

氏 名 Md, Akhtaruzzaman

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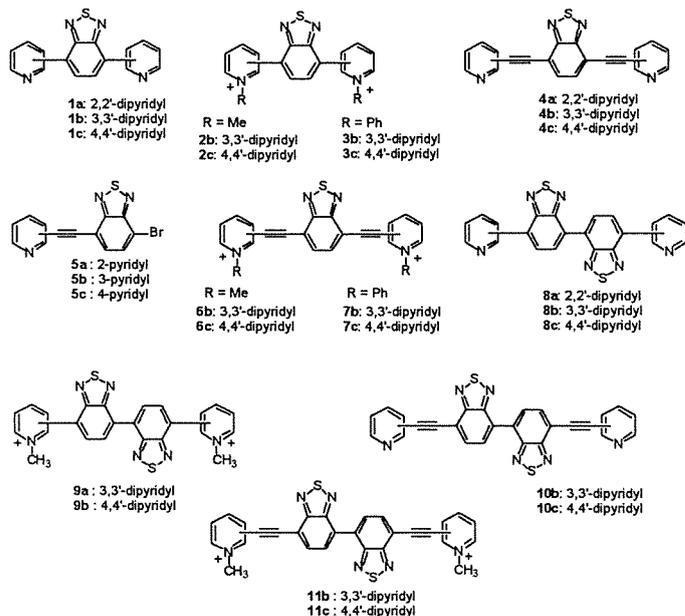
学位論文題目 Studies on Novel Linear  $\pi$ -Conjugated Molecules  
Containing Pyridyl Groups

論文審査委員 主査 教授 小林 速男  
教授 薬師 久彌  
助教授 井上 克也  
助教授 冨田 博一  
教授 山下 敬郎 (東京工業大学)  
教授 岡田 恵次 (大阪市立大学)

## 論文内容の要旨

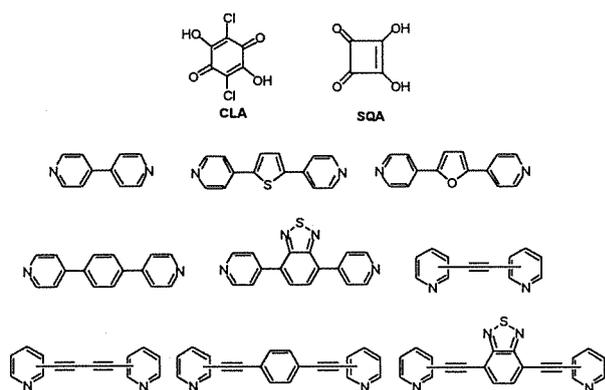
For the past forty years, inorganic silicon and gallium arsenide semiconductors, silicon dioxide insulators, and metals such as aluminium and copper have been the backbone of the semiconductor industry. However, there has been a growing research effort in “organic electronic” to improve the semiconducting, conducting and light emitting properties of organics (polymers, oligomers) and hybrids (organic-inorganic composites) through the novel synthesis and self-assembly techniques. This rich area of research has been benefited from studies on rational design based on crystal engineering, including supramolecular chemistry, and the interest to investigate the structures and properties of organic solids states. This research work was carried out to understand the intermolecular interactions and molecular recognition of solid state structures that might exhibit interesting electrical, magnetic and optical properties. For this purpose, molecules possessing pyridyl groups at the terminal positions have attracted much attention, and their derivatives have been reported by several groups since these molecules can afford supramolecular wires by coordination with metals and/or hydrogen bonding involving the nitrogen atoms of the pyridyl groups. In this context, linear  $\pi$ -conjugated molecules have now been synthesized by inserting benzothiadiazole as spacer units between the dipyridyl backbone. The introducing of 1,2,5-thiadiazole rings is of interest due to their extended  $\pi$ -conjugation and polarized heteroatoms which are expected to afford well-ordered crystal structures leading to intermolecular interactions such as heteroatom contacts or  $\pi$ - $\pi$  interactions. The compounds containing thiadiazole rings are well known as strong fluorescent materials. Highly fluorescent  $\pi$ -conjugated molecules are of interest from the application purposes such as EL (electroluminescence) devices and single molecular detection. Moreover, this heterocycle is electron-withdrawing and the compounds bearing this ring are possible candidates for electron carriers. The electron accepting conjugated molecules are also of interest from view points of the NDR (negative differential resistance) behaviours since recent studies have shown that oligo (phenyleneethylene)s containing an electron-withdrawing nitro group can be used as active redox centers responsible for the NDR behaviour in semiconductor devices.

