PD Research Report for the 2016 year

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Research Theme Synthetic Study of High-Ordered Iptycene Derivatives Using Isobenzofuran as a Reactive Platform

Research Period April 1st, 2016 ~ March 31st, 2017

Research Results

Isobenzofurans are useful building blocks in synthetic chemistry having 10π-electron systems with quinoid structures. Focusing on the high reactivity toward [4+2] cycloadditions with dienophiles, our group has developed the efficient synthetic methods and applications of highly functionalized isobenzofuran derivatives. For example, a donor–acceptor type isobenzofuran (**I**), bearing both electron donating and withdrawing groups exist in a molecule, enabling successive cycloaddition to construct polycyclic system. In addition, dual cycloaddition was available to lead polycycles using bis-isobenzofurans (**III**) as a key intermediate by the sequencial generation of isobenzofurans from bis-epoxynaphthalenes (**II**). Based on these previous results, our interest moved on to the tris-isobenzofuran (**V**) bearing triptycene skeleton in the core as a three dimensional building block.

Triptycenes (**IV**) are the simplest member in iptycene family, having [2.2.2]bicyclooctatriene bridgehead system with phenyl rings attached. The bicyclic core derives rigidity and creates prism-like geometry involving void spaces. Supramolecular interactions, opening a substantial potentiality in crystal engineering, host-guest complexes, molecular machines, polymers and liquid crystals.

In order to develop a novel three-dimensional π-extended molecule, our synthetic goal is synthesizing tris-polyacene (**VI**) utilizing triple [4+2] cycloaddition from tris-isobenzofuran (**V**).

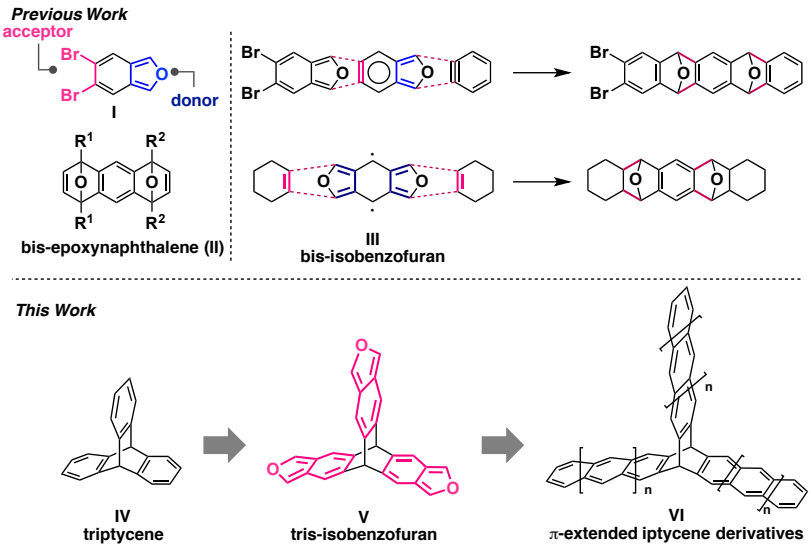


**Figure 1. Construction of polycyclic structure via isobenzofuran**

The key building block, tris-isobenzofuran (**4**), was synthesized from hexabromotriptycene (**1**). Upon the treatment of 4.0 equiv. of PhLi in toluene/THF co-solvent (conditions B), tris-epoxynaphthalene (**3**) was obtained in 41% yield. Mono-isobenzofuran (**5**) and bis-isobenzofuran (**6**) was also accessible (conditions A).

Using diphenylfuran (**10**) instead of **2**, isobenzofurans **7**, **8**, **9** were obtained. In this way, six different kinds of triptycene building blocks bearing isobenzofuran motif were synthesized.

