, *547*, 230–236.
- (50) Shen, J.; Chen, H.; Chen, K.; Qin, Y.; Lu, X.; Ouyang, P.; Fu, J. Atomic Layer Deposition of a Pt-Skin Catalyst for Base-Free Aerobic Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid. *Ind. Eng. Chem. Res.* **2018**, *57* (8), 2811–2818.
- (51) Donoeva, B.; Masoud, N.; de Jongh, P. E. Carbon Support Surface Effects in the Gold-Catalyzed Oxidation of 5-Hydroxymethylfurfural. *ACS Catal.* **2017**, *7* (7), 4581–4591.
- (52) Gao, Z.; Xie, R.; Fan, G.; Yang, L.; Li, F. Highly Efficient and Stable Bimetallic AuPd over La-Doped Ca–Mg–Al Layered Double Hydroxide for Base-Free Aerobic Oxidation of 5-Hydroxymethylfurfural in Water. *ACS Sustainable Chem. Eng.* **2017**, *5* (7), 5852–5861.
- (53) Chen, C.; Li, X.; Wang, L.; Liang, T.; Wang, L.; Zhang, Y.; Zhang, J. Highly Porous Nitrogen- and Phosphorus-Codoped Graphene: An Outstanding Support for Pd Catalysts to Oxidize 5-Hydroxymethylfurfural into 2,5-Furandicarboxylic Acid. *ACS Sustainable Chem. Eng.* **2017**, *5* (12), 11300–11306.
- (54) Rathod, P. V.; Jadhav, V. H. Efficient Method for Synthesis of 2,5-Furandicarboxylic Acid from 5-Hydroxymethylfurfural and Fructose Using Pd/CC Catalyst under Aqueous Conditions. *ACS Sustainable Chem. Eng.* **2018**, *6* (5), 5766–5771.
- (55) Yu, K.; Liu, Y.; Lei, D.; Jiang, Y.; Wang, Y.; Feng, Y.; Lou, L.-L.; Liu, S.; Zhou, W. M₃O(-Mn₄₊)₂ clusters in doped MnO_x catalysts as promoted active sites for the aerobic oxidation of 5-hydroxymethylfurfural. *Catal. Sci. Technol.* **2018**, *8* (9), 2299–2303.
- (56) Mishra, D. K.; Lee, H. J.; Kim, J.; Lee, H.-S.; Cho, J. K.; Suh, Y.-W.; Yi, Y.; Kim, Y. J. MnCo₂O₄ spinel supported ruthenium catalyst for air-oxidation of HMF to FDCA under aqueous phase and base-free conditions. *Green Chem.* **2017**, *19* (7), 1619–1623.
- (57) Tekautz, G.; Kirschneck, D.; Linhart, W. Process for the production of 2,5-furandicarboxylic acid (fdca). WO2017097843A1, 2017.
- (58) Gupta, K.; Rai, R. K.; Dwivedi, A. D.; Singh, S. K. Catalytic Aerial Oxidation of Biomass-Derived Furans to Furan Carboxylic Acids in Water over Bimetallic Nickel–Palladium Alloy Nanoparticles. *ChemCatChem* **2017**, *9* (14), 2760–2767.
- (59) Wang, K.-F.; Liu, C.-l.; Sui, K.-y.; Guo, C.; Liu, C.-Z. Efficient Catalytic Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid by Magnetic Laccase Catalyst. *ChemBioChem* **2018**, *19* (7), 654–659.
- (60) Xu, S.; Zhou, P.; Zhang, Z.; Yang, C.; Zhang, B.; Deng, K.; Bottle, S.; Zhu, H. Selective Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid Using O₂ and a Photocatalyst of Co-thiophopyrazine Bonded to g-C₃N₄. *J. Am. Chem. Soc.* **2017**, *139* (41), 14775–14782.
- (61) Fang, R.; Tian, P.; Yang, X.; Luque, R.; Li, Y. Encapsulation of ultrafine metal-oxide nanoparticles within mesopores for biomass-derived catalytic applications. *Chem. Sci.* **2018**, *9* (7), 1854–1859.
- (62) Zhou, B.; Song, J.; Zhang, Z.; Jiang, Z.; Zhang, P.; Han, B. Highly selective photocatalytic oxidation of biomass-derived chemicals

to carboxyl compounds over Au/TiO₂. *Green Chem.* **2017**, *19* (4), 1075–1081.

(63) Nam, D.-H.; Taitt, B. J.; Choi, K.-S. Copper-Based Catalytic Anodes To Produce 2,5-Furandicarboxylic Acid, a Biomass-Derived Alternative to Terephthalic Acid. *ACS Catal.* **2018**, *8* (2), 1197–1206.

(64) P, M.; Sermadurai, S.; Zimmermann, N.; Serum, E.; Ma, G.; Moorthy, R.; Kalliokoski, K. Novel monomers from biomass. *US2017233325*, 2017.

(65) Xianxiang, L.; Dulin, Y.; Kai, L.; Jinhua, L.; Qiong, X. Method for preparing 2,5-diformyl furan. *CN106967019*, 2017.

(66) Tong, X.; Yu, L.; Chen, H.; Zhuang, X.; Liao, S.; Cui, H. Highly efficient and selective oxidation of 5-hydroxymethylfurfural by molecular oxygen in the presence of Cu-MnO₂ catalyst. *Catal. Commun.* **2017**, *90*, 91–94.

(67) Xie, J.; Yin, K.; Serov, A.; Artyushkova, K.; Pham, H. N.; Sang, X.; Unocic, R. R.; Atanassov, P.; Datye, A. K.; Davis, R. J. Selective Aerobic Oxidation of Alcohols over Atomically-Dispersed Non-Precious Metal Catalysts. *ChemSusChem* **2017**, *10* (2), 359–362.

(68) Rapeyko, A.; Arias, K. S.; Climent, M. J.; Corma, A.; Iborra, S. Polymers from biomass: one pot two-step synthesis of furilydenepropanenitrile derivatives with MIL-100(Fe) catalyst. *Catal. Sci. Technol.* **2017**, *7* (14), 3008–3016.

(69) Cao, T.; Wu, M.; Ordonsky, V. V.; Xin, X.; Wang, H.; Métivier, P.; Pera-Titus, M. Selective Electrogenative Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandialdehyde. *ChemSusChem* **2017**, *10* (24), 4851–4854.

(70) Zhao, J.; Jayakumar, A.; Hu, Z.-T.; Yan, Y.; Yang, Y.; Lee, J.-M. MoO₃-Containing Protonated Nitrogen Doped Carbon as a Bifunctional Catalyst for One-Step Synthesis of 2,5-Diformylfuran from Fructose. *ACS Sustainable Chem. Eng.* **2018**, *6* (1), 284–291.

(71) Yan, Y.; Li, K.; Zhao, J.; Cai, W.; Yang, Y.; Lee, J.-M. Nanobelt-arrayed vanadium oxide hierarchical microspheres as catalysts for selective oxidation of 5-hydroxymethylfurfural toward 2,5-diformylfuran. *Appl. Catal., B* **2017**, *207*, 358–365.

(72) Ventura, M.; Lobefaro, F.; de Giglio, E.; Distaso, M.; Nocito, F.; Dibenedetto, A. Selective Aerobic Oxidation of 5-Hydroxymethylfurfural to 2,5-Diformylfuran or 2-Formyl-5-furancarboxylic Acid in Water by using MgO-CeO₂Mixed Oxides as Catalysts. *ChemSusChem* **2018**, *11* (8), 1305–1315.

