Studies on Novel Linear π-Conjugated Molecules Containing Pyridyl Groups

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Contents

Chapter 1 Introduction

1.1 General Introduction

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 electronics" to improve the semiconducting, conducting and light emitting properties of organics (polymers, oligomers) and hybrides (organic-inorganic composites) through the novel synthesis and self-assembly techniques. This rich area of research has been benefited from attempts to carry out rational design based on crystal engineering, including supramolecular chemistry and the interest to investigate the structures and properties of organic solids. 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. Recently, molecules possessing pyridyl groups at the terminal positions have attracted much attention and the derivatives have been reported by several groups since these molecules can afford supramolecular wires by coordination with metals[1] or hydrogen bonding.[2] They can afford interesting supramolecular architectures by intermolecular interactions involving the nitrogen atoms of the pyridyl groups.[2,3] In this context, the linear π-conjugated molecules have been synthesized by inserting benzothiadiazole as spacer units between the dipyridyl backbone. The introduction of 1,2,5-thiadiazole rings into this project is of interest due to their extended π-conjugation and polarized heteroatoms which are expected to afford well-ordered crystal structures leading to intermolecular interactions such as heteroatom contacts or π···π interactions.[4] The compounds containing thiadiazole rings are well known as strong fluorescent materials.[5] Highly fluorescent π–conjugated molecules are of interest from the application purposes such as EL (electroluminescence) devices[6] and single molecular detection.[7] 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(phenylenethylene)s containing an

electron-withdrawing nitro group can be used as active redox centers responsible for the NDR behaviour in semiconductor devices.[7] In this research work, the author designed some novel dipyridyl type compounds and their viologen analogues containing benzothiadiazole spacer units, and investigated their electronic properties, crystal structures, and established the relationship between the structures and fluorescence properties. The author also investigated their complexation with chloranilic acid, squaric acid and cyanuric acid through the hydrogen bonding networks. In this chapter, the author briefly describes some previous works related to intermolecular interactions in the field of crystal engineering as well as supramolecular chemistry, and the aim of present works.

1.2 Background Information

Crystals are composed of molecules or ions, and the physical and chemical properties of crystals depend upon the geometrical arrangement of these internal building blocks. Crystal engineering is to understand the nature, strength and directionality in various intermolecular interactions of solid states. For this reason, the experimental and theoretical generation of desired crystal structures is attracting the interest of an increasing number of research groups. The ultimate goal is to make crystals with a purpose. In 1970s G. M. J. Schmidt addressed (*design of organic solid*) that the crystal engineering is to predict structures in the context of organic solid state photochemical reactions of cinnamic acids.[9a] Later broad and more meaningful definition of crystal engineering was provided by G. R. Desiraju in 1989 who has defined it as "*the understanding of intermolecular interactions in the context of crystal packing and in the utilisation of such understanding in the design of new solids with desired physical and chemical properties*."[9b] Crystal engineering is now a rapidly developing interdisciplinary field with a wide scope for basic research and promising industrial applications which may also drive basic research efforts (for example, electronic materials and sensors, catalysis, optical materials, molecular modelling, drug design, supramolecular devices, nano and microporous materials). On the principal design, crystal engineering deals with the following two branches separately.

1. Inorganic solids (or coordination polymers) which are designed primarily by

considering metal coordination geometry, chemical structure of organic ligand, metal to ligands ratio, and the coordinating nature of the anions.

2. Organic solids which are designed by considering molecular shape, symmetry, and intermolecular interactions such as O····H, N····H, and C····H hydrogen bonding, or weaker halogen····halogen, electrostatic, or van der Waals interaction.[10-12]

Currently, the most efficient approach of crystal engineering in the field of inorganic solids is preparing well-arranged metal-containing macrocycles by the direct chemical combination of functional inorganic and organic components. For all practical purposes, the crystal structures are assumed to be networks, where the molecules, metals, ions etc., are considered as nodes and the intermolecular interactions or coordination bonds represent node connections. Therefore, the design of one, two, or three-dimensional crystalline networks is of utmost importance in crystal engineering which can be achieved by choosing the desired combination of nodes and connectors. For example, metal cations as the nodes with simple linear bifunctional ligands as connectors will form a variety of 1D, 2D, and 3D architectures depending upon the metal coordination geometries and metal to ligand ratio (Figure 1).[12]

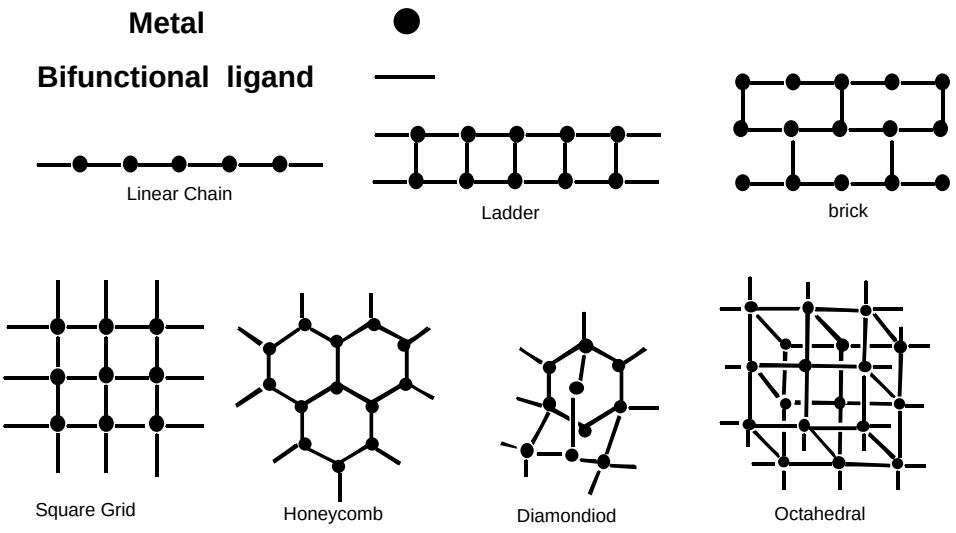

Figure 1. Control of metal ion coordination geometry and reaction stoichiometry can lead to controllable 1D, 2D, and 3D architectures.

Transition-metal-directed self-assembly has been used to construct crystalline

host-guest materials containing a cavity including ligands-bridged metallocycles (squares, rectangle, hexagon etc.) as nanoscale hosts in technological applications in the area of chemical recognition and sensing. Among these metallocycles, square-grid and rectangular-grid type architectures are promising because of their predictable pore sizes and selective inclusion of guest molecules. Initially these grids were reported in metal complexes of 4,4'-bipyridine with open and interpenetrated networks. The length, linear or nonlinear geometries, and conformationally rigid or nonrigid molecular skeletons of 4,4'-bipyridine can also be controlled by interconnecting spacers between the pyridyl groups. The conjugated π-systems containing ethynylene units and/or heteroaromatic ring spacers are currently of interest in developing fluorescence materials and are used as model compounds for electroluminescence and optical switching devices.[11-14] Fujita et. al, Stange et. al and many other research groups have reported many square structures based on transition metal centers such as Pd(II), Pt (II) and Cd (II), and pyridine-based bridging ligands. The 90º bonding angles between ligands in transition metal complexes provide an attractive feature for constructing macrocyclic structures (Figure 2a). Very recently, Alister J. Lees. et. al showed that the geometry of the macrocyclic compounds can be varied among squares, triangles, or dimers by simply modifying the bridging ligands (Figure 2b) and that their resulting electrochemical, photophysical, and photochemical properties and binding capabilities towards guest molecules are very different.[15]

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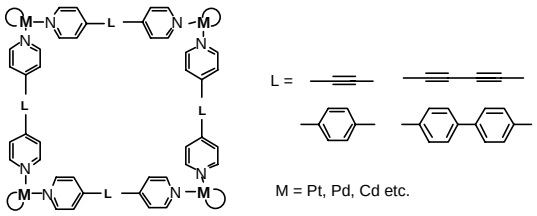

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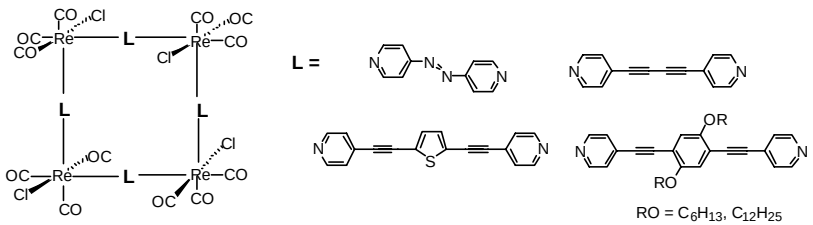

Figure 2. (a) Schematic diagram of Fujita et. al. (b) Schematic diagram of Lees et. al.

Since an organic crystal is a kind of supermolecule, thus the crystal engineering is an integral part of supramolecular chemistry, the chemistry of the 21st century. The voluminous (and ever growing) crystallographic information stored in the Cambridge Structural Database (CSD) is the primary source for an extremely reliable description of intermolecular interactions for the design of organic solids. For example, a very recent database study on the competition of hydrogen bond acceptors for the strong carboxyl donors shows that the recognition with CO_2H with pyridine is favoured 10 times more through an O–H····N hydrogen bond compared to dimer and catemer motifs with itself.[16] Desiraju has classified the intermolecular interactions in organic solid state into two types such as isotopic medium-range interactions which define shape, size and close packing, and anisotopic long-range interactions which are electrostatic and include hydrogen bonds and heteroatom interactions.[11] Isotropic interactions or van der Waals interactions are dispersive and repulsive and include C···C, C···H, and H···H contacts. Anisotropic interactions or directional interactions that operate in a supermolecule are strong hydrogen bonds (O-H···O, N-H···O, O-H···N), weak hydrogen bonds (C-H···O, C-H···N, O-H···π, C-H···halogen), ionic interactions and other interactions such as halogen···halogen, nitrogen···halogen and oxygen···halogen contacts. Among all these, the hydrogen bond is the most versatile and predictable and hence designable on the basis of molecular geometry and interactions topology. The general patterns of hydrogen bonds in crystal are tape, ribbon, and sheet like networks.[9] A tape will be formed when the functional groups involved in intermolecular interactions on a molecule are antiparallel or at 120° to each other, thus the molecule can interact with only two adjacent molecules in a linear or zigzag fashion (Figure 3a,b). In a ribbon pattern, the functional groups may be oriented in different directions, giving some flexibility in the recognition to adjacent molecules (Figure 3c). A sheet will involve the formation of two-dimensional arrays stabilised by intermolecular interactions (Figure 3e). The tapes and ribbons-like structures are of interest in crystal engineering due to various applications in materials science, because they can generate polarization through the intermolecular interactions in solid, which is a necessary condition for a number of physical properties. For example, *p*-nitroaniline leading to a tape structure has been studied for its non-linear optical properties. The sheet like pattern has received much interest to generate voids, which may in turn have

applications in the area of zeolite materials. For example, trimesic acid has been extensively studied for this purpose.

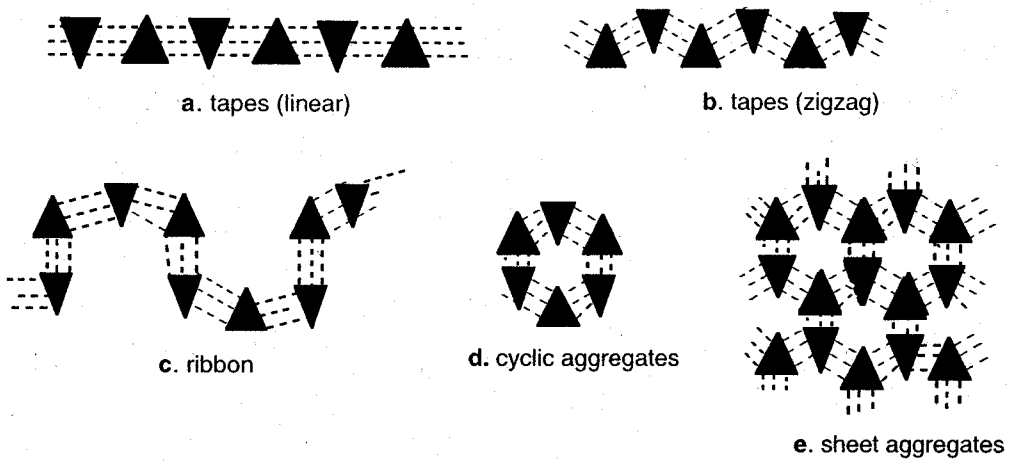

Figure 3. Schematic diagram of various types of hydrogen-bonding pattern.

Recently, a variety of supramolecular synthons have been drawn by Desiraju to identify the elements designed for intermolecular interactions in solid.[9b, 10] The carboxylic acids are commonly used as pattern controlling functional groups for the purpose of crystal engineering.[16] Since it possess hydrogen atoms for hydrogen bonding as well as electron-withdrawing carbonyl parts, it can readily form hydrogen bonds to give dimers (synthon **I**) or catemers (synthon **II**) motifs crystal structures. The formation of dimer synthon of carboxylic acid is preferred over the catemer chain. This was practised to construct a zero-dimensional dimer with benzoic acid, a 1-D chain with terephthalic acid or a zigzag chain with isophthalic acd, a 2-D sheet/honeycomb network with trimesic acid, a 3-D adamantoidal network with methanetetracarboxylic acid.[17] Specific noncovalent interactions between different functionalities seem to control single and multi-component crystallization. The cyclic dimer of synthon **III**, **IV** and **V** is formed whenever hetero-functional group recognition between a carboxylic acid and an amide is available which is notable for its robustness. *Peddy et. al.* showed that the combination of pyridines and carboxylic acids results in a heterodimer ring motif of **VI** [O-H···N, C-H···O]. In that report they also showed that O-H···N and N^{+}-H···O^{-} hydrogen bonding depend on the acidity of the CO_2H group and the basicity of the pyridyl moiety.[18] *Thalladi. et. al* also prepared the synthon of

VII using pyrazine and methyl substituted pyrazine and also showed that the nature of C-H···N/π interaction depends on the acidity of C-H group in pyrazine and the less acidity of C-H group leads to weaker interactions.[20]

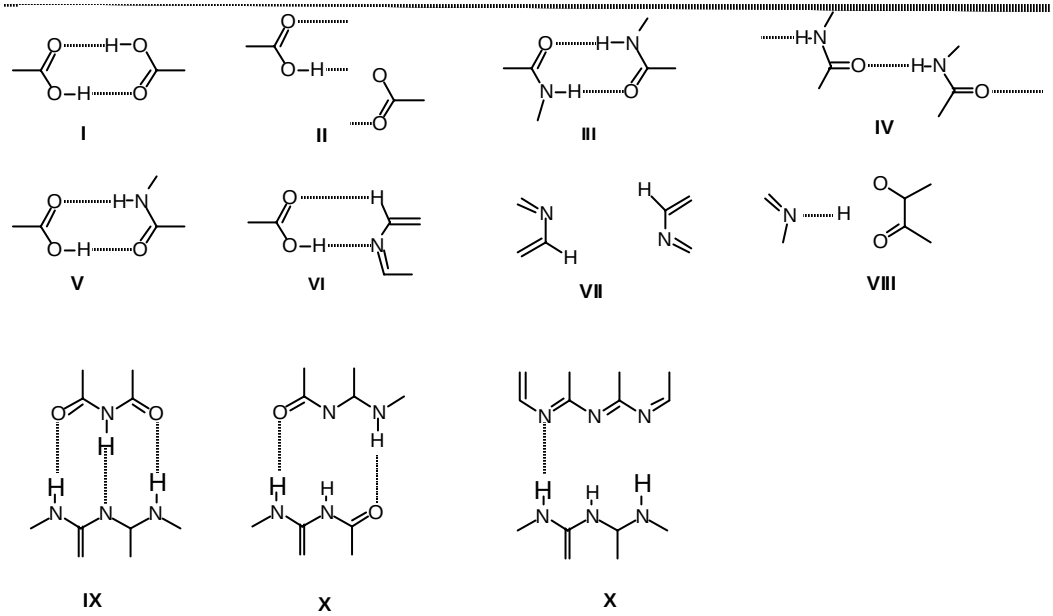

Figure 4. Some supramolecular synthons selected from the recent literature.

Very recently our group (*Zaman. et. al*) showed that the simple combination of chloranilic acids and dipyridyl compounds can create a new supramolecular synthon **VIII** as shown in Figure 4 through the hydrogen bonding network. It was revealed that the position of nitrogen atoms of dipyridyl compounds and spacer unit of dipyridyl compounds strongly influenced the solubility, hydrogen-bonding capability, ionicity, geometry, and stacking arrangement of the molecules. In this report they showed a bifurcated interionic N^{+}-H···O^{-} hydrogen bonding network between 2,2′-dipyridine (**2-DP**) and chloranilic acid (**CLA**) and this complex has a 1:2 (D/A) ratio in which two acidic protons are transferred from **CLA** to the nitrogen atoms of the acceptor molecules. In the complex of 4,4′-dipyridine (**4-DP**) and **CLA**, no proton is transferred from the acid to base molecules but intermolecular hydrogen-bonded H-O···N and =O···N create a new one dimensional molecular tape structure (Figure 5). When they used dipyridylacetylene (**DPA**) with **CLA** a drastic effect of the positions of the N-atoms in the dipyridylacetylene molecules was observed affording zigzag tape

(**2-DPA-CLA**), square grid (**3-DPA-CLA**), and linear chain (**4-DPA-CLA**) with different stacking arrangements and ionicity as shown in Figure 6.

