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**Solution and Solid-State Studies of Alkali Metal Aggregate Assemblies**

**John Jacob Morris**

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SOLUTION AND SOLID-STATE STUDIES OF ALKALI  
METAL AGGREGATE ASSEMBLIES

A Dissertation

Submitted to the Graduate School  
of the University of Notre Dame  
in Partial Fulfillment of the Requirements  
for the Degree of

Doctor of Philosophy

by

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# SOLUTION AND SOLID-STATE STUDIES OF ALKALI METAL AGGREGATE ASSEMBLIES

Abstract

by

John Jacob Morris

The work presented in this dissertation investigates the use of various alkali metal aggregates as secondary building units, SBUs, for the formation of extended framework materials. Three main avenues of research have been studied, which each consider different approaches to better understand this class of materials.

The first topic is concerned with the manipulation of extended supramolecular structure of lithium aryloxide complexes using either self-assembled mixed-anion species or solvent additives (Chapters 2 and 3). Our group has previously shown that molecular cage aggregates of *s*-block metal complexes can successfully be utilized as SBUs to direct network assembly. For example, tetrameric cubanes of specific lithium aryloxides may be designed such that each metal center has a single open site for coordination to a Lewis base. In turn, employment of a ditopic linker results in these aggregates acting as tetrahedral nodes to form 3D diamondoid, and related lower dimensionality polymers. Another level of sophistication to these systems is presented here through the control of the number of metal atoms within each aggregate that may act as points of network

extension. A set of zero-, one-, two-, and three-dimensional materials have been synthesized by systematically varying the stoichiometry of the two components, 2,4,6-Me<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>OLi (ArOLi) and Me<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>OLi (ROLi), within single aggregates while using 1,4-dioxane (diox) as a ditopic linker. The homoleptic complex  $[(\text{ArOLi})_4 \cdot (\text{diox})_2] \supset 3(\text{diox})]_{\infty}$  forms a 3D diamondoid extended structure, where Li<sub>4</sub>O<sub>4</sub> cubanes act as tetrahedral nodes. Attempts to rationally alter the dimensionality of the network through the sequential replacement of ArOLi vertices by potentially chelating ROLi units have succeeded. The mixed-anion complexes  $[(\text{ROLi})(\text{ArOLi})_3 \cdot (\text{diox})_{1.5}] \supset 1/2(\text{C}_6\text{H}_{14})]_{\infty}$  and  $[(\text{ROLi})_4(\text{ArOLi})_2 \cdot (\text{diox})]_{\infty}$ , adopt 2D hexagonal net and 1D chain structures, respectively. Furthermore, the two complexes  $[(\text{ROLi})_3(\text{ArOLi})_3 \cdot (\text{diox})_{0.5}](\text{C}_6\text{H}_{14})]_{\infty}$  and  $[(\text{ROLi})_5(\text{ArOLi}) \cdot (\text{diox})_{0.5}]_{\infty}$  both form unusual 0D molecular dumbbell structures in the solid state. Incorporation of multiple ROLi units in the mixed-anion complexes not only results in reducing the number of possible sites for polymer extension through chelation, but also changes the aggregation state of the building block from tetrametallic Li<sub>4</sub>O<sub>4</sub> units to hexametallic Li<sub>6</sub>O<sub>6</sub> units.

The second area of investigation explores the molecular aggregation and extended network chemistry of substituted aryloxide ligands in combination with the heavier alkali metals Na, K, Rb, and Cs (Chapters 4-6). In particular, we reasoned that aggregates containing the larger alkali metals were appealing candidates as SBUs for high-connectivity systems since they should allow multiple sites for network extension (increased metal solvation), leading to interesting or novel network topologies. Ring and cage aggregates containing the large alkali metals potassium or rubidium have proven to be excellent building blocks for the creation of high-connectivity nets, as demonstrated

by their use as septahedral and nonahedral nodes. Highlights from this work include the characterization of  $[(4\text{-Cl-2,6-Me}_2\text{-C}_6\text{H}_2\text{OK})_2\cdot(\text{dioxane})_{3.5}]_\infty$  and  $[(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2\text{OK})_5\cdot(\text{dioxane})_5]_\infty$ , which form two new types of 7-connected nets, and  $[2\text{-}^i\text{Pr-C}_6\text{H}_4\text{ORb})_6\cdot(\text{dioxane})_{4.5}]_\infty$ , which is the first ever example of a 9-connected net.

An expected finding during the study of the potassium 2-*tert*-butylphenoxide system was the encapsulation of molecular water inside a  $\text{K}_6\text{O}_6$  hexameric drum, forming  $[\{(2\text{-}t\text{Bu-C}_6\text{H}_4\text{OK})_6\supset(\text{H}_2\text{O})\}\cdot(\text{dioxane})_4]_\infty$ . Encapsulation of neutral molecules within alkali metal aggregates is rare. The scope and cause of this unusual behavior was studied in detail (Chapter 5).

The final part of the dissertation explores the synthesis of organometallic polymers assembled from cation- $\pi$  interactions (Chapter 7). The objective was to utilize ferrocene, the prototypical metallocene, as a neutral, linear, ditopic  $\pi$ -linker to bridge between preformed alkali metal aggregates. The combination of  $\text{M}(\text{HMDS})$ , where  $\text{M} = \text{Na, K, Rb, Cs}$ , with ferrocene gives rise to one-dimensional polymeric chains of dimeric ring amides bridged through ferrocene. In addition, the rubidium and cesium analogues have close intermolecular agostic interactions with neighboring chains, such that the supramolecular structures may be considered as two-dimensional  $4^4$ -nets. These studies demonstrate that cation- $\pi$  interactions can be used to rationally build extended networks using appropriate conditions.

For My Family and Niki  
Thank You For Everything

## CONTENTS

Figures.....	vii
Tables.....	xviii
Schemes .....	xx
Acknowledgments.....	xxi
Abbreviations.....	xxiii
Numbered compounds .....	xxvi
Chapter 1 Introduction .....	1
1.1 Outline.....	1
1.2 The Design of Coordination Frameworks.....	1
1.3 Applications of Porous Frameworks.....	5
1.4 Alkali Metals in Extended Networks.....	8
1.5 Alkali Metal Aggregates in Network Assembly.....	10
1.6 Use of Tetrameric $\text{Li}_4\text{O}_4$ Cubanes as SBUs.....	12
1.7 Use of Hexameric $\text{Na}_6\text{O}_6$ Aggregates as SBUs .....	14
1.8 Outline of Research.....	15
1.9 References.....	16
Chapter 2 Manipulation of Molecular Aggregation and Extended Structure	
Using Self-Assembled Lithiated Mixed-Anion Complexes .....	24
2.1 Introduction.....	24
2.2 Results and Discussion .....	27
2.2.1 Synthesis .....	27
2.2.2 Molecular Structures .....	28
2.2.3 Extended Supramolecular Structures.....	35
2.2.4 Synthesis of a Dimethylethanolamine Solvate .....	39
2.3 Summary .....	41
2.4 Experimental Section.....	43
2.4.1 General Procedures .....	43
2.4.2 X-ray Crystallography .....	43
2.4.3 Preparation and Characterization.....	44
2.5 References.....	47

