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Review

Diels–Alder Cycloadditions of Bio-Derived Furans with Maleimides as a Sustainable «Click» Approach towards Molecular, Macromolecular and Hybrid Systems

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Abstract: This mini-review highlights the recent research trends in designing organic or organic-inorganic hybrid molecular, biomolecular and macromolecular systems employing intermolecular Diels–Alder cycloadditions of biobased, furan-containing substrates and maleimide dienophiles. The furan/maleimide Diels–Alder reaction is a well-known process that may proceed with high efficiency under non-catalytic and solvent-free conditions. Due to the simplicity, 100% atom economy and biobased nature of many furanic substrates, this type of [4+2]-cycloaddition may be recognized as a sustainable "click" approach with high potential for application in many fields, such as fine organic synthesis, bioorganic chemistry, material sciences and smart polymers development.

Keywords: plant biomass; platform chemicals; biobased furans; maleimides; Diels–Alder reaction; dynamic systems; dynamers; covalent adaptable networks

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1. Introduction

Chemical modification of biomass-derived furanic platform chemicals furfural (FF) and 5-(hydroxymethyl)furfural (HMF) is a growing area of sustainable chemistry that is considered one of the general approaches for the replacement of traditional oil-based chemical production by biorefining based on renewable resources [1–5]. The major synthetic transformations of renewable furans are focused on the production of biofuels, chemicals and materials, in accordance with the sustainability concept [6–11]. Diels–Alder (DA) cycloaddition represents an important type of dynamic process that has found wide applications as a "click" reaction for the production of monomolecular products as well as for materials development [12–14]. The common mechanism of DA reactions includes the interaction of the highest occupied molecular orbital (HOMO) of the diene with the lowest unoccupied molecular orbital (LUMO) of dienophile, resulting in the formation of a new, six-membered ring. The relation between HOMO and LUMO energies determines the key characteristics of the DA reactions, such as regio- and diastereoselectivity, which strongly depend on the chemical structure of used substrates and reaction conditions [15]. The combination of diene and dienophile with opposite electronic characteristics is most favorable for DA reaction.

Electron-poor dienophiles (particularly maleimides) showed high activity in DA cycloadditions with many biobased furans. Some of these reactions proceed efficiently under solvent-free and non-catalytic conditions [16]. The DA reaction of a furanic diene and maleimide dienophile results in the formation of oxabicyclic core (oxanorbornene) as a single diastereomer or as a mixture of the kinetically favored *endo* form and the more thermodynamically stable *exo* product. The DA cycloadditions of donor-substituted furans with maleimides are thermodynamically favorable processes, while electron-poor furanic dienes display lower activity in these reactions [17,18].

The intermolecular furan/maleimide Diels–Alder (fmDA) reaction is an efficient approach for the formation of carbon–carbon bonds that was widely used for the construction of functional cyclic products with aliphatic or aromatic structures. On the other hand, the reversibility of fmDA cycloadditions that can be initiated by various stimuli (such as temperature, light, mechanical or magnetic force) is a prominent advantage when designing dynamic architectures. Due to its high efficiency, excellent selectivity, 100% atom economy and the biobased nature of most of the furanic substrates, the fmDA reaction may be considered as a sustainable «click» approach for the production of functional or dynamic molecular, biomolecular and macromolecular systems (Figure 1).

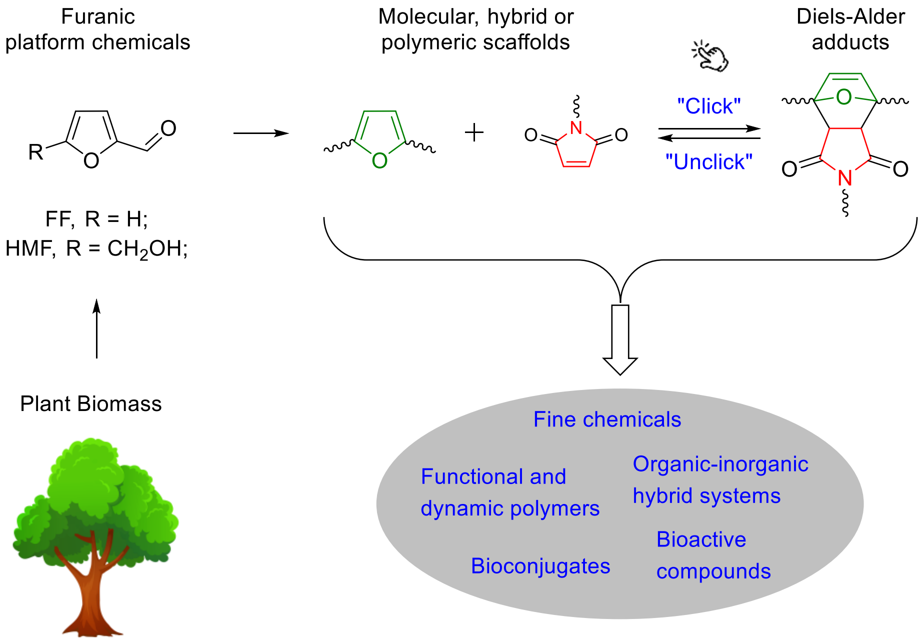


Figure 1. Intermolecular Diels–Alder cycloadditions of biobased furans with maleimides as a sustainable «click» approach towards practically important products.

Several recent reviews covered the scientific literature regarding the development of functional or dynamic macromolecular systems employing the fmDA approach [19–21]; other reviews provided detailed information about the reactivity of biobased furans in DA cycloadditions [16,22,23]; however, in the context of fmDA reactions, these coverages are not comprehensive or need updating. In this review, we briefly survey recent research trends in the application of the furan/maleimide-based «click» methodology for the production of functional or dynamic molecular, biomolecular and macromolecular systems. The information provided in this mini-review will be helpful to the scientists in many fields, including fine organic synthesis, medical and pharmaceutical research, polymers development and material sciences.

2. Application of fmDA "Click" Reaction for Synthesis of Functional Fine Chemicals

DA adducts of biobased monomeric furans and maleimide dienophiles have high synthetic potential as building blocks in fine organic synthesis. The general routes of applications include the synthesis of aliphatic or aromatic cyclic products, biologically active compounds, monomers and polyfunctional scaffolds. Reductions in the double bond in the furan-derived oxanorbornenes is a route to oxanorbornanes, structural analogs of the bioactive small molecules cantharidin (natural terpenoid isolated from Spanish fly blister beetles) and its synthetic analogs norcantharidin and norcantharimides, which also possesses strong biological activity (Figure 2) [24–29]. The introduction of a maleimide group instead of anhydride leads to an increase in the chemical stability of norcatharimides in comparison to cantharidines, but can lead to decreases in biological activity [30].