(73) Ma, B.; Wang, Y.; Guo, X.; Tong, X.; Liu, C.; Wang, Y.; Guo, X. Photocatalytic synthesis of 2,5-diformylfuran from 5-hydroxymethylfurfural or fructose over bimetallic Au-Ru nanoparticles supported on reduced graphene oxides. *Appl. Catal., A* **2018**, *552*, 70–76.

(74) Lagerblom, K.; Lagerspets, E.; Keskiäli, J.; Cook, C.; Ekholm, F.; Parviainen, A.; Repo, T. Practical Aerobic Oxidation of Alcohols: A Ligand-Enhanced 2,2,6,6-Tetramethylpiperidine-1-oxyl/Manganese Nitrate Catalyst System. *ChemCatChem* **2017**, *9* (20), 3880–3887.

(75) Biswas, S.; Dutta, B.; Mannodi-Kanakkithodi, A.; Clarke, R.; Song, W.; Ramprasad, R.; Suib, S. L. Heterogeneous mesoporous manganese/cobalt oxide catalysts for selective oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran. *Chem. Commun.* **2017**, *53* (86), 11751–11754.

(76) McKenna, S. M.; Mines, P.; Law, P.; Kovacs-Schreiner, K.; Birmingham, W. R.; Turner, N. J.; Leimkuhler, S.; Carnell, A. J. The continuous oxidation of HMF to FDCA and the immobilisation and stabilisation of periplasmic aldehyde oxidase (PaoABC). *Green Chem.* **2017**, *19* (19), 4660–4665.

(77) Han, G.; Jin, Y.-H.; Burgess, R. A.; Dickenson, N. E.; Cao, X.-M.; Sun, Y. Visible-Light-Driven Valorization of Biomass Intermediates Integrated with H₂ Production Catalyzed by Ultrathin Ni/CdS Nanosheets. *J. Am. Chem. Soc.* **2017**, *139* (44), 15584–15587.

(78) Özcan, L.; Yalçın, P.; Alagöz, O.; Yurdakal, S. Selective photoelectrocatalytic oxidation of 5-(hydroxymethyl)-2-furaldehyde in water by using Pt loaded nanotube structure of TiO₂ on Ti photoanodes. *Catal. Today* **2017**, *281*, 205–213.

(79) Liu, A.; Zhu, X.; Cheng, M.; Zhang, M. Preparation method of 2,5-furan diformaldehyde. *CN 106674162A*, 2017.

(80) Kashparova, V. P.; Klushin, V. A.; Zhukova, I. Y.; Kashparov, I. S.; Chernysheva, D. V.; Il'chibaeva, I. B.; Smirnova, N. V.; Kagan, E. S.;

Chernyshev, V. M. A TEMPO-like nitroxide combined with an alkyl-substituted pyridine: An efficient catalytic system for the selective oxidation of alcohols with iodine. *Tetrahedron Lett.* **2017**, *58* (36), 3517–3521.

(81) McGaff, R. W. Bridged phthalocyanine- and naphthalocyanine-metal complex catalysts and methods of using and purifying the same. *US20170022233*, 2017.

(82) Ning, L.; Liao, S.; Sun, Y.; Yu, L.; Tong, X. The Efficient Oxidation of Biomass-Derived 5-Hydroxymethyl Furfural to Produce 2,5-Diformylfuran Over Supported Cobalt Catalysts. *Waste Biomass Valorization* **2018**, *9* (1), 95–101.

(83) Martínez-Vargas, D. X.; Rivera De La Rosa, J.; Sandoval-Rangel, L.; Guzmán-Mar, J. L.; Garza-Navarro, M. A.; Lucio-Ortiz, C. J.; De Haro-Del Río, D. A. 5-Hydroxymethylfurfural catalytic oxidation under mild conditions by Co (II), Fe (III) and Cu (II) Salen complexes supported on SBA-15: Synthesis, characterization and activity. *Appl. Catal., A* **2017**, *547*, 132–145.

(84) Chatterjee, M.; Ishizaka, T.; Chatterjee, A.; Kawanami, H. Dehydrogenation of 5-hydroxymethylfurfural to diformylfuran in compressed carbon dioxide: an oxidant free approach. *Green Chem.* **2017**, *19* (5), 1315–1326.

(85) Jia, H.-Y.; Zong, M.-H.; Yu, H.-L.; Li, N. Dehydrogenase-Catalyzed Oxidation of Furanics: Exploitation of Hemoglobin Catalytic Promiscuity. *ChemSusChem* **2017**, *10* (18), 3524–3528.

(86) Zhang, X.-Y.; Zong, M.-H.; Li, N. Whole-cell biocatalytic selective oxidation of 5-hydroxymethylfurfural to 5-hydroxymethyl-2-furancarboxylic acid. *Green Chem.* **2017**, *19* (19), 4544–4551.

(87) Chen, C.-T.; Nguyen, C. V.; Wang, Z.-Y.; Bando, Y.; Yamauchi, Y.; Bazziz, T. S.; Fatehmulla, A.; Farooq, W. A.; Yoshikawa, T.; Masuda, T.; Wu, C.-W. Hydrogen Peroxide Assisted Selective Oxidation of 5-Hydroxymethylfurfural in Water under Mild Conditions. *ChemCatChem* **2018**, *10* (2), 361–365.

(88) Casanova, O.; Iborra, S.; Corma, A. Biomass into Chemicals: Aerobic Oxidation of 5-Hydroxymethyl-2-furfural into 2,5-Furandicarboxylic Acid with Gold Nanoparticle Catalysts. *ChemSusChem* **2009**, *2* (12), 1138–1144.

(89) Gupta, N. K.; Nishimura, S.; Takagaki, A.; Ebitani, K. Hydrotalcite-supported gold-nanoparticle-catalyzed highly efficient base-free aqueous oxidation of 5-hydroxymethylfurfural into 2,5-furandicarboxylic acid under atmospheric oxygen pressure. *Green Chem.* **2011**, *13* (4), 824–827.

(90) Pasini, T.; Piccinini, M.; Blosi, M.; Bonelli, R.; Albonetti, S.; Dimitratos, N.; Lopez-Sanchez, J. A.; Sankar, M.; He, Q.; Kiely, C. J.; Hutchings, G. J.; Cavani, F. Selective oxidation of 5-hydroxymethyl-2-furfural using supported gold-copper nanoparticles. *Green Chem.* **2011**, *13* (8), 2091–2099.

(91) Gorbanev, Y. Y.; Klitgaard, S. K.; Woodley, J. M.; Christensen, C. H.; Riisager, A. Gold-Catalyzed Aerobic Oxidation of 5-Hydroxymethylfurfural in Water at Ambient Temperature. *ChemSusChem* **2009**, *2* (7), 672–675.

(92) Davis, S. E.; Houk, L. R.; Tamargo, E. C.; Datye, A. K.; Davis, R. J. Oxidation of 5-hydroxymethylfurfural over supported Pt, Pd and Au catalysts. *Catal. Today* **2011**, *160* (1), 55–60.

(93) Parteneimer, W.; Grushin, V. V. Synthesis of 2,5-Diformylfuran and Furan-2,5-Dicarboxylic Acid by Catalytic Air-Oxidation of 5-Hydroxymethylfurfural. Unexpectedly Selective Aerobic Oxidation of Benzyl Alcohol to Benzaldehyde with Metal = Bromide Catalysts. *Adv. Synth. Catal.* **2001**, *343* (1), 102–111.

(94) Ma, J.; Du, Z.; Xu, J.; Chu, Q.; Pang, Y. Efficient Aerobic Oxidation of 5-Hydroxymethylfurfural to 2,5-Diformylfuran, and Synthesis of a Fluorescent Material. *ChemSusChem* **2011**, *4* (1), 51–54.