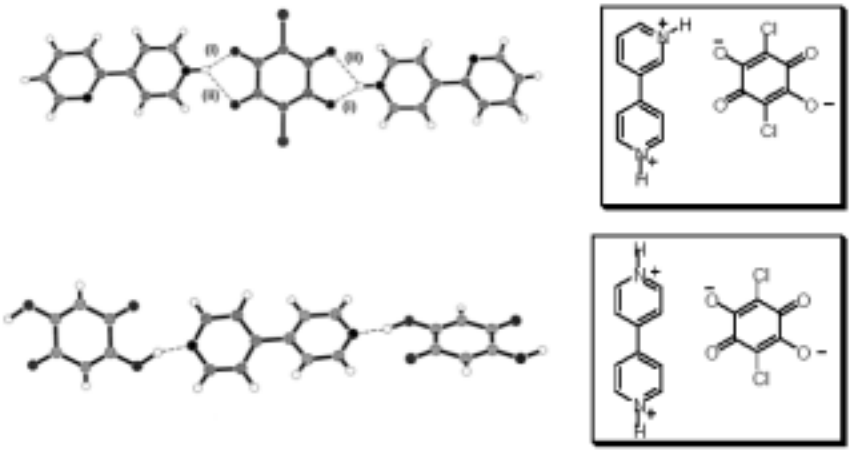

Figure 5. Zaman et. al. (*Chem. Commun.*, **1999**, 999)

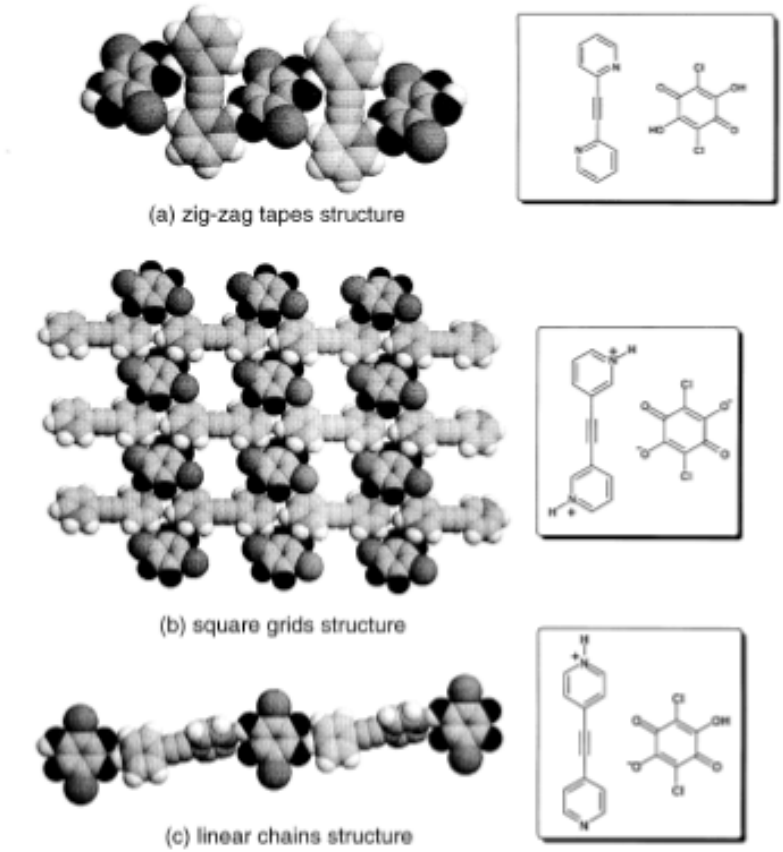

Figure 6. Zaman et. al. (*Org. Lett.*, **2000**, 2, 273)

The presence of two or more complementary hydrogen bonding donor and acceptor

sites in a recognition event, that is multipoint recognition, confers stability and robustness to the resulting supramolecular synthon **IX-XI**. For example, the crystal structure of melamine and cyanuric acid formed a two dimensional sheet structure through multi-hydrogen networks (*Melendez et. al.).*

Like hydrogen atoms mediated intermolecular interactions (hydrogen bonds), there exist other non-covalent interactions. These include halogen····halogen, N····Cl, N····Br, I····NO_2, C=N····Cl, and S····N interactions. These interactions occur due to anisotropically distributed electron density in the atoms or by induced polarisation. Very recently, *Yamashita et. al* showed that the highly polarized heteroatoms can be used as substituents to synthesize organic conducting materials which increase dimensionality as well as intermolecular interactions.[21] Nitrogen-containing heterocycles such as 1,2,5-thiadiazole are used as electron-accepting units in highly polarized donors. Negatively charged nitrogen atoms electrostatically interact with positively charged chalcogen atoms to form interesting molecular assembles. Interactions between the nitrogen and sulfur atoms of thiadiazole ring result in the formation of a molecular tape. Such type of intermolecular interactions can be used for crystal engineering.

1.3 Aim of the present work

Development of new materials is quite important for the progress in the field of materials science. The author has done the following synthetic works on the novel class of compounds which can afford supramolecular wires or molecular assemblies showing interesting physical properties. They would be also attractive as photonic materials due to their high quantum yields of fluorescence.

Chapter 2 describes the preparation, properties, and X-ray crystal structure analysis of 4,7-di(*n*-pyridyl)-2,1,3-benzothiadiazoles (*n* = 2, 3 and 4) (**1a-c**) and their viologen analogues (**2-3**), and 4,7-bis(*n*-pyridylethynyl)-2,1,3-benzothiadiazoles (*n* = 2, 3 and 4) (**4a-c, 5**) and their viologen analogues (**6-7**) as shown in Scheme 2. These compounds show high electron affinity, and high quantum yields of fluorescence. The absorption maxima appear in the longer wavelength region, showing the less aromaticity of benzothiadiazole ring and the narrow HOMO-LUMO band gaps. There are no

significant effects on the nitrogen positions of fluorescence properties. The compounds **1-3** are nonplanar due to the large steric effects between the benzothiadiazole and pyridine ring. So the intermolecular interactions become weak, and solid state fluorescence becomes strong. On the other hand, the compounds **4-7** are almost planar, and take columnar stacking arrangement. So the intermolecular interactions become stronger and solid state fluorescence becomes lower compared to the compounds **1-3**. The crystal structures of all these compounds are almost the same independent on the nitrogen position and no intermolecular short S···N contacts are observed. This result indicates that interheteroatom interactions are not involved in the crystallization and the nitrogen positions do not affect the crystal structures, suggesting that π···π intermolecular interactions are important for the crystallization of rigid long π-conjugated molecules.

In **chapter 3**, the author describes the preparation, properties, and X-ray crystal structure analysis of 7,7′-di(*n*-pyridyl)-4,4′-bis(2,1,3-benzothiadiazole) (*n* = 2, 3 and 4) (**8a-c**) and their viologen analogues (**9b,c**), and 7,7′-bis(*n*-pyridylethynyl)-4,4′-bis(2,1,3-benzothiadiazole) (*n* = 3, 4) (**10b,c**) and their viologen analogues (**11b,c**) as shown in Scheme 3. The absorption maxima of bis(benzothiadiazole) compounds (**8-11**) appear at longer wavelength than those of mono(benzothiadiazole) compounds due to the longer conjugation present in these compounds. The quantum yields are a little decreased compared to the mono(benzothiadiazole) compounds. There is no significant effect of the nitrogen position on the absorption and emission spectra of these compounds. The reduction potentials of these compounds show a stepwise one-electron-reduction wave due to the presence of two benzothiadiazole ring, and 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 a nonplanar structure due to the repulsion between the pyridine and benzothidiazole ring. There are short S···N contacts observed, leading to the molecular tape structures. It is noteworthy that the dihedral angle of their methyalted compounds are drastically decreased, and the dihedral angle between the pyridine and benzothidiazole ring is absolutely zero degree in the compound **11c**.

Chapter 4 is concerned on the development of new donor-acceptor (DA)

hydrogen bonding interactions in the field of crystal engineering as well as in supramolecular architecture. For this purpose, the author selected strong organic acids such as chloranilic acid (**CLA**), squaric acid (**SQA**) and cyanuric acid which are good proton donors and electron acceptors, and several organic base derivatives consisting of pyridyl substituents which are strong proton acceptors as shown in Scheme 5-7**.** Scheme 5 describes the complexes of 2,5-di(4-pyridyl)thiophene (**4-BPT**), 2,5-di(4-pyridyl)furan (**4-BPF**), 1,4-di(4-pyridyl)benzene (**4-BPB**) and 4,7-di(4-pyridyl)-2,1,3-benzothiadiazole (**4-BPBTD**) with 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (chloranilic acid, **CLA**) (**1-4**). Scheme 6 describes the complexes of 1,4-di(*n*-pyridyl)buta-1,3-diynes (*n* = 3, 4) (**DPDA**), 1,4-bis(*n*- pyridylethynyl)-benzene (*n* = 3, 4) (**BPBEB)** and 1,4-bis(4-pyridylethynyl)-1,2,3-benzothidaizole (**4-BPEBTD)** with **CLA** (**5-9**). Scheme 7 describes the complexes of **4-BPT**, **BPBEBs** and **4-DPDA** with 3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid,**SQA**) and 1,2,3-triazine-2,4,6-triol (cyanuric acid, **CNUA**) (**10-12**). The X-ray structure analyses of all these complexes revealed that the unusual molecular tape and sheet like structures are constructed through N-H···O, O-H···O, C-H···O and N-H···N hydrogen bonding networks, where a rare ten-membered hydrogen-bonded dimer of a squarate monoanion is formed. From these results, the aromatic spacer groups seem to play an important role in constructing the unique crystal structures.

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Chapter 2

Synthesis and Properties of Novel Bispyridyl Benzothidiazole Derivatives

Md. Akhtaruzzaman, Masaaki Tomura, Md. Badruz Zaman, Jun-ichi Nishida and Yoshiro Yamashita "Synthesis and Characterization of New Linear π–Conjugated Molecules Containing Bis(ethynylpyridine) Units with a Benzothiadiazole Spacer" *J. Org. Chem*., **2002**, 67, 7813-7818.

Md. Akhtaruzzaman, Masaaki Tomura, and Yoshiro Yamashita, "4,7-Bis(4-pyridylethynyl)-2,1,3-benzothiadiazole and its dipyridinium diperchlorate" *Acta Cryst*. **2001**, C57, 751.

Chapter 2. Synthesis and properties of novel bispyridyl benzothiadiazole derivatives

Abstract: Bispyridyl benzothiadiazole derivatives were synthesized through the coupling reaction of 4,7-dibromo-2,1,3-benzothiadiazole with the corresponding stannyl pyridines and ethynylpyridines in the presence of Pd (0) (**1a-c**) and Pd(II) (**4-5**) catalysts, respectively. Their viologen analogues **2, 3**, **6** and **7** were also prepared by methylation of pyridyl nitrogen atoms. X-ray analysis of these compounds was carried out to investigate the intermolecular interactions in the crystal structures, and found that the most of their structures are almost planar. The molecules of **4a-c** are stacked with unusual two dimensional columns which run in two direction of 45°. The dipyridinium dication molecules of **7d** stack along the a axis and form a dimmer with short S···N interoheteroatom contacts between the two 1,2,5-thiadiazole ring. The insertion of a benzothiadiazole moiety into this skeleton brings about a large increase in electron affinity and the bispyridyl compounds obtained here show high quantum yields of fluorescence. The structural analysis of these compound also shows that the solid-state fluorescence depends on the torsion angle between the benzothidiazole and pyridine rings.

2.1 Introduction

Long size π-conjugated molecules with rigid structures have attracted much attention due to their potential use as molecular wires.[1] Molecules with pyridyl substituents at the terminal positions are expected to be alligator clips for synthesis of molecular devices.[2] They can also afford interesting supramolecular architectures by intermolecular interactions such as hydrogen bonding[3] and coordination with metals.[4] In the dipyridyl compounds the structures and properties can be modified by changing the nitrogen positions and spacer groups. For example, Zaman, et. al have found that dipyridyl acetylenes afford one-dimensional molecular tapes by hydrogen bonding complexation with chloranilic acid, whose structures and electronic states are strongly

dependent on the nitrogen positions.[3a, 5] The 1,4-dipyridylbutadiyne molecules have often been used to construct interesting supramolecular structures.[4, 6] In this context, the author has now introduced a benzothiadiazole ring into this skeleton. There are the following advantages of the introduction of this group. First, this heterocycle is an electron-withdrawing and the compounds bearing this ring are possible candidates for electron carriers. Secondly, thiadiazole-containing compounds are expected to afford well-ordered crystal structures due to the highly polarized properties leading to intermolecular interactions such as heteroatom contacts or π···π interactions.[7] Thirdly, the compounds containing thiadiazole rings are well known as strong fluorescent materials.[8] Highly fluorescent π–conjugated molecules are of interest from the application purposes such as EL (electroluminescence) devices[9] and single molecular detection.[10] The author reports here the synthesis, structures and properties of the novel π-conjugated dipyridyl compounds containing a benzothiadiazole ring as a spacer unit. In addition, their dimethylated compounds and related dications have been prepared as viologen analogues. Viologens have been widely used in the basic study of electrochemical,[11] photoelectrochemical,[12] electrochromic materials[13] and the solar energy conversion,[14] and their π-extended analogues have been of much interest.[15] So the author has also described here the synthesis, structures and electronic properties of their viologen analogues.

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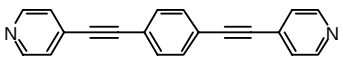
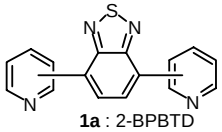
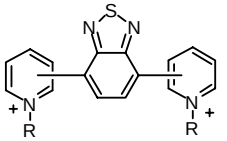


4-BPBEB

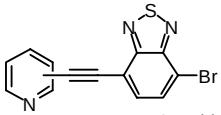


1a : 2-BPBTD
1b : 3-BPBTD
1c : 4-BPBTD

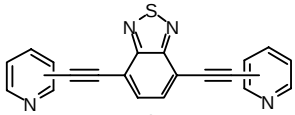


R = Me
2b : 3-BPBTDMe
2c : 4-BPBTDMe

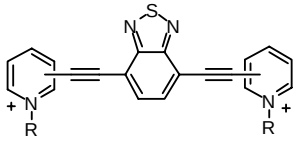
R = CH_2Ph
3c : 4-BPBTDPh



4a : 2-pyridyl
4b : 3-pyridyl
4c : 4-pyridyl

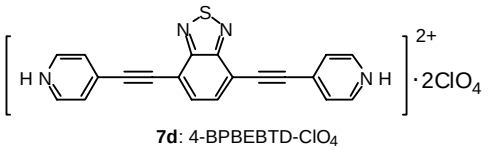


5a : 2-BPBEBTD
5b : 3-BPBEBTD
5c : 4-BPBEBTD



R = Me
6b : 3-BPBEBTDMe
6c : 4-BPBEBTDMe

R = CH_2Ph
7b : 3-BPBEBTDPh
7c : 4-BPBEBTDPh

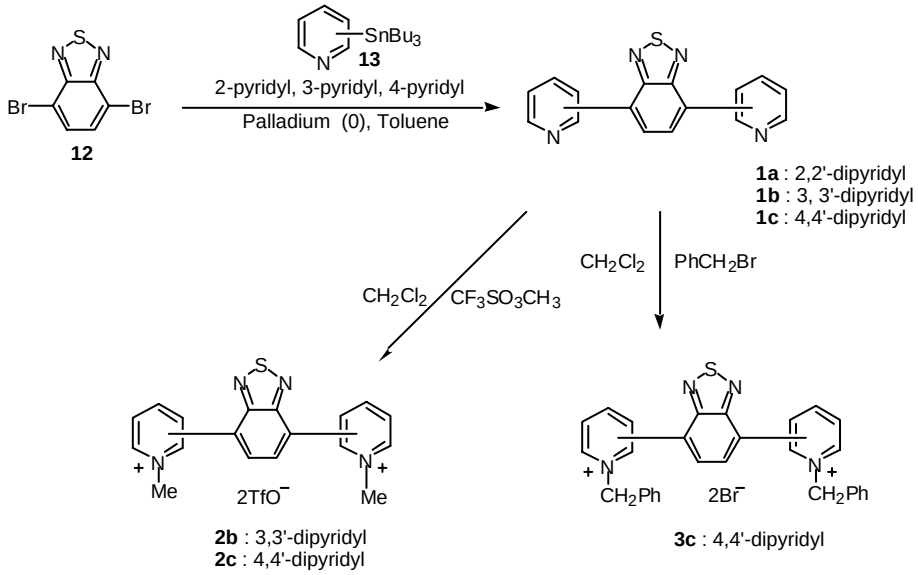


7d: 4-BPBEBTD-ClO_4

2.2 Results and Discussion

2.2.1 Synthesis of dipyridylbenzothiadiazole derivatives

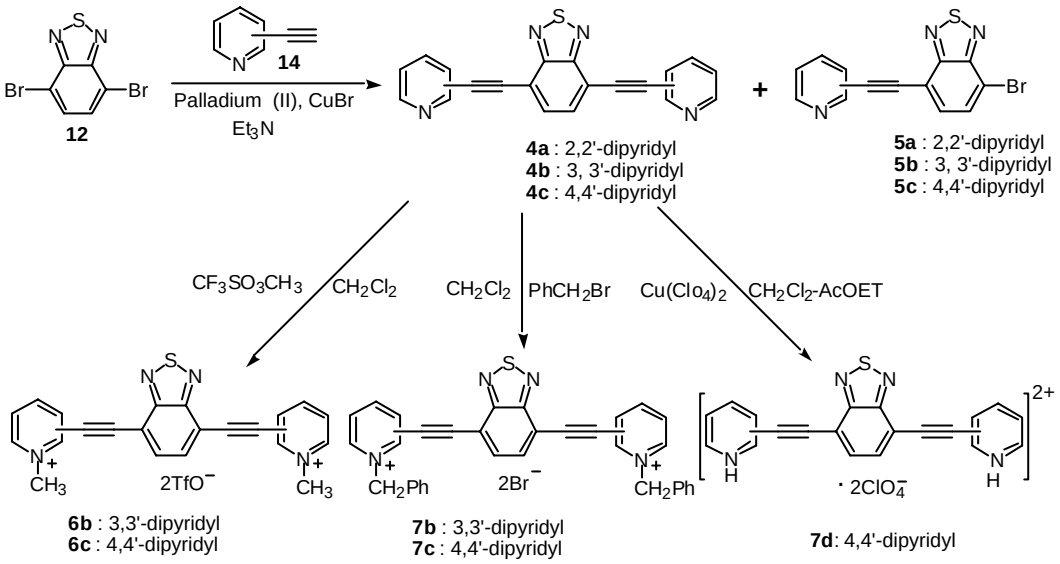
The synthesis of the compounds **1-3** is described in Scheme 1. A convenient one-pot procedure through the palladium-mediated cross coupling reaction of 4,7-dibromo 2,1,3-benzothiadiazole[16] with (tributylstanyl)pyridine[17] in dry toluene gave 4,7-di(*n*-pyridyl)-2,1,3-benzothiadiazole (*n* = 2,3,4) (**1a-c**) in 58-80%. Their viologen analogues **2b,c** and **3c** were also prepared by methylation and benzylation of pyridyl nitrogen atoms in CH_2Cl_2 in high yields, respectively.