Chapter 3	Systematic Study of Reaction Additives on the Molecular and Network Structure of Lithium 2,4,6-Trisubstituted Aryloxide Complexes.....	52
3.1	Introduction.....	52
3.2	Reactions of Lithium 4-Cl-2,6-Dimethylphenoxide .....	54
3.2.1	Synthesis .....	54
3.2.2	Solid-State Structures.....	55
3.3	Reactions of Lithium 4-Br-2,6-Dimethylphenoxide.....	71
3.3.1	Synthesis .....	71
3.3.2	Solid-State Structures.....	71
3.4	Solution Studies .....	77
3.4.1	Aggregate Size Determination By NMR .....	78
3.4.2	Aggregate Size Determination By Cryoscopy .....	81
3.5	Summary .....	83
3.6	Experimental Section .....	84
3.6.1	General Procedures .....	84
3.6.2	X-ray Crystallography .....	85
3.6.3	Cryoscopy Set-up.....	85
3.6.4	Preparation and Characterization.....	86
3.7	References .....	90
Chapter 4	Systematic Study of 2,4,6-Trisubstituted Alkali Metal Aryloxides Aggregates Highlighted by their sse in High-Connectivity Networks .....	93
4.1	Introduction.....	93
4.2	Network Topology .....	95
4.2.1	Strategies For Network Representation .....	96
4.3	Reactions of 4-(Cl/Br)-2,6-Dimethyphenol .....	99
4.3.1	Synthesis .....	99
4.3.2	Molecular Structures .....	100
4.3.3	Extended Structures .....	106
4.4	Reactions of 2,4,6-Trimethylphenol .....	113
4.4.1	Synthesis .....	113
4.4.2	Molecular Structures .....	114
4.4.3	Extended Structures .....	118
4.5	Summary .....	122
4.6	Experimental Section .....	123
4.6.1	General Procedures .....	123
4.6.2	X-ray Crystallography .....	124
4.6.3	Preparation and Characterization.....	124
4.7	References .....	128
Chapter 5	Systematic Study of <i>Ortho</i> -Substituted Alkali Metal Aryloxides Aggregates Highlighted by their Use in High-Connectivity Networks and Adventitious Water Encapsulation.....	131



5.1	Introduction.....	131
5.2	Reactions of 2- <i>tert</i> -Butylphenol .....	133
5.2.1	Synthesis .....	133
5.2.2	Molecular Structure of Potassium 2- <i>tert</i> -Butylphenoxide Dioxane.....	133
5.2.3	Crystallographic and Solution Studies of Potassium 2- <i>tert</i> - Butylphenoxide .....	139
5.2.4	Extended Structure of Potassium 2- <i>tert</i> -Butylphenoxide Dioxane.....	143
5.2.5	Characterization of Potassium 2- <i>tert</i> -Butylphenoxide THF .....	143
5.2.6	Structure of Rubidium and Sodium 2- <i>tert</i> -Butylphenoxide Dioxane .....	145
5.3	Reactions of 2-Isopropylphenol.....	150
5.3.1	Synthesis .....	150
5.3.2	Molecular Structures of Potassium 2-Isopropylphenoxide Dioxane.....	151
5.3.3	Solution Studies of Potassium 2-Isopropylphenoxide Dioxane.....	154
5.3.4	Extended Structure of Potassium 2-Isopropylphenoxide Dioxane .....	158
5.3.5	Structure of Rubidium 2-Isopropylphenoxide Dioxane.....	161
5.4	Reactions of 2-Ethylphenol and 2-Methylphenol.....	164
5.4.1	Synthesis .....	164
5.4.2	Structure of Potassium 2-Ethylphenoxide Dioxane.....	164
5.4.3	Structure of Potassium 2-Methylphenoxide Dioxane .....	168
5.5	Summary .....	171
5.6	Experimental Section.....	172
5.6.1	General Procedures .....	172
5.6.2	IR Spectroscopic Analysis .....	172
5.6.3	Computational Details .....	172
5.6.4	X-ray Crystallography .....	173
5.6.5	Neutron Data Collection .....	173
5.6.6	Preparation and Characterization.....	176
5.7	References.....	179
Chapter 6 Systematic Study of <i>Para</i> -Substituted Alkali Metal Aryloxide Aggregates Highlighted by Their Inorganic Connectivity.....		
6.1	Introduction .....	184
6.1.1	Hybrid Inorganic-Organic Frameworks.....	185
6.2	Coordination Frameworks From Discreet SBUs .....	188
6.2.1	Synthesis .....	188
6.2.2	Molecular Structures.....	188
6.2.3	Extended Structures .....	191
6.3	Coordination Frameworks Built From Inorganic Rods .....	195
6.3.1	Synthesis .....	195
6.3.2	Structures .....	196
6.4	Summary .....	203
6.5	Experimental Section.....	204
6.5.1	General Procedures .....	204

6.5.2	X-ray Crystallography .....	204
6.5.3	Preparation and Characterization.....	205
6.6	References .....	207
Chapter 7 Organometallic Polymers Assembled From Cation- $\pi$ Interactions .....		210
7.1	Introduction.....	210
7.2	Results and Discussion .....	214
7.2.1	Synthesis and Spectroscopic Analysis.....	214
7.2.2	Crystallographic Studies .....	215
7.2.3	Characterization of Arene Solvates .....	227
7.2.4	Characterization of a Bis(benzene)chromium Polymer.....	230
7.2.5	Computational Studies .....	233
7.3	Summary .....	242
7.4	Experimental Section .....	244
7.4.1	General Procedures .....	244
7.4.2	IR Spectroscopic Analysis .....	245
7.4.3	Computational Details .....	245
7.4.4	X-ray Crystallography .....	245
7.4.5	Preparation and Characterization.....	246
7.5	References .....	248
Appendix Crystallographic Information .....		257

## FIGURES

1.1	Coordination of metals with (a) convergent organic ligands to form molecular complexes, and (b) divergent ligands to give polymeric complexes. ....	2
1.2	(a) The molecular pyridine solvate of $\text{Ni}^{\text{II}}(\text{NO}_3)_2$ . The pyridyl groups are in an equatorial position. (b) The bipyridyl solvate of $\text{Ni}^{\text{II}}(\text{NO}_3)_2$ . The equatorial bipyridyl ligands bridge to other metals to give a square planar network. ....	3
1.3	The two different nodes in $[(\text{AgTMP})(\text{BF}_4)]_\infty$ showing (a) the tetrahedral silver center coordinated by four TMP ligands, and (b) the tetrahedral TMP ligand coordinating to four different silver centers. ....	3
1.4	The $[\text{Zn}_4\text{O}]^{6+}$ cluster with (a) benzene carboxylate as a terminal ligand, and (b) benzene dicarboxylate as a divergent linker.....	4
1.5	The dimeric $\text{Cu}_2\text{Cl}_2$ aggregate tetrasolvated by divergent bipyridine .....	5
1.6	(a) A 1D coordination polymer formed from $\text{Bu}_4\text{Li}_4$ tetramers and TMEDA. Only the $\alpha$ -carbon of the butyl group is shown for clarity. (b) A 2D sheet of $\text{Me}_4\text{Li}_4$ tetramers bridged by DEM. (c) The adamantane subunit of the 3D diamondoid network of $\text{Me}_4\text{Li}_4$ tetramers bridged by TMEDA. The blue tetrahedrons highlight the four lithium centers in the aggregate. ....	9
1.7	A one-dimensional coordination polymer formed from $(\text{LiHMDS})_2$ ring dimers solvated by 1,4-dioxane. ....	10
1.8	Relationship between selected metal aggregates and their nodal geometries: (a) disolvated ring dimer, (b) trisolvated ring trimer, (c) tetrasolvated tetrameric cubane, and (d) hexasolvated prismatic hexamer.....	11
1.9	Molecular structures of a series of THF-solvated lithium aryloxides, $[(\text{ArOLi})\cdot(\text{THF})]_n$ .....	12
1.10	Sections of the polymeric structures of the: (a) 1D zig-zag chain, (b) framework atoms of the 2D hexagonal network with two guest solvent	