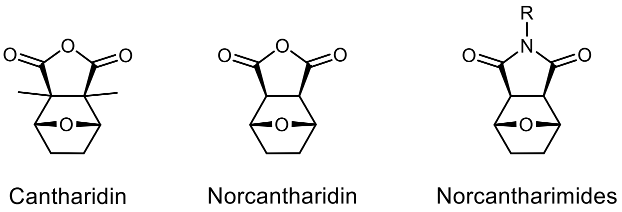
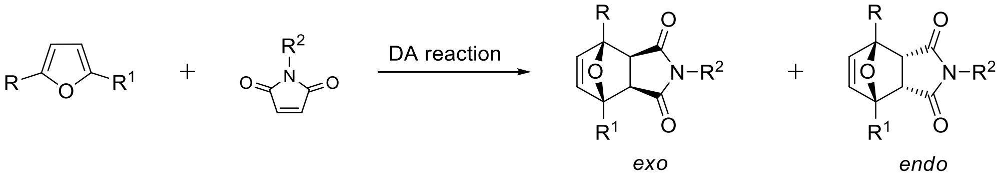


Figure 2. Chemical structures of cantharidin, norcantharidin and norcantharimides.

An important parameter of the fmDA reaction that should be taken into account in the development of bioactive compounds is diastereoselectivity, because *endo* and *exo* diastereomers can exhibit different biological activity [31]. The literature data on the diastereoselectivity of the DA reactions between the most common biobased furans and *N*-alkyl or *N*-aryl maleimides are summarized in Tables 1 and 2. Based on these data, some typical patterns for the furan/alkene DA reaction [16] were also found for DA reactions with maleimides as dienophiles.

Table 1. Results of the DA reactions of maleimide and *N*-alkyl maleimides with biobased furans (selected examples).



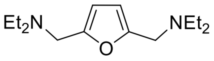
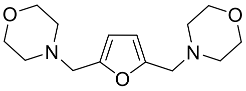
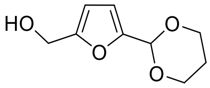
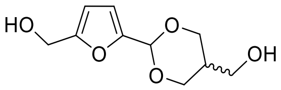
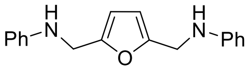
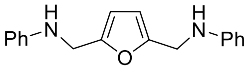
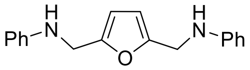
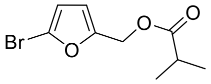
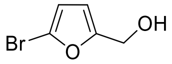
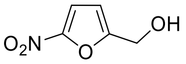
№	R^2	Furan	Conditions	*Endo*/*Exo* Ratio	Yield of DA Adducts (%), Citation
1	H	2-MF	Et_2O, RT, 3 days	N.d.	21 (*endo*), [32]
2	H	2-MF	THF, reflux, 4 h	0:100	94 [1], [33]
3	H	DMF	CH_3CN, 60 °C, overnight	1:4	N.d., [34]
4	H	BHMF	Ethyl acetate, 24 °C, 16 h	>99:1	83, [35]
5 [2]	H	BHMF	H_2O, 24 °C, 16 h	>99:1	75, [35]
6 [2]	H	BHMF diethyl ester	Ethyl acetate, 24 °C, 32 h	>99:1	62, [35]
7	H	BAMF	Ethyl acetate, 24 °C, 24 h	>97:3	42, [35]
8 [2]	H	BAMF	Ethyl acetate, 24 °C, 32 h	>97:3	76, [35]
9 [2]	H		Ethyl acetate, 24 °C, 32 h	N.d.	51, [35]
10 [2]	H		Ethyl acetate, 24 °C, 32 h	N.d.	42, [35]
11	H	HMF dioxolane acetal	THF, 50 °C, 3 days	4:1	64.1 [3], [36]
12	H		THF, 50 °C, 3 days	4:1	94.7 [3], [36]
13	H		THF, 50 °C, 3 days	5:1	95.2 [3], [36]
14	H		Et_2O, 24 °C	N.d.	35 (*endo*), [30]
15 [2]	H		THF, RT	N.d.	51 (*endo*), [30]
16	Me	2-MF	Toluene, 90 °C	0:100	92, [37]
17	Me	FA	Et_2O, 90 °C	21:79	43, [38]
18	Me	FA acetate	CH_2Cl_2, 23 °C	77:23	N.d., [39]
19	Me	FA allyl ester	Toluene, 50 °C, 24 h	N.d.	65 (*endo*), [40]
20	Me	FA *tert*-butyl ester	CH_2Cl_2, 23 °C	71:29	N.d., [39]
21	Me	Furfural dioxolane acetal	CH_2Cl_2, 23 °C	87:13	N.d., [39]

Table 1. *Cont.*

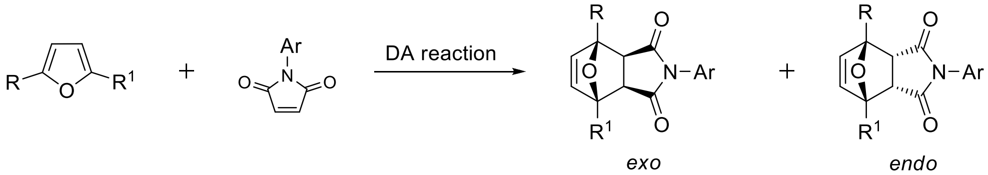
№	R^2	Furan	Conditions	*Endo*/*Exo* Ratio	Yield of DA Adducts (%), Citation
22	Me	R^1 = Me, R^2 = CH_2OAc	CH_2Cl_2, 23 °C	73:27	N.d., [39]
23	Et	2-MF	H_2O, 65 °C	1.4: 1	100, [41]
24	Et	DMF	H_2O, RT	3:2	100, [41]
25 [2]	Pr		THF, RT	4:1	66, [30]
26	Pr	FA *iso*-propyl ester	$CHCl_3$, 55 °C	60:40	N.d., [42]
27	Pr		$CHCl_3$, 55 °C	100:0	N.d., [42]
28	^{t}Bu	2-MF	H_2O, 65°C	0:100	100, [41]
29	^{t}Bu	DMF	H_2O, RT	1:8	100, [41]
30	^{t}Bu	FA *iso*-propyl ester	$CHCl_3$, 55 °C	51:49	N.d., [42]
31	Bn	FA	CH_3CN, 35 °C	70:30	75, [43]
32	Bn	FA *iso*-propyl ester	$CHCl_3$, 55 °C	44:56	N.d., [42]
33	Bn		CH_3CN, 70 °C	3:1	31 [4], [44]
34	Bn		CH_3CN, 70 °C, 16 h	N.d.	69 (*endo*), 21 (*exo*), [44]
35	2-Hydroxyethyl	FA	Benzene, reflux	0:100	86, [45]
36	2-Hydroxyethyl	DMF	CH_3CN, 65 °C	1:4	100, [46]
37	2-Carboxyethyl	2-MF	$CHCl_3$, 38 °C	28:72	100, [46]
38	2-Carboxyethyl	DMF	CH_2Cl_2, RT	78:22	100, [46]
39	2-Carboxyethyl	DMF	CH_3CN, 60 °C	22:78	100, [46]
40	3-Hydroxypropyl	FA	Toluene, 80 °C	30:70 [5]	77, [47]
41	Methoxy-2-propyl	FA acetate	CH_2Cl_2, 23 °C	76:24	N.d., [39]

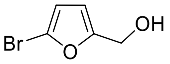
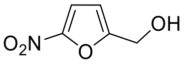
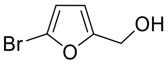
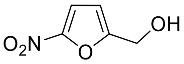
[1] Yield of crude product. [2] One-pot DA/hydrogenation on Pd/C. [3] Determined by NMR. [4] Was obtained as an inseparable mixture of the *endo* and *exo* (2:1) cycloadducts. [5] Slowly transformed to the pure *exo* isomer over a period of several months. N.d.—not determined.