Scheme 1

Scheme 2 shows the synthesis of the compounds **4-7**. The compouds **4-5** were synthesized using a convenient one-pot consecutive Sonogashira cross-coupling reaction of 4,7-dibromo-2,1,3-benzothiadiazole (**12**) with 2-, 3- and 4-ethynylpyridines (**13**)[18] in the presence of $PdCl_2(PPh_3)_2$ and CuBr catalyst in Et_3N at 90 ^oC. The reaction produced bis-coupling products **4a-c** along with mono-coupling products **5a-c**. They were isolated and purified by column chromatography on silica-gel using chloroform-ethyl acetate as eluent. Monobrominated compounds **5a-c** obtained as bi-products are expected to be key starting materials to afford longer conjugated

oligomers. The pyridinium compounds of **4b** and **4c** were obtained as trifluoromethanesulfonate (TfO) salts **6b** and **6c** in high yields by mixing **4b** and **4c** with MeOTf (Methyl trifluoromethanesulfonate) (1:3 stoichi- ometry) in dichloromethane, respectively. The benzylated compounds **7b** and **7c** were also obtained in good yields by mixing **4b** and **4c** with $PhCH_2Br$ (1:3 stoichiometry) in dichloromethane, respectively. The author also obtained **7d**, dipyridium salt of **4c** as a single crystal by mixing **4c** and $Cu(ClO_4)_2$ in CH_2Cl_2-AcOET. The methylation reaction of the 2,2'-dipyridyl derivative has not been successful probably due to its weak basicity.



Scheme 2

2.2.2 Crystal Structures

In order to investigate the intermolecular interactions in the crystal structures, X-ray structure analysis was carried out. The single crystals of **1a-c** suitable for X-ray analysis were obtained from recrystallization from a mixed solvent of acetonitrile-chloroform. All crystal data and a summary of data collection parameters are shown in Table 1-4.

The molecules **1a** are twisted with 26.0 (1) and 38.7 (1)º of the angles between

the pyridine and benzothiadiazole planes. The crystal structure of **1a** with the space group of the monoclinic $P2_1/n$ is shown in Fig. 7**.** The molecules are stacked along the a-axis where the distance between the molecular planes is 3.5 Å. No short S····N contacts are observed, while a large number of C–H····N interactions form a planar molecular sheet.

The molecules **1b** are twisted with 45.2 (1) and 35.6 (1)º of the angles between the pyridine and benzothiadiazole planes. The crystal structure of **1b** with the space group of the monoclinic $P2_1/c$ is as shown in Fig. 8. The molecules are stacked along a-axis where the distance between the molecular planes is 3.55 Å. No short S····N contacts are observed, while a large number of C–H····N interactions (H····N, 2.54 and C····N 3.45 Å) form a planar molecular sheet.

The molecules **1c** are twisted with 40.0 (5) and 33.7 (4) º of the angles between the pyridine and benzothiadiazole planes. The crystal structure of **1c** with the space group of the monoclinic $P2_1/c$ is as shown in Fig. 9. The molecules are stacked along a-axis where the distance between the molecular planes is 3.64 Å. Within the stacking, the molecules overlap in a head-to-tail fashion. The short S····N contacts [3.003 (2) Å] are observed between the sulfur atom of the thiadiazole ring and the nitrogen atom of the pyridine ring.

The single crystals of **2b** including water molecules suitable for X-ray analusis were obtained from acetonitrile-ethanol solution. The crystal structure of **2b** with the space group of the triclinic $P\bar{1}$ is as shown in Fig**.** 10. The molecule of **2b** are twisted 38.7(1) and 27.3(2) º of the angles between the pyridine and benzothiadiazole planes, the angles are smaller than those of the corresponding neutral compounds **1b**. The triflate anion molecules are disordered and interact with the solvated water molecules. The molecules are stacked along a-axis where the distance between the molecular planes is 3.15 Å.

The single crystal of **3c** suitable for X-ray analysis were obtained from acetonitrile-dichloromethane solvent. The crystal structure of **3c** with the space group of orthorhombic *Pbcn* is shown in Fig. 11. The molecules are stacked in an unusual manner as shown in figure 11c along the c-axis, where the benzyl groups as well as the main heterocyclic unit are involved in the stacking. The angle between both units is 74.2(1)°, leading to a two-dimensional stairs-like stacking.

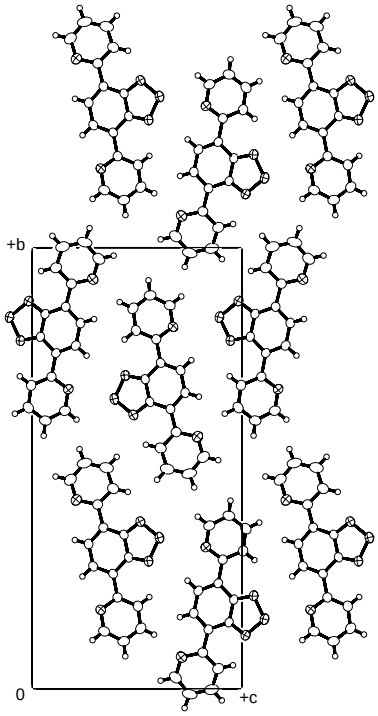


Figure 7. Crystal structure of **1a** viewed along the a axis.

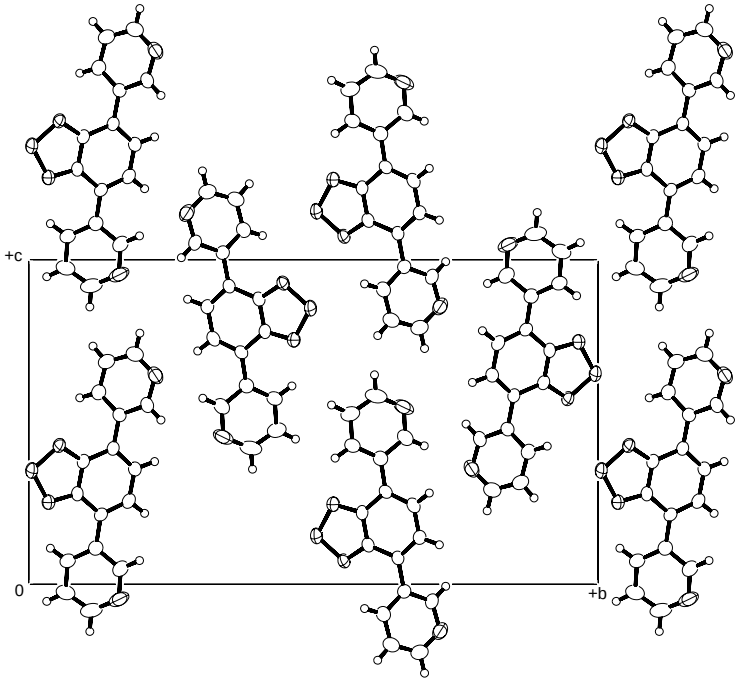


Figure 8. Crystal structure of **1b** viewed along the b axis.

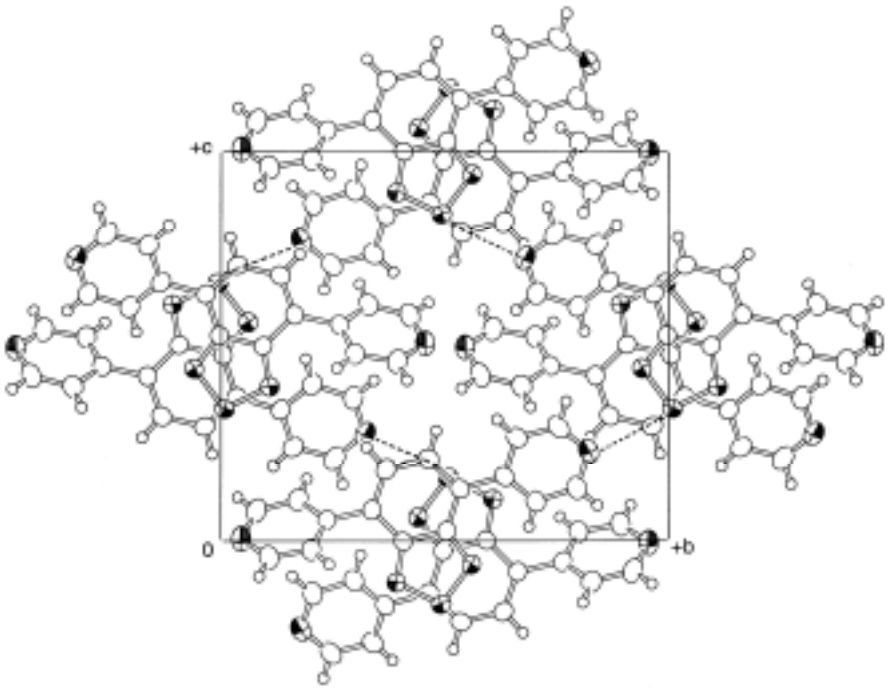


Figure 9. Crystal structure of **1c** viewed along the a axis (dotted line show the short S···N contacts).

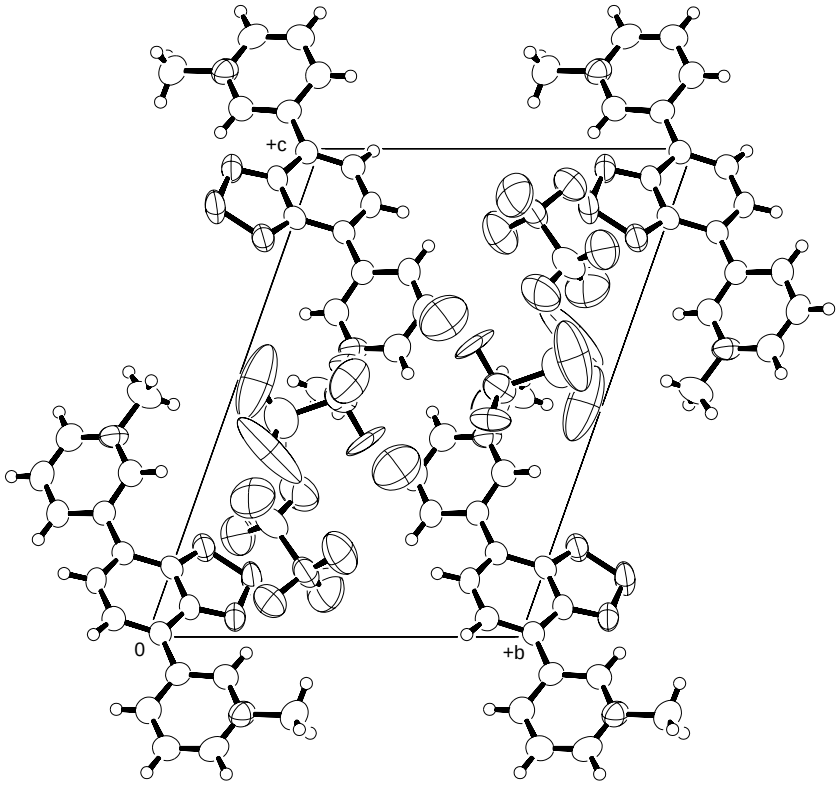


Figure 10. Crystal structure of **2b** viewed along the a axis.

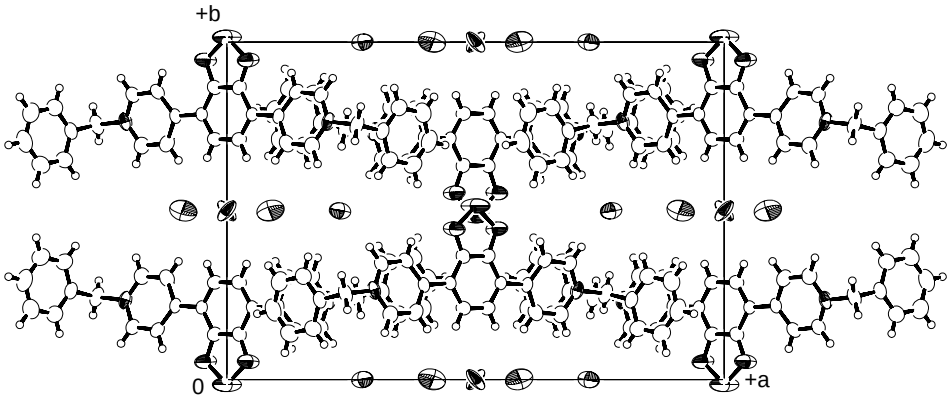


Figure 11a. Crystal structure of **3c** viewed along the a axis.

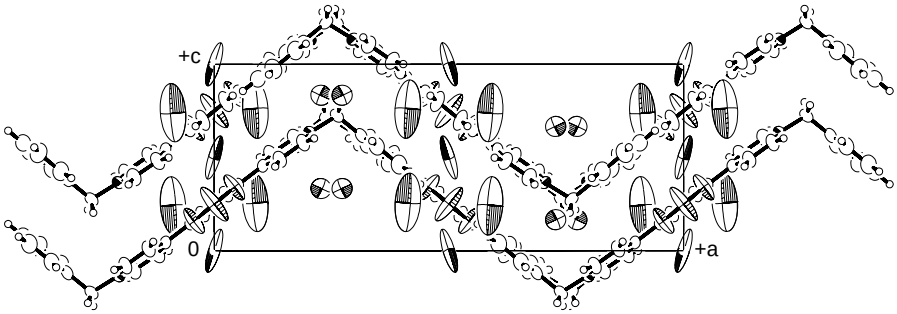


Figure 11b. Crystal structure of **3c** viewed along the b axis.

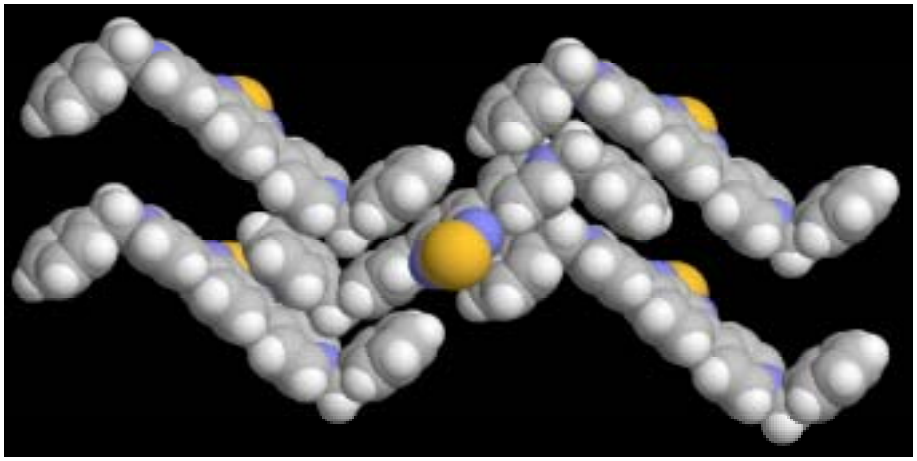


Figure 11c. Two dimensional stair-like stacking along the c axis of the crystal structure of **3c**.

The single crystals of **4** suitable for X-ray analysis were obtained from recrystallization from a mixed solvent of acetonitrile-ethyl acetate. The molecules **4a-c** are linear with 16.6-18.3 Å lengths and a little twisted with 1.5-15.2^{o} of the angles

between the pyridine and benzothiadiazole planes. The crystal structure of **4a** with the space group of the orthorhombic *Pbcn* is shown in Fig. 12, where a half of molecule is independent. 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 **4b** and **4c** are similar to that of **4a** although the space groups are different. The molecule **4b** crystallizes in the monoclinic *Cc* space group with two independent molecules. The molecule **3c** crystallizes in the monoclinic $P2_1/a$ space group with one independent molecule. This result indicates that interhetero atom interactions are not involved in the crystallization and the nitrogen positions do not affect the crystal structures, suggesting that π···π intermolecular interactions are important for the crystallization of rigid long π-conjugated molecules.

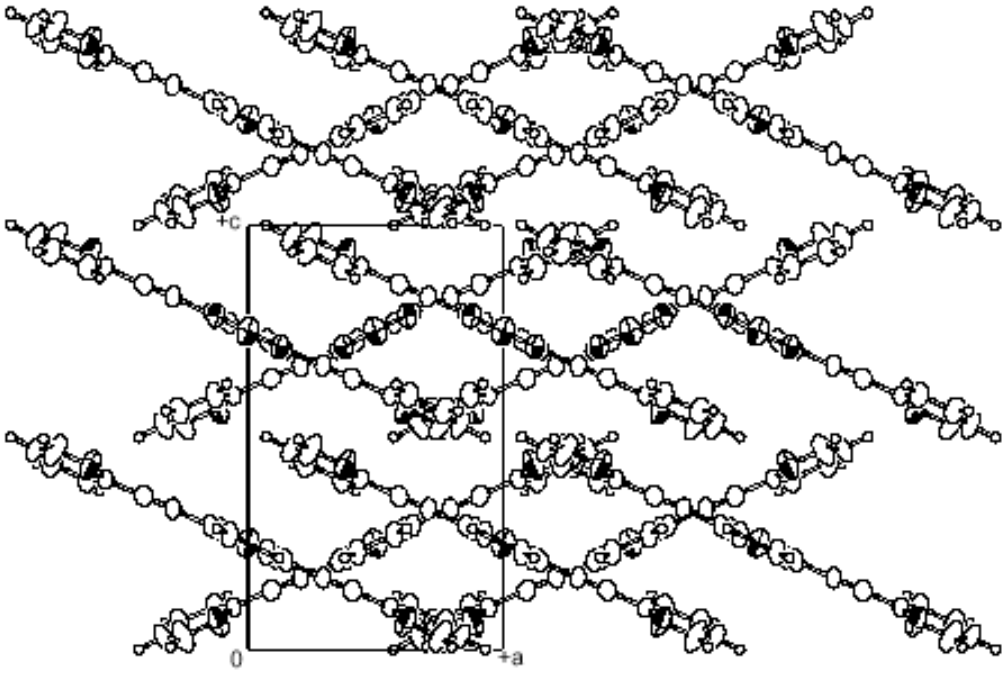


Figure 12. Crystal structure of **4a** viewed along the b axis.

