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-Me₃-C₆H₂OLi (ArOLi) and Me₂N(CH₂)₂OLi (ROLi), within single aggregates while using 1,4-dioxane (diox) as a ditopic linker. The homoleptic complex [{{(ArOLi)}₄·(diox)}₂·3(diox)}]∞ forms a 3D diamondoid extended structure, where Li₄O₄ 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 [{{(ROLi)(ArOLi)}₃·(diox)}₁.₅·(C₆H₁₄)}]∞ and [(ROLi)₄(ArOLi)₂·(diox)]∞, adopt 2D hexagonal net and 1D chain structures, respectively. Furthermore, the two complexes [{{(ROLi)₃(ArOLi)₃·(diox)}₀.₅}·(C₆H₁₄)}]∞ and [(ROLi)₅(ArOLi)·(diox)]₀.₅]∞ 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 Li₄O₄ units to hexametallic Li₆O₆ 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 \([(4-\text{Cl}-2,6-\text{Me}_2\text{C}_6\text{H}_2\text{OK})_2\cdot(\text{dioxane})_{3.5}]_{\infty}\) 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 \([2-\text{^1Pr-C}_6\text{H}_4\text{ORb}_6\cdot(\text{dioxane})_{4.5}]_{\infty}\), which is the first ever example of a 9-connected net.

An expected finding during the study of the potassium 2-\text{^}{\text{tert}}-\text{butylphenoxide} system was the encapsulation of molecular water inside a K\text{\textsubscript{6}}O\text{\textsubscript{6}} hexameric drum, forming \[\{\{2-\text{tBu-C}_6\text{H}_4\text{OK}\}_6\supseteq(\text{H}_2\text{O})\}\cdot(\text{dioxane})_4]_{\infty}.\] 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 M(HMDS), where M = 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\textsuperscript{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
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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-ζ
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 – Methyl lithium
MOF – Metal Organic Framework
MS – Mass Spectrometry
NaOAr – Sodium aryloxide
NMR – Nuclear Magnetic Resonance
PCU – Primitive Cubic
PMD – Pyrimidine
PMDTA – 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-Me3-C6H2OLi)4·(diox)2]∞
2.2 [(Me2NC2H4OLi)(2,4,6-Me3-C6H2OLi)3·(diox)1.5]∞ 1/2(C6H14)∞
2.3 [(Me2NC2H4OLi)3(2,4,6-Me3-C6H2OLi)3·(diox)0.5]∞ (C6H14)∞
2.4 [(Me2NC2H4OLi)4(2,4,6-Me3-C6H2OLi)2·(diox)]∞
2.5 [(Me2NC2H4OLi)5(2,4,6-Me3-C6H2OLi)·(diox)0.5]∞
2.6 [(2,4,6-Me3-C6H2OLi)·(Me2NC2H4OH)·(diox)0.5]∞
3.1 [(4-Cl-2,6-Me2-C6H2OLi)2·(dioxane)2]∞
3.2 [(4-Cl-2,6-Me2-C6H2OLi)2·(dioxane)2.5]∞
3.3 [(4-Cl-2,6-Me2-C6H2OLi)4·(dmf)4]
3.4 [(4-Cl-2,6-Me2-C6H2OLi)4·(dioxane)·(dmf)2]∞
3.5 [(4-Cl-2,6-Me2-C6H2OLi)4·(dioxane)2]∞
3.6 [(4-Cl-2,6-Me2-C6H2OLi)2·(dioxolane)2]∞
3.7 [(4-Br-2,6-Me-C6H2OLi)2·(dioxane)2]∞ [(4-Br-2,6-Me-C6H2OLi)2·(dioxane)2.5]∞
3.8 [(4-Br-2,6-Me-C6H2OLi)4·(dioxane)1·(dmf)2]∞
3.9 [(4-Br-2,6-Me-C6H2OLi)4·(dmf)4]
3.10 [(4-Br-2,6-Me-C6H2OLi)2·(dioxolane)2]∞
4.1 [(4-Cl-2,6-Me-C6H2ONa)2·(dioxane)3]∞
4.2 [(4-Br-2,6-Me-C6H2ONa)2·(dioxane)3]∞
4.3 [(4-Cl-2,6-Me₂C₆H₂OK)₂·(dioxane)₃]∞
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4.7 [(4-Cl-2,6-Me₂C₆H₂OCs)₇·(dioxane)]∞
4.8 [(2,4,6-Me₃C₆H₂OK)₅·(dioxane)]∞
4.9 [(2,4,6-Me₃C₆H₂ORb)₅·(dioxane)]∞
4.10 [(2,4,6-Me₃C₆H₂OK)₄·(thf)]∞
5.1 [(2-tBu-C₆H₄OK)₆·(H₂O)]·(dioxane)₄]∞
5.1₁ [(2-tBu-C₆H₄OK)₆·(H₂O)]·(dioxane)₄]∞
5.2 [(2-tBu-C₆H₄OK)₆·(H₂O)]·(THF)₆]
5.3 [(2-tBu-C₆H₄ORb)₆·(H₂O)]·(dioxane)₄]·(dioxane)]∞
5.4 [(2-tBu-C₆H₄ONa)₆·(H₂O)]·(dioxane)₃]∞
5.5 [(2-iPr-C₆H₄OK)₆·(H₂O)]·(dioxane)₃]·(dioxane)]∞
5.6 [(2-iPr-C₆H₄OK)₆·(dioxane)]∞
5.7 [(2-iPr-C₆H₄OK)₆·(H₂O)]·(dioxane)₅]∞
5.8 [2-iPr-C₆H₄ORb)₆·(dioxane)₄]∞
5.1₀ [(2-Me-C₆H₄OK)₄·(dioxane)]∞
6.1 [(4-F-C₆H₄OK)₆·(dioxane)]∞
6.2 [(4-I-C₆H₄OK)₆·(dioxane)]∞
6.3 [(4-I-C₆H₄ORb)₆·(dioxane)]∞
6.4 [(4-Cl-C₆H₄OK)₃·(dioxane)]∞
6.5 [(4-Br-C₆H₄OK)₂·(dioxane)₀]∞
6.6 [(4-Br-C₆H₄ORb)₅·(dioxane)₃]∞