	molecules per macrocycle, and (c) 3D diamondoid network. Vertices of the blue tetrahedra represent the four lithium centers within each cubane.....	13
1.11	Sections of the polymeric structures of the: (a) 1D linear chain, (b) 2D square net (framework atoms only), and (c) 3D cubic lattice (framework atoms showing a single cubic unit), formed from triple-stack Na <sub>6</sub> O <sub>6</sub> SBUs bridged by dioxane.....	15
2.1	Tetrameric cubane SBU in <b>2.1</b> , showing all four lithium centers connected to dioxane. Hydrogen atoms removed for clarity. ....	28
2.2	Mixed-anion (3:1) tetrametallic SBU in <b>2.2</b> , showing one chelated and three dioxane-solvated lithium centers. Hydrogen atoms removed for clarity. ....	29
2.3	Mixed-anion (3:3) hexametallic SBU in <b>2.3</b> , showing three chelated, one dioxane-solvated and two unsolvated lithium centers. Hydrogen atoms removed for clarity.....	30
2.4	Octameric structure of [Me <sub>2</sub> N(CH <sub>2</sub> ) <sub>2</sub> OLi)] <sub>8</sub> , <b>2.7</b> , with chelate rings highlighted in red and the methyl groups on nitrogen removed for clarity. ....	30
2.5	Mixed-anion (2:4) hexametallic SBU of <b>2.4</b> , showing four chelated and two dioxane-solvated lithium centers. Hydrogen atoms removed for clarity. ....	31
2.6	Mixed-anion (1:5) hexametallic SBU of <b>2.5</b> , showing five chelated and one dioxane-solvated lithium centers. Hydrogen atoms removed for clarity. ....	32
2.7	Possible chelation modes of homoleptic lithium aminoethoxide aggregates with resulting (a) S <sub>6</sub> and (b) D <sub>3</sub> symmetry.....	32
2.8	Views of a single adamantane subunit of <b>2.1</b> , and the extended 3D diamondoid network highlighting the I-shaped open channels (enclathrated dioxane molecules are removed for clarity).....	35
2.9	Extended 2D 6 <sup>3</sup> -net of <b>2.2</b> showing only the Li <sub>4</sub> O <sub>4</sub> cubanes and the other framework atoms. ....	36
2.10	Section of the 1D linear chain polymer of <b>2.4</b> composed of linked hexametallic aggregates.....	38
2.11	The 0D molecular dumbbell structures of <b>2.5</b> . Hydrogen atoms are removed for clarity.....	38

2.12	The 0D molecular dumbbell structure of <b>2.3</b> . Hydrogen atoms are removed for clarity.....	39
2.13	(a) The asymmetric unit of monomeric <b>2.6</b> . (b) The supramolecular dimer of <b>2.6</b> formed by the bridging dioxane molecule. Only the proton found in the electron difference map is shown for clarity.....	39
2.14	The extended structure of <b>2.6</b> highlighting (a) the hexagonal ring formed by a combination of hydrogen bonds and bridging dioxane, and (b) the two-dimensional 6 <sup>3</sup> -net. ....	41
3.1	Relationship between selected metal aggregates and their potential nodal geometries: (a) tetrasolvated tetrameric cubane, (b) hexasolvated prismatic hexamer, (c) tetrasolvated ring dimer. ....	53
3.2	(a) The tetrasolvated dimeric aggregate of <b>3.1</b> with two dioxane molecules solvating each lithium center. (b) Illustration of the dimeric aggregate as a square planar node with bridging dioxane shown as blue arrows. (c) The extended two-dimensional network of <b>3.1</b> with a 4 <sup>4</sup> -net topology. (d) Simplification of the 4 <sup>4</sup> -network with the dimeric aggregates shown as blue spheres and the dioxanes as the gray connections. ....	56
3.3	(a) Tetrasolvated dimeric aggregate of <b>3.2</b> with two dioxane molecules solvating each lithium center (b) Illustration of the dimeric aggregate as a trigonal node with the three bridging dioxane shown as blue arrows and the one terminal dioxane shown as a red arrow. (c) The extended two-dimensional network of <b>3.2</b> with 6 <sup>3</sup> -net topology. The terminal dioxane molecule on each dimer has been removed for clarity. (d) Simplification of the 6 <sup>3</sup> -network with the dimeric aggregates shown as blue spheres and the bridging dioxane as the gray connections. ....	58
3.4	<sup>1</sup> H NMR titration with (a) DMF in dioxane solvent with a <i>d</i> <sub>12</sub> -cyclohexane spike, (b) 0.125 equivalents DMF added to a solution of lithium 4-Cl-2,6-dimethylphenoxide in dioxane with a <i>d</i> <sub>12</sub> -cyclohexane spike, (c) 0.25 equivalents DMF added, (d) 0.65 equivalents DMF added, (e) 1.3 equivalents DMF added, (f) 2 equivalents DMF added.....	61
3.5	Calculation of solvent exchange reaction of the tetrasolvated lithium ring dimer with DMF replacing dioxane. Calculation at B3LYP/6-31G* level of theory. ....	62
3.6	(a) The tetrameric cubane aggregate of <b>3.3</b> with all four lithium centers solvated by a DMF molecule. Hydrogen atoms are removed for clarity. (b) Illustration of the tetramer with DMF molecules shown as terminal red arrows.....	63

3.7	(a) Tetrameric aggregate of <b>3.5</b> with two of the lithium centers solvated by bridging dioxane, one lithium solvated by a terminal dioxane, and the fourth lithium completely unsolvated. (b) Illustration of the aggregate showing the two bridging dioxanes as blue arrows and the terminal dioxane shown as a red arrow. (c) Extended structure of <b>3.5</b> with a 1D zigzag chain topology. Hydrogen atoms removed for clarity.....	66
3.8	(a) Tetrameric aggregate of <b>3.4</b> with two of the lithium centers solvated by dioxane and the other two lithium centers solvated by DMF. (b) Illustration of the tetrameric aggregate with bridging dioxane shown as blue arrows and terminal DMF shown as red arrows. (c) The extended 1D zigzag chain of <b>3.4</b> . ....	68
3.9	(a) The dimeric aggregate of <b>3.6</b> with two dioxolane molecules solvating each metal center. (b) Illustration of the dimeric aggregate as a tetrahedral node with the bridging dioxolane shown as blue arrows. (c) Adamantane subunit of the extended structure of <b>3.6</b> . Only the $\text{Li}_2\text{O}_2$ dimers and bridging dioxolane molecules needed to build the adamantane unit are shown for clarity. (d) The extended structure with diamondoid topology. The dimeric aggregates are shown as blue spheres. The adamantane subunit of the net is highlighted in red.....	70
3.10	(a) The two unique dimeric aggregates within <b>3.7</b> , with both dimers tetrasolvated by dioxane. (b) Schematic view of the two types of dimeric SBUs present. The tetrahedral node is shown in blue and the trigonal node is shown in green. The bridging dioxanes are shown as red arrows and the terminal dioxane is shown as a black arrow. (c) Section of the bilayer of <b>3.7</b> viewed through the plane of the chair shaped hexagonal nets. Dioxane pillars can be seen bridging between the two layers. Only the oxygen atoms of the aryloxides are shown. Green = lithium, red = oxygen, gray = carbon. (d) A topological representation of <b>3.7</b> highlighting the connectivities of the tetrahedral (blue) and trigonal (green) nodes. ....	73
3.11	(a) Tetrameric aggregate of <b>3.8</b> with two of the lithium centers solvated by dioxane and the other two solvated by DMF. (b) Illustration of the tetrameric aggregate with bridging dioxane shown as blue arrows and terminal DMF shown as red arrows. (c) The extended 1D zigzag chain of <b>3.8</b> .....	75
3.12	(a) Tetrameric cubane aggregate of <b>3.9</b> with all lithium centers solvated by DMF. Hydrogen atoms are removed for clarity. (b) Illustration of the tetramer with DMF molecules shown as terminal red arrows. ....	76
3.13	(a) Dimeric aggregate of <b>3.10</b> with two dioxolane molecules solvating each metal center. (b) Illustration of the dimeric aggregate as a tetrahedral	