Single crystals of **6b,c** including water and **7b** were obtained from acetonitrile-ethanol and their crystal structures have been solved. The molecular

structures of the methylated compounds are more planar than **4**. Thus, the dihedral angles between the pyridines and the benzothiadiazole are 1.4 and 6.5^{o} for **6b** and 5.3^{o} for **6c**. Their crystal structures include π···π stacking of long molecules. The crystal structure of **6b·H$_2$O** is shown in Fig. 13, where a uniform stacking with 3.41 Å distance is observed. A number of intermolecular O–H···O, C–H···O and C–H···F interactions are also found in this structure. On the other hand, the herringbone structure with the interstack distances of 3.40 and 3.45 Å is observed in **6c** as shown in Fig. 14. The different crystal structures of **6b** and **6c** can be attributed to the steric interactions of methyl groups. The crystal structure of **7b.H$_2$O** is shown in Fig. 15 viewed along the b axis. The dication part except the benzyl groups was planar with 2.4 (3) and 4.9 (3)º of the dihedral angles between the pyridine and the benzothiadiazole rings. The diheral angles between the pyridine and the phenyl ring of benzyl groups are 98.9(4) and 72.9(4)º. The benzyl groups hold the upper and lower molecules via C–H·····π interaction (2.48-2.89 Å for H···π distances) to form the unique stacking with 3.45 Å of the interstack distance as shown in Fig. 16. The C–H·····π interactions between the stacks were also observed [2.74 (1) Å for H·····π distance]. The compound **7d** crystallized in the $P2_1/c$ space groups, with one molecule in the asymmetric units. The molecules are stacked along the a-axis and the interstack distance between the two 2,1,3-benzothidiazole ring planes within the stack is 3.40 (1) Å. The crystal structure of **7d** shows the existence of short S····N intereroheteroatom contacts [3.146 (4) Å] between the two 2,1,3-thiadiazole rings. Thus the dipyridinium dication molecules form S····N contacts, which are planar and lie in a plane within deviation of 0.09 (1) Å. No short S····N interheteroatom contact within the sum of van der Waals radii of the S and N atoms was observed in the corresponding neutral crystal structure of **4c**. Interestingly, the dimer is surrounded by the perchlorate anions as shown in Figure 16a, where observed a large number of intermolecular N-H·····O and C-H·····O hydrogen bonds are observed. The intermolecular O···O distances of the perchlorates are in the range of 3.044 (6)-3.286 (6) Å.

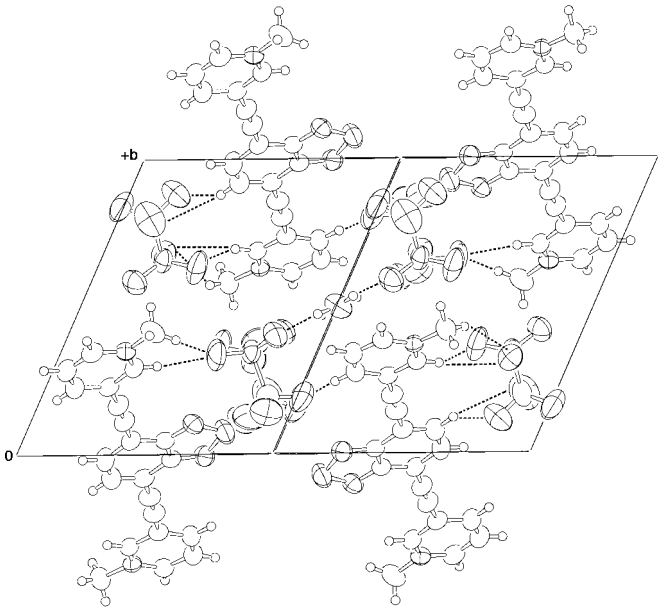


Figure 13. Crystal structure of **6b·H_2O** viewed along the [1 0 -1] direction. Dotted lines show the intermolecular O-H···O, C-H···O and C-H···F interactions.

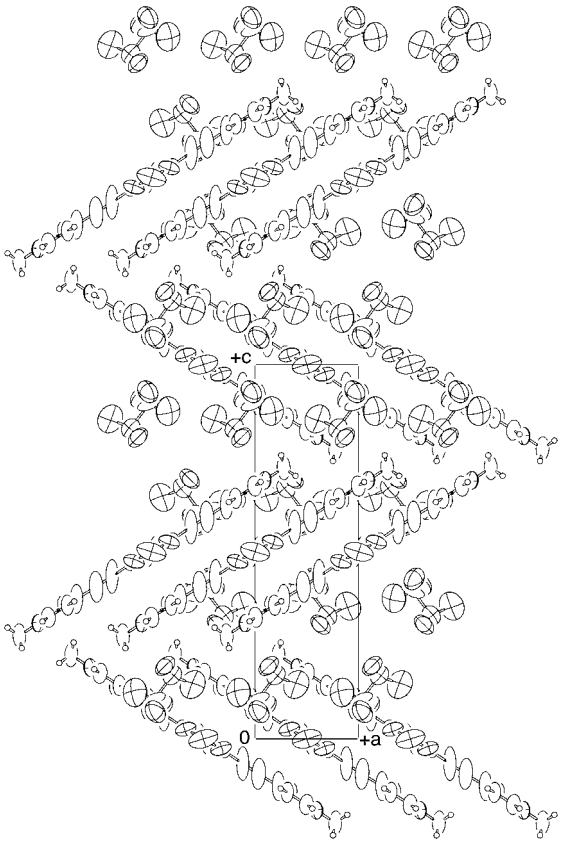


Figure 14. Crystal Structure of **6c** viewed along b axis.

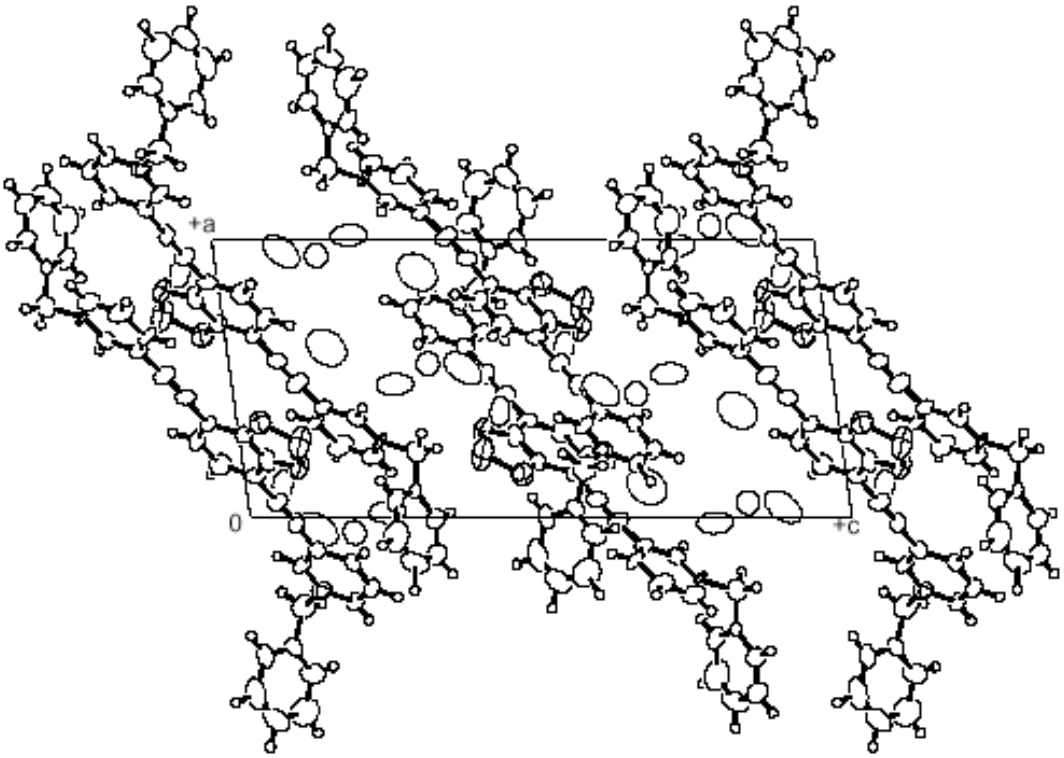


Figure 15. Crystal structure of **7b·3H$_2$O** viewed along the b axis.

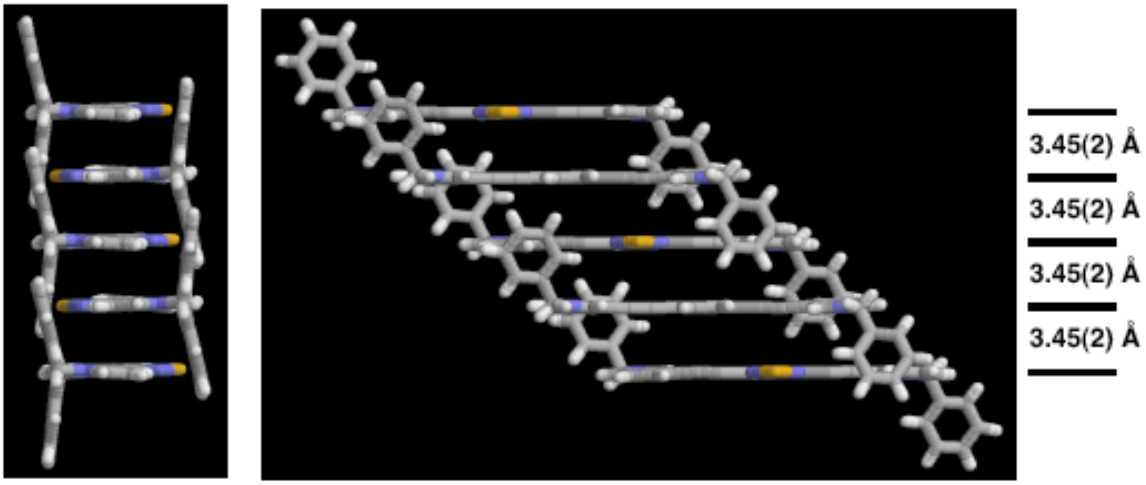


Figure 16. The benzyl groups hold the upper and lower molecules via C-H···π interactions to form the unique stacking of **7b.**

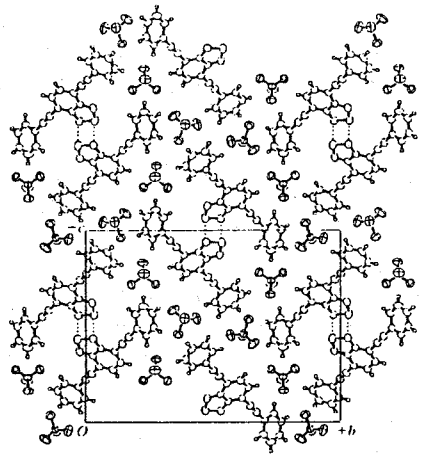


Figure 16a. Packing diagram of **7d** viewed along a axis. Dotted lines show the short S····N interheteroatoms contacts.

Table 1 Crystal data and summary of data collection parameters

		1a	**1b**	**1c**
Molecular formula		$C_{16}H_{10}N_4S$	$C_{16}H_{10}N_4S$	$C_{16}H_{10}N_4S$
Molecular weight		290.34	290.34	290.34
Crystal dimensions (mm^3)		0.25 x 0.15 x 0.10	0.20 x 0.10 x 0.10	0.40 x 0.10 x 0.10
Crystal system		monoclinic	monoclinic	monoclinic
Space group		$P2_1/n$	$P2_1/c$	$P2_1/c$
Temp. (K)		296	296	296
Unit cell	a (Å)	3.7763(2)	3.8113(13)	7.3213(3)
	b (Å)	27.0492(11)	24. 552(6)	14.3519(3)
	c (Å)	12.9087(4)	14.056(5)	12.4801(6)
	α (°)	90	90	90
	β (°)	94.877(3)	94.123(11)	90.206(3)
	γ (°)	90	90	90
	V ($Å^3$)	1313.80(10)	1311.9(7)	1311.33(9)
Z		4	4	4
Density calc. ($g\ cm^{-3}$)		1.468	1.470	1.471
Absorption coeff. (mm^{-1})		2.164	0.244	2.168
Radiation		Mo-Kα	Cu-Kα	Cu-Kα
Measured reflections		3085	9779	2870
Independent reflections		2676	2954	2662
Reflections with $I > 2\sigma(I)$		1834	2146	-
R_1		0.0441	0.1071	0.0338
wR_2		0.1109	0.2485	0.0921
GOF		1.012	1.206	1.028

Table 2. Crystal data and summary of data collection parameters

		2b	**3c**
Molecular formula		$C_{20}H_{16}N_4O_7S_3$	$C_{30}H_{30}N_4O_3SBr_2$
Molecular weight		634.55	686.40
Crystal dimensions (mm^3)		0.50 x 0.25 x 0.20	0.20 x 0.10 x 0.10
Crystal system		Triclinic	Monoclinic
Space group		$P2_1/n$	$P2_1$/c
Temp. (K)		296	296
Unit cell	a (Å)	8.7475(13)	22.3292(18)
	b (Å)	11.3927(15)	15. 1543(10)
	c (Å)	14.991(2)	8.8149(8)
	α(°)	67.544(17)	
	β(°)	77.59(2)	
	γ(°)	67.938(2)	
	V (Å3)	1275.20(3)	2982.8(4)
Z		2	4
Density calc. (g cm^{-3})		1.653	
Absorption coeff. (mm^{-1})		0.384	
Radiation		Mo-Kα	Cu-Kα
Measured reflections		12817	
Independent reflections		5622	
Reflections with $I > 2\sigma(I)$		3765	2003
R_1		0.1030	0.0872
wR_2		0.2673	0.2603
GOF		1.167	1.846

Table 3. Crystal data and summary of data collection parameters

		4a	**4b**	**4c**
Molecular formula		$C_{20}H_{10}N_4S$	$C_{20}H_{10}N_4S$	$C_{20}H_{10}N_4S$
Molecular weight		338.38	338.38	338.38
Crystal dimensions (mm^3)		0.55 x 0.20 x 0.05	0.30 x 0.20 x 0.15	0.50 x 0.30 x 0.10
Crystal system		orthorhombic	monoclinic	monoclinic
Space group		*Pbcn*	*Cc*	$P2_1/a$
Temp. (K)		296	296	296
Unit cell	*a* (Å)	8.980(5)	15.3862(10)	12.487(2)
	b (Å)	12.163(5)	17. 5790(7)	7.5477(13)
	c (Å)	14.926(4)	12.1370(4)	17.513(3)
	α(°)	90	90	90
	β(°)	90	103.690(3)	105.22(2)
	γ(°)	90	90	90
	V ($Å^3$)	1630.3(12)	3189.48(17)	1592.8(5)
Z		4	8	4
Density calc. (g cm^{-3})		1.379	1.409	1.411
Absorption coeff. (mm^{-1})		0.208	0.212	1.875
Radiation		Mo-Kα	Cu-Kα	Cu-Kα
Measured reflections		1875	3280	3416
Independent reflections		1875	3280	3254
Reflections with $I > 2\sigma(I)$		-	-	1902
R_1		0.0606	0.0458	0.064
wR_2		0.1546	0.1159	0.1697
GOF		0.972	0.893	1.036

Table 4. Crystal data and summary of data collection parameters

	6b	**6c**	**7b**
Molecular formula	$C_{24}H_{18}F_6N_4O_7S_3$	$C_{24}H_{16}F_6N_4O_6S_3$	$C_{34}H_{24}Br_2N_4O_3S$
Molecular weight	684.60	666.59	728.46
Crystal dimensions (mm^3)	0.55 x 0.25 x 0.10	0.40 x 0.25 x 0.05	0.60 x 0.05 x 0.03
Crystal system	Triclinic	0rthorhombic	Monoclinic
Space group	*P*-1	*Pn2n*	-
Temp. (K)	296	296	296
Unit cell *a* (Å)	11.1998(8)	6.3555(4)	9.912(2)
b (Å)	12.2723(8)	9. 470(2)	15.683(3)
c (Å)	12.3784(9)	23.335(3)	21.418(5)
α(°)	67.740(6)	90	90
β(°)	67.542(6)	90	97.983(10)
γ(°)	72.373(5)	90	90
V ($Å^3$)	1430.08(17)	1404.5(4)	3297.00(1)
Z	2	2	4
Density calc. (g cm^{-3})	1.590	1.576	1.467
Absorption coeff. (mm^{-1})	3.201	3.216	1.875
Radiation	Mo-Kα	Cu-Kα	Mo-Kα
Measured reflections	6146	1277	27365
Independent reflections	5832	1277	7509
Reflections with $I > 2\sigma(I)$	-	-	
R_1	0.0528	0.1240	0.1435
wR_2	0.1442	0.3322	
GOF	1.024	2.295	1.368

