

Table of Contents

Kurzzusammenfassung.....	1
Abstract	2
1 Introduction	3
1.1 Zeolites and Metal-Organic Frameworks.....	4
1.2 Crystalline Organic Frameworks	8
1.2.1 Classification of COFs	9
1.2.2 Applications	12
1.2.2.1 Gas Storage	13
1.2.2.2 Catalysis	13
1.2.2.3 Other Applications	14
1.2.3 Controlling Crystallinity	14
1.2.4 Nitroxide Exchange Reaction.....	16
1.2.4.1 Synthesis of Alkoxyamines.....	17
1.2.4.2 Synthesis of Nitroxides	19
1.3 Amorphous Organic Frameworks	19
1.4 Azides and Nitrenes	22
1.4.1 Synthesis of Azides	22
1.4.2 Nitrene Chemistry	24
2 Objective	27
3 Results and Discussion.....	29
3.1 Core Structures.....	29
3.1.1 Trigonal Planar Cores.....	30
3.1.2 Tetraphenylmethane as Tetrahedral Core.....	32
3.1.3 Tetraphenylethylene as Rectangular Planar Core	37
3.1.4 Hexakis(phenyl)- <i>para</i> -xylene as Pseudo-Octahedral Core.....	37
3.2 Synthesis of Alkoxyamines and Nitroxides	39

3.2.1	Synthesis of Multidimensional Alkoxyamines	39
3.2.1.1	Friedel-Crafts acylation.....	40
3.2.1.2	Introduction of the Hydroxy Groups	46
3.2.1.3	Introduction of the Bromo Functionality	52
3.2.1.4	Conversion into Alkoxyamines	53
3.2.2	Synthesis of Multidimensional Nitroxides	59
3.2.2.1	Synthesis of Linear Dinitroxides	59
3.2.2.2	Synthesis of Trigonal and Tetrahedral Nitroxides	62
3.2.3	Integration into Complex Frameworks	73
3.2.4	Monoalkoxyamine Library	80
3.2.4.1	Synthesis of the Monoalkoxyamines.....	83
3.2.4.2	NMR Effects, Crystal Structures, and Calculations	87
3.3	Synthesis and Thermolysis of Polyazides	93
3.3.1	Synthesis of Polyazides.....	93
3.3.1.1	Polyazides on Rigid Aromatic Core Structures.....	93
3.3.1.2	Polyazides on Porphyrin and Phthalocyanine	98
3.3.2	Synthesis and Characterization of ATFs	106
3.3.2.1	Macroscopic Properties of the ATFs.....	107
3.3.2.2	Thermogravimetric Analysis.....	109
3.3.2.3	IR and Elemental Analysis	111
3.3.2.4	Determination of Surface Area and Pore Size.....	115
3.3.2.5	Scanning Electron Microscopy	118
4	Summary and Outlook	127
4.1	Alkoxyamines and Nitroxides	127
4.2	Multifunctional Azides and ATFs.....	131
5	Experimental Section	137
5.1	General Remarks	137

5.2	Procedures	142
5.2.1	Procedures and Analytical Data of Core Structures	142
5.2.2	Procedures and Analytical Data of Multifunctional Alkoxyamines	156
5.2.3	Procedures and Analytical Data of Multifunctional Nitroxides	213
5.2.4	Procedures and Analytical Data of Monoalkoxyamines	235
5.2.5	Procedures and Analytical Data of Azides	253
5.2.6	Characterization of Azide Thermolysis Frameworks	272
5.2.6.1	Adsorption Isotherms	273
5.3	Crystal Structures	276
6	List of Abbreviations	287
7	Bibliography	293
8	Appendix	311
8.1	Curriculum Vitae	311
8.2	List of Publications	313
8.3	Acknowledgments	314