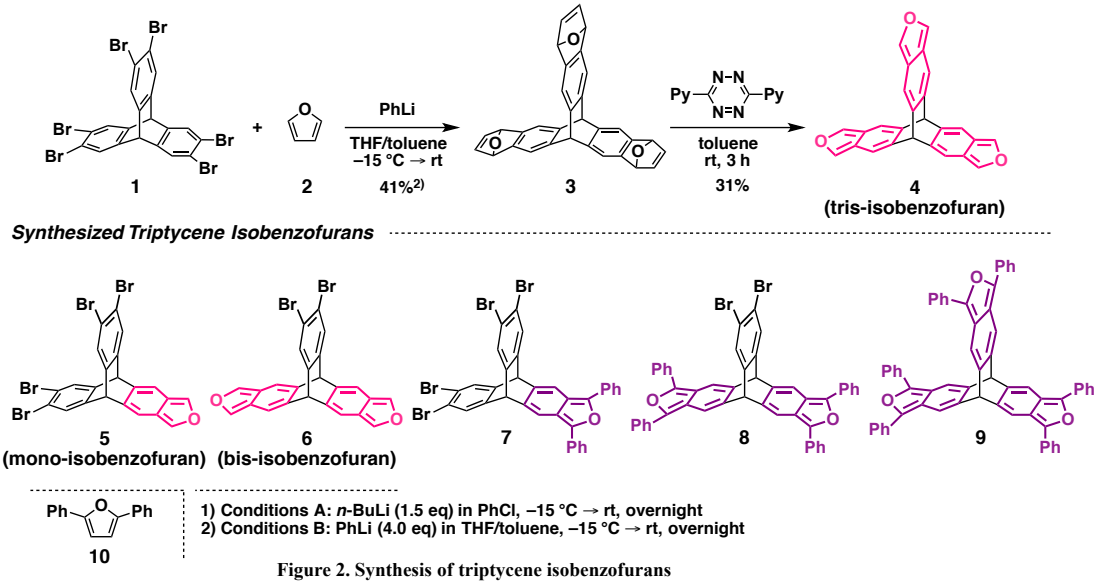


**Figure 2. Synthesis of triptycene isobenzofurans**

Next, cycloaddition of tris-isobenzofuran (**4**) and anthraquinone (**11**) was conducted and following aromatization in acidic conditions gave the tris-pentacenequinone (**12**) in 14% as a two-step yield. Further transformation toward pentacene derivatives was also performed. TIPS ethynyl group was added to the **12**, then upon the treatment of $SnCl_2$ and 10% HCl in THF solution gave the desired tris-pentacene (**13**) in 16% yield (2 steps). Further studies toward electronic and photochemical characteristics of **13** will be studied.

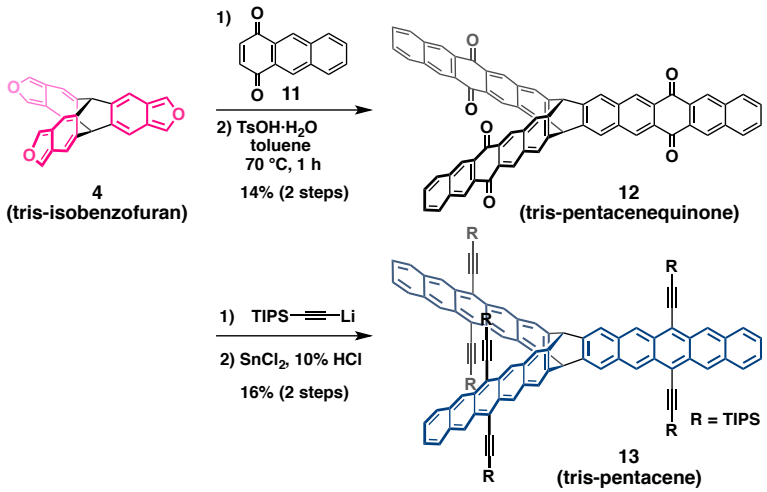


**Figure 3. Synthesis of tris-pentacenequinone and tris-pentacene**

In conclusion, the highly reactive triptycene based isobenzofurans were synthesized and applied to the synthesis of tris-pentacene derivative, a high-ordered iptycene derivative. We will continue our study on supermolecular activity of this three-dimensional π-extended iptycenes as a potential organic material.

Conference Presentations

(1) Sunna Jung and Toshiyuki Hamura, "Synthetic Study of High-Ordered Iptycene Derivatives Using Isobenzofuran as a Reactive Platform", Spring CSJ meeting, 2F1-19 (Presentation), Kanagawa, Japan, **2017**, March. (*English*)