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Synthesis of Dendrimers Containing 1,3,4-Oxadiazoles

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Introduction

Polymers[1,2] containing 1,3,4-oxadiazoles are accessible by several preparative methods and are known[3−6] to be useful as electron transporting layers in organic light emitting diodes (LEDs). Charge transport through thin layers of these materials occurs via a so-called hopping mechanism. Because of their highly branched structures, dendritic molecules can be even more advantageous as the electrons have an enhanced probability to find an energetically favored pathway to hop from one to another.

The usual way to prepare 2,5-diaryl-1,3,4-oxadiazoles starts from an aroyl hydrazide **5**. After the introduction of a second aroyl group, the resulting 1,2-bis(aroyl)-hydrazide **6** can be cyclized, for instance with $POCl_3$ or $SOCl_2$, to form a 1,3,4-oxadiazole **4**. This reaction sequence is rather difficult to apply to dendrimer synthesis since the polar intermediates are not easy to purify. A better way is the Huisgen route,[7] which involves the aroylation of 5-aryltetrazoles **2**. These tetrazoles themselves are easily accessible starting from benzonitriles **1** (Scheme 1). However, even this reaction was not effective enough to go beyond the first-generation stage.[8−11] Therefore, we decided to prepare the 1,3,4-oxadiazole ring prior to the dendrimer propagation step and to use the nucleophilic aromatic substitution reaction (NAS) as the key step in the propagation of our dendrons. The well-known[1] electron-withdrawing capacity of 1,3,4-oxadiazoles makes this reaction possible. We used a convergent strategy to build up higher generation dendrimers.

Synthesis

Scheme 1. General Synthesis of 1,3,4-Oxadiazoles

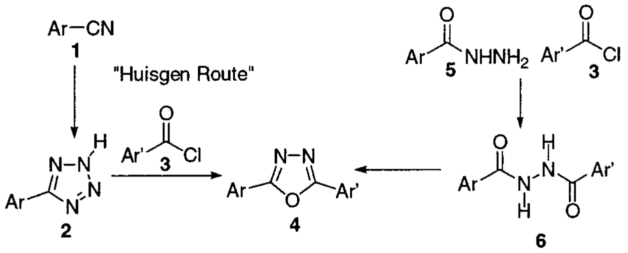

Table 1. Yields of the Different Generation Dendrimers

core	G$_0$	G$_1$	G$_2$
17a	60	74	
18a	64	48	47
19a	85	71	75
20a	70	75	56

Table 2. Mass Spectrometry Data[2]

compd	generation	calcd mass	exptl mass (ESI-MS)
14	G$_1$	606.36	606.6^a
16	G$_2$	1590.79	1592.0^b
17b	G$_0$	630.38	630.6^a
17c	G$_1$	1430.76	1432.2^b
18b	G$_0$	1122.60	1123.6^b
18c	G$_1$	2323.17	2324.1^b
18d	G$_2$	5276.46	
19b	G$_0$	693.49	694.5^a
19c	G$_1$	1894.06	1896.1 (*m/e*); 948.8 (m/2e)^b
19d	G$_2$	4847.35	2426.4 (m/2e); 1617.7 (m/3e)^b
20b	G$_0$	732.41	732.8^a
20c	G$_1$	1532.79	1535.2^b
20d	G$_2$	3501.66	3505.5 (*m/e*); 1752.9 (m/2e)^b

^{a} Taken with EI-MS. ^{b} Taken with ESI-MS.

In a first step, the peripheral group **14** was prepared from 5-(3,5-bis-*tert*-butylphenyl)tetrazole **10** and 5-methoxyisophthalic acid chloride **7**. The tetrazole **10** was prepared from the known aldehyde[12] via the nitrile intermediate **8**. Next, 4 equiv of BBr_3 was needed for the deprotection of the methoxy group of **12** to obtain compound **14** in a quantitative yield. This product **14** will be called the first-generation dendron because a first branching point is introduced. A comparable synthetic route starting from 5-(4-fluorophenyl)tetrazole **11** gave rise to the monomer **13**, which contains two fluorine functions where NAS can take place. To prepare the second-generation dendron **16**, 2 equiv of the peripheral product **14** were attached to the monomer **13** via a NAS reaction. For the deprotection of the methoxy group of compound **15**, 10 equiv of BBr_3 were necessary (Scheme 2).