Crystal data and summary of data collection of **7d**

Molecular formula	$C_{20}H_{12}N_4S^{2+}.2ClO_4$	Density calc. (g cm^{-3})	1.590
Molecular weight	539.30	Absorption coeff. (mm^{-1})	0.824
Crystal dimensions (mm^3)	0.35 x 0.15 x 0.05	Radiation	Cu-Kα
Crystal system	Monoclinic	Measured reflections	4684
Space group	$P2_1/c$	Independent reflections	4543
Temp. (K)	296	Reflections with $I > 2\sigma(I)$	2774
Unit cell			
a (Å)	5.1097(3)	R_1	0.061
b (Å)	24.4522(16)	wR_2	0.205
c (Å)	17.8489(13)	GOF	1.00
β(°)	92.281(5)		
V ($Å^3$)	2228.3(3)		
Z	4		

2.2.3 Physical Properties

The physical properties of the compounds **1a-c** and their salts **2-3** along with 1,4-bis(4-pyridyl)benzene(**4-BPB**)**,** the compounds **4a-c** and their salts **6-7** along with 1,4-bis(4-pyridylethynyl)benzene (**4-BPBEB**) are summarized in Table 5**.** Their absorption maxima are significantly red-shifted compared with those of BPB and BPBEB. This can be explained by the PM3 calculation method.[19] The LUMO energy levels of **1a-c** and **4a-c** are lower than those of **4-BPB** and **4-BPBEB**, respectively, due to the electron-withdrawing thiadiazole ring, while the HOMO energies are not so different among them. This fact is supported by the PM3 calculations (shown in Table 6), indicating that the LUMO levels of **1** and **4** are lower than those of **4-BPB** and **4-BPBEB**. The calculations also show that the HOMO-LUMO differences are smaller in **1** and **4** than in **BPB** and **BPBEB**, respectively. The absorption spectra of **1a-c** and **4a-c** are dependent on the solvent. In polar solvents blue shifts are observed as shown in Table 7. This result shows that the ground states of these molecules are more polar as compared to the excited states. All the heterocycles obtained here exhibit strong fluorescence.[20] Interestingly, the emission maxima are prominently red-shifted compared to those of **BPB** and **BPBEB** due to the large Stokes shifts. They emit blue luminescence and the quantum yields are very high. The absolute quantum yield of **4c** is 0.87 ± 0.05. There is no significant effect of the nitrogen positions on the quantum yields. The compounds **4a-c** are more planar and columnar stacked molecular structures are formed, leading to stronger intermolecular interactions compared to the compounds **1a-c**. So the solid-state fluorescence of **1a-c** is stronger than those of **4a-c**. It is also noteworthy that the salts **6b, c** and **7b, c** display high quantum yields but the salts **2c** and **3b,c** show very low quantum yields of fluorescence. The reduction potentials listed in Table 5 show that the thiadiazole containing compounds **1** and **4** have stronger electron affinities compared with the reference compounds **4-BPB** and **4-BPBEB,** respectively, due to the electron–withdrawing properties of the thiadiazole ring. The salts **2, 3**, **5** and **6** show higher reduction potentials than their corresponding neutral compounds because of the dication species. Since they have high fluorescence quantum yields, they are expected to work as strong electron acceptors in photo-induced electron transfer reactions.

Table 5. Absorption maxima,[a] fluorescence maxima,[b] quantum yields[b] and reduction potentials[c] for dipyridyl compounds

Compound	λ_{max}/nm (log ε)	$\lambda_{em,\ max}$ /nm	Φ_{em}	E_{red}/V
4-BPB	278 (4.51) -			-1.98, -2.14
1a	377 (4.12)	469	0.80	- 1.25
1b	366 (4.06)	467	0.90	- 1.30
1c	356 (5.03)	448	0.68	- 1.19
2b	350 (4.08)	441	0.24	- 0.84, -1.12
2c	362 (4.71)	427	0.11	- 0.51, -0.63
3c	366[d]	432	0.08	-0.35
4-BPBEB	334 (4.22)	344	0.71	- 1.75
4a	393 (4.48)	473	0.87	- 1.18
4b	396 (4.45)	479	0.80	- 1.08
4c	388 (4.43)	464	0.87	- 1.00
6b	384 (4.50)	449	0.85	- 0.52
6c	398 (4.57)	437	0.82	- 0.62
7b	387[d]	459	0.75	- 0.84
7c	401[d]	442	0.97	- 0.57

4-BPB : 1,4-bis(4-pyridylethynyl)benzene[21], **4-BPEB**: 1,4-bis(4-pyridylethynyl) benzene.[22] [a] In MeCN. [b] In MeCN solution, λ_{ex} = 299 nm. The Φ_{em} values of 0.83 for **3-BPEB** and 0.49 for **4-BPEB** in toluene are reported.[23] [c] 0.1 mol dm^{-3} *n*-Bu_4NPF_6 in MeCN, Pt electrode, scane rate 100 mV s^{-1}, V vs SCE. [d] Absorption coefficients could not be measured due to their low solubility in solvents.

Table 6. HOMO and LUMO energies of dipyridyl compounds calculated by the PM3 method

Dipyridyl compounds	HOMO / eV	LUMO / eV
4-BPB	-9.19	-1.14
1a	-8.80	-1.82
1b	-8.91	-2.20
1c	-9.16	-2.34
4-BPBEB	-9.04	-1.20
4a	-8.80	-1.99
4b	-8.88	-2.17
4c	-9.04	-2.24

Table 7. Absorption and emission maxima and fluorescence quantum yields of **1b** and **4c** in a series of solvents

Solvent	**1b**			**4c**		
	λ_{max}/nm	$\lambda_{em,\ max}$/nm[a]	Φ_{em}	λ_{max}/nm	$\lambda_{em,\ max}$/nm[a]	Φ_{em}
Ethanol	366	469	0.89	390	474	0.92
Acetonitrile	366	471	0.77	388	464	0.87
Chloroform	370	467	0.90	396	469	0.95
Cyclohexane	372	455	0.93	395	441	0.61

[a] λ_{ex} 299 nm.

2.2.4 Summary

In this chapter, the author has explored novel dipyridyl compounds with electron-withdrawing properties and high fluorescence quantum yields. The bipyridinium compounds, viologens analogues, have been found to be easily obtained and show higher electron affinities. Further studies on construction of supramolecular systems composed of these compounds using hydrogen bonding and metal coordination are currently in progress.

2.3 Experimental

Preparation of 4,7-di(2-pyridyl)-2,1,3-benzothiadiazole (1a). To a solution of 4,7-dibromo 2,1,3-benzothiadiazole (**12**) (300mg, 1.04 mmol) in dry toluene (10 ml) were added 2-stannylpyridine (950mg, 2.58 mmol) and the tetrakis(triphenylphosphine) palladium ($Pd(PPh_3)_4$ (235mg, 0.20 mmol) under an argon atmosphere. The resulting mixture was heated under reflux overnight. After being cooled to room temperature, the reaction mixture was quenched with 1.0 mol dm^{-3} of aqueous ammonia and extracted with chloroform. The combined extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with $CHCl_3$-EtOH as eluent afforded compound **1a**. Recrystalization from ethanol gave a yellow solid (81% yield): mp 145-147 °C; IR (KBr) ν_{max} 2992, 1581, 1548, 1499, 1431, 1348, 1296, 1054, 994, 892, 773, 737, 643 cm^{-1}. UV (MeCN) λ_{max} nm (log ε) 289(4.28), 314 (4.02), 323 (4.04), 377 (4.12); ^1H NMR ($CDCl_3$, 300 MHz): δ 8.82 (d, J = 6.0 Hz, 2H), 8.71 (d, J = 8.1 Hz, 2H), 8.6 (s, 2H), 7.92-7.86 (m, 2H); 7.37-7.27 (m, 2H); ^{13}C NMR ($CDCl_3$; 75 MHz) δ, 123.13, 125.15, 129.66, 132.34, 136.59, 149.82, 153.80, 154.07; MS (EI): *m/z* (%) 290 (M^+, 100). Anal. Calcd for $C_{16}H_{10}N_4S$: C, 66.19; H, 3..47; N, 19.30; S, 11.04; Found: C, 65.98; H, 3.64; N, 19.34; S, 11.04.

Preparation of 4,7-Di(3-pyridyl)-2,1,3-benzothiadiazole (1b): Following the same procedure as that for **1a**, the compound **1b** was obtained. Recrystallization from $CHCl_3$-EtOH gave a yellow solid (69% yield): mp 219-221 °C; IR (KBr) ν_{max} 3022, 1588, 1556, 1472, 1411, 1326, 1195, 1027, 931, 885, 799, 705, 616 cm^{-1}. UV (MeCN) λ_{max} nm (log ε) 237 (4.23), 268 (4.32), 307 (4.07), 316 (4.12), 366 (4.06); ^1H NMR (300 MHz, $CDCl_3$): δ 9.18 (d, J = 2.4 Hz,, 2H), 8.73 (d, J = 6.6 Hz, 2H), 8.40-8.36 (m, 2H), 7.87 (s, 2H), 7.53-7.48 (m, 2H); ^{13}C NMR ($CDCl_3$; 75 MHz) δ, 123.38, 128.16, 130.83, 132.87, 136.62, 149.56, 149.77, 153.84; MS (EI): *m/z* (%) 290 (M^+, 100); Anal. Calcd for $C_{16}H_{10}N_4S$: C, 66.19; H, 3..47; N, 19.30; S, 11.04; Found: C, 66.37; H, 3.74; N, 19.33; S, 11.05.

Preparation of 4,7-Di(4-pyridyl)-2,1,3-benzothiadiazole (1c): Following

the same procedure as that for **1a**, the compound **1c** was obtained. Recrystalization from $CHCl_3$-EtOH gave a yellow solid (58% yield): mp 258-260 °C; IR (KBr) ν_{max} 3044, 1594, 1538, 1477, 1410, 1310, 1217, 1070, 993, 818, 713, 624 cm^{-1}. UV (MeCN) λ_{max} nm (log ε) 272 (5.23), 318 (5.08), 356 (5.03); ^1H NMR (300 MHz, $CDCl_3$): δ 8.91 (br. s, 2H), 8.64 (br. s, 2H), 7.96-7.98 (m, 2H), 7.87 (d, J = 3.9 Hz, 2H), 7.34-7.39 (m, 2H); ^{13}C NMR ($CDCl_3$; 300 MHz) δ 123.55, 123.57, 128.48, 131.98, 144.16, 150.30, 153.50, MS (EI): *m/z* (%) 338 (M^+, 100); Anal. Calcd for $C_{16}H_{10}N_4S$: C, 66.19; H, 3..47; N, 19.30; S, 11.04; Found: C, 66.11; H, 3.77; N, 19.23; S, 10.93.

Methylation of 4,7-Di(3-pyridyl)-2,1,3-benzothiadiazole 1b: Tetrafluromethanesulfonic acid (360 mg, 2.2 mmol) was added to a solution of **1b** (100 mg, 0.35 mmol) in CH_2Cl_2 (20 ml). The mixture was stirred for 3h at room temperature. The resulting solid was filtered and washed with CH_2Cl_2 to give a yellow solid **2b** (80% yield): mp 145-147 °C; UV (MeCN) λ_{max} nm (log ε) 246 (4.16), 277(3.98), 319 (4.13), 350 (4.08); ^1H NMR (300 MHz, CD_3CN): δ 8.94 (s, 2H), 8.60-8.66 (m, 4H), 8.05-8.09 (m, 4H), 4.40 (s, 6H).

Methylation of 4,7-Di(4-pyridyl)2,1,3-benzothiadiazole 1c: Following the same procedure as above, the dimethylated compound **2c** was obtained as a yellow solids (93%): mp 289-291 °C; IR (KBr) ν_{max} 3547, 3063, 1643, 1525, 1474, 1269, 1157, 1031, 841, 754, 637, 519 cm^{-1}; UV (MeCN) λ_{max} nm (log ε) 303 (3.46), 362 (4.71); ^1H NMR (300 MHz, CD_3CN): δ 8.83 (d, J = 6.5 Hz, 4H), 8.75 (d, J = 7.2 Hz, 4H), 8.40 (s, 2H), 4.38 (s, 6H); ^{13}C NMR ($CDCl_3$; 75 MHz) δ 49.00, 128.45, 130.83, 132.20, 146.49, 152.77, 153.92; Anal. Calcd for $C_{20}H_{18}N_4S_3F_6O_7$: C, 37.74; H, 2.84; N, 8.80; S, 15.11; O, 17.59; F, 17.91; Found: C, 38.31; H, 2.90; N, 8.97; S, 15.12; O, 17.51; F, 18.00.

Benzylation of 4,7-Di(4-pyridyl)-2,1,3-benzothiadiazole 1c: Benzylbromide (0.36 g, 2.11 mmol) was added to a solution of **1c** (0.05 g, 0.17 mmol) in CH_2Cl_2 (10 ml). The mixture was stirred for 2 d at room temp. The resulting solid was filtered and washed with CH_2Cl_2-ether to give a yellow solid **3c** (79% yield): mp 182-183 °C; IR (KBr) ν_{max} 3344, 3016, 1634, 1556, 1520, 1455, 1316, 1232, 1168, 1114, 849, 818,

756, 701, 622, 518 ^{1}cm^{-1}; H NMR (300 MHz, DMSO-d_6): δ 9.45 (d, J = 6.6 Hz , 4H), 8.92 (d, J = 6.6 Hz, 4H), 8.59 (s, 2H), 7.48-7.63 (m, 10H), 5.96 (s, 4H); ^{13}C NMR (DMSO-d_6; 300 MHz) δ 62.94, 127.69, 128.81, 129.24, 129.39, 131.33, 134.25, 144.84, 151.17, 147.64, 152.26.

Preparation of 4,7-Bis[(2-pyridyl)ethynyl]-2,1,3-benzothiadiazole (4a): To a solution of 2-ethynylpyridine (0.302 g, 2.93 mmol) and 4,7-dibromo-2,1,3-benzothiadiazole (0.411 g, 1.4 mmol) in triethylamine (15 ml), bis(triphenylphosphine) palladium(II) dichloride (0.023 g, 0.0327 mmol) and copper(I) bromide were added. After stirring for 1 h at 60 °C, the reaction mixture was further stirred for 2 d at 90 °C under argon. Triethylamine was removed in vacuo and the residue was dissolved in $CHCl_3$. The solution was washed with aqueous K_2CO_3 and dried over Na_2SO_4. After filtration the solvent was removed to give brown solids. Chromatography on silica gel with chloroform–ethyl acetate as eluent afforded the compound **4a**. Recrystalization from toluene: Yellow solid (47% yield): mp 232-234 °C; IR (KBr) ν_{max} 2214, 1582, 1497, 1459, 1383, 1240, 1149, 988, 895, 860, 779, 547 cm^{-1}; UV ($CHCl_3$) λ_{max} nm (log ε) 242 (4.21), 306 (4.55), 399 (4.42); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.72 (br. s, 2H), 7.9-7.93 (m, 2H), 7.70-7.80 (m, 4H), 7.30-7.34 (m, 2H); ^{13}C NMR ($CDCl_3$; 300 MHz) δ 84.53, 96.46, 117.05, 123.47, 127.76, 133.10, 136.27, 142.79, 150.36, 154.36; MS (EI): m/z (%) 338 (M^+, 100). Anal. Calcd for $C_{20}H_{10}N_4S$: C, 70.99; H, 2.98; N, 16.56; S, 9.48; Found: C, 70.79; H, 3.20; N, 16.51; S, 9.11.

Preparation of 4,7-Bis[(3-pyridyl)ethynyl]-2,1,3-benzothiadiazole (4b): Following the same procedure as that for **4a,** the compound **4b** was obtained. Recrystalization from toluene: Yellow solid (57% yield): mp 189-191 °C; IR (KBr) ν_{max} 2356, 1564, 1538, 1470, 1182, 1022, 886, 807, 705, 547, 506 cm^{-1}; UV ($CHCl_3$) λ_{max} nm (log ε) 242 (4.35), 304 (4.54), 403 (4.39); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.91 (br. s, 2H), 8.64 (br. s, 2H), 7.96-7.98 (m, 2H), 7.87 (d, J = 3.9 Hz, 2H), 7.34-7.39 (m, 2H); ^{13}C NMR ($CDCl_3$; 300 MHz) δ 88.18, 94.05, 117.02, 119.67, 123.11, 132.68, 138.80, 149.37, 152.52, 154.20; MS (EI): m/z (%) 338 (M^+, 100); Anal. Calcd for $C_{20}H_{10}N_4S$: C, 70.99; H, 2.98; N, 16.56; S, 9.48; Found: C, 71.24; H, 3.28; N, 16.43; S, 9.44.

Preparation of 4,7-Bis[(4-pyridyl)ethynyl]-2,1,3-benzothiadiazole (4c): Following the same procedure as that for **4a**, the compound **4c** was obtained. Recrystalization from toluene: Yellow solid (78% yield); mp 243-245 °C; IR (KBr) ν_{max} 2353, 2212, 1592, 1538, 1504, 806, 853, 816, 660, 543 cm^{-1}; UV ($CHCl_3$) λ_{max} nm (log ε) 243 (4.39), 301 (4.67), 396 (4.56); ^1H NMR (270 MHz, $CDCl_3$): δ 7.55 (d, J = 5.9 Hz, 4H), 7.88 (s, 2H), 8.69 (d, J = 5.9 Hz, 4H); ^{13}C NMR ($CDCl_3$; 270 MHz) δ 89.05, 94.64, 117.09, 125.71, 130.49, 133.04, 149.99, 154.21; MS (EI): *m/z* (%), 338 (M^+, 100); Anal. Calcd for $C_{20}H_{10}N_4S$: C, 70.99; H, 2.98; N, 16.56; S, 9.48; Found: C, 71.29; H, 3.12; N, 16.58; S, 9.37.

