

附件一

行政院國家科學委員會補助專題研究計畫 成果報告
 期中進度報告

低聚反式（亞芳香基亞乙烯）衍生物和尿素衍生物的合成與研究

計畫類別： 個別型計畫 整合型計畫

計畫編號：NSC 91-2113 M-002 -024

執行期間：2000年8月1日至2003年7月31日

計畫主持人：梁文傑

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計畫參與人員：

成果報告類型(依經費核定清單規定繳交)： 精簡報告 完整報告

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執行單位：台大化學系

中華民國 92 年 10 月 15 日

中文摘要

本計劃的目的可分為(1)分子辨識與協統行為;(2)光電材料的設計與合成。第一部分集中在尿素衍生物的合成與研究。在第二部分我們開發電化學聚合法,合成光電有機聚合物。

英文摘要

Our ongoing research was divided into two directions: (1) Molecular recognition and cooperative interactions. (2) Design and synthesis of novel opto-electronic materials. In the first topics, we focused on the binding behavior of bis-urea and oligoaminopyridine. In the second part, we have developed electropolymerization techniques on opto-electronic material synthesis.

關鍵: 分子辨識, 協統行為, 電化學聚合法, 光電有機聚合物。Molecular recognition; cooperative interactions; Electropolymerization; opto-electronic materials

報告內容:

Introduction:

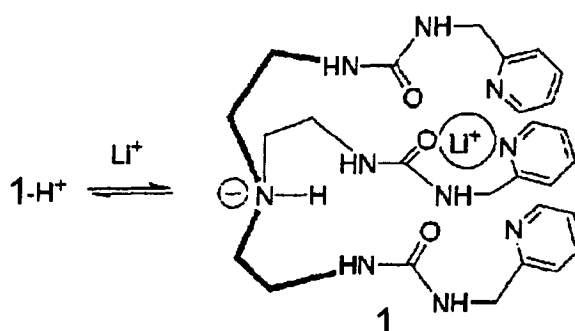
During the last few years, our ongoing research was divided into two directions: (1) Molecular recognition and cooperative interactions. (2) Design and synthesis of novel opto-electronic materials. About ten related papers have been published. Herein we summarized some of our major work that have been done for the proposal.

- (I) Cooperative binding behavior of organic ureas.
- (II) Zipperic dimerization through hydrogen bonding interaction.
- (III) Solubilization of conjugated polymers by aryl side-chain.
- (IV) Electro-polymerization of triarylamine derivatives

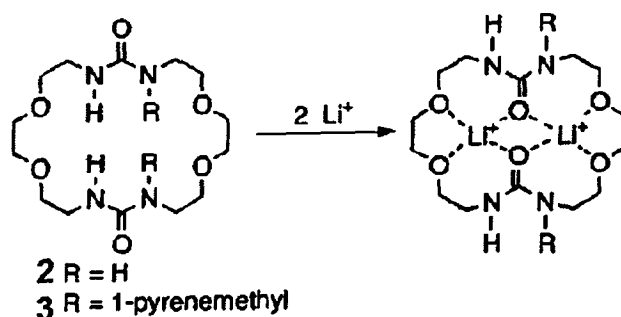
Major Achievements

Cooperative binding behavior of organic ureas.

Reference 1 reported that tris(2-((pyrid-2-ylmethyl)ureido)ethyl)amine (1) and its perchlorate salt, 1-HClO₄, bind with Li⁺ in nitromethane in a 1:1 fashion. The stability constants of $K(\text{Li}^+)$ and $K_{\text{H}}(\text{Li}^+)$ were found to be 112 ± 25 and $130 \pm 30 \text{ M}^{-1}$ in CD₃NO₂, respectively. Formation of the 1:1 complexes were further evidenced by electrospray ionization mass spectrometry (ESI-MS). The slight increase, or at least the same order of magnitude, of $K_{\text{H}}(\text{Li}^+)$ compared to $K(\text{Li}^+)$ points to a remarkable preorganization of the protonated podand in 1-HClO₄, that essentially overcomes the increased Columbic repulsion occurring on complexation to Li⁺.