With the G$_1$- and G$_2$-dendrons **14** and **16** it is possible to carry out a final coupling reaction to a suitable core molecule, obtaining G$_1$- and G$_2$-dendrimers. Model compounds (G$_0$) were prepared by coupling the commercially available 3,5-bis(*tert*-butyl)phenol as a branch to different core reagents and gave us an idea about the reactivity of the core molecules. Bi- and tridirectional oxadiazole cores, 2,5-bis-(4-fluorophenyl)-1,3,4-oxadiazole **17a** and 1,3,5-tris-(2-(4-fluorophenyl)-1,3,4-oxadiazol-5-yl)benzene **18a**, were prepared from 5-(4-fluorophenyl)-tetrazole

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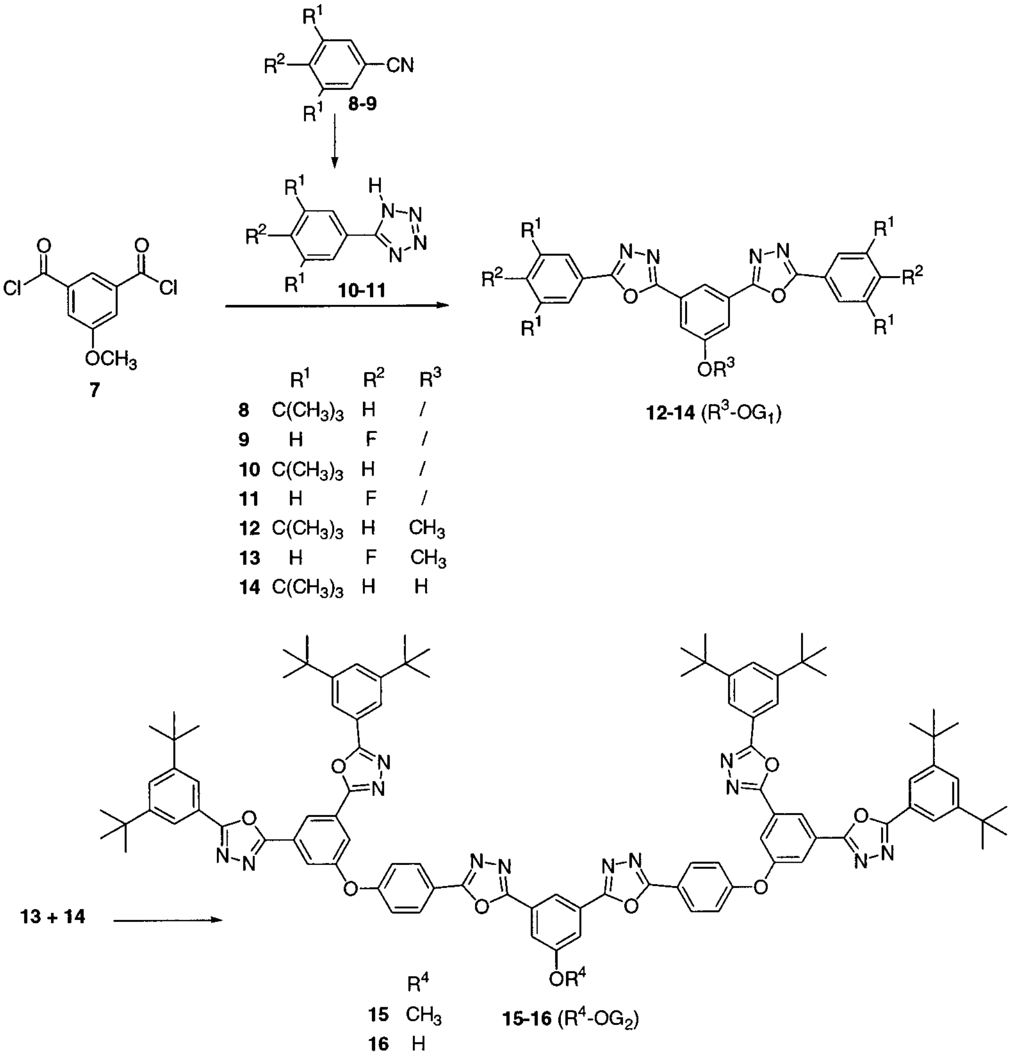
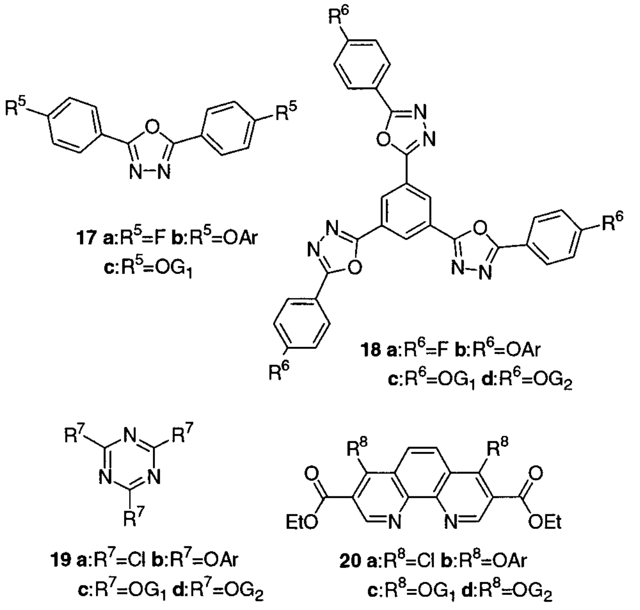
Scheme 2. Propagation of G_1- and G_2-Dendrons