(95) Carlini, C.; Patrono, P.; Galletti, A. M. R.; Sbrana, G.; Zima, V. Selective oxidation of 5-hydroxymethyl-2-furaldehyde to furan-2,5-dicarboxaldehyde by catalytic systems based on vanadyl phosphate. *Appl. Catal., A* **2005**, *289* (2), 197–204.

(96) Srivastava, S.; Jadeja, G. C.; Parikh, J. Synergism studies on alumina-supported copper-nickel catalysts towards furfural and 5-

hydroxymethylfurfural hydrogenation. *J. Mol. Catal. A: Chem.* **2017**, *426*, 244–256.

(97) Puylaert, P.; van Heck, R.; Fan, Y.; Spannenberg, A.; Baumann, W.; Beller, M.; Medlock, J.; Bonrath, W.; Lefort, L.; Hinze, S.; de Vries, J. G. Selective Hydrogenation of α,β -Unsaturated Aldehydes and Ketones by Air-Stable Ruthenium NNS Complexes. *Chem. - Eur. J.* **2017**, *23* (35), 8473–8481.

(98) Lima, S.; Chadwick, D.; Hellgardt, K. Towards sustainable hydrogenation of 5-(hydroxymethyl)furfural: a two-stage continuous process in aqueous media over RANEY® catalysts. *RSC Adv.* **2017**, *7* (50), 31401–31407.

(99) Gupta, D.; Saha, B. Carbon nanosphere supported Ru catalyst for the synthesis of renewable herbicide and chemicals. *Catal. Commun.* **2017**, *100*, 206–209.

(100) Li, X.-L.; Zhang, K.; Chen, S.-Y.; Li, C.; Li, F.; Xu, H.-J.; Fu, Y. A cobalt catalyst for reductive etherification of 5-hydroxymethylfurfural to 2,5-bis(methoxymethyl)furan under mild conditions. *Green Chem.* **2018**, *20*, 1095.

(101) Upare, P. P.; Hwang, Y. K.; Hwang, D. W. An integrated process for the production of 2,5-dihydroxymethylfuran and its polymer from fructose. *Green Chem.* **2018**, *20* (4), 879–885.

(102) Li, H.; Fang, Z.; He, J.; Yang, S. Orderly Layered Zr-Benzylphosphonate Nanohybrids for Efficient Acid–Base-Mediated Bifunctional/Cascade Catalysis. *ChemSusChem* **2017**, *10* (4), 681–686.

(103) Chilukuri, S. V. V.; Nagpure, A. S. Transition metal(s) catalyst supported on nitrogen-doped mesoporous carbon and its use in catalytic transfer hydrogenation reactions. WO2017042838A1, 2017.

(104) Li, H.; Liu, X.; Yang, T.; Zhao, W.; Saravanamurugan, S.; Yang, S. Porous Zirconium–Furandicarboxylate Microspheres for Efficient Redox Conversion of Biofurans. *ChemSusChem* **2017**, *10* (8), 1761–1770.

(105) Li, H.; Yang, T.; Fang, Z. Biomass-derived mesoporous Hf-containing hybrid for efficient Meerwein-Ponndorf-Verley reduction at low temperatures. *Appl. Catal., B* **2018**, *227*, 79–89.

(106) Townsend, T. M.; Kirby, C.; Ruff, A.; O'Connor, A. R. Transfer hydrogenation of aromatic and linear aldehydes catalyzed using Cp*Ir(pyridinesulfonamide)Cl complexes under base-free conditions. *J. Organomet. Chem.* **2017**, *843*, 7–13.

(107) Zhang, Z.; Wang, F.; Jiang, L. Method for preparing furfuryl alcohol by utilizing hydrogen transfer reaction to catalyze furfural. CN106543115, 2017.

(108) Xing, T.; Junnan, W.; Yong, S.; Xianhai, Z.; Lu, L.; Tingzhou, L. Synthetic method of 2,5-furan dimethanol and etherified product of 2,5-furan dimethanol. CN106946820, 2017.

(109) Nguyen, H.; Xiao, N.; Daniels, S.; Marcella, N.; Timoshenko, J.; Frenkel, A.; Vlachos, D. G. Role of Lewis and Brønsted Acidity in Metal Chloride Catalysis in Organic Media: Reductive Etherification of Furans. *ACS Catal.* **2017**, *7* (10), 7363–7370.

(110) He, J.; Li, H.; Riisager, A.; Yang, S. Catalytic Transfer Hydrogenation of Furfural to Furfuryl Alcohol with Recyclable Al–Zr@Fe Mixed Oxides. *ChemCatChem* **2018**, *10* (2), 430–438.

(111) Rojas-Buzo, S.; Garica-Garcia, P.; Corma, A. Catalytic Transfer Hydrogenation of Biomass-Derived Carbonyls over Hafnium-Based Metal–Organic Frameworks. *ChemSusChem* **2018**, *11* (2), 432–438.

(112) Sibi, M. P.; Sermadurai, S.; Zimmermann, N.; Serum, E.; Ma, G.; Moorthy, R.; Kalliokoski, K. Novel monomers from biomass. US20170233325, 2017.

(113) Kucherov, F. A.; Galkin, K. I.; Gordeev, E. G.; Ananikov, V. P. Efficient route for the construction of polycyclic systems from bioderived HMF. *Green Chem.* **2017**, *19* (20), 4858–4864.

(114) Dunbabin, A.; Subrizi, F.; Ward, J. M.; Sheppard, T. D.; Hailes, H. C. Furfurylamines from biomass: transaminase catalysed upgrading of furfurals. *Green Chem.* **2017**, *19* (2), 397–404.

(115) Li, Y.-M.; Zhang, X.-Y.; Li, N.; Xu, P.; Lou, W.-Y.; Zong, M.-H. Biocatalytic Reduction of HMF to 2,5-Bis(hydroxymethyl)furan by HMF-Tolerant Whole Cells. *ChemSusChem* **2017**, *10* (2), 372–378.

(116) Iriando, A.; Mendiguren, A.; Güemez, M. B.; Requies, J.; Cambra, J. F. 2,5-DMF production through hydrogenation of real and

synthetic 5-HMF over transition metal catalysts supported on carriers with different nature. *Catal. Today* **2017**, *279*, 286–295.

(117) Yang, Y.; Liu, Q.; Li, D.; Tan, J.; Zhang, Q.; Wang, C.; Ma, L. Selective hydrodeoxygenation of 5-hydroxymethylfurfural to 2,5-dimethylfuran on Ru–MoO_x/C catalysts. *RSC Adv.* **2017**, *7* (27), 16311–16318.

(118) Li, J.; Liu, J.-l.; Liu, H.-y.; Xu, G.-y.; Zhang, J.-j.; Liu, J.-x.; Zhou, G.-l.; Li, Q.; Xu, Z.-h.; Fu, Y. Selective Hydrodeoxygenation of 5-Hydroxymethylfurfural to 2,5-Dimethylfuran over Heterogeneous Iron Catalysts. *ChemSusChem* **2017**, *10* (7), 1436–1447.

(119) Srivastava, S.; Jadeja, G. C.; Parikh, J. Influence of supports for selective production of 2,5-dimethylfuran via bimetallic copper-cobalt catalyzed 5-hydroxymethylfurfural hydrogenolysis. *Chin. J. Catal.* **2017**, *38* (4), 699–709.

(120) Insyani, R.; Verma, D.; Kim, S. M.; Kim, J. Direct one-pot conversion of monosaccharides into high-yield 2,5-dimethylfuran over a multifunctional Pd/Zr-based metal-organic framework@ sulfonated graphene oxide catalyst. *Green Chem.* **2017**, *19* (11), 2482–2490.