A high *endo*-diastereoselectivity may be reached under kinetic control of the reaction, while *exo* products are more thermodynamically favorable [16,48]. The nature of the substituents at the furan ring and *N*-atom of maleimide have a significant influence on the efficiency and selectivity of cycloaddition. In some cases, HMF-derived furans showed higher *endo*-selectivity in DA reactions with maleimides than furfural-derived furans (Table 1, entries 4–8, 11–13). *N*-Aryl maleimides typically showed lower diastereoselectivity in cycloadditions with furans than *N*-alkyl maleimides. However, a high *exo*-diastereoselectivity for *N*-phenyl maleimide was reached by conduction of the DA reaction with FA under solvent-free conditions at high temperatures (Table 2, entry 5).

A high level of progress was recently achieved for DA reactions with low reactive acceptor-substituted furans by Bruijnincx and co-workers. They found a significant increase in the efficiency of the DA reaction of maleimides with furanic aldehydes, furoic acids and derivatives when water was used as a solvent (the results of these reactions are presented in Table 3) [17,18]. The impact of water on the efficiency of the DA reaction was multiple and depended on the nature of the furanic substrates and their physical properties. In the case of water-soluble substrates (such as furoic acids), this role can be attributed to the stabilization of the transition state and DA adduct by H-bonding with water [18]. A hydrophobic effect and hydrogen bonding with water molecules at the interface may play an activating role in DA reaction for water-insoluble furanic substrates [18]. Furanic aldehydes react with maleimides in water due to the possibility of hydration of the aldehyde group that stabilizes the cycloadducts [17]. DFT calculations showed that the formation of furanic aldehyde–maleimide adducts is possible if hydration occurs either prior to (which led to an increase in the rate of the DA reaction) or after the cyclization step (which led to a decrease in the rate of the retro-DA reaction) [17]. It should be noted that furanic derivatives containing electron-withdrawing substituents usually showed a high *exo*-diastereoselectivity in DA reactions with maleimides (Table 3).

Table 2. Results of the reactions of *N*-aryl maleimides with biobased furans (selected examples).

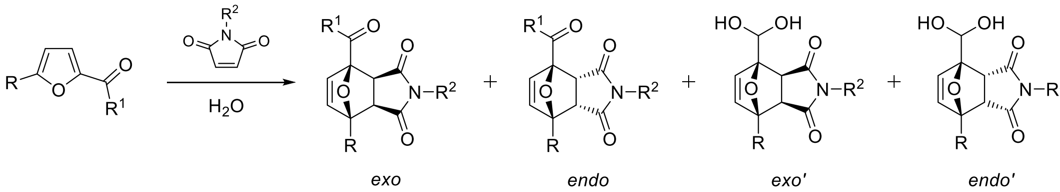


№	Ar	Furan	Conditions	*Endo*/*Exo* Ratio	Yield of DA Adducts (%), Citation
1	Ph	2-MF	H_2O, 65 °C	1.6:1	100, [41]
2	Ph	2-MF	4:1 toluene/benzene, RT, 1.1 GPa	1.66:1	85, [49]
3	Ph	2-MF	$CDCl_3$, 60 °C	*Exo* with traces of *endo*	90, [50]
4	Ph	2-MF	Hexane or heptane, TFA, glass beads, 80 °C, 5–8 days [1]	(−)-*Exo*, 86–90 *ee*	80, [50]
5	Ph	FA	Neat, 140 °C, 8 min	*Exo*	82, [51]
6	Ph	FA	RT, 12 h	71:29	66, [51]
7	Ph	FA allyl ester	Toluene, 50 °C, 24 h	N.d.	26 (*exo*), [40]
8	Ph	FA acetate	CH_2Cl_2, 23 °C	65:35	N.d., [39]
9	Ph	FA vinyl ester	Et_2O, 22–24 °C	1:2.8	47, [52]
10	Ph	FA vinyl ester	Toluene, 80 °C	4:1	66, [52]
11	Ph	DMF	H_2O, RT	1.3:1	100, [41]
12	*p*-Tolyl	DMF	toluene, 60 °C, 3 h	*Exo*	50, [53]
13	*p*-Tolyl	DMF	Neat, 94 °C, 1 h	*Exo*	60, [54]
14	*m*-Tolyl	FA *iso*-butyl ester	$CHCl_3$, 55 °C	67:33	N.d., [42]
15	PhF_5	2-MF	Neat, reflux	*Exo*	50, [55]
16	4-Hydroxyphenyl	FA	Acetone, 55 °C	*Exo*	71, [56]
17	4-Hydroxyphenyl	FA	CH_3CN, 35 °C	80:20	N.d., [56]
18	*p*-Methoxyphenyl	FA	CH_3CN, 35 °C, 18 h	N.d.	>85 (*endo*), [44]
19	*p*-Methoxyphenyl	FA acetate	CH_2Cl_2, 23 °C	67:33	N.d., [39]
20	*p*-Methoxyphenyl	DMF	Neat, 94 °C, 1 h	17:83	25, [54]
21	*p*-Methoxyphenyl		CH_3CN, 75 °C,	N.d.	61 (*endo*), <5 (*exo*) [44]
22	*p*-Methoxyphenyl		CH_3CN, 75 °C, 8 h	N.d.	<5 (*endo*), 63 (*exo*) [44]
23	*p*-Chlorophenyl	DMF	Neat, 94 °C, 1 h	6:94	46, [54]
24	*m*-Nitrophenyl	DMF	Neat, 94 °C, 1 h	5:95	14, [54]
25	*p*-Nitrophenyl	FA	CH_3CN, 40 °C	70:23	52, [44]
26	*p*-Nitrophenyl	FA acetate	CH_2Cl_2, 23 °C	55:45	N.d., [39]
27	*p*-Nitrophenyl		CH_3CN, 50 °C, 72 h	N.d.	26 (*endo*), <5 (*exo*), [44]
28	*p*-Nitrophenyl		CH_3CN, 80 °C	N.d.	<5 (*endo*), 31 (*exo*) [44]
29	BMI as dienophile	FA	Toluene, 75–80 °C, two days	Mostly *exo*	92, [57]
30	BMI as dienophile	FA *iso*-propyl ester	$CHCl_3$, 55 °C	19:81	N.d., [42]

[1] Reaction was conducted under dynamic enantiomeric crystallization conditions. BMI—4,4′-bis(maleimido)diphenylmethane. N.d.—not determined.