	R^1	R^2	R^3
8	$C(CH_3)_3$	H	/
9	H	F	/
10	$C(CH_3)_3$	H	/
11	H	F	/
12	$C(CH_3)_3$	H	CH_3
13	H	F	CH_3
14	$C(CH_3)_3$	H	H

	R^4
15	CH_3
16	H

Scheme 3. Core Molecules and G_1-and G_2-Dendrimers[a]


17 a:R^5=F **b**:R^5=OAr **c**:R^5=OG_1

18 a:R^6=F **b**:R^6=OAr **c**:R^6=OG_1 **d**:R^6=OG_2

19 a:R^7=Cl **b**:R^7=OAr **c**:R^7=OG_1 **d**:R^7=OG_2

20 a:R^8=Cl **b**:R^8=OAr **c**:R^8=OG_1 **d**:R^8=OG_2

[a] OAr = 3,5-bis(*tert*-butyl)phenoxy.

11 and 4-fluorobenzoyl chloride or 1,3,5-benzenetricarboxylic acid chloride, respectively (Scheme 3). Alternatively, the commercial cyanuric chloride **19a** or the 1,10-phenanthroline **20a** can be used as reactive core molecules. Yields of all dendrimers prepared are summarized in Table 1.

Characterization

Because of the high symmetry of the dendritic molecules all ^1H and ^{13}C NMR spectra could be quite easily interpreted. All prepared dendrimers were completely characterized in this way. Electrospray mass spectrometry (ESI-MS) gave in most cases good results (except for **18d**), and data are summarized in Table 2.

Conclusions

The preparation of dendrimers containing the 1,3,4-oxadiazole group, using the nucleophilic aromatic substitution reaction as the propagation step, was studied. Dendrimers up to the second generation containing three different oxadiazole layers were synthesized. All dendrimers were characterized using NMR spectroscopy as well as mass spectroscopy (EI-MS or ESI-MS).

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Supporting Information Available: Printouts of the ^{1}H NMR spectra for compounds **8** and **10**–**20** and ^{13}C NMR spectra of compounds **8**, **10**, **12**, **14**–**17**, **20a**, **17b**, **18b**, **19b**, and **20b**–**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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