	node with the bridging dioxolane shown as blue arrows. (c) Extended structure with a diamondoid topology. The dimeric aggregates are shown as blue spheres. The adamantane subunit of the net is highlighted in red. (d) Section of the extended structure of <b>3.10</b> showing a view down the hexagonal <i>pseudo</i> -channels. Only oxygen centers of the aryloxides are shown and all hydrogen atoms are removed for clarity. Green=lithium, red=oxygen and grey=carbon. ....	77
3.14	General set-up of cryoscopy apparatus .....	86
4.1	2,4,6-Trisubstitued phenols highlighted in this chapter.....	94
4.2	Stepwise deconstruction of the dioxane coordinated pentameric aggregate, <b>4.10</b> , showing (a) the full pentameric aggregate with ten coordinated dioxane molecules, (b) the aggregate with carbon atoms of the aryloxide removed for clarity, (c) illustration of the aggregate showing the eight unique points of network extension, (d) the pentameric aggregate linked to eight neighboring aggregates to give the <b>bcu</b> topology, (e) reduction of the pentameric aggregates and bridging dioxanes to ball and stick representation, (f) ball and stick view of <b>bcu</b> net. ....	97
4.3	Dimeric aggregate of <b>4.1</b> coordinated by six divergent dioxane molecules. Hydrogen atoms are removed for clarity. ....	101
4.4	(a) Full dimeric aggregate of <b>4.3</b> with seven coordinated dioxane, and (b) the dimeric aggregate of <b>4.3</b> with carbon atoms of the aryloxide removed for clarity. Hydrogen atoms in both representations are removed for clarity. ....	102
4.5	(a) Full dimeric aggregate of <b>4.5</b> with seven coordinated dioxane, and (b) the dimeric aggregate of <b>4.5</b> with carbon atoms of the aryloxide removed for clarity. Hydrogen atoms in both representations are removed for clarity. ....	103
4.6	Complete series of dimeric alkali metal 4-Cl-2,6-dimethylphenoxide coordinated by (a) four dioxanes in <b>3.1</b> , (b) six dioxane in <b>4.1</b> , (c) seven dioxanes in <b>4.3</b> , and (d) seven dioxanes in <b>4.5</b> . Only the coordinating oxygen of the dioxane molecules are shown for clarity. ....	105
4.7	Structure of <b>4.1</b> showing (a) the dimeric aggregate with six coordinated dioxane molecules, (b) the dimeric aggregate bridged to five other aggregates through four single bridges and one double bridge, (c) the dimeric aggregate, shown in red, with the nine 5-membered rings and one 7-membered ring created by the coordination to five neighboring aggregates, and (d) extended 5 <sup>9</sup> .7-net with helical channels shown in red.....	107

4.8	Structure of <b>4.3</b> showing (a) the dimeric aggregate coordinated by seven dioxanes with the carbon atoms of the aryloxy removed for clarity, (b) illustration of the dimeric aggregate with 7 points of extension, (c) the dimeric aggregate represented as a blue node connected to seven other aggregates, (d) the extended 7-connected network with 3 <sup>3</sup> .4 <sup>12</sup> .5 <sup>5</sup> .6 topology. ....	109
4.9	Asymmetric unit of <b>4.7</b> with seven unique cesiums and aryloxides. There is one free molecule of dioxane (not shown) per asymmetric unit in the channel of the extended structure. ....	110
4.10	(a-g) Bonding environments of the seven cesium atoms in <b>4.7</b> . (h) Asymmetric unit (highlighted in yellow) with all points of extension through Cs-OAr interactions. Carbon atoms of the aryloxy backbones are removed for clarity.....	111
4.11	(a) Twenty-four membered ring building unit of <b>4.7</b> built through Cs-O interactions. (b) Four 24-membered rings connected through a Cs1-Cs2 dimer. ....	112
4.12	(a) Extended star-shaped tube structure of <b>4.7</b> built through cesium aryloxy interactions. (b) Packing of the one-dimensional tubes stabilized through cation- $\pi$ interactions. ....	113
4.13	Structure of <b>4.8</b> showing (a) the full pentameric aggregate with nine coordinated dioxane molecules, and (b) the pentameric aggregate with dioxane molecules removed for clarity.....	114
4.14	(a) Pentameric aggregate of <b>4.8</b> , and (b-j) core structures of related pentameric aggregates. ....	116
4.15	Structure of <b>4.9</b> showing (a) the full pentameric aggregate with ten coordinated dioxane molecules, and (b) the pentameric aggregate with dioxane molecules removed for clarity.....	117
4.16	(a) Tetrameric ladder structure of <b>4.10</b> which is coordinated by four THF molecules. (b) Extended 1D structure built through cation- $\pi$ interactions. ....	118
4.17	Structure of <b>4.8</b> showing (a) the pentameric aggregate coordinated by nine dioxanes, (b) an illustration of the aggregate showing eight bridging and one terminal dioxane, (c) two 4 <sup>4</sup> -net layers of the extended structure showing the top layer (yellow) connected to the bottom layer (blue) through a combination of single and double dioxane bridges, (d) the extended structure with pentameric aggregates shown as blue spheres. ....	119



4.18	Extended structures of the three known 7-connected topologies showing (a) <b>4.3</b> , (b) <b>4.13</b> , and (c) <b>4.8</b> . ....	120
4.19	Structure of <b>4.9</b> showing (a) the pentameric aggregate coordinated by 10 dioxanes, (b) an illustration of aggregate showing eight unique points of extension, (c) the pentameric aggregate bridged through dioxane to eight neighboring aggregates, (d) the extended structure with <b>bcu</b> topology.....	122
5.1	<i>Ortho</i> -substituted phenols used in this chapter. ....	131
5.2	Structure of $[(2\text{-}t\text{Bu-C}_6\text{H}_4\text{OK})_6\supset(\text{H}_2\text{O})]\cdot(\text{dioxane})_4$ , <b>5.1</b> , showing (a) the asymmetric unit with hydrogen atoms removed for clarity, and (b) the prismatic hexamer highlighting the two disordered water sites within the aggregate and the six coordinated dioxanes. The carbon atoms of the aryloxide backbone are removed for clarity. ....	134
5.3	Structure of $[(2\text{-}t\text{Bu-C}_6\text{H}_4\text{OK})_6\supset(\text{H}_2\text{O})]\cdot(\text{dioxane})_4$ , <b>5.1<sub>n</sub></b> , showing (a) the asymmetric unit with hydrogen atoms removed for clarity, and (b) the prismatic hexamer highlighting one water site within the aggregate with non-water hydrogens and dioxanes removed for clarity.....	135
5.4	Ball and stick, and CPK space-filling views of the $[\text{K}_6\text{O}_6\supset\text{H}_2\text{O}]$ core of the calculated structure. ....	138
5.5	Water addition to <b>5.1</b> in THF- <i>d</i> <sub>8</sub> . ....	142
5.6	The extended two-dimensional 4 <sup>4</sup> -net of <b>5.1<sub>n</sub></b> resulting from four bridging and two terminal dioxane molecules per hexameric aggregate. ....	143
5.7	Structure of $[(2\text{-}t\text{Bu-C}_6\text{H}_4\text{OK})_6\supset(\text{H}_2\text{O})]\cdot(\text{THF})_6$ , <b>5.2</b> , showing (a) the full hexameric aggregate with one of the water sites, and (b) the prismatic hexamer highlighting one water site within the aggregate, with non-water hydrogens and dioxanes removed for clarity. ....	145
5.8	Structure of <b>5.3</b> , showing (a) the asymmetric unit with the encapsulated water molecule, and (b) the prismatic hexamer highlighting both of the water sites within the aggregate with hydrogens and dioxanes removed for clarity. ....	147
5.9	Structure of <b>5.4</b> , showing (a) half of the hexameric aggregate with encapsulated water molecule, and (b) the prismatic hexamer highlighting both of the water sites within the aggregate, with hydrogens and dioxanes removed for clarity.....	148
5.10	(a) The prismatic hexamer <b>5.3</b> highlighting the eight coordinated dioxanes, and (b) the eight linked aggregates that form part of the extended three-	