Methylation of 4,7-Bis[(3-pyridyl)ethynyl]-2,1,3-benzothiadiazole 4b: Tetrafluromethanesulfonic acid (0.080 g, 0.49 mmol) was added to a solution of **4b** (0.051 g, 0.15 mmol) in CH_2Cl_2 (20 ml). The mixture was stirred for 2 h at room temperature. The resulting solid was filtered and washed with CH_2Cl_2 to give a yellow solid **6b** (82% yield): mp 289-291 °C; ^1H NMR (300 MHz, CD_3CN): δ 8.94 (s, 2H), 8.60-8.66 (m, 4H), 8.05-8.09 (m, 4H), 4.40 (s, 6H); ^{13}C NMR ($CDCl_3$; 300 MHz) δ 49.69, 89.83, 93.05, 117.12, 117.32, 124.59, 129.25, 135.29, 146.02, 148.21, 148.63, 154.94; Anal. Calcd for $C_{24}H_{16}F_6N_4O_6S_3$: C, 43.25; H, 2.42; N, 8.41; S, 14.43; Found: C, 43.19; H, 2.84; N, 8.47; S, 14.41.

Methylation of 4,7-Bis[(4-pyridyl)ethynyl]-2,1,3-benzothiadiazole 4c: Following the same procedure as above, the dimethyalted compound **6c** was obtained as a yellow solid (86% yield): mp 229-232 °C; ^1H NMR (300 MHz, CD_3CN): δ 8.68 (d, J = 6.3 Hz, 4H), 8.14 (s, 2H), 8.11 (d, J = 6.6 Hz, 4H), 4.55 (s, 6H); ^{13}C NMR ($CDCl_3$; 270 MHz) δ 49.25, 92.63, 98.18, 117.12, 117.48, 130.67, 135.88, 139.85, 146.43, 154.80; Anal. Calcd for $C_{24}H_{16}F_6N_4O_6S_3$: C, 43.25; H, 2.42; N, 8.41; S, 14.43; Found: C, 43.09; H, 2.84; N, 8.47; S, 14.41.

Benzylation of 4,7-Bis[(3-pyridyl)ethynyl]-2,1,3-benzothiadiazole 4b: Benzylbromide (0.085 g, 0.50 mmol) was added to a solution of **4b** (0.05 g, 0.15 mmol) in CH_2Cl_2 (20 ml). The mixture was stirred for 2 d at 40 °C. The resulting solid was filtered and washed with CH_2Cl_2 to give a yellow solid **7b** (62% yield): mp 234-236

°C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.76 (br. s, 2H), 9.29 (dd, J = 6.3 Hz, 2H), 8.90 (dd, J = 6.9 Hz, 2H), 8.32 (dd, J = 8.1 Hz, 2H), 8.2 (s, 2H), 7.61-7.62 (m, 4H), 7.47-7.49 (m, 6H), 5.93 (br. s, 4H); ^{13}C NMR (DMSO-d_6; 300 MHz) δ 63.65, 89.79, 91.58, 115.63, 122.65, 128.73, 129.02, 129.22, 129.50, 133.86, 134.35, 144.76, 147.16, 147.64, 153.29; Anal. Calcd for $C_{34}H_{24}Br_2N_4S\cdot(H_2O)_{2.5}$: C, 56.29; H, 4.02; N, 7.72; S, 4.42; Found: C, 56.05; H, 3.94; N, 7.78; S, 4.3.

Benzylation of 4,7-Bis[(4-pyridyl)ethynyl]-2,1,3-benzothiadiazole 4c:

Following the same procedure as above, **7c** was obtained as a yellow solid (86% yield): mp 374-376 °C; ^{1}H NMR (300 MHz, DMSO): δ 9.29 (dd, J = 9 Hz, 4H), 8.41 (dd, J = 6.9 Hz, 4H), 8.29 (s, 2H), 7.45-7.55 (m, 10H), 5.89 (br. s, 4H). ^{13}C NMR (DMSO-d_6; 270 MHz) δ 63.31, 92.29, 96.89, 115.85, 128.90, 129.27, 129.47, 130.08, 134.00, 135.11, 138.03, 145.12, 153.24; Anal. Calcd for $C_{34}H_{24}Br_2N_4S\cdot(H_2O)_{1.5}$: C, 57.73; H, 3.84; N, 7.92; S, 4.53; Found: C, 57.53; H, 3.90; N, 8.17; S, 4.59.

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Chapter 3

Synthesis and Properties of Novel Bispyridyl Bis(benzothiadiazole) Derivatives.

Md. Akhtaruzzaman, Masaaki Tomura, J. Nishida and Yoshiro Yamashita "Linear molecules with ethynylpyridine and bisbenzothiadiazole units" *Synth. Met.* **2003**, 137, 873.

Chapter 3. Synthesis and properties of bispyridyl-bisbenzothiadiazole derivatives

Abstract. Bispyridylbis(benzothiadiazole) derivatives (**8-11**) were synthesized using the palladium-mediated cross coupling reaction of 7,7′-dibromo-4,4′-bis(2,1,3-benzothiadiazole). X-ray structure analysis of these derivatives revealed the linear molecular structures with unusual tape-like networks. They showed high electron affinities and fluorescence properties with large Stokes shifts. Their viologen analogues were also prepared by methylation of the dipyridyl nitrogen atoms and their properties were investigated.

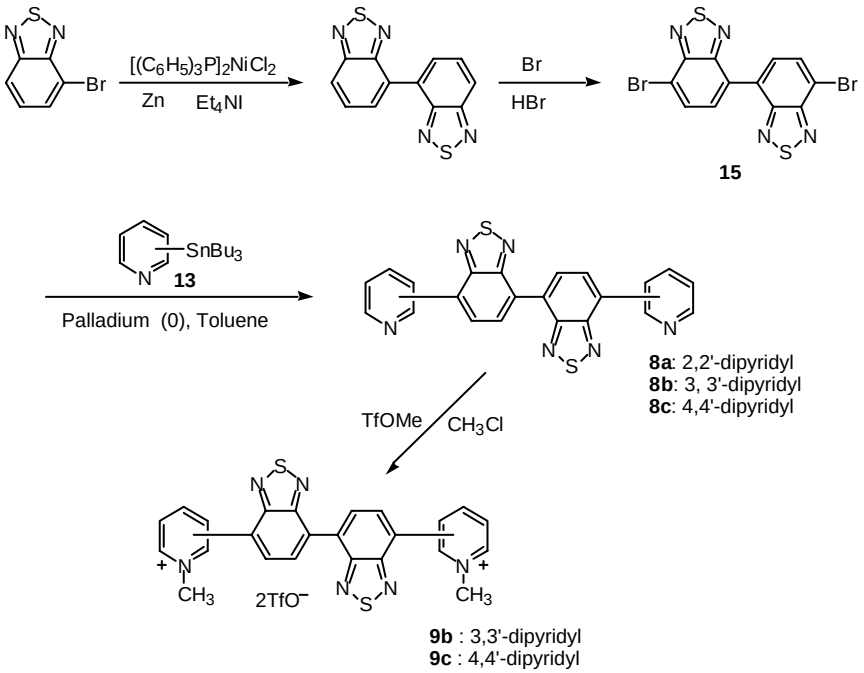
3.1 Introduction

Molecules with pyridyl substituents at the terminal positions can afford supramolcular architectures using intermolecular interactions such as hydrogen bonding and coordination with metals.[1] The author has described in chapter 2 that the compounds containing one benzothiadiazole unit show high electron affinity and high quantum yields of fluorescence. The crystal structures of the compounds **1-4** are almost the same independent on the nitrogen position. This is attributed to the efficient π–π interactions of the long size π-conjugation molecules. On the other hand, the tape-like networks by intermolecular S····N contacts are observed in the structures of 4,4'-bis(2,1,3-benzothiadiazole) derivatives.[2] With this in mind, the author has alsosynthesized the compounds **8-11** (Scheme 3 & 4), and describes their structures and electronic properties in this chapter.

3.2 Results and Discussion

3.2.1 Synthesis of Bispyridylbisbenzothiadiazole Derivatives

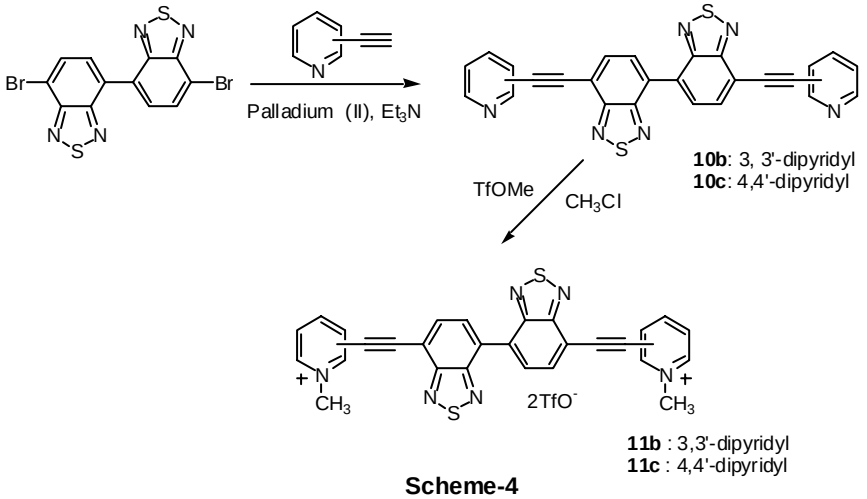
The compounds **8a-c** were synthesized (shown in Scheme **3**) by using a palladium mediated cross coupling reaction of 7,7′-dibromo-4,4′-bis(2,1,3-benzothiadiazole) (**15**)[3] with (tributylstanyl)pyridine[4] in dry toluene gave 7,7′-bis(*n*-pyridyl)-4,4′-bis(2,1,3-benzothiadiazole) (*n* = 2, 3, 4) in 59-61%. Their viologen analogues were also obtained as trifluromethanesulfonate (**TfO**) salts **9b** and **9c** in high yields by mixing **8b** and **8c** with MeOTf (1: 6 stoichiometry) in chloroform, respectively.



Scheme-3

Scheme 4 describes the synthesis of 7,7′-bis(*n*-pyridylethynyl)-4,4′-bis(2,1,3-benzothiadiazole) (*n* = 3, 4) (**10b,c),** and their viologen analogues **11b,c**. The compounds **10b,c** were obtained by using the Sonogashira cross coupling reaction of **15** with the corresponding ethynylpyridine (**14**)[5] in the presence of $PdCl_2(PPh_3)_2$ and CuBr in triethylamine. The dimethylated compouds of **10b,c** which are analogues of methyl viologen, were obtained as trifluoromethanesulfonate (**TfO**) salts **11b** and **11c** in high yields by mixing **10b** and **10c**

with MeOTf (1: 3 stoichiometry) in dichloromethan, respectively.



Scheme-4

3.2.2 Crystal structures

In order to investigate the structures of the long π-conjugated molecules, X-ray analyses of **10c** and **11c** were carried out (Table 8). The crystal structure of **10c** with the space group of triclinic $P\bar{1}$ is shown in Fig. 17. There exist two crystallographically independent molecules (molecule I and II) in the crystal. The dihedral angles between the two benzothiadiazole rings of the molecule I and II are 26.4(1)° and 26.9(1)°, and those between the pyridine and benzothiadiazole rings are 18.5(1)° and 6.1(1)° for the molecule I, and 24.59(1)° and 6.8(1)° for the molecule II, respectively (Fig. 18a). It should be noted that there is a steric interaction between the nitrogen and hydrogen atoms in the two benzothiadiazole rings leading to the torsion. In the crystal structures of **4** (in Chapter 2), π-stacking is favored and no short heteroatom contacts are observed. In contrast, the crystal **10c** contains short S···N contacts (3.00 and 3.10 Å for the molecule I, 2.97 and 3.09 Å for the molecule II) between the thiadiazole rings leading to the molecular tape structure as shown in Fig. 18b.

The crystal structure of **11c** with the space group of triclinic $P\bar{1}$ is shown in Fig. 19. The molecular structure of **11c** is almost planar and the dihedral angles between the two benzothiadiazole rings and the pyridine and benzothiadiazole rings are 0° and

2.9(3)°, respectively (Fig. 19a). It should be noted that the molecules becomes more planar in the dication state. The molecular length between the two N-methyl atoms of **11c** is 23.7 Å. The short S···N contacts [2.99(1) Å] are observed in the structure, leading to the molecular tape structure as shown in Fig. 19b.

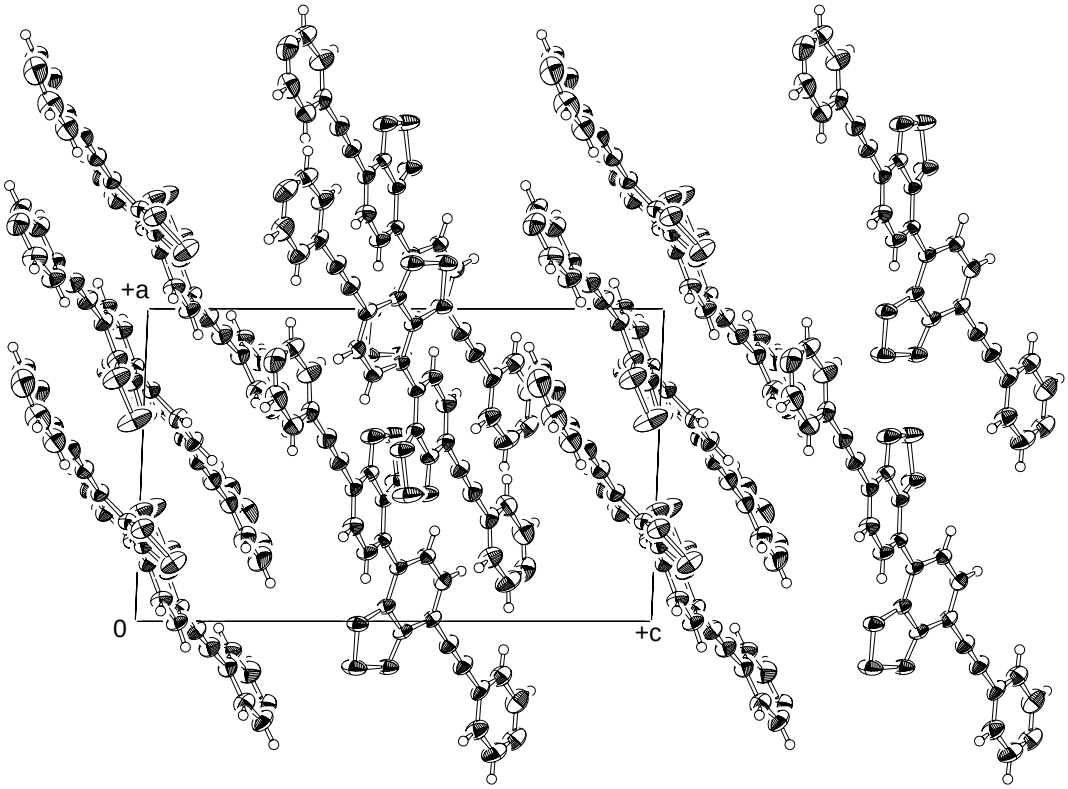
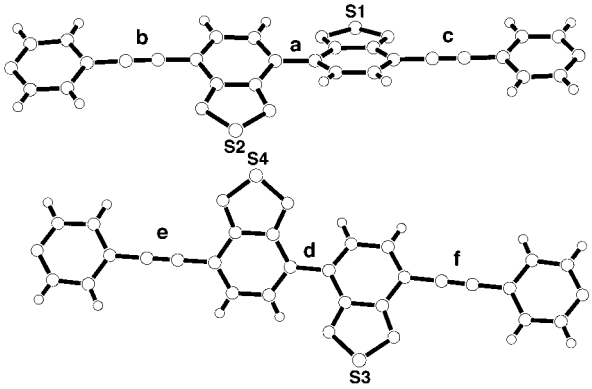
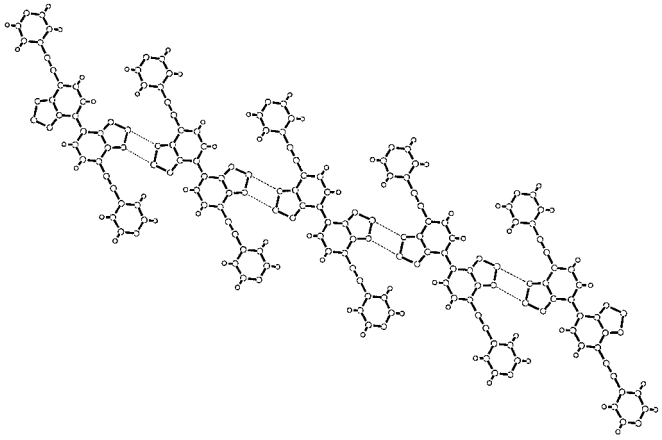


Figure 17. Crystal structure of **10c** viewed along the b axis.

(a)



(b)



(c)

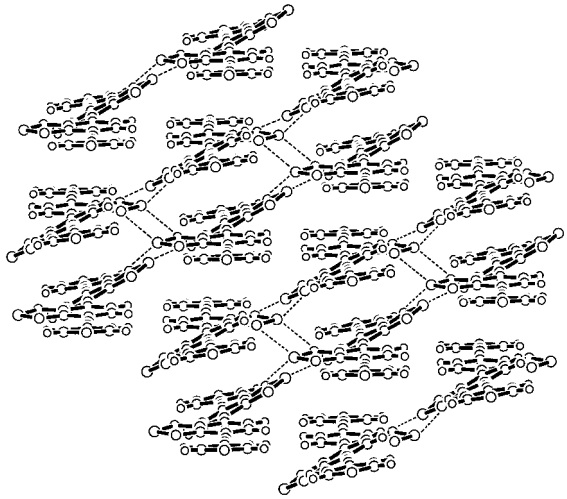


Figure 18. (a) Dihedral angles of the molecule **10c**; a; 26.4(1)°, b; 6.1(1)°, c; 18.5(1)°, d; 29.6(1)°, e; 24.5(1)°, f; 6.8(1)°. (b) Tape-like networks by S···N contacts of **10c**. (c) Columnar structure of **10c**.