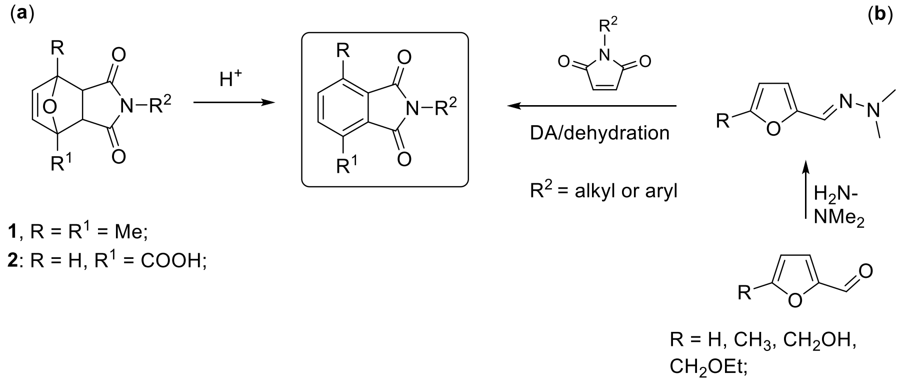
Acid- or base-catalyzed dehydration of the furan-derived oxanorbornenes is an important approach to access a renewable aromatics [15,22,23]. In the case of furan–maleimide-derived oxanorbornenes, this reaction led to the formation of renewable phtalimides (Scheme 1). The few examples of this reaction are presented in the scientific literature involving oxanorbornenes obtained from DMF [53] or furoic acid [18]. However, in the case of FF- or HMF-derived dimethyl hydrazones reacting with maleimides, aromatization proceed without any catalysts via spontaneous ring-opening/aromatization process (Scheme 1b) [58] and led to adducts in a high yields using green solvents such as water [59] or ionic liquids [60].

Table 3. The results of water-mediated DA cycloadditions of acceptor-substituted furans with maleimides.



№	Furanic Substrate	R^2	Conditions	Conversion [1]/ Isolated Yield	Selectivity [1]
1	R = R^1 = H	H	H_2O, 60 °C, 16 h	38 [2]	*endo*/*exo* 8:30, *endo′*/*exo′* 0:0
2	R = R^1 = H	Me	H_2O, 60 °C, 16 h	63 [2]	*endo*/*exo* 18:40, *endo′*/*exo′* 1:3
3	R = R^1 = H	Et	H_2O, 60 °C, 16 h	43 [2]	*endo*/*exo* 8:28, *endo′*/*exo′* 1:6
4	R = R^1 = H	^{n}Pr	H_2O, 60 °C, 16 h	20 [2]	*endo*/*exo* 1:7, *endo′*/*exo′* 1:11
5	R = R^1 = H	Ph	H_2O, 60 °C, 16 h	7 [2]	*endo*/*exo* 0:1, *endo′*/*exo′* 1:5
6	R = Me, R^1 = H	Me	H_2O, 60 °C, 16 h	14 [2]	*endo*/*exo* 3:8, *endo′*/*exo′* 0:3
7	R = CH_2OH, R^1 = H	Me	H_2O, 60 °C, 16 h	50 [2]	*endo*/*exo* 37:13, *endo′*/*exo′* 0:0
8	R = CH_2OMe, R^1 = H	Me	H_2O, 60 °C, 16 h	18 [2]	*endo*/*exo* 7:5, *endo′*/*exo′* 3:3
9	R = H, R^1 = CH_3	Me	H_2O, 60 °C, 16 h	32/32	*endo*/*exo* trace:32
10	R = H, R^1 = OH	H	NaOH, H_2O, 50 °C, 16 h	95/68	*endo*/*exo* trace:95
11	R = H, R^1 = OH	Me	NaOH, H_2O, 50 °C, 16 h	98/92	*endo*/*exo* 1:97
12	R = H, R^1 = OH	^{n}Pr	NaOH, H_2O, 50 °C, 16 h	96/72	*endo*/*exo* 3:93
13	R = H, R^1 = OH	Ph	NaOH, H_2O, 50 °C, 16 h	51/21	*endo*/*exo* trace:51
14	R = H, R^1 = OH	Cy	NaOH, H_2O-MeOH, 50 °C, 16 h	56/31	*endo*/*exo* 3:53
15	R = H, R^1 = OMe	H	H_2O, 50 °C, 16 h	67/43	*endo*/*exo* 2:65
16	R = H, R^1 = OMe	Me	H_2O, 50 °C, 16 h	70/52	*endo*/*exo* 5:65
17	R = H, R^1 = OMe	Et	H_2O, 50 °C, 16 h	65/47	*endo*/*exo* 4:61
18	R = H, R^1 = OEt	Me	H_2O, 50 °C, 16 h	63/29	*endo*/*exo* 4:59
19	R = H, R^1 = O^{i}Pr	Me	H_2O, 50 °C, 16 h	54/26	*endo*/*exo* 4:50
20	R = H, R^1 = O^{t}Bu	Me	H_2O, 50 °C, 16 h	54/25	*endo*/*exo* 3:51
21	R = H, R^1 = NH_2	Me	H_2O, 50 °C, 16 h	94/77	*endo*/*exo* 3:91
22	R = H, R^1 = NMe_2	Me	H_2O, 50 °C, 16 h	81/41	*endo*/*exo* 4:77
23	R = H, R^1 = NHOH	Me	H_2O, 50 °C, 16 h	92/69	*endo*/*exo* 16:76
24	R = Me, R^1 = OH	Me	NaOH, H_2O, 50 °C, 16 h	93/75	*endo*/*exo* 5:88
25	R = CH_2OH, R^1 = OH	Me	NaOH, H_2O, 50 °C, 16 h	91/51 [3]	*endo*/*exo* 19:72
26	R = CH_2OH, R^1 = OH	Ph	NaOH, H_2O, 50 °C, 16 h	28/11	*endo*/*exo* trace:28
27 [4]	R = CHO, R^1 = OH	Me	NaOH, H_2O, 50 °C, 16 h	<10/N.d.	*endo*/*exo* trace:~5
28 [4]	R = COOH, R^1 = OH	Me	NaOH, H_2O, 50 °C, 16 h	20/N.d.	*endo*/*exo* 0:20
29 [4]	R = COOH, R^1 = OH	Me	NaOH, H_2O, 50 °C, 16 h	56/N.d.	*endo*/*exo* 0:56