	dimensional network with <b>bcu</b> topology. Hydrogen atoms and the carbon atoms of the aryloxides are removed for clarity. ....	149
5.11	(a) The prismatic hexamer <b>5.4</b> highlighting the six coordinated dioxanes, and (b) the six linked aggregates that form part of the extended three-dimensional network with <b>pcu</b> topology. Hydrogen atoms and the carbon atoms of the aryloxides are removed for clarity. ....	150
5.12	Structure of <b>5.5</b> , showing (a) the asymmetric unit with hydrogen atoms removed for clarity, (b) the prismatic hexamer highlighting one of the water sites within the aggregate. The six dioxane molecules are removed for clarity.....	151
5.13	The water-free hexameric aggregate of <b>5.6</b> with dioxane molecules and hydrogens removed for clarity. ....	152
5.14	The dihydrated hexameric aggregate of <b>5.7</b> highlighting the one water molecule encapsulated within the aggregate and the second water molecule coordinated on the outer face. Dioxane molecules and non-water hydrogen atoms are removed for clarity. ....	154
5.15	Water addition to <b>5.6</b> in $\text{CDCl}_2$ .....	156
5.16	Aromatic region of <b>5.7</b> in $\text{CD}_2\text{Cl}_2$ .....	157
5.17	Variable temperature study of <b>5.7</b> in $\text{CD}_2\text{Cl}_2$ .....	158
5.18	The extended three-dimensional network of <b>5.5</b> with primitive cubic topology resulting from six bridging and two terminal dioxane molecules per hexameric aggregate. ....	159
5.19	(a) The hexameric triple stack of dimers of <b>5.6</b> highlighting the eight coordinated dioxane and (b) the extended three-dimensional network with <b>pcu</b> topology resulting from six bridging and two terminal dioxane molecules per hexameric aggregate. Hydrogen atoms and the carbon atoms of the aryloxides are removed for clarity. ....	160
5.20	(a) Hexameric aggregate of <b>5.7</b> highlighting the eight coordinated dioxane. The carbon atoms of the aryloxide backbone are removed for clarity. (b) The extended two-dimensional bilayer structure resulting from five bridging and three terminal dioxane molecules per hexameric aggregate. The blue spheres represent the centroid of the hexameric aggregate. ....	160
5.21	Structure of <b>5.8</b> , showing (a) the full hexameric aggregate with hydrogen atoms removed for clarity, and (b) a simplified view of the aggregate with the nine dioxane molecules and hydrogen atoms removed for clarity.....	161

5.22	(a) Hexameric aggregate of $[2\text{-}i\text{Pr-C}_6\text{H}_4\text{ORb})_6\bullet(\text{diox})_{4.5}]_\infty$ , <b>5.8</b> coordinated by nine dioxanes. The carbon atoms of the aryl ligand and hydrogen atoms are removed for clarity (b) Illustration of the nine points of network extension (c) Dioxane bridges to nine other aggregates. (d) The extended <b>ncd</b> network showing the framework with the $4^4$ -nets in blue and the $(3.4^3)(3^2.4^3)$ -nets in red. (e) Section of the $(3.4^3)(3^2.4^3)$ -net. (f) Offset pattern of the two $(3.4^3)(3^2.4^3)$ -nets intersecting with a $4^4$ -net. ....	163
5.23	Structure of <b>5.10</b> , showing the two hexameric and one dimeric aggregate that make up the extended structure. The dioxane molecules and hydrogen atoms removed for clarity. ....	165
5.24	(a) The three aggregates of <b>5.10</b> coordinated by twenty dioxane molecules. The carbon atoms of the aryl ligand and hydrogen atoms are removed for clarity (b) Illustration of the points of network extension from each aggregate. (c) Extended network showing the dimeric (red) and hexameric (blue and green) aggregates as spheres. (d) Section of the three subnets with $4^4$ , $4^4$ , and $(3.5.3.5)_2(3.5^2.3.5^2)$ topology. ....	167
5.25	Structure of <b>5.10</b> , showing (a) the full tetrameric aggregate with eight coordinated dioxanes, and (b) a simplified view of the aggregate with dioxane molecules and hydrogen atoms removed for clarity. ....	168
5.26	(a) Tetrameric aggregate of <b>5.10</b> coordinated by eight dioxanes. The carbon atoms of the aryl ligand and hydrogen atoms are removed for clarity. (b) Illustration of the eight bridging dioxanes. The four single dioxane bridges are shown in blue and the four dioxane double bridges are shown in green. (d) The 3D <b>sxc</b> net topology showing the framework with the $4^4$ -nets in red and blue and the $6^4$ -nets in gray. (e) The <b>pcu</b> net topology used for comparison.....	170
6.1	<i>Para</i> -substituted phenols highlighted in this chapter.....	185
6.2	The extended structure of nickel succinate containing 1D inorganic chains, bridged by organic ligands along a second dimension to form sheets. $\text{NiO}_6$ octahedra in green with carbon and oxygen as black and red sphere, respectively. ....	186
6.3	Structure of <b>6.1</b> showing (a) the full hexameric aggregate with eight coordinated dioxane molecules, and (b) the hexameric aggregate with dioxane molecules removed for clarity.....	189
6.4	Structure of <b>6.2</b> showing (a) the full hexameric aggregate with twelve coordinated dioxane molecules, and (b) the hexameric aggregate with dioxane molecules removed for clarity.....	191