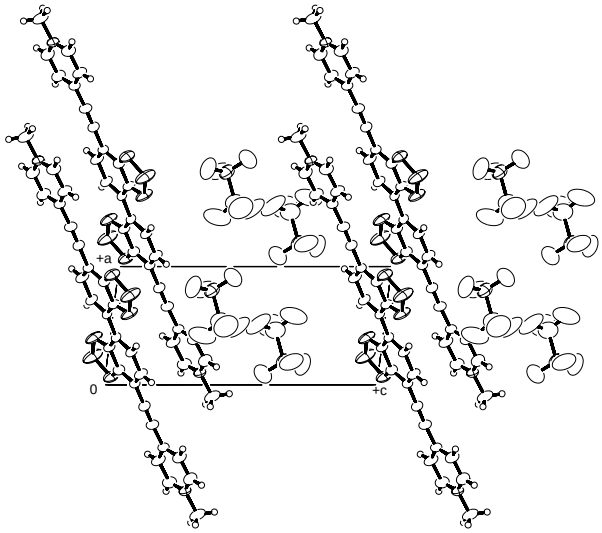
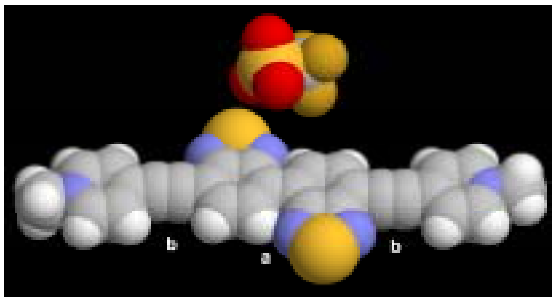


Figure 19. Crystal structure of **11c** viewed along the b axis.

(a)



(b)

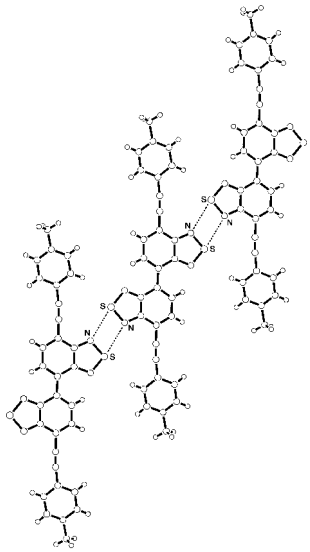


Figure 19. (a) Dihedral angles of the molecule **11c**, where a; 0°, b; 2.9(3)°; (b) Tape-like networks by S···N contacts of **11c**.

Table 8. Crystal data and summary of data collection parameters

		10c	**11c**
Molecular formula		$C_{26}H_{12}N_6S_2$	$C_{30}H_{18}F_6N_6O_6S_4$
Molecular weight		472.54	800.74
Crystal dimensions (mm^3)		0.30 x 0.15 x 0.05	0.25 x 0.15 x 0.02
Crystal system		Triclinic	Triclinic
Space group		*p*1	*p*1
Temp. (K)		296	296
Unit cell	*a* (Å)	11.1338(4)	6.631(6)
	b (Å)	11.0455(3)	8. 311(6)
	c (Å)	17.9630(14)	15.252(10)
	(°)	87.638(4)	82.94(7)
	(°)	87.227(4)	82.13(10)
	(°)	77.316(3)	83.61(10)
	V ($Å^3$)	2151.57(19)	822.5(11)
Z		4	1
Density calc. (g cm^{-3})		1.459	1.617
Absorption coeff. (mm^{-1})		2.477	0.378
Radiation		Mo-K□	Cu-K□
Measured reflections		9248	8211
Independent reflections		8770	3616
Reflections with $I > 2$	(*I*)	-	1467
R_1		0.0470	0.0877
wR_2		0.1211	0.1730
GOF		1.00	0.983

3.2.3 Physical properties

All the electronic properties of the compounds **8-11** are summarised in Table 9. The absorption maxima of bis(benzothidiazole) compounds **8** and **10** are observed at longer wavelengths than those of mono(benzothiadiazole) containing units compounds, due to the longer conjugation in the two benzothiadiazole units containing compounds. The structures of these molecule are polarized in the ground state as deduced from the red-shift in less polar solvents (shown in Table 10). The compounds **8** and **10** exhibit strong fluorescence emission in solution. The Stokes shifts are larger and the quantum yields decrease compared to the mono(benzothiadiazole) containing compounds (in Chapter two). The absorption maxima of **10** are red shifted compared to **8** due to the larger conjugation**.** The quantum yields of **8** is lower than **10**. The dication salts show lower quantum yields and a little red-shift of emmision maxima compared to the corresponding neutral compounds. There are no significant effects of the nitrogen

positions on the absorption and emission spectra in these compounds. The bis(benzothidiazole) containing compounds show higher reduction potential compared to the mono(benzothidiazole) containing compounds. This is attributed to the electron withdrawing property of the thiadiazole ring. The compounds **10** show stepwise one-electron-reduction waves since they contain two benzothiadiazole units. The methyalted compounds show higher reduction potentials than the neutral compounds.

Table 9: Absorption maxima, fluorescence maxima, quantum yields and reduction potentials for dipyridyl compounds

Compounds	$\lambda_{abs,max}$/nm	$\lambda_{em,\ max}$/nm	Φ_e	E_{red}/V
8a	401	484	0.26	-1.28, -1.48
8b	397	481	0.21	–
8c	389	469	0.24	–
9b	387	493	0.10	-0.53, -0.86
9c	397	480	0.15	-0.40, -0.86
10b	416	503	0.32	-1.10, -1.34
10c	412	486	0.46	-1.07, -1.27
11b	411	492	0.26	-0.93
11c	422	508	0.30	-0.67

##Absorption maxima, fluorescence maxima, quantum yields of **8** and **9-11** were measured in $CHCl_3$ and MeCN, respectively.

Reduction potentials of methylated compounds (**9, 11**) and the neutral compounds (**8a**, **10**) were measured in MeCN and CH_2Cl_2, respectively (0.1 mol dm^{-3} *n*-Bu_4NPF_6 in solution Pt electrode, scane rate 100 mV s^{-1}, V vs SCE).

The reduction potential of **8b,c** were not measured due to bad solubility.

Table 10. Absorption maxima, fluorescence maxima and quantum yields in various solvents.

solvents	**8a**			**10c**		
	$\lambda_{abs,\,max}$/nm,	$\lambda_{em,\,max}$ /nm,	Φ_e,	$\lambda_{abs,\,max}$/nm,	$\lambda_{em,\,max}$ /nm,	Φ_e,
$CHCl_3$	401	484	0.26	420	484	0.34
MeCN	398	497	0.35	414	486	0.46
EtOH	399	485	0.27	413	485	0.27

λ_{ex} 299 nm

3.2.4 Summary

In this chapter, the author has prepared novel π– conjugated compounds with terminal pyridyl groups. They have also show high electron affinity and high fluorescence in a longer wavelength region. They are expected to afford unique molecular assemblies by heteroatom contacts and/or hydrogen bonding.

3.3 Experimental section.

7,7′-Di(2-pyridyl)-4,4′-bis(2,1,3-benzothiadiazole) (8a). To a solution of 7,7′-dibromo-4,4′-bis(2,1,3-benzothiadiazole) (**15**) (600 mg, 1.40 mmol) in dry toluene (70ml) were added 2-stannylpyridine (1500 mg, 4.0 mmol) (**13**) and the tetrakis(triphenylphos- phine) palladium ($Pd(PPh_3)_4$ (440 mg, 0.38 mmol) under an argon atmosphere. The resulting mixture was heated under reflux overnight. After being cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was washed with hexane. The crude product was purified by sublimation to give a yellow solid (60% yield): mp 281-283 ^oC; IR (KBr) V_{max} 2996, 1591, 1548, 1462, 1432, 1331, 1260, 1150, 1094, 1052, 995, 904, 840, 773, 743, 623 cm^{-1}; UV ($CHCl_3$) λ_{max} 242, 266, 309; 401 nm; MS (EI): *m/z* (%) 424 (M^+, 100); Anal. Calcd for Anal. $C_{22}H_{12}N_6S_2$: C, 62.25; H, 2.85; N, 19.80; S, 15.11; Found: C, 62.81; H, 3.04; N, 19.88; S, 15.09.

7,7′-Di(3-pyridyl)-4,4′-bis(2,1,3-benzothiadiazole) (8b). Following the same procedure as that for **8a**, the compound **8b** was obtained as a yellow solid (61% yield): mp 343-345 ^{o}C; IR (KBr) V_{max} 3021, 1588, 1549, 1473, 1419, 1330, 1194, 1026, 943, 900, 874, 842, 807, 709, 614 cm^{-1}; UV ($CHCl_3$) λ_{max} 244, 266, 310, 318, 397 nm; MS (EI): *m/z* (%) 424 (M^+, 100); Anal. Calcd for $C_{22}H_{12}N_6S_2$: C, 62.25; H, 2.85; N, 19.80; S, 15.11; Found: C, 62.94; H, 3.19; N, 19.99; S, 15.28.

7,7′-Di(4-pyridyl)-4,4′-bis(2,1,3-benzothiadiazole) (8c). Following the same procedure as that for **8**a, the compound **8c** was obtained as a yellow solid (61% yield): mp 444-446 ^{o}C; IR (KBr) V_{max} 3019, 1600, 1551, 1478, 1414, 1338, 1270, 1220, 1076, 993, 817, 746, 640 cm^{-1}; UV ($CHCl_3$) λ_{max} 242, 268, 311, 318, 389 nm; MS (EI): *m/z* (%) 424 (M^+, 100); Anal. Calcd for $C_{22}H_{12}N_6S_2$: C, 62.25; H, 2.85; N, 19.80; S, 15.11; Found: C, 62.58; H, 3.11; N, 19.88; S, 15.08.

Methylation of 7,7′-di(3-pyridyl)-4,4′-bis(2,1,3-benzothiadiazole) 8b:
Tetrafluromethane sulfonic acid (70 mg , 0.43 mmol) was added to a solution of **8b** (30 mg, 0.071 mmol) in $CHCl_3$ (10 ml). The mixture was stirred overnight at 50° C. The resulting solid was filtered and washed with $CHCl_3$ and ether to give a yellow solid **9b** (90% yield): mp 145-147 ^{o}C; IR (KBr) V_{max} 3088, 2857, 1634, 1555, 1468, 1283, 1164, 1030, 908, 848, 815, 759, 638, 518 cm^{-1}; UV (MeCN) λ_{max} 229, 253, 317, 387 nm; ^{1}H NMR (300 MHz, DMSO-d$_6$): δ 9.73(s, 2H), 9.31(d, J = 7.8 Hz, 2H), 9.10-8.98(m, 4H), 8.56 (d, J = 7.5 Hz, 2H), 8.40 (s, 2H), 4.51 (s, 6H).

Methylation of 7,7′-di(3-pyridyl)-4,4′-bis(2,1,3-benzothiadiazole) 8c:
Following the same procedure as above, the dimethylated compounds **9c** was obtained as a yellow solids (92%): mp 145-147 ^{o}C; IR (KBr) V_{max} 3071, 2855, 1634, 1546, 1379, 1255, 1168, 1028, 906, 818, 760, 641, 516 cm^{-1}; UV (MeCN) λ_{max} 229, 253, 317, 387 nm; ^{1}H NMR (300 MHz, CD_3CN): δ 8.88-8.10(br, 8H), 8.64 (d, J = 7.2 Hz, 2H), 8.44(d, J = 7.2 Hz, 2H), 3.12 (s, 6H).

7,7′-Bis(3-pyridylethynyl)-4,4′-bis(2,1,3-benzothiadiazole) (10b). To a solution of 3-ethynylpyridine (220 mg, 2.12 mmol) (**14**) and

7,7′-dibromo-4,4′-bis(2,1,3-benzothia-diazole) (**15**) in triethylamine (40 ml), bis(triphenylphosphine) palladium(II) dichloride (45 mg, 0.064 mmol) and copper(I) bromide (15 mg, 0.079) were added. After stirring for 1 h at 60 ^{o}C, the reaction mixture was further stirred for 3 d at 90 ^{o}C under argon. Triethylamine was removed in vacuo and the residue was dissolved in $CHCl_3$. The solution was washed with aqueous K_2CO_3 and dried over Na_2SO_4. After filtration the solvent was removed to give a dark yellow solid. Chromatography on silica gel with chloroform–ethyl acetate as eluent afforded the compound **10b**. Recrystalization from toluene gave a yellow solid (53% yield): mp 232-234^{o}C; IR (KBr) V_{max} 3027, 2205, 1561, 1486, 1409, 1343, 1186, 1025, 907, 844, 803, 700, 630, 543, 501 cm^{-}1; UV ($CHCl_3$) λ_{max} nm (log ε) 242 (4.0), 300 (4.3), 426 (4.2); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.72 (br. s, 2H), 7.9-7.93 (m, 2H), 7.70-7.80 (m, 4H), 7.30-7.34 (m, 2H); MS (EI): *m/z* (%) 472 (M^{+}, 100)

7,7′-Bis(4-pyridylethynyl)-4,4′-bis(2,1,3-benzothiadiazole) (10c). Following the same procedure as that for **10b**, the compound **10c** was obtained. Recrystalization from toluene gave a yellow solid (49%); mp 305-307 ^{o}C; IR (KBr) V_{max} 3037, 2205, 1538, 1492, 1411, 1357, 1219, 1081, 1035, 989, 909, 810, 717, 668, 544 cm^{-}1; UV ($CHCl_3$) λ_{max} nm (log ε) 241 (4.44), 293 (4.57), 419 (4.52); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.68 (br. s, 4H), 8.50 (s, 2H), 8.05 (s, 2H), 7.55 (br. s, 4H); MS (EI): *m/z* (%) 472 (M^{+}, 100)

Methylation of 7,7′-bis(3-pyridyl)-4,4′-bis(2,1,3-benzothiadiazole) 10b: Tetrafluromethanesulfonic acid (114 mg, 0.70 mmol) was added to a solution of **10b** (50 mg, 0.11 mmol) in CH_2Cl_2 (40 ml). The mixture was stirred for 2 h at room temperature. The resulting solid was filtered and washed with CH_2Cl_2 to give a yellow solid **11b** (78% yield): mp 285-287 ^{o}C; IR (KBr) V_{max} 3072, 2217, 1632, 1557, 1507, 1362, 1256, 1160, 1031, 925, 845, 757, 674, 639, 574, 518 cm^{-}1; UV (MeCN) λ_{max} 231, 296, 416 nm; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.96 (s, 2H), 8.73-8.66 (m, 4H), 8.54 (d, J = 7.5 Hz, 2H), 8.24 (d, J = 7.5 Hz, 2H), 8.10-8.06 (m, 2H), 4.36 (s, 6H).

Methylation of 7,7′-bis(4-pyridyl)-4,4′-bis(2,1,3-benzothiadiazole) 10c:

Following the same procedure as above, the dimethyalted compound **11c** was obtained as yellow solid (83%). mp 289-291 ^{o}C; IR (KBr) V_{max} 3058, 2210, 1637, 1518, 1268, 1159, 1029, 854, 637, 518 cm^{-}1; UV (MeCN) λ_{max} 231, 295, 416 nm; ^{1}H NMR (300 MHz, CD_3CN): δ 8.84-8.78 (m, 8H), 8.64-8.59 (m, 2H), 8.45-8.42 (m, 2H), 4.38 (s, 6H).

3.4 References

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Chapter 4

Studies on the Crystal Engineering as well as Supramolecular Architecture based on Organic Acids and Dipyridyl Compounds.

Md. Akhtaruzzaman, Masaaki Tomura, and Yoshiro Yamashita, "One-dimensional hydrogen-bonded molecular tapes in 1,4-bis[(4-pyridinium)ethynyl]benzene chloranilate" *Acta Cryst*. **2001**, E57, o353.

Md. Akhtaruzzaman, Masaaki Tomura, Kazuko Takahashi**,** Jun-ichi Nishida and Yoshiro Yamashita "Unusual Hydrogen Bonding Networks Consisted of π–Extended 4,4′-Bipridines and Chloranilic Acid" *Supramol. Chem.* accepted.

Chapter 4. Studies on the crystal engineering as well as supramolecular architecture based on organic acids and dipyridyl compounds.

Abstract: In this chapter, the author attempted to include both ionic and hydrogen-bonding interactions in a system that can form a variety of supramolecular structures and mediate electron-proton transfer between organic acid and base materials. For such a purpose he has selected strong organic acids such as chloranilic acid (**CLA**), squaric acid (**SQA**) and cyanuric acid (**CNUA**) which are good hydrogen-bonding donors, and several organic base derivatives consisting of pyridyl substituents at the terminal position should be strong proton acceptors as shown in Scheme 5, 6 and 7**.** Scheme 5 describes the complexes of 2,5-di(4-pyridyl)thiophene (**4-BPT**), 2,5-di(4-pyridyl)furan (**4-BPF**), 1,4-di(4-pyridyl)benzene (**4-BPB**) and 4,7-di(4-pyridyl)-2,1,3-benzothiadiazole(**4-BPBTD**) with 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (chloranilic acid, **CLA**) (**1-4**). In Scheme 6 have been described the complexes of 1,4-di(*n*-pyridyl)buta-1,3-diynes (*n* = 3, 4) (**DPDAs**), 1,4-bis(n-pyridylethynyl)benzene (*n* = 3,4) (**BPBEBs),** and 1,4-bis(4-pyridylethynyl)-2,1,3-benzothiadiazole (**4-BPBEBTD)** with **CLA**. The complexes of **4-BPT**, **DPDAs** and **BPBEBs** and with 3,4-dihydroxy-3-cyclobutehe-1,2-dione (squaric acid, **SQA**) (**9-11**) and the complex of **4-DPDA** with 1,3,5-triazine-2,4,6-triol (cyanuric acid, **CNUA**) (**12**) are described in Scheme 7. The X-ray structure analyses of all these complexes show the unusual molecular tape and sheet structures by N-H···O, O-H···O, C-H···O and N-H···N hydrogen bonds, where a rare ten-membered hydrogen-bonded ring is formed between the two monoanions of **SQA**. The structure of **8** could not be solved yet due to the disorder. From these results, the aromatic spacer groups seem to play an important role in the formation of unique crystal structures.