(121) Mani, C. M.; Braun, M.; Molinari, V.; Antonietti, M.; Fechner, N. A High-Throughput Composite Catalyst based on Nickel Carbon Cubes for the Hydrogenation of 5-Hydroxymethylfurfural to 2,5-Dimethylfuran. *ChemCatChem* **2017**, *9* (17), 3388–3394.

(122) Chen, B.; Li, F.; Huang, Z.; Yuan, G. Carbon-coated Cu–Co bimetallic nanoparticles as selective and recyclable catalysts for production of biofuel 2,5-dimethylfuran. *Appl. Catal., B* **2017**, *200*, 192–199.

(123) Luo, J.; Monai, M.; Wang, C.; Lee, J. D.; Duchon, T.; Dvorak, F.; Matolin, V.; Murray, C. B.; Fornasiero, P.; Gorte, R. J. Unraveling the surface state and composition of highly selective nanocrystalline Ni–Cu alloy catalysts for hydrodeoxygenation of HMF. *Catal. Sci. Technol.* **2017**, *7* (8), 1735–1743.

(124) Priece, P.; Endot, N. A.; Carà, P. D.; Lopez-Sanchez, J. A. Fast Catalytic Hydrogenation of 2,5-Hydroxymethylfurfural to 2,5-Dimethylfuran with Ruthenium on Carbon Nanotubes. *Ind. Eng. Chem. Res.* **2018**, *57* (6), 1991–2002.

(125) Kong, X.; Zhu, Y.; Zheng, H.; Zhu, Y.; Fang, Z. Inclusion of Zn into Metallic Ni Enables Selective and Effective Synthesis of 2,5-Dimethylfuran from Bioderived 5-Hydroxymethylfurfural. *ACS Sustainable Chem. Eng.* **2017**, *5* (12), 11280–11289.

(126) Siddiqui, N.; Roy, A. S.; Goyal, R.; Khatun, R.; Pendem, C.; Chokkapu, A. N.; Bordoloi, A.; Bal, R. Hydrogenation of 5-hydroxymethylfurfural to 2,5 dimethylfuran over nickel supported tungsten oxide nanostructured catalyst. *Sustainable Energy & Fuels* **2018**, *2* (1), 191–198.

(127) Zhang, F.; Liu, Y.; Yuan, F.; Niu, X.; Zhu, Y. Efficient Production of the Liquid Fuel 2,5-Dimethylfuran from 5-Hydroxymethylfurfural in the Absence of Acid Additive over Bimetallic PdAu Supported on Graphitized Carbon. *Energy Fuels* **2017**, *31* (6), 6364–6373.

(128) Zhang, J.; Chen, J. Selective Transfer Hydrogenation of Biomass-Based Furfural and 5-Hydroxymethylfurfural over Hydroxycalcite-Derived Copper Catalysts Using Methanol as a Hydrogen Donor. *ACS Sustainable Chem. Eng.* **2017**, *5* (7), 5982–5993.

(129) Li, W.; Fan, G.; Yang, L.; Li, F. Highly efficient synchronized production of phenol and 2,5-dimethylfuran through a bimetallic Ni–Cu catalyzed dehydrogenation-hydrogenation coupling process without any external hydrogen and oxygen supply. *Green Chem.* **2017**, *19* (18), 4353–4363.

(130) Masse, C. E.; Greenwood, J. R.; Romero, D. L.; Harriman, G. C.; Wester, R. T.; Shelley, M.; Kennedy-Smith, J. J.; Dahlgren, M.; Mondal, S. Tyk2 inhibitors and uses thereof. WO2017040757, 2017.

(131) Yoshii, K.; Yamada, A. Method for producing a tetrahydrofuran compound. JP6168044B2, 2017.

(132) Duan, Y.; Zheng, M.; Li, D.; Deng, D.; Ma, L.-F.; Yang, Y. Conversion of HMF to methyl cyclopentenolone using Pd/Nb₂O₅ and Ca–Al catalysts via a two-step procedure. *Green Chem.* **2017**, *19* (21), 5103–5113.

(133) Li, G.; Sun, Z.; Yan, Y.; Zhang, Y.; Tang, Y. Direct Transformation of HMF into 2,5-Diformylfuran and 2,5-Dihydrox-

ymethylfuran without an External Oxidant or Reductant. *ChemSusChem* **2017**, *10* (3), 494–498.

(134) Balakrishnan, M.; Sacia, E. R.; Bell, A. T. Etherification and reductive etherification of 5-(hydroxymethyl)furfural: 5-(alkoxymethyl)furfurals and 2,5-bis(alkoxymethyl)furans as potential bio-diesel candidates. *Green Chem.* **2012**, *14* (6), 1626–1634.

(135) Thananathanachon, T.; Rauchfuss, T. B. Efficient Production of the Liquid Fuel 2,5-Dimethylfuran from Fructose Using Formic Acid as a Reagent. *Angew. Chem., Int. Ed.* **2010**, *49* (37), 6616–6618.

(136) Chen, B.; Li, F.; Huang, Z.; Yuan, G. Carbon-coated Cu-Co bimetallic nanoparticles as selective and recyclable catalysts for production of biofuel 2,5-dimethylfuran. *Appl. Catal., B* **2017**, *200*, 192–199.

(137) Pezzetta, C.; Veiros, L. F.; Oble, J.; Poli, G. Murai Reaction on Furfural Derivatives Enabled by Removable N,N'-Bidentate Directing Groups. *Chem. - Eur. J.* **2017**, *23* (35), 8385–8389.

(138) Xu, G. G.; Pagare, P. P.; Ghatge, M. S.; Safo, R. P.; Gazi, A.; Chen, Q.; David, T.; Alabbas, A. B.; Musayev, F. N.; Venitz, J.; Zhang, Y.; Safo, M. K.; Abdulmalik, O. Design, Synthesis, and Biological Evaluation of Ester and Ether Derivatives of Antisickling Agent 5-HMF for the Treatment of Sickle Cell Disease. *Mol. Pharmaceutics* **2017**, *14* (10), 3499–3511.

(139) Romashov, L. V.; Ananikov, V. P. Alkynylation of Bio-Based 5-Hydroxymethylfurfural to Connect Biomass Processing with Conjugated Polymers and Furanic Pharmaceuticals. *Chem. - Asian J.* **2017**, *12* (20), 2652–2655.

(140) Stensrud, K. S., Brennan Preparation of a sugar-derived ester, glycol and polymers therefrom. WO2017065980, 2017.

(141) Ding, Z.; Luo, X.; Ma, Y.; Chen, H.; Qiu, S.; Sun, G.; Zhang, W.; Yu, C.; Wu, Z.; Zhang, J. Eco-friendly synthesis of 5-hydroxymethylfurfural (HMF) and its application to the Ferrier-rearrangement reaction. *J. Carbohydr. Chem.* **2018**, *37* (2), 81–93.

(142) Shinde, S.; Rode, C. Cascade Reductive Etherification of Bioderived Aldehydes over Zr-Based Catalysts. *ChemSusChem* **2017**, *10* (20), 4090–4101.

(143) Braun, M.; Antonietti, M. A continuous flow process for the production of 2,5-dimethylfuran from fructose using (non-noble metal based) heterogeneous catalysis. *Green Chem.* **2017**, *19* (16), 3813–3819.

(144) Antunes, M. M.; Lima, S.; Fernandes, A.; Magalhães, A. L.; Neves, P.; Silva, C. M.; Ribeiro, M. F.; Chadwick, D.; Hellgardt, K.; Pillinger, M.; Valente, A. A. MFI Acid Catalysts with Different Crystal Sizes and Porosity for the Conversion of Furanic Compounds in Alcohol Media. *ChemCatChem* **2017**, *9* (14), 2747–2759.