6.5	Structure of <b>6.1</b> showing (a) the hexameric aggregate with the eight bridging dioxanes shown as well as the eight aryloxy ligands that bridge through K-F <sub>Ar</sub> interactions. (b) Illustration of the aggregate showing the eight bridging dioxane (blue arrows) and eight bridging aryl ligands (green arrows). (c) The hexameric aggregate bridged to neighboring aggregates through 8 double bridges. (d) The extended structure with <b>bcu</b> topology. The hexameric aggregates are shown as blue spheres and both types of bridges are shown as sticks. ....	193
6.6	Structure of <b>6.3</b> showing (a) the hexameric aggregate coordinated by 12 bridging dioxane molecules. The carbon atoms of the aryloxy are removed for clarity. (b) Illustration of the aggregate showing the twelve bridging dioxanes (blue arrows). (c) The hexameric aggregate bridged to neighboring aggregates through 6 dioxane double bridges. (d) The extended structure with <b>pcu</b> topology. The hexameric aggregates are shown as blue spheres and dioxanes are shown as red and grey sticks. ....	195
6.7	(a) Structure of <b>6.4</b> showing a slice of the extended inorganic structure formed through K-O <sub>Ar</sub> interactions. (b) Simplified view of the inorganic chain showing only the K-O <sub>Ar</sub> interactions. (c) Expanded view of the extended structure showing the inorganic rods bridged by dioxanes to give parallel stacks of 4 <sup>4</sup> -nets. ....	197
6.8	(a) Structure of <b>6.4</b> showing a slice of the extended inorganic structure formed through K-O <sub>Ar</sub> interactions. (b) Simplified view of the inorganic chain showing only the K-O <sub>Ar</sub> interactions. ....	199
6.9	(a) Structure of <b>6.6</b> showing a slice of the extended inorganic structure formed through K-O <sub>Ar</sub> interactions. (b) Simplified view of the inorganic chain showing only the K-O <sub>Ar</sub> and K-O <sub>diox</sub> interactions. (c) View of the K-O <sub>Ar</sub> inorganic chain highlighting the helical structure. (d) Expanded view of the extended structure showing the isolated inorganic rods. ....	201
7.1	Cationic moiety of [K·(Cp <sub>2</sub> Fe) <sub>2</sub> ·(Tol) <sub>2</sub> ] <sup>+</sup> [Mg(HMDS) <sub>3</sub> ] <sup>-</sup> . ....	211
7.2	Sections of the ferrocene-bridged polymers (a) [(Cp <sub>2</sub> Fe)·(Ga <sub>2</sub> Cl <sub>4</sub> )] <sub>∞</sub> and (b) [(Cp <sub>2</sub> Fe)·{(o-C <sub>6</sub> F <sub>4</sub> Hg) <sub>3</sub> } <sub>2</sub> ] <sub>∞</sub> . ....	212
7.3	Top: Section of the polymeric structure of <b>7.1</b> highlighting the dimeric Na <sub>2</sub> N <sub>2</sub> ring core η <sup>5</sup> -coordinated to two ferrocene molecules. Bottom: Extended section of <b>7.2</b> showing the linear polymeric chain structure. Hydrogen atoms are omitted for clarity. ....	217
7.4	Top: Section of the polymeric structure of <b>7.3</b> highlighting the dimeric Rb <sub>2</sub> N <sub>2</sub> ring core η <sup>5</sup> -coordinated to two ferrocene molecules in a tilted	

	fashion. Bottom: Extended section of <b>7.4</b> showing the zig-zag polymeric chain structure. Hydrogen atoms are omitted for clarity. ....	218
7.5	Sections of the polymeric structures of (a) $[\text{Na}(\text{Fc pz})]_{\infty}^{-}$ , <b>7.10</b> , and (b) $[\text{M}_2(\text{Fc pz}) \cdot (\text{DME})_3]_{\infty}$ , M = K ( <b>7.11</b> ), Rb ( <b>7.12</b> ), Cs ( <b>7.13</b> ). ....	221
7.6	Extended section of <b>7.3</b> showing the combination of cation- $\pi$ and agostic Rb-C interactions leading to the 2D sheet assembly. Hydrogen atoms are omitted for clarity. ....	224
7.7	Section of the molecular structure of <b>7.5</b> showing the relative positions of the partially occupied ferrocene and toluene molecules. ....	225
7.8	Section of the extended structure of <b>7.6</b> showing two alternative solvation modes within the crystal: (i) bridging of the amide dimers by ferrocene and (ii) terminal binding of toluene on two adjacent dimers. ....	226
7.9	Molecular Structure of <b>7.14</b> highlighting the dimeric $\text{K}_2\text{N}_2$ ring core $\eta^6$ -coordinated to two <i>tert</i> -butylbenzene molecules. ....	228
7.10	Molecular Structure of <b>7.15</b> highlighting the dimeric $\text{K}_2\text{N}_2$ ring core $\eta^6$ -coordinated to two mesitylene molecules. ....	228
7.11	Section of the polymeric structure of <b>7.17</b> showing the charge-separated potassium cation and the magnesium tris(amide)amide anion. Hydrogen atoms are omitted for clarity. ....	232
7.12	Section of the polymeric structure of <b>7.17</b> highlighting the $6^3$ -sheet formed by the trigonal potassium cation nodes and the bis(benzene)chromium bridges. The magnesium tris(amide) anions and hydrogen atoms are omitted for clarity. ....	233
7.13	Geometry optimized structures of the cation- $\pi$ solvated sodium and potassium amide dimers. Hydrogen atoms are omitted for clarity. ....	238

## TABLES

2.1	Key Bond Lengths [ $\text{\AA}$ ] and Angles ( $^{\circ}$ ) For <b>2.1-2.5</b> and <b>2.7</b> . Mean Parameters are Shown in Brackets.....	34
3.1	Key Bond Lengths [ $\text{\AA}$ ] And Angles ( $^{\circ}$ ) For <b>3.1-3.10</b> . Mean Parameters are Shown in Brackets..	59
3.2	$^{13}\text{C}$ NMR Chemical Shift Difference $\Delta\delta_{(4)}$ for Lithium Phenolates in Dioxane (25 $^{\circ}\text{C}$ , ~0.5 M) and Corresponding Structure. ....	79
3.3	$^{13}\text{C}$ NMR Chemical Shifts $\Delta\delta_{(4)}$ for Lithium 4-Br-2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>2</sub> O- in Dioxolane (~0.5 M). ....	81
3.4	Degree Of Aggregation for Lithium 4-Br-2,6-Dimethylphenoxide in Dioxane .....	83
4.1	Key Bond Lengths [ $\text{\AA}$ ] and Angles ( $^{\circ}$ ) for <b>4.1-4.12</b> . Mean Parameters are Shown in Brackets. ....	104
5.1	Key Bond Lengths [ $\text{\AA}$ ] for <b>5.1-5.10</b> . Mean Parameters are Shown in Brackets.....	137
5.2	Key Bond Lengths [ $\text{\AA}$ ] and Water Occupancy for <b>5.1</b> and <b>I-XVI</b> .....	140
6.1	Key Bond Lengths [ $\text{\AA}$ ] and Angles ( $^{\circ}$ ) for <b>6.1-6.7</b> . Mean Parameters are Shown in Brackets. ....	202
7.1	Key Bond Lengths [ $\text{\AA}$ ] and Angles ( $^{\circ}$ ) for <b>7.1-7.6</b> .....	216
7.2	Comparison of Selected Bond Lengths [ $\text{\AA}$ ] and Angles [ $^{\circ}$ ] for M(HMDS) (M = Na, K, Rb, Cs) Compounds .....	219
7.3	Comparison of Selected Bond Lengths [ $\text{\AA}$ ] and Angles [ $^{\circ}$ ] for the Calculated Structures .....	236
7.4	Selected Experimental and Calculated IR Data [ $\text{cm}^{-1}$ ] .....	241
A.1	Crystallographic Parameters for Compounds <b>2.1-2.5</b> .....	286

A.2	Crystallographic Parameters for Compounds <b>2.6, 3.1-3.4</b> .....	287
A.3	Crystallographic Parameters for Compounds <b>3.5-3.9</b> .....	288
A.4	Crystallographic Parameters for Compounds <b>3.10, 4.1-4.4</b> .....	289
A.5	Crystallographic Parameters for Compounds <b>4.5-4.9</b> .....	290
A.6	Crystallographic Parameters for Compounds <b>4.10, 5.1-5.3</b> .....	291
A.7	Crystallographic Parameters for Compounds <b>5.4-5.8</b> .....	292
A.8	Crystallographic Parameters for Compounds <b>5.10, 6.1-6.4</b> .....	293
A.9	Crystallographic Parameters for Compounds <b>6.5-6.7</b> .....	294
A.10	Crystallographic Parameters for Compounds <b>7.1-7.5</b> .....	295
A.11	Crystallographic Parameters for Compounds <b>7.6, 7.14, 7.15</b> .....	296