In this research work, the author designed some new dipyridyl compounds and their viologen analogues containing benzothiadiazole spacer units as shown in general scheme 1, and investigated their electronic properties, crystal structures, and established the relationship between the structures and fluorescence properties. The compounds of 4,7-di(*n*-pyridyl)-1,2,3-benzothiadiazole (*n* = 2, 3, and 4) (**1a-c**) show high quantum yields of fluorescence and high electron affinities. They also show solid-state fluorescence due to weak intermolecular interactions caused by their large torsion angle between the benzothiadiazole and pyridyl rings. There is no significant effect of the nitrogen positions of the pyridyl ring on the quantum yield of fluorescence. The crystal structures of the compounds **1a-c** have the similar space group with overlapping the stacked molecules in a head-to-tail fashion. The reduction potentials of their viologen analogues **2-3** are higher than their corresponding neutral compounds. The quantum yields of fluorescence of these compounds are low due to decrease of the torsion angles.



The compounds 4,7-bis(*n*-pyridylethynyl)-1,2,3-benzothiadiazole (*n* = 2, 3, and 4) (**4a-c**) also show high electron affinities and high quantum yields of fluorescence. The absolute quantum yield of **4c** is  $0.87 \pm 0.05$ . The solid-state fluorescence of these compounds is lower compared to the compounds **1a-c**. This can be explained by the planarity of the molecular structures. X-ray structures analysis revealed that the torsion angles between the benzothiadiazole and pyridine ring are smaller than those of the compounds **1a-c**. So the intermolecular interactions becomes stronger and the solid-state fluorescence decreases. The molecules are stacked to afford unusual two-dimensional columns where the distance between the molecular planes is 3.79 Å. The columns run in two directions with 45°. No short heteroatom contacts such as S...N are observed. The crystal structures of **4a-c** are similar although the space groups are different. The noncentrosymmetric space group is interesting from the standpoint of nonlinear optical properties. The molecular structures of their methylated compounds are more planar than the corresponding neutral compounds. Their crystal structures include  $\pi \cdots \pi$  stacking of long molecules. A number of intermolecular O-H...O, C-H...O, and C-H...F interactions are also found in the methylated structures.

The absorption maxima of bis(benzothiadiazole) compounds (**8-11**) are observed at longer wavelengths than those of mono(benzothiadiazole) compounds due to longer conjugation in these compounds. The quantum yields are a little decreased compared to the mono(benzothiadiazole) compounds. There is no significant effect of the nitrogen positions on the absorption and emission spectra on these compounds. The reduction potentials of these compounds show stepwise one-electron reduction waves due to the presence of two benzothiadiazole ring, and also higher than those of mono benzothiadiazole derivatives. This is attributed to the electron withdrawing property of the thiadiazole ring. X-ray structure analysis reveals that the bis(benzothiadiazole) derivatives are nonplanar structures due to the repulsion between the pyridine and benzothiadiazole ring. There are short S...N contacts observed, leading to the molecular tape structures. It is noteworthy that the dihedral angles of their methylated compounds are drastically decreased, and the dihedral angle between the pyridine and benzothiadiazole ring is absolutely zero degree in the methylated compound **11c**.



**Scheme 2**

Finally, the author used dipyrrolyl compounds containing  $\pi$ -conjugated groups as proton acceptor as shown in general Scheme 2, and investigated their complexation with chloranilic(CLA) and squaric (SQA) acid by hydrogen-bonding interactions which are very important in the field of crystal engineering as well as in supramolecular chemistry. The introduction of a  $\pi$ -conjugated spacer to dipyrrolyl compounds have been considered to increase intermolecular  $\pi$ - $\pi$  interactions and decrease Coulombs repulsion in the dication states. The crystal structures are strongly dependent on the spacer group. Although the details of relationship between the crystal structures and spacer group are still ambiguous, it should be noted that the structure of the complexes of the twisted molecules are completely different from those of the planar molecules. The author believed that more elaborated crystal engineering would be possible by changing the spacer group and/or substituents of anilic acid.

