

Self-Assembly of Fluorinated Boronic Esters and 4,4'-Bipyridine into 2:1 N→B Adducts and Inclusion of Aromatic Guest Molecules in the Solid State: Application for the Separation of *o,m,p*-Xylene

Published as part of a *Crystal Growth and Design* virtual special issue on π - π Stacking in Crystal Engineering: Fundamentals and Applications

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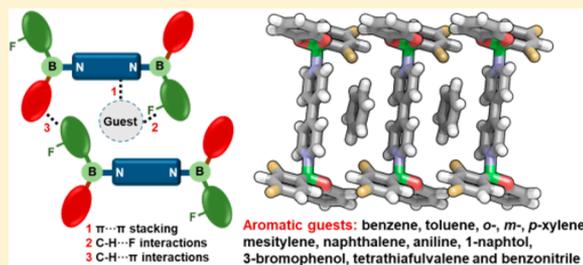
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Supporting Information

ABSTRACT: A series of 2:1 fluorinated arylboronic ester adducts with 4,4'-bipyridine sustained by N→B dative bonds have been synthesized. The degree of fluorination in the arylboronic esters derived from catechol is shown to modulate the molecular conformation of the coordinated boronic ester moieties and the intermolecular interactions by means of C–H⋯F and F⋯F contacts that sustain the crystal lattices. The adduct derived from the catechol ester of 2,4-difluorophenylboronic acid was chosen to examine the formation of inclusion complexes with a large number of aromatic guests, affording solvates, cocrystals, and a cocrystal solvate. Six different crystal structure types with 1:1, 1:2, and 1:2:2 N→B adduct–guest ratios were observed, whose supramolecular organization is strongly influenced by the formation of sandwich-type complexes between the host and guest molecules. The host–guest interactions involve π ⋯ π interactions with the bipyridine linkers and additional contacts with the catecholate and B-aryl_F substituents, indicating a large flexibility of the N→B adducts to adapt to the guest stereochemistry. The versatility of the crystallization system was employed to isolate *o*-xylene from an equimolar mixture of *o*-, *m*-, and *p*-xylene.



1. INTRODUCTION

The rational design of supramolecular architectures based on the self-assembly of building blocks (tectons)^{1,2} has led to the generation of diverse functional molecular systems, such as macrocycles, cages, capsules, rotaxanes, calixarenes, and metal–organic frameworks (MOFs).^{3–6} The assemblies are frequently metal–organic constructs with coordinate covalent bonds being the essential element of junction between the tectons. More recently, supramolecular structures with a high level of organization based on weak noncovalent intermolecular interactions have become increasingly valuable with applications in host–guest chemistry^{7,8} and crystal engineering.⁹ In the context of ion and molecular recognition, much attention has been directed toward the sensing and/or removal of toxic chemicals, including small aromatic hydrocarbons^{10,11} and polycyclic aromatic hydrocarbons (PAHs),^{12,13} for which most of the current techniques rely on costly processes.¹⁴

Easily accessible boronic acids have been a useful tool for the rational design of functional materials due to the capability of forming hydrogen-bonded homo- and heterodimeric synthons^{15,16} as well as aggregates with reversible covalent B–O bonds.^{17–19} Among others, boronic acids have been employed to assemble discrete and infinite systems capable of recognizing anions (i.e., F[−], CN[−]) and neutral molecules including aromatic compounds.^{20–24} Moreover, in the presence of N-containing ligands, the formation of boron-based supramolecular aggregates through coordinate covalent N→B bonds gives access to more diversified systems including coordination polymers, nanostructures, and gels.^{25–27} Recent examples are 2:1 Lewis type N→B adducts formed from boronic esters and diamines, of which the former are derived from arylboronic acids and

Received: September 26, 2017

Revised: March 22, 2018

Published: April 3, 2018