(145) Arias, K. S.; Garcia-Ortiz, A.; Climent, M. J.; Corma, A.; Iborra, S. Mutual Valorization of 5-Hydroxymethylfurfural and Glycerol into Valuable Diol Monomers with Solid Acid Catalysts. *ACS Sustainable Chem. Eng.* **2018**, *6* (3), 4239–4245.

(146) Páez, A.; Rojas, H. A.; Portilla, O.; Sathicq, G.; Afonso, C. A. M.; Romanelli, G. P.; Martínez, J. J. Preyssler Heteropolyacids in the Self-Etherification of 5-Hydroxymethylfurfural to 5,5'-(Oxybis(methylene))bis-2-furfural Under Mild Reaction Conditions. *ChemCatChem* **2017**, *9* (17), 3322–3329.

(147) Vicente, A.; Coelho, J.; Simeonov, S.; Lazarova, H.; Popova, M.; Afonso, C. Oxidation of 5-Chloromethylfurfural (CMF) to 2,5-Diformylfuran (DFF). *Molecules* **2017**, *22* (2), 329 DOI.

(148) Bizet, B.; Hornung, C. H.; Kohl, T. M.; Tsanaktisidis, J. Synthesis of Imines and Amines from Furfurals Using Continuous Flow Processing. *Aust. J. Chem.* **2017**, *70* (10), 1069–1072.

(149) Kanai, S.; Nagahara, I.; Kita, Y.; Kamata, K.; Hara, M. A bifunctional cerium phosphate catalyst for chemoselective acetalization. *Chem. Sci.* **2017**, *8* (4), 3146–3153.

(150) Zhao, Q.; Zou, Y.; Huang, C.; Lan, P.; Zheng, J.; Ou, S. Formation of a Hydroxymethylfurfural–Cysteine Adduct and Its Absorption and Cytotoxicity in Caco-2 Cells. *J. Agric. Food Chem.* **2017**, *65* (45), 9902–9908.

(151) Li, H.; Yang, T.; Riisager, A.; Saravanamurugan, S.; Yang, S. Chemoselective Synthesis of Dithioacetals from Bio-aldehydes with

Zeolites under Ambient and Solvent-free Conditions. *ChemCatChem* **2017**, *9* (6), 1097–1104.

(152) Fakhouri, L.; Cook, C. D.; Al-Hunuti, M. H.; Console-Bram, L. M.; Hurst, D. P.; Spano, M. B. S.; Nasrallah, D. J.; Caron, M. G.; Barak, L. S.; Reggio, P. H.; Abood, M. E.; Croatt, M. P. Design, synthesis and biological evaluation of GPR55 agonists. *Bioorg. Med. Chem.* **2017**, *25* (16), 4355–4367.

(153) Crockatt, M.; Urbanus, J. H. WO 2017146581, 2017.

(154) Guan, Z.; Ding, M.; Sun, Y.; Yu, S.; Zhang, A.; Xia, S.; Hu, X.; Lin, Y. The synthesis of two long-chain N-hydroxy amino coumarin compounds and their applications in the analysis of aldehydes. *RSC Adv.* **2017**, *7* (32), 19707–19716.

(155) Liu, Q.; Zhang, C.; Shi, N.; Zhang, X.; Wang, C.; Ma, L. Production of renewable long-chained cycloalkanes from biomass-derived furfurals and cyclic ketones. *RSC Adv.* **2018**, *8* (25), 13686–13696.

(156) Li, S.; Chen, F.; Li, N.; Wang, W.; Sheng, X.; Wang, A.; Cong, Y.; Wang, X.; Zhang, T. Synthesis of Renewable Triketones, Diketones, and Jet-Fuel Range Cycloalkanes with 5-Hydroxymethylfurfural and Ketones. *ChemSusChem* **2017**, *10* (4), 711–719.

(157) Witczak, Z. J.; Bielski, R.; Mencer, D. E. Concise and efficient synthesis of E-stereoisomers of exo-cyclic carbohydrate enones. Aldol condensation of dihydrolevoglucosone with five-membered aromatic aldehydes Part 1. *Tetrahedron Lett.* **2017**, *58* (43), 4069–4072.

(158) Xu, J.; Li, N.; Yang, X.; Li, G.; Wang, A.; Cong, Y.; Wang, X.; Zhang, T. Synthesis of Diesel and Jet Fuel Range Alkanes with Furfural and Angelica Lactone. *ACS Catal.* **2017**, *7* (9), 5880–5886.

(159) Taylor, K. M.; Taylor, Z. E.; Handy, S. T. Rapid synthesis of auronones under mild conditions using a combination of microwaves and deep eutectic solvents. *Tetrahedron Lett.* **2017**, *58* (3), 240–241.

(160) Park, H. S.; Nelson, D. E.; Taylor, Z. E.; Hayes, J. B.; Cunningham, K. D.; Arivett, B. A.; Ghosh, R.; Wolf, L. C.; Taylor, K. M.; Farone, M. B.; Handy, S. T.; Farone, A. L. Suppression of LPS-induced NF- κ B activity in macrophages by the synthetic aurone, (Z)-2-((5-(hydroxymethyl) furan-2-yl) methylene) benzofuran-3(2H)-one. *Int. Immunopharmacol.* **2017**, *43*, 116–128.

(161) Fan, W.; Queneau, Y.; Popowycz, F. HMF in multicomponent reactions: utilization of 5-hydroxymethylfurfural (HMF) in the Biginelli reaction. *Green Chem.* **2018**, *20* (2), 485–492.

(162) Zongchao, Z.; Zhanwei, X.; Lu, W.; Peifang, Y. Furandiolamine compound and preparation method thereof. CN106632166, 2017.

(163) Zhu, M.-M.; Tao, L.; Zhang, Q.; Dong, J.; Liu, Y.-M.; He, H.-Y.; Cao, Y. Versatile CO-assisted direct reductive amination of 5-hydroxymethylfurfural catalyzed by a supported gold catalyst. *Green Chem.* **2017**, *19* (16), 3880–3887.

(164) Jagadeesh, R. V.; Murugesan, K.; Alshammari, A. S.; Neumann, H.; Pohl, M.-M.; Radnik, J.; Beller, M. MOF-derived cobalt nanoparticles catalyze a general synthesis of amines. *Science* **2017**, *358* (6361), 326–332.

(165) Komanoya, T.; Kinemura, T.; Kita, Y.; Kamata, K.; Hara, M. Electronic Effect of Ruthenium Nanoparticles on Efficient Reductive Amination of Carbonyl Compounds. *J. Am. Chem. Soc.* **2017**, *139* (33), 11493–11499.

(166) Ramos, R.; Grigoropoulos, A.; Perret, N.; Zanella, M.; Katsoulidis, A. P.; Manning, T. D.; Claridge, J. B.; Rosseinsky, M. J. Selective conversion of 5-hydroxymethylfurfural to cyclopentanone derivatives over Cu-Al₂O₃ and Co-Al₂O₃ catalysts in water. *Green Chem.* **2017**, *19* (7), 1701–1713.

(167) Xu, Y.-J.; Shi, J.; Wu, W.-P.; Zhu, R.; Li, X.-L.; Deng, J.; Fu, Y. Effect of Cp*Ir(III) Complex and acid co-catalyst on conversion of furfural compounds to cyclopentanones or straight chain ketones. *Appl. Catal., A* **2017**, *543*, 266–273.

(168) Wozniak, B.; Spannenberg, A.; Li, Y.; Hinze, S.; de Vries, J. G. Cyclopentanone Derivatives from 5-Hydroxymethylfurfural via 1-Hydroxyhexane-2,5-dione as Intermediate. *ChemSusChem* **2018**, *11* (2), 356–359.