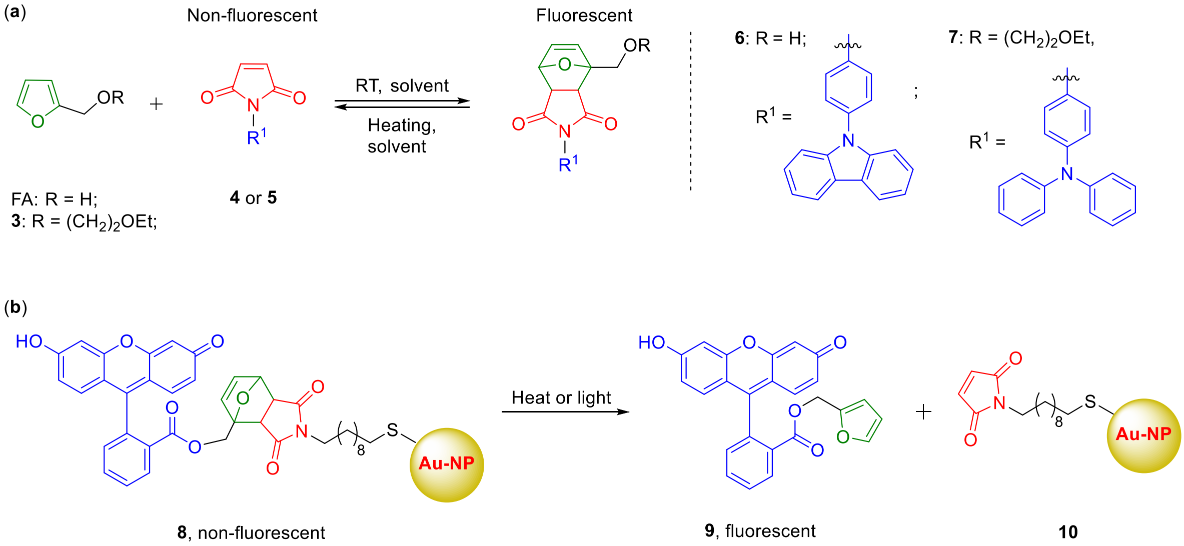
[1] Determined by NMR. [2] Products were not isolated. [3] After hydrogenation on Pd/C. [4] Extensive hydrolysis of *N*-substituted maleimide to maleic acid. N.d.—not determined. Data for entries 1–9 were obtained from reference [17]. Data for other entries were obtained from reference [18].



Scheme 1. (**a**) Synthesis of renewable phtalimides by dehydration of oxanorbornenes. Reaction conditions: *N*-(*p*-tolyl)-maleimide, *p*-TsOH, toluene, 80 °C, 16 h, 100% yield for dehydration of oxanorbornene **1**; *N*-Me-maleimide, HBr in AcOH, RT to 60 °C, 66% yield for dehydration of oxanorbornene **2**. (**b**) General scheme for the synthesis of renewable phtalimides starting from FF- or HMF-derived dimethyl hydrazones by spontaneous DA/dehydration reactions.

3. Application of a fmDA "Click" Approach for the Development of Dynamic Molecular, Biomolecular and Organic-Inorganic Hybrid Systems

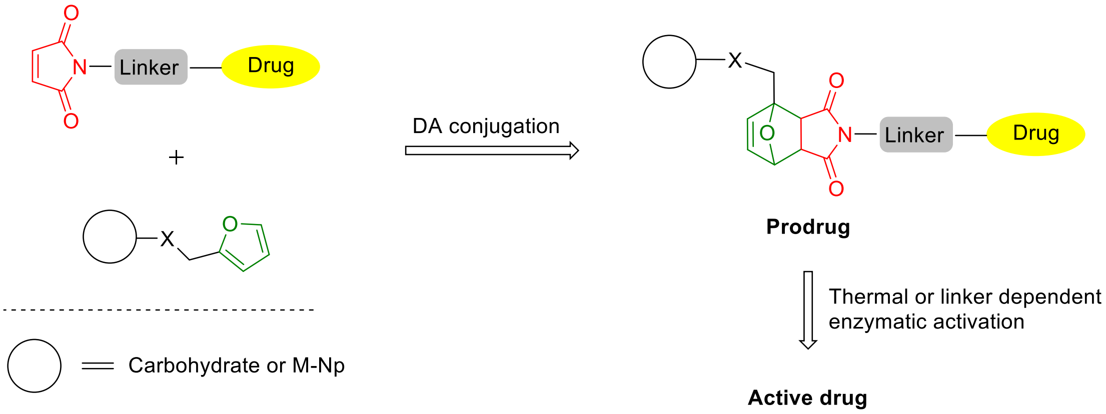
The reversibility of the fmDA cycloadditions used to link diverse chemical, biochemical and inorganic scaffolds was widely applied in the design of dynamic molecular, biomolecular and organic–inorganic hybrid architectures. The DA reaction of an FA or FA ester **3** with maleimides containing aromatic amine groups led to cycloadducts **6** or **7, **which exhibit fluorescent behavior and decompose back into non-fluorescent furan and maleimide upon heating (Scheme 2a) [61,62]. Thus, DA cyclization promotes fluorescence in these systems, and thermally induced rDA reaction quenches it. Cycloadduct **7** displays amphiphilic properties due to the presence of hydrophobic maleimide moiety and hydrophilic oxanorbornene fragment [62].



Scheme 2. Dynamic molecular (**a**) and hybrid (**b**) light-emitting dye systems based on fmDA cycloaddition. The dye fragment is highlighted by blue color in a molecular structure.

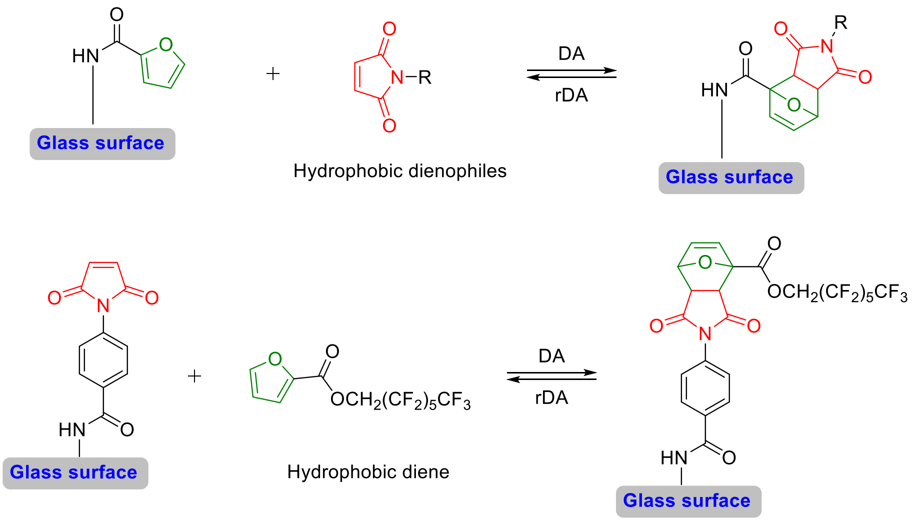
If the fluorescent molecule remains close to the surface of the aurum nanoparticles (Au-NPs), the fluorescence emission from the dye molecule is efficiently quenched by Au-NPs [63]. The photothermal rDA reaction of non-fluorescent conjugate **8** led to the release of dye **9** from the nanoparticle surface, providing fluorescence that was turned "On" (Scheme 2b) [63]. The use of one diastereomer was advantageous for this dynamic photothermally induced dye-emission system. Isomer **8**-*endo* decomposed in 63% yield after 5 h compared to 45% after 8 h for its *exo* counterpart. Monomolecular or hybrid dynamic light-emitting systems have high potential in sensor applications or molecular imaging.