Reference 2 reported that ureylene crown ethers 2 and 3 bind with 2 equiv of Li⁺ cooperatively and selectively over other alkali metal ions such as Na⁺, K⁺, and Cs⁺. The binding constant for 3



was found to be 3.0×10^7 (L/mol)². In a series of competition experiments, addition of the same amounts of Na⁺, K⁺, or Cs⁺ would not affect the ratios of I_f/I_{ex} for **3**, indicating the preference for Li⁺ binding. In particular, the ratio of I_f/I_{ex} for **3** is not significantly altered even in the presence of a 100-fold excess of Na⁺ and drops to only one half in the presence of an 850-fold excess of Na⁺. All these observations suggested a high selectivity of **3** toward Li⁺ binding.

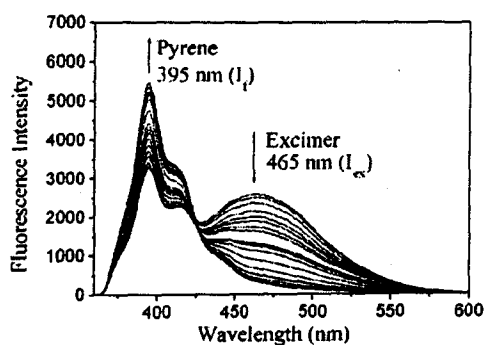
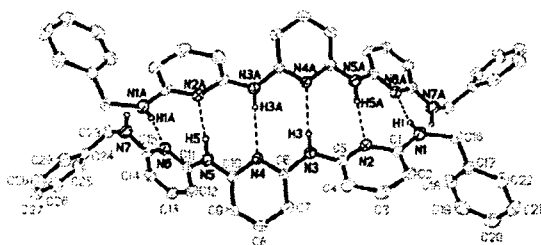
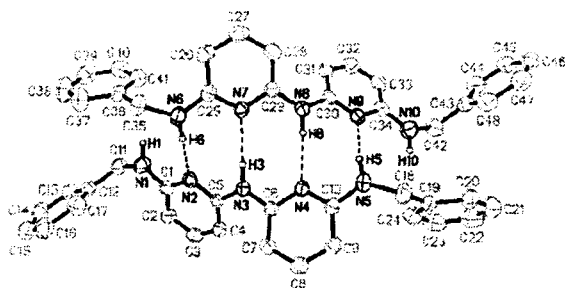


Figure 1. Fluorescence titration experiments of **3** at 2×10^{-6} M in CH₃CN with LiClO₄ as the titrant. Addition of LiClO₄ to a solution of **3** reduces the intensity of the excimer.

Zipperic dimerization through hydrogen bonding interaction

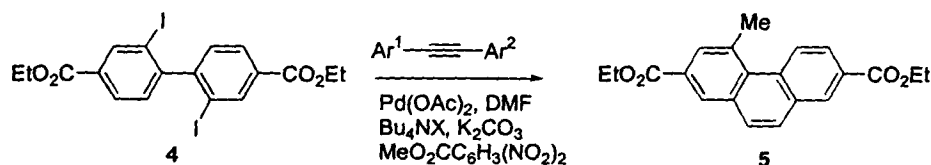
A new class of hydrogen-bonded ladders based on hydrogen-bonded dimerization of oligo-2-aminopyridines has been demonstrated in reference 3. Jorgensen's model can be successfully applied to this hydrogen bonding system in non-polar solvents. The results show the competitive enthalpy/entropy compensation relationship upon dimerization. Although increasing the number of hydrogen-bonding interactions would enhance the hydrogen-bonding stabilization enthalpy, this stabilization enthalpy per unit would be partially sacrificed to compensate for the entropy loss due to dimerization. These results clearly support the importance of preorganization in designing hydrogen-bonding guest-host molecules.