## SCHEMES

2.1	Proposed sequential replacement of aryloxide anions (ArO) by chelating dimethylaminoethoxide units, and the effect on the resulting supramolecular structure. The blue arrows represent the sites for polymer extension. ....	26
2.2	Preparation of <b>2.1-2.5</b> .....	27
2.3	Molecular SBUs in <b>2.1, 2.2, 2.4</b> and <b>2.5</b> illustrating their use as tetrahedral, trigonal, linear and single-bridging nodes. ....	41
3.1	Proposed sequential replacement of dioxane by DMF starting with the tetrasolvated dimeric aggregate <b>3.1</b> . The amount of each Lewis base is relative to the dimer. The dioxane is half the amount of DMF in each step because it is a divergent solvate that bridges between aggregates.....	57
3.2	Proposed sequential replacement of dioxane by DMF starting with a dioxane solvated tetramer. The amount of each Lewis base is relative to the tetramer. The dioxane is half the amount of DMF in each step because it is a divergent solvate that bridges between aggregates. ....	65
5.1	Energetics of water encapsulation for the hexameric aggregate (HF/6-31G*). ....	138
7.1	Energetics of cation- $\pi$ solvation for the metal amide dimers with ferrocene and toluene (B3LYP/6-31G*). ....	235



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## ABBREVIATIONS

**1D** – One dimensional

**2D** – Two dimensional

**3D** – Three dimensional

**Bipy** – 4, 4'-Bipyridine

**BCU** – Body-Centered Cubic

**BDC** – Benzenedicarboxylate

**BPE** – Trans-bis(4-pyridyl)ethylene

**BTB** – 1,3,5-benzenetribenzoate

**BTC** – 1,3,5-benzenetricarboxylate

**BuLi** – Butyllithium

**CSD** – Cambridge Structural Database

**Cp** – Cyclopentadienyl

**DEM** – diethoxymethane

**Dia** – Diamondoid

**Diox** – 1,4-Dioxane

**DMF** – Dimethylformamide

**DME** – Dimethoxyethane

**DMF** – Dimethylformamide

**DMSO** – Dimethylsulfoxide

**DFT** – Density Functional Theory

**DZ** – Double- $\zeta$

**EQ** – Equation

**FAU** – Faujasite

**Fc** – Ferrocene

**FCU** – Face-Centered Cubic

**FMA** – fumarate

**HMDS** – Hexamethyldisilazide

**HMPA** – Hexamethylphosphoramide

**IP** – Isophthalate

**IR** – Infrared

**L-lac** – Lactate

**LiOAr** – Lithium aryloxide

**MeLi** – Methyllithium

**MOF** – Metal Organic Framework

**MS** – Mass Spectrometry

**NaOAr** – Sodium aryloxide

**NMR** – Nuclear Magnetic Resonance

**PCU** – Primitive Cubic

**PMD** – Pyrimidine

**PMDTA** – N, N, N', N'', N''-Pentamethyldiethylene triamine

**Pyr** – Pyridine

**Pz** – Pyrazolyl

**RCSR** - Reticular Chemistry Structure Resource

**SBU** – Secondary Building Unit

**SCO** – Spin crossover

**THF** – Tetrahydrofuran

**Tol** – Toluene

**TMEDA** – N,N,N',N'-Tetramethylethylenediamine

**TPM** – Tetra-(4-pyridyl)methane

**TPT** – 2,4,6-tris(4-pyridyl)triazine

**XRD** – X-ray diffraction

## NUMBERED COMPOUNDS

- 2.1** [ $\{(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2\text{OLi})_4 \cdot (\text{diox})_2\} \supset 3(\text{diox})$ ] $_{\infty}$
- 2.2** [ $\{(\text{Me}_2\text{NC}_2\text{H}_4\text{OLi})(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2\text{OLi})_3 \cdot (\text{diox})_{1.5}\} \supset 1/2(\text{C}_6\text{H}_{14})$ ] $_{\infty}$
- 2.3** [ $\{(\text{Me}_2\text{NC}_2\text{H}_4\text{OLi})_3(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2\text{OLi})_3 \cdot (\text{diox})_{0.5}\}(\text{C}_6\text{H}_{14})$ ] $_{\infty}$
- 2.4** [ $(\text{Me}_2\text{NC}_2\text{H}_4\text{OLi})_4(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2\text{OLi})_2 \cdot (\text{diox})$ ] $_{\infty}$
- 2.5** [ $(\text{Me}_2\text{NC}_2\text{H}_4\text{OLi})_5(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2\text{OLi}) \cdot (\text{diox})_{0.5}$ ] $_{\infty}$
- 2.6** [ $(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2\text{OLi}) \cdot (\text{Me}_2\text{NC}_2\text{H}_4\text{OH}) \cdot (\text{diox})_{0.5}$ ] $_{\infty}$
- 3.1** [ $(4\text{-Cl-}2,6\text{-Me}_2\text{-C}_6\text{H}_2\text{OLi})_2 \cdot (\text{dioxane})_2$ ] $_{\infty}$
- 3.2** [ $(4\text{-Cl-}2,6\text{-Me}_2\text{-C}_6\text{H}_2\text{OLi})_2 \cdot (\text{dioxane})_{2.5}$ ] $_{\infty}$
- 3.3** [ $(4\text{-Cl-}2,6\text{-Me}_2\text{-C}_6\text{H}_2\text{OLi})_4 \cdot (\text{dmf})_4$ ]
- 3.4** [ $(4\text{-Cl-}2,6\text{-Me}_2\text{-C}_6\text{H}_2\text{OLi})_4 \cdot (\text{dioxane}) \cdot (\text{dmf})_2$ ] $_{\infty}$
- 3.5** [ $(4\text{-Cl-}2,6\text{-Me}_2\text{-C}_6\text{H}_2\text{OLi})_4 \cdot (\text{dioxane})_2$ ] $_{\infty}$
- 3.6** [ $(4\text{-Cl-}2,6\text{-Me}_2\text{-C}_6\text{H}_2\text{OLi})_2 \cdot (\text{dioxolane})_2$ ] $_{\infty}$
- 3.7** [ $\{(4\text{-Br-}2,6\text{-Me-C}_6\text{H}_2\text{OLi})_2 \cdot (\text{dioxane})_2\} \{ (4\text{-Br-}2,6\text{-Me-C}_6\text{H}_2\text{OLi})_2 \cdot (\text{dioxane})_{2.5} \}$ ] $_{\infty}$
- 3.8** [ $(4\text{-Br-}2,6\text{-Me}_2\text{-C}_6\text{H}_2\text{OLi})_4 \cdot (\text{dioxane})_1 \cdot (\text{dmf})_2$ ] $_{\infty}$
- 3.9** [ $(4\text{-Br-}2,6\text{-Me}_2\text{-C}_6\text{H}_2\text{OLi})_4 \cdot (\text{dmf})_4$ ]
- 3.10** [ $(4\text{-Br-}2,6\text{-Me}_2\text{-C}_6\text{H}_2\text{OLi})_2 \cdot (\text{dioxolane})_2$ ] $_{\infty}$
- 4.1** [ $(4\text{-Cl-}2,6\text{-Me}_2\text{-C}_6\text{H}_2\text{ONa})_2 \cdot (\text{dioxane})_3$ ] $_{\infty}$
- 4.2** [ $(4\text{-Br-}2,6\text{-Me}_2\text{-C}_6\text{H}_2\text{ONa})_2 \cdot (\text{dioxane})_3$ ] $_{\infty}$