Akhtaruzzaman さんの提出論文の題名は「Studies on Novel Linear  $\pi$ -Conjugated Molecules Containing Pyridyl Groups」である。

両末端にピリジル基を有する直線状 $\pi$ 共役分子は、長い剛直な共役系分子としての物性に興味を持たれる他に、金属への配位や水素結合のプロトン受容体としての性質を持つことから、超分子体構築のユニットとしても期待される。また、これら分子の両末端にピリジル基を結ぶ $\pi$ 共役スペーサー部やピリジン環の窒素の位置を変えることで、分子や超分子体の構造・物性を制御することが可能である。Akhtaruzzaman さんは新しい機能性分子物質の開発を目指して、スペーサー部にベンゾチアジアゾール環やアセチレンユニットなどを有する分子を新規に合成し、それらの分子の性質や結晶構造を検討した。

Akhtaruzzaman さんはビスピリジルエチニル化合物については Sonogashira 反応を、芳香環に直接ピリジル基を置換した分子は Still カップリング反応を用いて合成し、ピリジル基の導入法を確立させた。分子構造を単結晶構造解析で明らかにし、アセチレンユニットを導入すると立体障害がなくなるために平面性がよくなり、結晶内で $\pi$ - $\pi$ の相互作用を持ったスタック構造をとりやすくなることを明らかにした。スペーサー部にベンゾチアジアゾールユニットを導入することで電子受容性と蛍光特性の向上、最高被占軌道と最低空軌道間のエネルギー差の減少が見られた。溶液の蛍光の量子収率は 100%のものもあり、興味深い光学的性質が見られた。また、立体障害を利用して分子を非平面構造とすると、固体状態での蛍光効率が上昇することも見いだしているが、この結果は固体での蛍光物質の開発に重要な知見を与えるものである。更に、スペーサー部にベンゾチアジアゾールユニットを2つ導入することにより共役系をさらに拡大させると、結晶内の隣接分子間の S $\cdots$ N 相互作用により分子がテープ状に連なった興味深い分子配列が構築される事が判った。一部のジピリジル分子ではN位をメチル化することでジカチオン体を得られる。これらは $\pi$ 電子系が拡大したメチルピオローゲン類縁体であり、蛍光特性などに興味深い物性が期待される。

分子物質の機能性の発現には分子配列・結晶構造制御が極めて重要である事は言うまでもない。Akhtaruzzaman さんは水素結合を用いた構造制御を目的として、ジピリジル化合物をプロトン受容体、クロラニル酸や四角酸などの有機酸をプロトン供与体とする超分子錯体を作成し、それらの構造研究を行った。ジピリジル化合物の $\pi$ 共役スペーサー、窒素原子の位置の効果、有機酸の効果などを系統的に研究し、種々の特異な結晶構造を明らかにし、共通の「構造部品」により、多様な構造が構築できることを示した。現在のところ、新機能の発現は実現されていないが、プロトン移動によりジカチオン、モノカチオン、中性の状態を選択的に生成できるので、今後プロトン移動と電子移動が共存による新物性の実現が期待される。

このように Akhtaruzzaman さんの論文では拡張 $\pi$ 電子系を有するジピリジニル化合物を合成し、蛍光特性などの興味ある物性を明らかにし、また、これらの分子を用いて水素結合超分子体の構築に成功した。この研究成果は複素環化学、材料化学ならびに超分子化学に貢献するものであり、博士論文に値するものと判断された。

審査会では約1時間にわたる論文の説明の後、約1時間の質疑応答の中で博士論文に関

する専門分野ならびに基礎的な知識に関する質問を行った。Akhtaruzzamanさんは超分子分野の研究の背景をよく理解していると同時に、有機化学、複素環化学の基礎知識も修得していると判断された。また、学位論文は英語で書かれ、論文説明、質疑応答も英語で行われた。

以上、Akhtaruzzamanさんは博士論文を中心としてその周辺分野まで含めて幅広い学識を有しているものと判断される。また、公開発表会でも明解な発表をし、審査委員全員一致して合格と判定した。