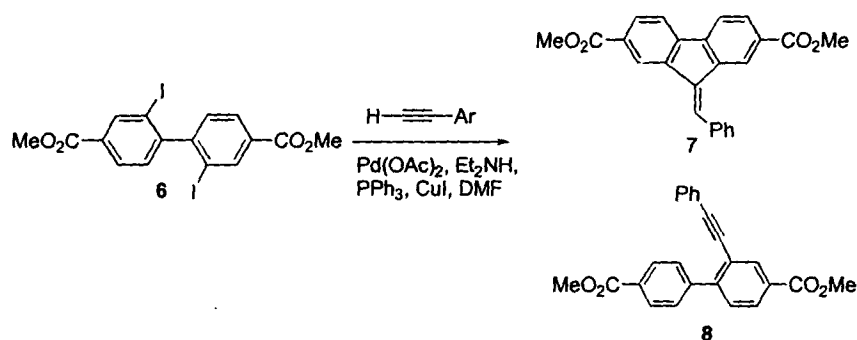
Solubilization of conjugated polymers by aryl side-chain.

In this section, we are interested in synthesizing soluble fully aromatic conjugated polymers for LED purpose. Compound **4** is considered as a useful starting material because it contains two iodo side-groups that could be further functionalized as aromatic side chains. During the development of the synthetic strategy, we have discovered two new reactions. Reference 4 described that the reaction of diethyl 2,2'-diiodo-4,4'-biphenyldicarboxylate (**4**) with diarylacetylenes in the presence of 3,5-(NO₂)₂C₆H₃CO₂Me (MeDNB) or 4-(NO₂)C₆H₄CO₂Me (MePNB), Pd(OAc)₂ (10 mol%), K₂CO₃, and Bu₄NBr, in DMF at 100°C, gives 4-methyl-9,10-diaryl-2,7-phenanthrenedicarboxylic acid diethyl esters **5** in good yields. The methyl group at position 4 originates from the electron deficient methyl nitrobenzoates. High regioselectivity for the annulation of **4** with nonsymmetrical diarylalkynes was observed with the selectivity controlled mainly by electronic factors rather than by steric factors. A competitive kinetic isotope study was carried out using a 1:1 mixture of MePNB and MePNB-*d*₃ in the annulation reaction of **4** which gave 4-methyl- and 4-(methyl-*d*₃)phenanthrene in a 67:33 ratio,

leading to an apparent value of k_H/k_D) 1.26. Possible mechanisms for the methyl transferring process are discussed.



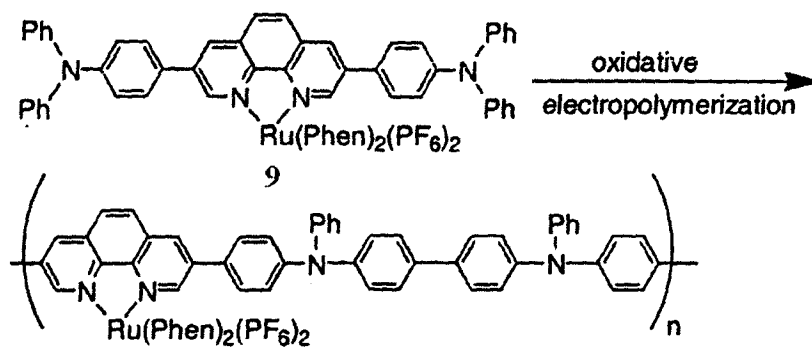
Reference 5 reported that 2,2'-Diiodobiphenyl-4,4'-dicarboxylic acid dimethyl ester (**6**) undergoes either a ring-closure reaction with phenylacetylene to give **7** or hydrodeiodo phenylethylation to give **8** under the catalytic conditions of Pd(OAc)₂/CuI/phosphine in amines. In these reactions, the amine and the phosphine ligands play important roles in controlling the reactivity. Among the ligands we used, tris(*o*-tolyl)phosphine is the best ligand for hydrodeiodo phenylethylation, while the bidentate phosphine ligand retards both of the reactions. On the basis of our results, we propose that **6** is formed through a fast hydrodeiodination, followed by a Sonogashira phenylethylation. The results of the deuterium labeling experiments show that proton exchange between the acetylenic proton and the alkyl protons of amine occurs effectively under the reaction conditions. In addition, the hydrogen that replaces the iodide in the hydrodeiodination process arises mainly from the acetylenic proton.



Electro-polymerization of triarylamine derivatives

Reference 6 reported that the diphenylamino group is an effective handle for

electropolymerization to give electron donor-acceptor conjugated polymers. For example, **9** could be effectively electropolymerized to give electroactive polymer which shows interesting electrochromic and photoresponsive behavior.



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