- 4.3** [(4-Cl-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>OK)<sub>2</sub>·(dioxane)<sub>3.5</sub>]<sub>∞</sub>
- 4.4** [(4-Br-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>OK)<sub>2</sub>·(dioxane)<sub>3.5</sub>]<sub>∞</sub>
- 4.5** [(4-Cl-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>ORb)<sub>2</sub>·(dioxane)<sub>3.5</sub>]<sub>∞</sub>
- 4.6** [(4-Br-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>ORb)<sub>2</sub>·(dioxane)<sub>3.5</sub>]<sub>∞</sub>
- 4.7** [(4-Cl-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>OCs)<sub>7</sub>·(dioxane)<sub>1</sub>]<sub>∞</sub>
- 4.8** [(2,4,6-Me<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>OK)<sub>5</sub>·(dioxane)<sub>5</sub>]<sub>∞</sub>
- 4.9** [(2,4,6-Me<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>ORb)<sub>5</sub>·(dioxane)<sub>5</sub>]<sub>∞</sub>
- 4.10** [(2,4,6-Me<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>OK)<sub>4</sub>·(thf)<sub>4</sub>]<sub>∞</sub>
- 5.1** [{(2-*t*Bu-C<sub>6</sub>H<sub>4</sub>OK)<sub>6</sub>⊃(H<sub>2</sub>O)}·(dioxane)<sub>4</sub>]<sub>∞</sub>
- 5.1<sub>n</sub>** [{(2-*t*Bu-C<sub>6</sub>H<sub>4</sub>OK)<sub>6</sub>⊃(H<sub>2</sub>O)}·(dioxane)<sub>4</sub>]<sub>∞</sub>
- 5.2** [{(2-*t*Bu-C<sub>6</sub>H<sub>4</sub>OK)<sub>6</sub>⊃(H<sub>2</sub>O)}·(THF)<sub>6</sub>]
- 5.3** [{(2-*t*Bu-C<sub>6</sub>H<sub>4</sub>ORb)<sub>6</sub>⊃(H<sub>2</sub>O)}·(dioxane)<sub>4</sub>·(dioxane)]<sub>∞</sub>
- 5.4** [{(2-*t*Bu-C<sub>6</sub>H<sub>4</sub>ONa)<sub>6</sub>⊃(H<sub>2</sub>O)}·(dioxane)<sub>3</sub>]<sub>∞</sub>
- 5.5** [{(2-*i*Pr-C<sub>6</sub>H<sub>4</sub>OK)<sub>6</sub>⊃(H<sub>2</sub>O)}·(dioxane)<sub>5</sub>·(dioxane)]<sub>∞</sub>
- 5.6** [(2-*i*Pr-C<sub>6</sub>H<sub>4</sub>OK)<sub>6</sub>·(dioxane)<sub>5</sub>]<sub>∞</sub>
- 5.7** [{(2-<sup>*i*</sup>Pr-C<sub>6</sub>H<sub>4</sub>OK)<sub>6</sub>·(H<sub>2</sub>O)<sub>2</sub>}·(dioxane)<sub>5.5</sub>]<sub>∞</sub>
- 5.8** [2-<sup>*i*</sup>Pr-C<sub>6</sub>H<sub>4</sub>ORb)<sub>6</sub>·(dioxane)<sub>4.5</sub>]<sub>∞</sub>
- 5.10** [(2-Me-C<sub>6</sub>H<sub>4</sub>OK)<sub>4</sub>·(dioxane)<sub>4</sub>]<sub>∞</sub>
- 6.1** [(4-F-C<sub>6</sub>H<sub>4</sub>OK)<sub>6</sub>·(dioxane)<sub>4</sub>]<sub>∞</sub>
- 6.2** [(4-I-C<sub>6</sub>H<sub>4</sub>OK)<sub>6</sub>·(dioxane)<sub>6</sub>]<sub>∞</sub>
- 6.3** [(4-I-C<sub>6</sub>H<sub>4</sub>ORb)<sub>6</sub>·(dioxane)<sub>6</sub>]<sub>∞</sub>
- 6.4** [(4-Cl-C<sub>6</sub>H<sub>4</sub>OK)<sub>3</sub>·(dioxane)]<sub>∞</sub>
- 6.5** [(4-Br-C<sub>6</sub>H<sub>4</sub>OK)<sub>2</sub>·(dioxane)<sub>0.5</sub>]<sub>∞</sub>

- 6.6** [(4-Br-C<sub>6</sub>H<sub>4</sub>ORb)<sub>5</sub>·(dioxane)<sub>5</sub>]<sub>∞</sub>
- 6.7** [(4-<sup>i</sup>Pr-C<sub>6</sub>H<sub>4</sub>OK)<sub>2</sub>·(dioxane)<sub>0.5</sub>]<sub>∞</sub>
- 7.1** [{(Me<sub>3</sub>Si)<sub>2</sub>NNa}<sub>2</sub>·(Cp<sub>2</sub>Fe)]<sub>∞</sub>
- 7.2** [{(Me<sub>3</sub>Si)<sub>2</sub>NK}<sub>2</sub>·(Cp<sub>2</sub>Fe)]<sub>∞</sub>
- 7.3** [{(Me<sub>3</sub>Si)<sub>2</sub>NRb}<sub>2</sub>·(Cp<sub>2</sub>Fe)]<sub>∞</sub>
- 7.4** [{(Me<sub>3</sub>Si)<sub>2</sub>NCs}<sub>2</sub>·(Cp<sub>2</sub>Fe)]<sub>∞</sub>
- 7.5** [{(Me<sub>3</sub>Si)<sub>2</sub>NRb}<sub>2</sub>·(Cp<sub>2</sub>Fe)<sub>0.6</sub>·(C<sub>7</sub>H<sub>8</sub>)<sub>0.8</sub>]<sub>∞</sub>
- 7.6** [{(Me<sub>3</sub>Si)<sub>2</sub>NCs}<sub>2</sub>·(Cp<sub>2</sub>Fe)<sub>0.5</sub>·(C<sub>7</sub>H<sub>8</sub>)]<sub>∞</sub>
- 7.7** [(Me<sub>3</sub>Si)<sub>2</sub>NK·(Tol)]<sub>2</sub>
- 7.8** [{(Me<sub>3</sub>Si)<sub>2</sub>NCs}<sub>2</sub>·(Tol)]<sub>∞</sub>
- 7.9** [K·(Cp<sub>2</sub>Fe)<sub>2</sub>·(Tol)<sub>2</sub>]<sup>+</sup>[Mg(HMDS)<sub>3</sub>]<sup>-</sup>
- 7.10** [{Na(Fcpz)}·{Na(DME)<sub>3</sub>}]<sub>∞</sub>
- 7.11** [K<sub>2</sub>(Fcpz)·(DME)<sub>3</sub>]<sub>∞</sub>
- 7.12** [Rb<sub>2</sub>(Fcpz)·(DME)<sub>3</sub>]<sub>∞</sub>
- 7.13** [Cs<sub>2</sub>(Fcpz)·(DME)<sub>3</sub>]<sub>∞</sub>
- 7.14** [{(Me<sub>3</sub>Si)<sub>2</sub>NK}·(<sup>t</sup>Bu-C<sub>6</sub>H<sub>5</sub>)]<sub>2</sub>
- 7.15** [{(Me<sub>3</sub>Si)<sub>2</sub>NK}·(Me<sub>3</sub>-C<sub>6</sub>H<sub>3</sub>)]<sub>2</sub>
- 7.16** [{K·((C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Cr)<sub>2</sub>}]<sup>+</sup>[Mg(HMDS)<sub>3</sub>]<sup>-</sup>]<sub>∞</sub>
- 7.17** [{K·((C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Cr)<sub>1.5</sub>·(Mes)}]<sup>+</sup>[Mg(HMDS)<sub>3</sub>]<sup>-</sup>]<sub>∞</sub>