An important application of fmDA "click" methodology is designing organic or hybrid conjugate systems for drug-delivery purposes [64]. The targeted delivery of bioactive molecule can be carried out using fmDA conjugation of functionalized drug with biocompatible support such as carbohydrate [65–67] or metal nanoparticles [68,69] (Scheme 3). The controllable release of drugs in vitro can be realized by the introduction of enzymatically active linkers. Some conjugates of Doxorubicin with furan-containing oligosaccharides (glyco-prodrugs) were synthesized by DA conjugation with maleimide-functionalized Doxorubicin containing enzymatically cleavable linkers [67]. In vitro experiments demonstrated an efficient, controllable release of the cytotoxic Doxorubicin-containing molecule from glyco-prodrug upon enzymatic cleavage. An alternative approach to drug release is thermally induced rDA cleavage, which has been efficiently demonstrated for hybrid systems containing drug and magnetically active NPs [68].



Scheme 3. Design of drug-delivery systems using fmDA "click" conjugation. M-Np—metal nanoparticle.

Thermo-responsive non-wetting surfaces were prepared using the fmDA reaction of hydrophobic maleimides or polyfluorinated furan with DA counterparts attached to a glass slides and capillaries (Scheme 4) [70]. However, attempts to demonstrate a self-purging capillary were unsuccessful due to the incomplete surface functionalization or surface rearrangement. As suggested by the authors, residual functional groups such as amines, amides, esters or ethers were most likely involved in H-bonding, resulting in a residual H2O layer that inhibits the self-purging phenomenon [70].



Scheme 4. Synthesis of thermo-responsive non-wetting glass surfaces by fmDA "click" approach used in work [70].

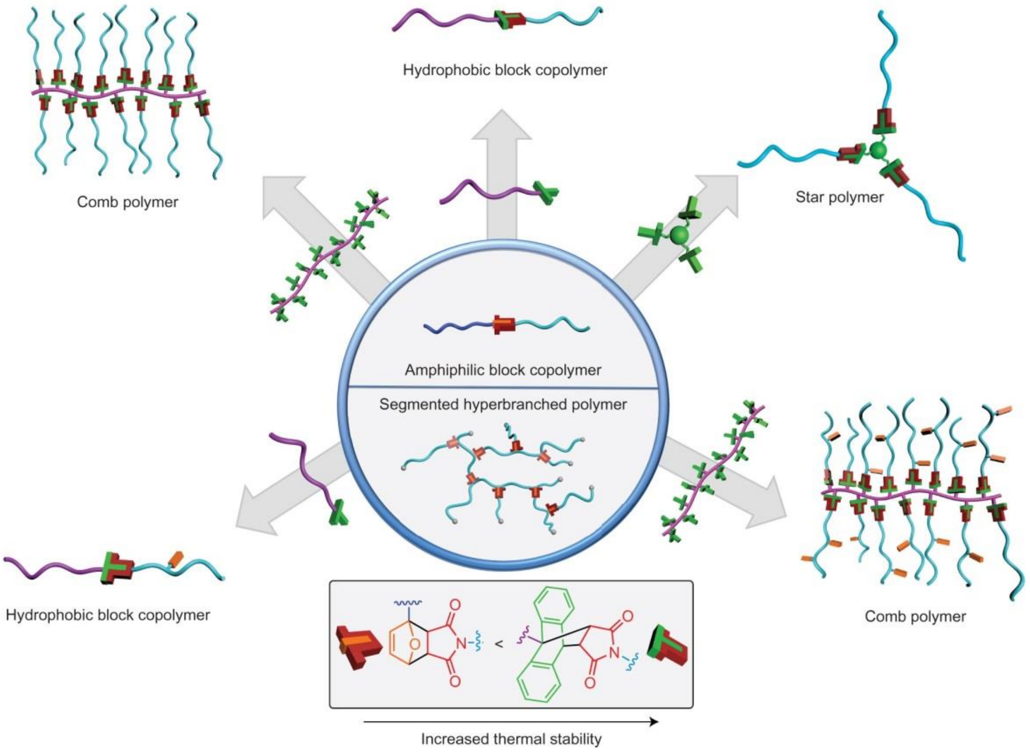
4. Application of fmDA Cycloaddition for the Preparation of Functional or Dynamic Polymers

Some oxanorbornenes, obtained by the DA reaction of C2-alkyl furans with maleimides, showed high reactivity in Ru-catalyzed ring-opening metathesis polymerization (ROMP) [37,38,71]. It is important to note that *endo* end *exo* oxanorbornenes can exhibit different reactivity in ROMP. For example, *exo* oxanorbornene, formed from 2-alkyl furans and *N*-methyl maleimide, underwent efficient homo-polymerization in the presence of G3 catalyst, while the *endo* isomer could not be polymerized [72].

The combination of several types of dienic structures with different reactivities in DA reactions with maleimides could provide sequence-controlled polymerization and self-assembly. Sun and co-workers described the topological transformations of a linear amphiphilic fmDA block co-polymer or a segmented hyperbranched polymer into various macromolecular architectures via the diene (furan or anthracene) displacement reaction (Scheme 5) [73]. Han et al. reported a one-shot, sequence-controlled copolymerization of styrene with several maleimides using differences in the temperature of rDA deprotection in corresponding *endo* and *exo* fmDA adducts [74].

The reversibility of the fmDA reaction allows for dynamic polymers (dynamers) characterized by interesting properties such as self-healing or shape memory effects. The low activity of acceptor-substituted furans in the fmDA reaction explains its low applicability in the development of fmDA-based dynamic materials. Dynamic polymers containing furanic ester [75,76] amide [77] or oxime [78] functionalities showed only moderate self-healing efficiency. *Endo*/*exo* isomerism is a major concern in the development of dynamers because the low diastereoselectivity of fmDA polymerization or cross-linking may influence the physical properties of resulting dynamers [42,79].

The broad investigations describing the synthesis of various dynamic polymeric materials and composites using DA reactions (such as structural materials, supramolecular systems, hydrogels, coatings with tunable adhesion), which have promising potential for biomedical applications or smart materials development, were highlighted in some recent reviews [80–83]. Dynamers with many different structural types can be synthesized using the fmDA approach depending on the structure and ratio of the initial components. The application of furan- and maleimide-functionalized bifunctional monomers or end-capped linear pre-polymers provides the formation of linear dynamic polymers and co-polymers, while the incorporation of three or more furanic or maleimide functionalities into the structure of monomers leads to the formation of branched, hyperbranched or cross-linked architectures [20,81]. Several types of dendritic compound were also prepared using the fmDA approach [20,84].



Scheme 5. Example of macromolecular sequence-controlled metamorphosis via diene (furan or anthracene) displacement reactions [73] (reproduced from ref. [73] with permission from Nature Publishing Group, copyright 2017).