(169) Wozniak, B.; Li, Y.; Hinze, S.; Tin, S.; de Vries, J. G. Efficient Synthesis of Biomass-Derived N-Substituted 2-Hydroxymethyl-5-

Methyl-Pyrroles in Two Steps from 5-Hydroxymethylfurfural. *Eur. J. Org. Chem.* **2018**, 2018 (17), 2009–2012.

(170) Mingyuan, Z.; Bin, X.; Jifeng, P.; Ruiyan, S.; Xinsheng, L.; Aiqin, W.; Xiaodong, W.; Tao, Z. Method for preparing 1,6-hexanediol through catalytic conversion of 5-hydroxymethyl furfural. CN106866360, 2017.

(171) Buntara, T.; Noel, S.; Phua, P. H.; Melian-Cabrera, I.; de Vries, J. G.; Heeres, H. J. Caprolactam from Renewable Resources: Catalytic Conversion of 5-Hydroxymethylfurfural into Caprolactone. *Angew. Chem., Int. Ed.* **2011**, 50 (31), 7083–7087.

(172) Li, X.; Ho, B.; Lim, D. S. W.; Zhang, Y. Highly efficient formic acid-mediated oxidation of renewable furfural to maleic acid with H₂O₂. *Green Chem.* **2017**, 19 (4), 914–918.

(173) Dibenedetto, A.; Ventura, M.; Williamson, D.; Lobefaro, F.; Jones, M. D.; Mattia, D.; Nocito, F.; Aresta, M. Sustainable synthesis of oxalic (and succinic) acid via aerobic oxidation of C₆ polyols by using M@CNT/NCNT (M = Fe, V) based catalysts in mild conditions. *ChemSusChem* **2018**, 11, 1073–1081.

(174) Han, M.; Liu, X.; Zhang, X.; Pang, Y.; Xu, P.; Guo, J.; Liu, Y.; Zhang, S.; Ji, S. 5-Hydroxymethyl-2-vinylfuran: a biomass-based solvent-free adhesive. *Green Chem.* **2017**, 19 (3), 722–728.

(175) Sharma, U. K.; Gemoets, H. P. L.; Schröder, F.; Noël, T.; Van der Eycken, E. V. Merger of Visible-Light Photoredox Catalysis and C–H Activation for the Room-Temperature C-2 Acylation of Indoles in Batch and Flow. *ACS Catal.* **2017**, 7 (6), 3818–3823.

(176) Hirapara, P.; Riemer, D.; Hazra, N.; Gajera, J.; Finger, M.; Das, S. CO₂-assisted synthesis of non-symmetric [small alpha]-diketones directly from aldehydes via C-C bond formation. *Green Chem.* **2017**, 19 (22), 5356–5360.

(177) Chatterjee, M.; Ishizaka, T.; Kawanami, H. Accelerated decarbonylation of 5-hydroxymethylfurfural in compressed carbon dioxide: a facile approach. *Green Chem.* **2018**, 20, 2345.

(178) Li, X.; Jia, X.; Ma, J.; Xu, Y.; Huang, Y.; Xu, J. Catalytic Amidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxamide over Alkali Manganese Oxides. *Chin. J. Chem.* **2017**, 35 (6), 984–990.

(179) Li, X.; Ma, J.; Jia, X.; Xia, F.; Huang, Y.; Xu, Y.; Xu, J. Al-Doping Promoted Aerobic Amidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxamide over Cryptomelane. *ACS Sustainable Chem. Eng.* **2018**, DOI: 10.1021/acssuschemeng.8b01617.

(180) Kumalaputri, A. J.; Randolph, C.; Otten, E.; Heeres, H. J.; Deuss, P. J. Lewis Acid Catalyzed Conversion of 5-Hydroxymethylfurfural to 1,2,4-Benzenetriol, an Overlooked Biobased Compound. *ACS Sustainable Chem. Eng.* **2018**, 6 (3), 3419–3425.

(181) Ohyama, J.; Ohira, Y.; Satsuma, A. Hydrogenative ring-rearrangement of biomass derived 5-(hydroxymethyl)furfural to 3-(hydroxymethyl)cyclopentanol using combination catalyst systems of Pt/SiO₂ and lanthanoid oxides. *Catal. Sci. Technol.* **2017**, 7 (14), 2947–2953.

(182) Zhang, Y.; Li, T.; Xie, Z.; Han, J.; Xu, J.; Guo, B. Synthesis and Properties of Biobased Multiblock Polyesters Containing Poly(2,5-furandimethylene succinate) and Poly(butylene succinate) Blocks. *Ind. Eng. Chem. Res.* **2017**, 56 (14), 3937–3946.

(183) Vijjamarr, S.; Streed, S.; Serum, E. M.; Sibi, M. P.; Du, G. Polymers from Bioderived Resources: Synthesis of Poly(silyl ether)s from Furan Derivatives Catalyzed by a Salen–Mn(V) Complex. *ACS Sustainable Chem. Eng.* **2018**, 6 (2), 2491–2497.

(184) Zhang, D.; Dumont, M.-J. Synthesis, characterization and potential applications of 5-hydroxymethylfurfural derivative based poly([small beta]-thioether esters) synthesized via thiol-Michael addition polymerization. *Polym. Chem.* **2018**, 9 (6), 743–756.

(185) Kieber, R. J.; Silver, S. A.; Kennemur, J. G. Stereochemical effects on the mechanical and viscoelastic properties of renewable polyurethanes derived from isohexides and hydroxymethylfurfural. *Polym. Chem.* **2017**, 8 (33), 4822–4829.

(186) Ding, J.; Rahman, O. u.; Wang, Q.; Peng, W.; Yu, H. Sustainable Graphene Suspensions: A Reactive Diluent for Epoxy Composite Valorization. *ACS Sustainable Chem. Eng.* **2017**, 5 (9), 7792–7799.

(187) Shen, X.; Liu, X.; Wang, J.; Dai, J.; Zhu, J. Synthesis of an Epoxy Monomer from Bio-Based 2,5-Furandimethanol and Its Toughening via Diels–Alder Reaction. *Ind. Eng. Chem. Res.* **2017**, 56 (30), 8508–8516.

(188) Hu, L.; Xu, J.; Zhou, S.; He, A.; Tang, X.; Lin, L.; Xu, J.; Zhao, Y. Catalytic Advances in the Production and Application of Biomass-Derived 2,5-Dihydroxymethylfuran. *ACS Catal.* **2018**, 8 (4), 2959–2980.

(189) Galkin, K.; Kucherov, F.; Markov, O.; Egorova, K.; Posvyatenko, A.; Ananikov, V. Facile Chemical Access to Biologically Active Norcantharidin Derivatives from Biomass. *Molecules* **2017**, 22 (12), 2210 DOI.

(190) Yen, A.; Choo, K.-L.; Yazdi, S. K.; Franke, P. T.; Webster, R.; Franzoni, I.; Loh, C. C. J.; Poblador-Bahamonde, A. I.; Lautens, M. Rhodium-Catalyzed Enantioselective Isomerization of meso-Oxabenzonorbornadienes to 1,2-Naphthalene Oxides. *Angew. Chem., Int. Ed.* **2017**, 56 (22), 6307–6311.

(191) Li, C.; Xu, G.; Liu, X.; Zhang, Y.; Fu, Y. Hydrogenation of Biomass-Derived Furfural to Tetrahydrofurfuryl Alcohol over Hydroxyapatite-Supported Pd Catalyst under Mild Conditions. *Ind. Eng. Chem. Res.* **2017**, 56 (31), 8843–8849.