6.7 [(4-Pr-C₆H₄OK)₂·(dioxane)₀.₅]∞

7.1 [((Me₃Si)₂NNa)₂·(Cp₂Fe)]∞

7.2 [((Me₃Si)₂NK)₂·(Cp₂Fe)]∞

7.3 [((Me₃Si)₂NRb)₂·(Cp₂Fe)]∞

7.4 [((Me₃Si)₂NCs)₂·(Cp₂Fe)]∞

7.5 [((Me₃Si)₂NRb)₂·(Cp₂Fe)₀.₆·(C₇H₈)₀.₈]∞

7.6 [((Me₃Si)₂NCs)₂·(Cp₂Fe)₀.₅·(C₇H₈)]∞

7.7 [(Me₃Si)₂NK·(Tol)]₂

7.8 [((Me₃Si)₂NCs)₂·(Tol)]∞

7.9 [K·(Cp₂Fe)₂·(Tol)₂]⁺[Mg(HMDS)₃]⁻

7.10 [Na(Fcpz)]⁻·[Na(DME)₃]∞

7.11 [K₂(Fcpz)·(DME)₃]∞

7.12 [Rb₂(Fcpz)·(DME)₃]∞

7.13 [Cs₂(Fcpz)·(DME)₃]∞

7.14 [((Me₃Si)₂NK)·(t-Bu-C₆H₅)]₂

7.15 [((Me₃Si)₂NK)·(Me₃-C₆H₃)]₂

7.16 [K·((C₆H₆)₂Cr)]⁺{Mg(HMDS)₃}∞

7.17 [K·((C₆H₆)₂Cr)₁.₅·(Mes)]⁺{Mg(HMDS)₃}∞