Below, we have covered the general approaches to the preparation of dynamers using the fmDA "click" methodology. The selection predominantly includes representative examples and most recent investigations dedicated to the synthesis of linear and three-dimensional polymeric structures.

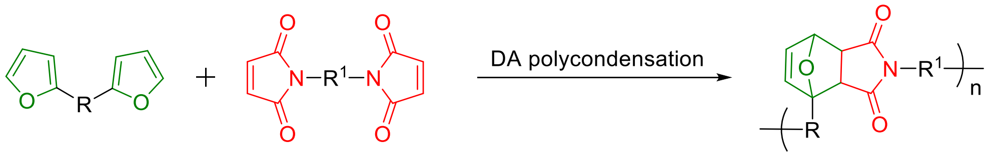
4.1. Synthesis of Dynamic Linear Polymers Using the fmDA "Click" Reaction

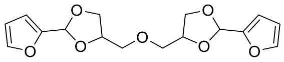
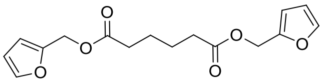
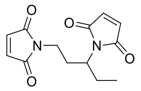
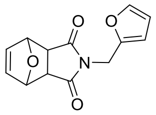
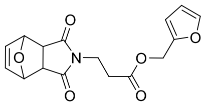
Polycondensation by fmDA reaction using bifunctional linear monomers (bis-furans and bis-maleimides) or polymerization of maleimide-substituted furans was applied in the development of various linear dynamers [85–88], including polymers with switchable optical properties [89,90] or magnetically active conjugates [91]. A significant limitation of this approach is the low degrees of polymerization by fmDA reaction (Table 4). Other approaches that may be used for the synthesis of high-molecular-weight linear polymers include the DA polymerization of linear oligomers or pre-polymers end-capped with the furan- or maleimide functional groups [92–95], or co-polymerization of bifunctional fmDA adducts [96].

4.2. Synthesis of Cross-Linked Dynamers Using the fmDA "Click" Reaction

The synthesis of dynamic cross-linked polymers, the so-called covalent adaptable networks (CANs), has been paid significant attention in recent years due to the relatively low decoupling energy provided through the retro-DA reaction, providing the possibility of the easy thermal reprocessing and chemical recycling of CANs compared to traditional covalently crosslinked thermosets [82]. Several approaches were used for the synthesis of CANs using fmDA reaction. The synthesis of highly reprocessable cross-linked polymers may be carried out using monomolecular substrates containing three or more furanic and/or maleimide functional groups [99–101]. Depending on the structure and ratio of the monomers, polycondensation by fmDA reaction can lead to branched or cross-linked polymers [102]. One of the most studied types of CANs is dynamic thermoset polymers containing classical non-dynamic covalent polymers cross-linked by dynamic oxanorbornene groups. Two general pathways used for the preparation of such polymers include the cross-linking of functionalized pre-polymers (Scheme 6a,b) or polycondensation of bifunctional fmDA adducts (Scheme 6c).

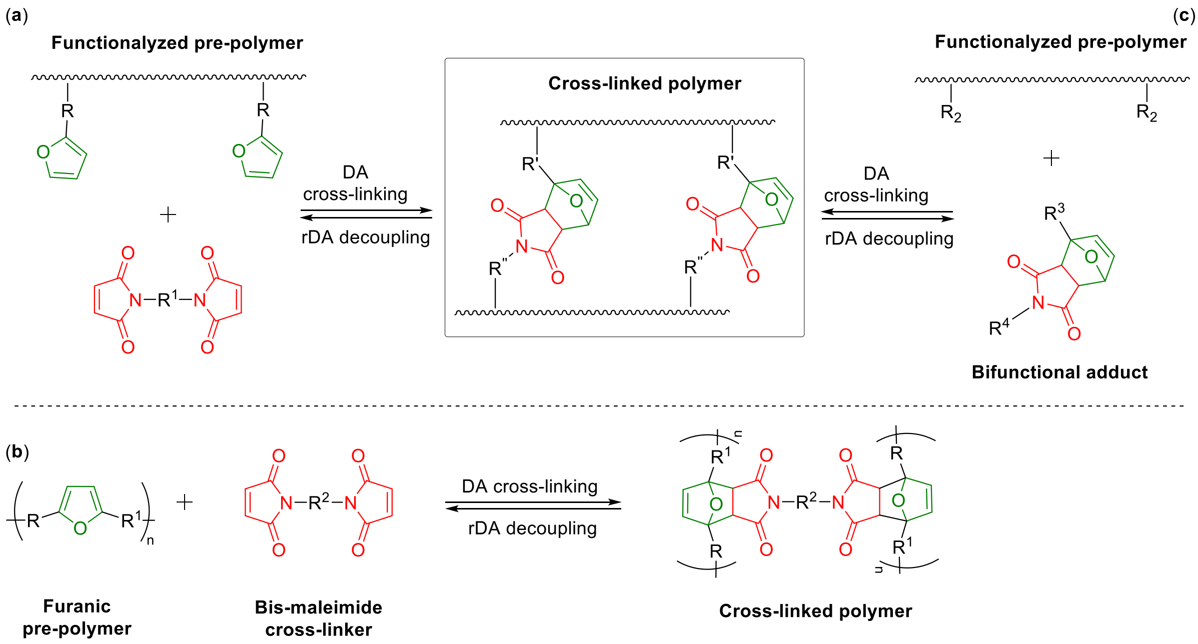
Table 4. Synthesis of linear polymers using the fmDA polycondensation.



№	Furan	Maleimide	Conditions	Mn (g mol^{-1})	PDI	rDA (°C) [1]	Citation
1	R = CH_2	$R^1 = (CH_2)_3$	THF, reflux, 24 h	3650	2.45	100–122	[85]
2	R = CH_2-O-CH_2	$R^1 = (CH_2)_3$	THF, reflux, 24 h	4540	2.31	140–161	[85]
3	R = CH_2-S-CH_2	$R^1 = (CH_2)_3$	THF, reflux, 24 h	5660	1.72	118–130	[85]
4	R = CH_2-NH-CH_2	$R^1 = (CH_2)_3$	THF, reflux, 24 h	2920	2.76	123–140	[85]
5	R = CH_2-O-$(CH_2)_{10}$-O-CH_2	BMI	1,2-dichloroethane, 60 °C	2900–7800	1.66–2.86	110–150	[95]
6	R = CH_2-(O-$(CH_2$-$CH_2)_3$-O-CH_2	BMI	1,2-dichloroethane, 60 °C	18,000–38,000	3.5–5.81	110	[95]
7		BMI	$CHCl_3$, 60 °C, 48 h	2200	2.45	140–170	[88]
8		$(CH_2)_6$	$CHCl_3$, 55 °C, 48 h	5920	1.5	~124	[42]
9			$CHCl_3$, 55 °C, 48 h	3700	1.43	~124	[42]
10		BMI	$CHCl_3$, 55 °C, 48 h	1900	1.37	~124	[42]
11		-	TCE, 110 °C, 5 h, then 60 °C, 72 h	~1800	N.d.	150	[97]
12		-	TCE, 110 °C, 24 h, then 65 °C, 72 h	1900	2.2	N.d.	[98]

[1] Was determined by GS, DSC, TGA or NMR. TCE—1,1,2,2-tetrachloroethane. N.d.—not determined.