(192) Xu, Y.; Jia, X.; Ma, J.; Gao, J.; Xia, F.; Li, X.; Xu, J. Efficient Synthesis of 2,5-Dicyanofuran from Biomass-Derived 2,5-Diformylfuran via an Oximation–Dehydration Strategy. *ACS Sustainable Chem. Eng.* **2018**, 6 (3), 2888–2892.

(193) Yan, D.; Xin, J.; Zhao, Q.; Gao, K.; Lu, X.; Wang, G.; Zhang, S. Fe-Zr-O catalyzed base-free aerobic oxidation of 5-HMF to 2,5-FDCA as a bio-based polyester monomer. *Catal. Sci. Technol.* **2018**, 8 (1), 164–175.

(194) Girka, Q.; Hausser, N.; Estrine, B.; Hoffmann, N.; Le Bras, J.; Marinkovic, S.; Muzart, J. [small beta]-Amino acid derived gemini surfactants from diformylfuran (DFF) with particularly low critical micelle concentration (CMC). *Green Chem.* **2017**, 19 (17), 4074–4079.

(195) Akocak, S.; Lolak, N.; Nocentini, A.; Karakoc, G.; Tufan, A.; Supuran, C. T. Synthesis and biological evaluation of novel aromatic and heterocyclic bis-sulfonamide Schiff bases as carbonic anhydrase I, II, VII and IX inhibitors. *Bioorg. Med. Chem.* **2017**, 25 (12), 3093–3097.

(196) Crockatt, M.; Urbanus, J. H. Aromatic compounds from furanics. WO2017146581A1, 2017.

(197) Civcir, P. Ü.; Kurtay, G.; Sarıkavak, K. Experimental and theoretical investigation of new furan and thiophene derivatives containing oxazole, isoxazole, or isothiazole subunits. *Struct. Chem.* **2017**, 28 (3), 773–790.

(198) Wang, Z.; Bae, E. J.; Han, Y. T. Synthesis and anti-inflammatory activities of novel dihydropyranoaurone derivatives. *Arch. Pharmacol. Res.* **2017**, 40 (6), 695–703.

(199) Cheng, F.; He, C.; Yu, S.; Yin, H. Highly selective SCN–fluorescent sensing by a Ru(II) complex containing functionalized polypyridine. *Inorg. Chim. Acta* **2017**, 462, 43–49.

(200) Mohamed, O. G.; Khalil, Z. G.; Capon, R. J. Prolinimines: N-Amino-l-Pro-methyl Ester (Hydrazine) Schiff Bases from a Fish Gastrointestinal Tract-Derived Fungus, *Trichoderma* sp. CMB-F563. *Org. Lett.* **2018**, 20 (2), 377–380.

(201) Chua, M. H.; Kim, T.; Lim, Z. L.; Gopalakrishna, T. Y.; Ni, Y.; Xu, J.; Kim, D.; Wu, J. BODIPY-Based Antiaromatic Macrocycles: Facile Synthesis by Knoevenagel Condensation and Unusual Aggregation-Enhanced Two-Photon Absorption Properties. *Chem. - Eur. J.* **2018**, 24 (9), 2232–2241.

(202) Werpy, T.; Petersen, G.; Aden, A.; Bozell, J.; Holladay, J.; White, J.; Manheim, A.; Eliot, D.; Lasure, L.; Jones, S. *Top Value Added Chemicals from Biomass. Vol. 1—Results of Screening for Potential Candidates from Sugars and Synthesis Gas*. Department of Energy: Washington, DC, USA, 2004.

(203) van Berkel, J. G. Process for enhancing the molecular weight of a polyester by solid state polymerization. WO2017043974A1, 2017.

(204) Dai, J.; Ma, S.; Teng, N.; Dai, X.; Shen, X.; Wang, S.; Liu, X.; Zhu, J. 2,5-Furandicarboxylic Acid- and Itaconic Acid-Derived Fully

Biobased Unsaturated Polyesters and Their Cross-Linked Networks. *Ind. Eng. Chem. Res.* **2017**, *56* (10), 2650–2657.

(205) Howard, S. J.; Stensrud, K. Oligomers of fdca and glycols from a one-pot esterification-transesterification process using water-tolerant metal triflate catalyst. WO2017091412A1, 2017.

(206) Hagberg, E.; Howard, S. J.; Stensrud, K. Oligomerizations of fdca and glycols in a one-pot esterification-transesterification process catalyzed by homogeneous organometallic lewis acids. WO2017091435A1, 2017.

(207) Marotta, A.; Ambrogi, V.; Cerruti, P.; Mija, A. Green approaches in the synthesis of furan-based diepoxy monomers. *RSC Adv.* **2018**, *8* (29), 16330–16335.

(208) Kucherov, F. A.; Gordeev, E. G.; Kashin, A. S.; Ananikov, V. P. Three-Dimensional Printing with Biomass-Derived PEF for Carbon-Neutral Manufacturing. *Angew. Chem., Int. Ed.* **2017**, *56* (50), 15931–15935.

(209) Metkar, P. S.; Ozer, R.; Sacia, E. R. Process for producing 2,5-furandicarboxylic acid dialkyl ester. WO2017019431A1, 2017.

(210) Cipot-Wechsler, J. H.; Metkar, P. S.; Ozer, R. Low pressure, high temperature process for forming 2,5-furandicarboxylic acid dialkyl ester. WO2017019444A1, 2017.

(211) Elliott, B. A.; Liao, K.-H.; Brandon Shiflett, M. Gas separation membrane using furan-based polymers. WO2017019435A1, 2017.

(212) Long, Y.; Zhang, R.; Huang, J.; Wang, J.; Jiang, Y.; Hu, G.-h.; Yang, J.; Zhu, J. Tensile Property Balanced and Gas Barrier Improved Poly(lactic acid) by Blending with Biobased Poly(butylene 2,5-furan dicarboxylate). *ACS Sustainable Chem. Eng.* **2017**, *5* (10), 9244–9253.

(213) Long, Y.; Zhang, R.; Huang, J.; Wang, J.; Zhang, J.; Rayand, N.; Hu, G.-h.; Yang, J.; Zhu, J. Retroreflection in binary bio-based PLA/PBF blends. *Polymer* **2017**, *125*, 138–143.

(214) Soares, M. J.; Dannecker, P.-K.; Vilela, C.; Bastos, J.; Meier, M. A. R.; Sousa, A. F. Poly(1,20-eicosanediyl 2,5-furandicarboxylate), a biodegradable polyester from renewable resources. *Eur. Polym. J.* **2017**, *90*, 301–311.

(215) Shen, Y.; Yao, B.; Yu, G.; Fu, Y.; Liu, F.; Li, Z. Facile preparation of bio-based polyesters from furandicarboxylic acid and long chain diols via asymmetric monomer strategy. *Green Chem.* **2017**, *19* (20), 4930–4938.

(216) Matos, M.; Sousa, A. F.; Silvestre, A. J. D. Improving the Thermal Properties of Poly(2,5-furandicarboxylate)s Using Cyclohexylene Moieties: A Comparative Study. *Macromol. Chem. Phys.* **2017**, *218* (5), 1600492.

(217) Lingier, S.; Spiesschaert, Y.; Dhanis, B.; De Wildeman, S.; Du Prez, F. E. Rigid Polyurethanes, Polyesters, and Polycarbonates from Renewable Ketal Monomers. *Macromolecules* **2017**, *50* (14), 5346–5352.

(218) Poulat, F.; Reutenauer, P. Pet polymer with an anti-crystallization comonomer that can be bio-sourced. WO2017098296A1, 2017.