The preparation of dynamers by cross-linking functionalized pre-polymers using the fmDA "click" reaction usually contains several steps: synthesis of pre-polymer and cross-linker (monomolecular or polymeric), functionalization or the end-capping of pre-polymer by a furanic or maleimide groups and thermally induced cross-linking. Synthesis of the functionalized pre-polymers may be carried out by co-polymerization with a furan- or maleimide containing monomers. These approaches were widely used in recent investigations for the preparation of cross-linked polyurethanes [103], polyacrylates [42,104,105] (including photoactive polymers [106,107]), cross-linked polysaccharides [108], and other types of CANs. Linear polymers containing C2,C5-disubstituted furans as repeated units also can undergo cross-linking with bis-maleimides [109–113]. Although disubstituted furans might have a lower reactivity for the fmDA reaction than monosubstituted FF-derived analogs, the presence of additional functionality at the furan ring provides additional opportunities for the synthesis of cross-linked CANs using HMF-derived monomers. Thus, Chang and co-workers reported the preparation of self-remendable polyurethane by cross-linking the linear fmDA bridged pre-polymer (obtained by the reaction of a difuran containing hydroxymethyl groups at the furan rings with BMI) with bis-isocyanate [114].



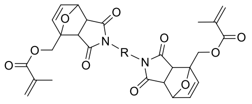
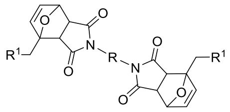
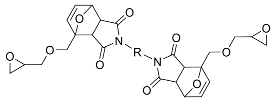
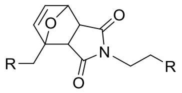
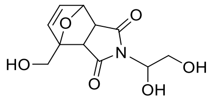
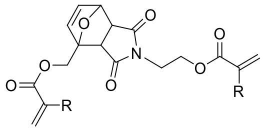
Scheme 6. General approaches to the synthesis of CANs using fmDA "click" approach: cross-linking of pre-polymers with bis-maleimides (**a**,**b**) or with bifunctional fmDA adducts (**c**).

An alternative strategy for the synthesis of CANs with a high degree of cross-linking is the application of bifunctional fmDA adducts for the synthesis of linear or cross-linked pre-polymers [115–117], or as co-monomers [47,104,118]. Recently reported representative examples of the bifunctional adducts and types of obtained CANs are presented in Table 5. Depending on the nature of functional groups involved in adducts, various common dynamers were obtained, including polyacrylates, polyurethanes, epoxy resins and silicones.

The relatively high temperature of polymerization and cross-linking and the low gap between coupling and decoupling temperatures (typically, coupling begins at 50–60 °C and decoupling at 100–120 °C) are significant limitations in the practical application of dynamic polymers based on fmDA reaction. A possible means of overcoming these limitations is the combination of slowly exchanging covalent dynamic DA bonds with weakly supramolecular cross-links, such as Van-der-Waals interactions or H-bonding. The presence of H-bonding in polymeric molecules reduces the temperature of rDA decoupling, used for the development of room-temperature-remendable materials. In these materials, supramolecular cross-links provided partial healing at room temperature and showed an almost complete recovery at elevated temperatures [104,105,119,120].

Besides thermal initiation, rDA reaction in CANs can be driven by other stimuli, such as light [107], mechanical [138] or magnetic force [139]. Light-responsive CANs based on a photocontrolled DA reaction could be obtained by the introduction of the fluorescent fragment into diene or dienophile [107,140,141]. Mechanochemical activation originating in the overlap of dynamic bonds in furan-derived oxanorbornene fragment with the force vector was used in the development of smart force-responsive materials and devices [142–146]. A comparison of the rate of coupling for some fmDA adducts has shown that the efficiency of thermal and mechanical activation is not equal and depends on the regio- and stereo structure of the adducts: some diastereomers can be mechano-resistant due to misalignment of the dynamic DA bonds with the force vector providing ineffective mechanochemical interactions [147].

Table 5. Examples of the bifunctional fmDA adducts and types of prepared CANs.

№	Type of Bifunctional Adduct	R, R^1	Type of Prepared CAN, Citation
1		BMI as a precursor	Polyacrylates [121]
2		BMI as a precursor, R^1 = OH	Polyurethanes [122,123]
3		BMI as a precursor, $R^1 = NH_2$	Epoxy resins [124]
4		$R = (CH_2)_8$, $R^1 = NH_2$	Epoxy resin [125]
5		$R = (CH_2)_6$	Epoxy thermosets [126]
6		BMI as a precursor	Polysiloxanes [66]
7		R = OH	Polyurethanes [116,127–130], dendrimers [131]
8		$R = NH_2$	Epoxy resins [132,133]
9		-	Polyurethanes [24,25]
10		R = H	Polyacrylates [45,134–136]
11		R = Me	Polyacrylates [137]

5. Conclusions

The recent trend towards sustainable development provided an increased number of research articles related to the application of bioderived substrates as sources to practically important products. The fmDA "click" cycloadditions involving biobased substrates is a valuable approach used for the production of various smart systems, with high potential in many fields, including fine organic synthesis, biochemistry, or materials development. The easy functionalization of many different types of substrates by furan and maleimide moieties, and the ability to fine-tune the reaction parameters of furan/maleimide DA and rDA reactions, provides wide opportunities for the creation of monomolecular, polymeric or hybrid architectures combining the properties of both clickable scaffolds. Thus, fmDA conjugation of lipophilic and hydrophilic components could lead to the formation of amphiphilic systems.

The increased number of publications and emergence of the novel fmDA "click" methodologies indicate the rapid progress in these fields. However, many important areas, including the development of room-temperature self-remendable polymers, application of acceptor-substituted furans for the synthesis of fine chemicals and materials, need further study. Moreover, new, industrially relevant technologies towards the production of biobased smart molecular systems, materials and devices based on fmDA "click" approach are required.

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Abbreviations

2-MF	2-methylfuran
BAMF	2,5-bis(acetoxymethyl)furan
BHMF	2,5-bis(hydroxymethyl)furan
BMI	4,4′-bis(maleimido)diphenylmethane
Bn	benzyl
CAN	covalent adapfigure network
DA	Diels–Alder
DFT	density functional theory
DMF	2,5-dimethylfuran
FA	furfuryl alcohol
FF	furfural
fmDA	furan/maleimide Diels–Alder
HMF	5-(hydroxymethyl)furfural
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
N.d.	not determined
NMR	nuclear magnetic resonance
NP	nanoparticle
PDI	polydispersity index
rDA	retro-Diels–Alder
ROMP	ring-opening metathesis polymerization
RT	room temperature
TFA	trifluoroacetic acid
THF	tetrahydrofuran
Ts	tosyl

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