(219) Konstantopoulou, M.; Terzopoulou, Z.; Nerantzaki, M.; Tsagkalias, J.; Achilias, D. S.; Bikiaris, D. N.; Exarhopoulos, S.; Papageorgiou, D. G.; Papageorgiou, G. Z. Poly(ethylene furanoate-co-ethylene terephthalate) biobased copolymers: Synthesis, thermal properties and cocrystallization behavior. *Eur. Polym. J.* **2017**, *89*, 349–366.

(220) Wang, J.; Liu, X.; Jia, Z.; Liu, Y.; Sun, L.; Zhu, J. Synthesis of bio-based poly(ethylene 2,5-furandicarboxylate) copolyesters: Higher glass transition temperature, better transparency, and good barrier properties. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55* (19), 3298–3307.

(221) Wang, G.; Jiang, M.; Zhang, Q.; Wang, R.; Tong, X.; Xue, S.; Zhou, G. Biobased copolyesters: Synthesis, sequence distribution, crystal structure, thermal and mechanical properties of poly(butylene sebacate-co-butylene furandicarboxylate). *Polym. Degrad. Stab.* **2017**, *143*, 1–8.

(222) Jia, Z.; Wang, J.; Sun, L.; Zhu, J.; Liu, X. Fully bio-based polyesters derived from 2,5-furandicarboxylic acid (2,5-FDCA) and dodecanedioic acid (DDCA): From semicrystalline thermoplastic to amorphous elastomer. *J. Appl. Polym. Sci.* **2018**, *135* (14), 46076.

(223) Cai, X.; Yang, X.; Zhang, H.; Wang, G. Aliphatic-aromatic poly(carbonate-co-ester)s containing biobased furan monomer: Synthesis and thermo-mechanical properties. *Polymer* **2018**, *134*, 63–70.

(224) Sousa, A. F.; Guigo, N.; Pozycka, M.; Delgado, M.; Soares, J.; Mendonca, P. V.; Coelho, J. F. J.; Sbirrazzuoli, N.; Silvestre, A. J. D. Tailored design of renewable copolymers based on poly(1,4-butylene 2,5-furandicarboxylate) and poly(ethylene glycol) with refined thermal properties. *Polym. Chem.* **2018**, *9* (6), 722–731.

(225) Wang, G.; Jiang, M.; Zhang, Q.; Wang, R.; Zhou, G. Biobased multiblock copolymers: Synthesis, properties and shape memory performance of poly(ethylene 2,5-furandicarboxylate)-b-poly(ethylene glycol). *Polym. Degrad. Stab.* **2017**, *144*, 121–127.

(226) Percec, S.; Bair, S. N. A solvent-free melt polycondensation process of making furan-based polyamides. WO2017106405A1, 2017.

(227) Cousin, T.; Galy, J.; Rousseau, A.; Dupuy, J. Synthesis and properties of polyamides from 2,5-furandicarboxylic acid. *J. Appl. Polym. Sci.* **2018**, *135* (8), 45901.

(228) Ma, K.; Chen, G.; Wang, W.; Zhang, A.; Zhong, Y.; Zhang, Y.; Fang, X. Partially bio-based aromatic polyimides derived from 2,5-furandicarboxylic acid with high thermal and mechanical properties. *J. Polym. Sci., Part A: Polym. Chem.* **2018**, *56* (10), 1058–1066.

(229) Martino, L.; Guigo, N.; van Berkel, J. G.; Sbirrazzuoli, N. Influence of organically modified montmorillonite and sepiolite clays on the physical properties of bio-based poly(ethylene 2,5-furandicarboxylate). *Composites, Part B* **2017**, *110*, 96–105.

(230) Miao, J.-T.; Yuan, L.; Guan, Q.; Liang, G.; Gu, A. Biobased Heat Resistant Epoxy Resin with Extremely High Biomass Content from 2,5-Furandicarboxylic Acid and Eugenol. *ACS Sustainable Chem. Eng.* **2017**, *5* (8), 7003–7011.

(231) Dreischarf, A. C.; Lammert, M.; Stock, N.; Reinsch, H. Green Synthesis of Zr-CAU-28: Structure and Properties of the First Zr-MOF Based on 2,5-Furandicarboxylic Acid. *Inorg. Chem.* **2017**, *56* (4), 2270–2277.

(232) Sapchenko, S. A.; Demakov, P. A.; Samsonenko, D. G.; Dybtsev, D. N.; Schröder, M.; Fedin, V. P. A Cryptand Metal–Organic Framework as a Platform for the Selective Uptake and Detection of Group I Metal Cations. *Chem. - Eur. J.* **2017**, *23* (10), 2286–2289.

(233) Du, X.; Fan, R.; Qiang, L.; Wang, P.; Song, Y.; Xing, K.; Zheng, X.; Yang, Y. Encapsulation and Sensitization of Ln³⁺ within Indium Metal–Organic Frameworks for Ratiometric Eu³⁺ Sensing and Linear Dependence of White-Light Emission. *Cryst. Growth Des.* **2017**, *17* (5), 2746–2756.

(234) Zhao, S.; Hao, X.-M.; Liu, J.-L.; Wu, L.-W.; Wang, H.; Wu, Y.-B.; Yang, D.; Guo, W.-L. Construction of Eu(III)- and Tb(III)-MOFs with photoluminescence for sensing small molecules based on furan-2,5-dicarboxylic acid. *J. Solid State Chem.* **2017**, *255*, 76–81.

(235) Gruter, G. J. M.; Van Der Waal, J. C.; Magnée, L. Process for the manufacture of an adipic acid product. WO2017061858A1, 2017.

(236) Chacón-Huete, F.; Mangel, D.; Ali, M.; Sudano, A.; Forgione, P. High-Value Biomass-Derived 2,5-Furandicarboxylic Acid Derivatives Obtained by a Double Decarboxylative Cross-Coupling. *ACS Sustainable Chem. Eng.* **2017**, *5* (8), 7071–7076.

(237) Serum, E. M.; Selvakumar, S.; Zimmermann, N.; Sibi, M. P. Valorization of 2,5-furandicarboxylic acid. Diels–Alder reactions with benzyne. *Green Chem.* **2018**, *20* (7), 1448–1454.

(238) Figure 9 shows analysis of the articles covered in the present review (starting from January 2017), Figure 10 shows the trends for other years as indicated.

(239) Ciriminna, R.; Pandarus, V.; Béland, F.; Pagliaro, M. Sol–gel Entrapped Nitroxyl Radicals: Catalysts of Broad Scope. *ChemCatChem* **2018**, DOI: 10.1002/cctc.201701910.

(240) Galkin, K. I.; Krivodaeva, E. A.; Romashov, L. V.; Zalesskiy, S. S.; Kachala, V. V.; Burykina, J. V.; Ananikov, V. P. Critical Influence of 5-Hydroxymethylfurfural Aging and Decomposition on the Utility of Biomass Conversion in Organic Synthesis. *Angew. Chem., Int. Ed.* **2016**, *55* (29), 8338–8342.

(241) Kashin, A. S.; Galkin, K. I.; Khokhlova, E. A.; Ananikov, V. P. Direct Observation of Self-Organized Water-Containing Structures in the Liquid Phase and Their Influence on 5-(Hydroxymethyl)furfural

Formation in Ionic Liquids. *Angew. Chem., Int. Ed.* **2016**, *55* (6), 2161–2166.

(242) Yoshida, S.; Hiraga, K.; Takehana, T.; Taniguchi, I.; Yamaji, H.; Maeda, Y.; Toyohara, K.; Miyamoto, K.; Kimura, Y.; Oda, K. A bacterium that degrades and assimilates poly(ethylene terephthalate). *Science* **2016**, *351* (6278), 1196–1199.