4.1 Introduction

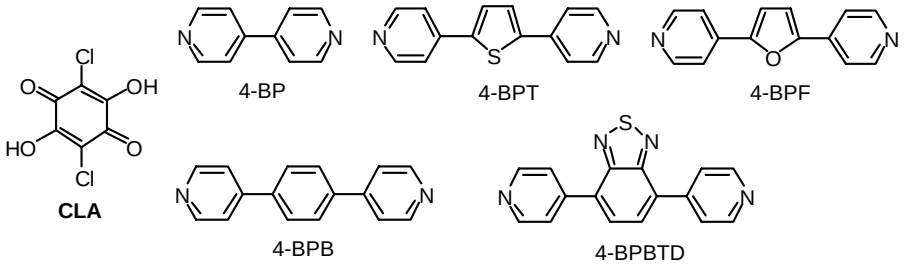
Hydrogen bonds are flexible in binding strength and selectivity, and particularly in molecular and supramolecular geometry compared to the coordination bonds and rigid covalent bonds.[1] Among intermolecular interactions, hydrogen bonding has been the most important one in the supramolecular chemistry[2] as well as in crystal engineering studies.[3] The hydrogen bonding interactions have been used for the development of tailor-making materials with desired and controllable properties for electronic, magnetic, optical, and catalytic systems.[2-4] Many examples using hydrogen bonding interactions to control the self-assembling of molecules and prepare well-defined aggregates have been reported during the past decade.[1,3] However, there are only a few of hydrogen bonding systems involving intermolecular electron-transfer interactions.[5] Benzoquinones containing dihydroxy and halide/cyanide groups can afford such systems because they have excellent proton donating and electron accepting properties and undergo multi-stage deprotonation and protonation processes.[6,7] They can be associated with various proton-acceptors and electron donors for the design and control of new supramolecular architectures.[6] *Zaman et. al* have recently shown that the simple combination of chloranilic acid (**CLA**) with dipyridyl compounds affords a variety of hydrogen bonding networks such as linear chain, zigzag tapes and square grids structures,[8] where charge transfer interactions between molecules take place. They have also shown that the formation of their neutral, monoanion, and dianion states can be controlled by proton transfer.[9] The structures and properties of the hydrogen bonding complexes are tuned by the substituents of anilic acids.[10] On the other hand, they are expected to strongly depend on the dipyridyl compounds. The author has now used dipyridyl compounds containing π-conjugated groups as proton acceptor and have investigated complexation with chloranilic acid (**CLA**), squaric acid (**SQA**) and cyanuric acid (**CNUA**) which work as proton donors (in Scheme 5-7). Introduction of a π-conjugated spacer is expected to increase intermolecular π-π interactions and decrease Coulombic repulsion in the dication states.

4.2 *EXPERIMENTAL*

4.2.1 Preparation

4,4'-Dipyridyl compounds containing thiophene, furan, benzene as spacer were prepared on the basis of palladium-catalyzed cross-coupling procedures.[11] The compounds 1,4-bis[(*n*-pyridyl)ethynyl]benzene (where *n* = 3, 4) and 1,4-di(*n*-pyridyl)buta-1,3-diyne (where *n* = 3, 4) were synthesized according to the published method.[12] To obtain the target supramolecular complexes, equal molar ratio of dipyridyl subtituents compound and **CLA** / **SQA / CNUA** were placed at the bottom of H-shaped two tubes and filled with solvents. The complexes **1-12** were obtained as single crystals by using acetonitrile, methanol, and a mixture of acetonitrile-aceton as solvents. All crystal data and summary of data collections parameters are shown in Table 11-12.

4.2.2 Result and Discussion.



Scheme 5

Complex 1: 4-BPT and CLA

Complex 2: 4-BPF and CLA

Complex 3: 4-BPB and CLA

Complex 4: 4-BPBTD and CLA

Complex **1** has a composition of (dication of **4-BPT**)·(monoanion of **CLA**)$_2$ and crystallizes in a monoclinic space group *C*2/*c*. It involves bifurcated N^+-H···O hydrogen bonds on both sides of **4-BPT** with a thiophene ring and an O-H···O hydrogen bond between the **CLA** molecules. No infinite molecular tape structure is observed. In addition, a molecular sheet structure is formed via C-H···O hydrogen bonds between **4-BPT** and **CLA**. Between the molecular sheet, two types of overlaps for the

monoanion of **CLA** exist. The distances between the ring planes for CLA-CLA and CLA-pyridine are 3.15(1) and 3.32(2) Å, respectively. The structural views and their intermolecular hydrogen bond distances are depicted in Fig. 20.[13] It should be noted that one proton of **CLA** is transferred to the nitrogen atoms of **4BPT** to produce the monoanion of **CLA** and the dication of **4-BPT**. The bond distances of **CLA** support the monoanion structures.[14]

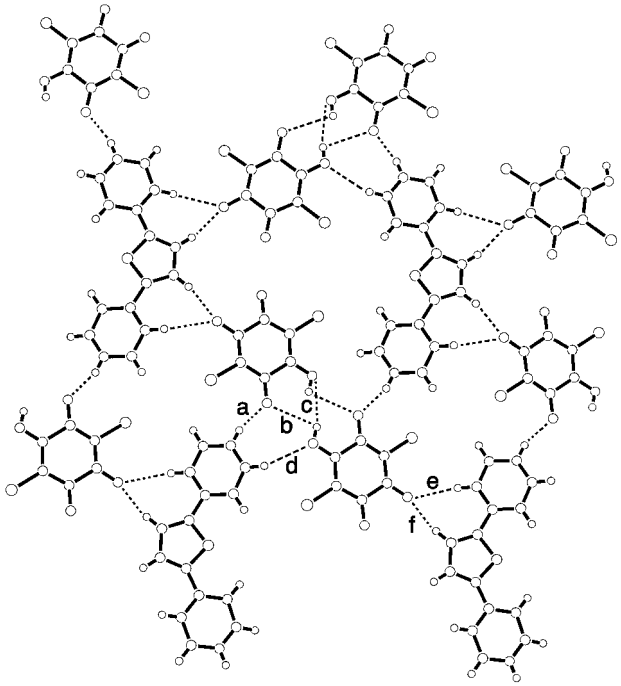
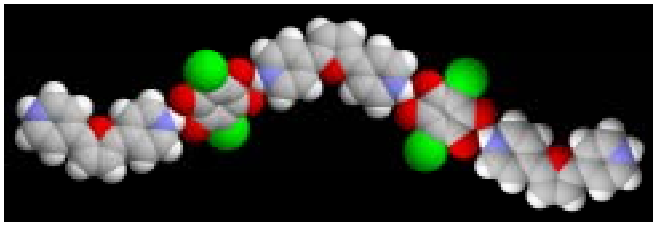


Figure 20. Intermolecular contacts in the molecular sheet of complex **1**, where a (N-H···O): H···O 1.93, N···O 2.74; b (O-H···O): H···O 2.68, O···O 2.98; c (O-H···O): H···O 2.62, O···O 3.41; d (C-H···O): H···O 2.62, C···O 3.51; e (C-H···O): H···O 2.60, C···O 3.50; f (C-H···O): H···O 2.18, C···O 3.09 Å.

Complex **2** has a composition of (dication of **4-BPF**)·(dianion of **CLA**)·(MeOH) with triclinic $P\bar{1}$ space group. Both the pyridyl rings of **4-BPF** are protonated to form a molecular tape structure via bifurcated interionic N^{+}-H···O and N^{+}-H···O^{-} hydrogen bonds with **CLA** molecules (Fig. 21). These hydrogen bond motifs are robust and similar to the supramolecular synthon that Zaman. et. al previously reported to afford tape-like networks. [6] The dipyridyl molecule **4-BPF** is nearly planar as shown by the small dihedral angles [3.5(1)° and 7.6(1)°] between the pyridine and

furan rings. Although one **CLA** molecule is almost coplanar to **4-BPF** with a small dihedral angle of 5.9(2)°, another molecule is twisted with a dihedral angle of 47.5(2)°. The tape structures stack along the b axis, where the intertape distance is 3.27(1) Å.

(a)



(b)

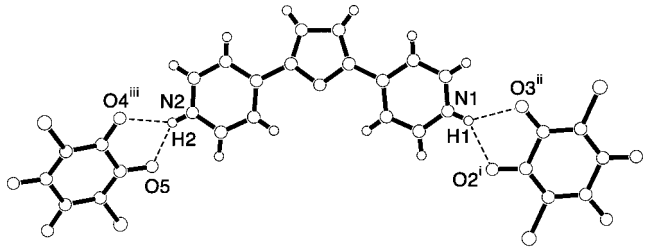
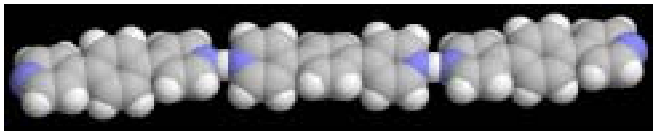


Figure 21. (a) Molecular tape structure of complex **2**. (b) Hydrogen bonding pattern of complex **2.**

Complex **3** has a composition of (**4-BPB**)·(dication of **4-BPB**)·(dianion of **CLA**)·$(H_2O)_6$. X-ray structure analysis reveals the existence of a tape-like structure consisted of only **4-BPB** and a sheet like structure consisted of **CLA** and water molecules. The tape structure is formed by N^+-H···N hydrogen bonding between neutral **4-BPB** and diprotonated **4-BPB** as shown in Fig. 22 where the H···N and N^+···N distances are 1.48(5) and 2.680(3) Å, respectively. The neutral and dication structures of **4-BPB** are nonplanar and the dihedral angles between the benzene ring and dipyridyl groups [29.8(2) and 32.1(2)°] are larger compared to the corresponding angles of **4-BPT** and **4-BPF** in the complexes **1** and **2**. This is due to the larger steric interaction of benzene ring. The hydrogen bonding between the two pyridyl groups is almost linear with the angle of 178(4)°. Such a hydrogen bonding tape-like network formed by neutral and dication molecules is the first example to the best of my knowledge. This type of hydrogen bonding is of interest from the viewpoint of proton transfer since a

mixed protonated state seems to be easily achieved due to the small activation energy of proton transfer.[16]

(a)



(b)

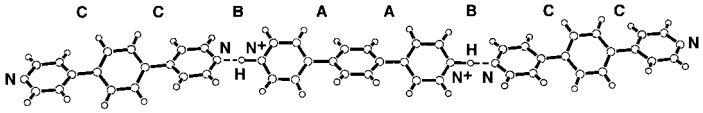


Figure 22 (a) Molecular tape structure of complex **3**. (b) Hydrogen bonding pattern and the dihedral angles between the ring planes of complex **3**, where N^{+}-H 1.20(5), H···N 1.48(5), N^{+}···N 2.680(3) Å, N^{+}-H···H 178(4)°; dihedral angle A: 29.8(2), B: 25.4(1), C: 32.1(2)°.

The planar sheet-like network formed by hydrogen bonds between dianion of **CLA** and water molecules is also observed (Fig. 23). The intermolecular O···O distances in the molecular sheet lie between the range of 2.714(3)-2.981(3) Å. This type of unusual two-dimensional hydrogen bonding networks is also the first example in the **CLA** complexes. The molecular tape of **4-BPB** is stacked in a manner of neutral-dication-neutral to form a two-dimensional columnar structure as shown in Fig. 24a. The molecular sheet consisted of the **CLA** and water molecules is obliquely located between the columns of **4-BPB** (Fig. 24b). The dihedral angles between the **CLA** ring and the benzene ring are 82.5(2)° for dicaton **4-BPB** and 61.5(2)° for neutral **3**. The C-H····π intermolecular interactions are also observed between the tapes of **4-BPB** and the sheets of **CLA**. The C-H····π distances between the least-square planes of the **CLA** dianions and the hydrogen and carbon atoms in the benzene ring of neutral **3** are 2.73(2) (H····π) and 3.44(1) (C····π) Å

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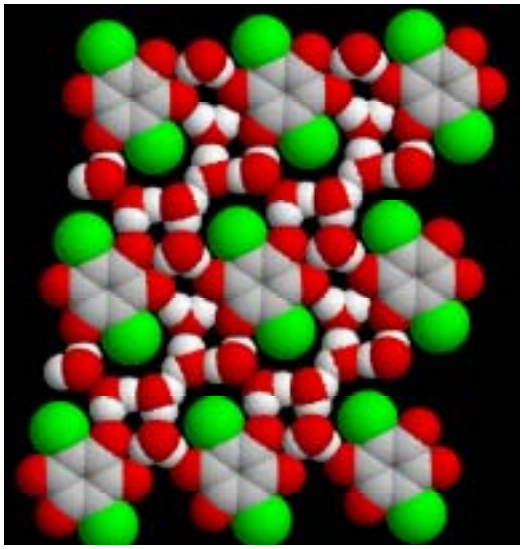
a)



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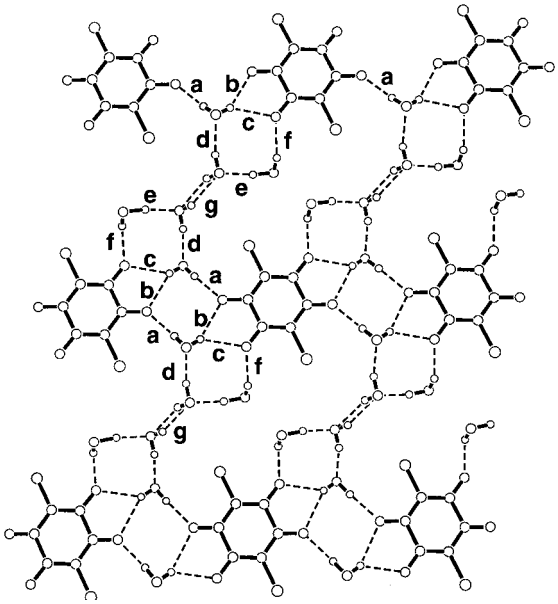
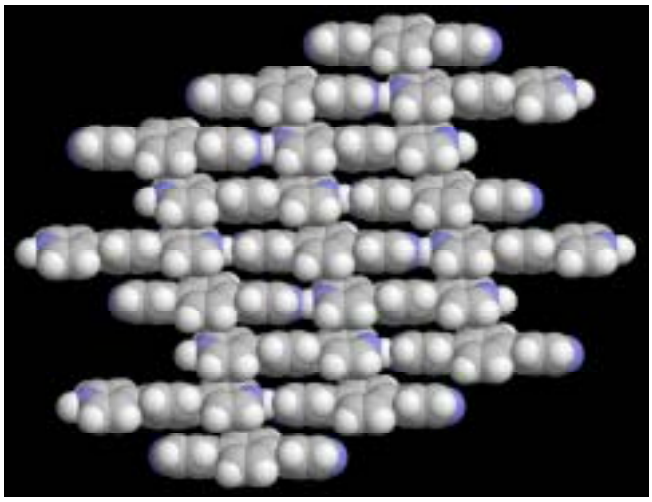


Figure 23 (a) Two-dimensional hydrogen bonding sheet by **CA** and water molecules of **complex 3**. (b) Intermolecular O···O distances in the hydrogen bonding sheet of complex **3**, where a: 2.83, b: 2.98, c: 2.89, d: 2.78, e: 2.73, f: 2.71, g: 2.75 Å.

(a)



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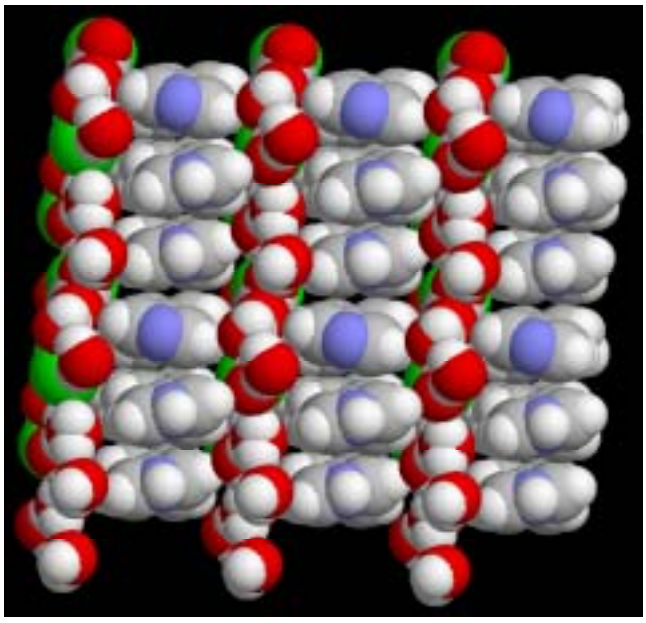


Figure 24 (a) Stacking of the molecular tape structure of complex **3**. (b) Crystal structure of complex **3**. The angles between the **CA** ring and the benzene ring of dication and neutral **3** are 82.5(2)° and 61.5(2)°, respectively.

Complex **4** has a composition of **4-BPBTD** and **CLA** with monoclinic space group $P2_1/c$ and contained three molecules of water. Both of the hydrogen atoms of

chloranilic acid have transferred to the pyridine rings. Thus the complex consists of the dication of **4-BPBTD** and the dianion of **CLA.** A planar one-dimensional molecular tape structure was observed along the [1 0 1] direction. The angles between the pyridinium ring and the benzothiadiazole ring are 15.3(1) and 31.0(1)°, and those between the pyridinium ring and the plane of the chloranilate in the tapes are 9.3(1) and 25.3(1)°, as shown in Figure 25. The lengths of the N-H···O hydrogen bonds between the pyridinium ring and the chloranilate are 2.741(5), 2.761(5), 2.793(5) and 2.858(5) Å. The tape structure stacks in an alternate fashion and forms a mixed stacking. The interstack distance of the tape is 3.3 Å. The chloranilate dianion and the three water molecules form a two-dimensional hydrogen bonding network (molecular sheet) with a large number of O-H···O and O-H···Cl bondings. The averages of O···O distances in the O-H···O bonds and O···Cl distances in the O-H···Cl bonds are 2.96 and 3.55 Å, respectively.

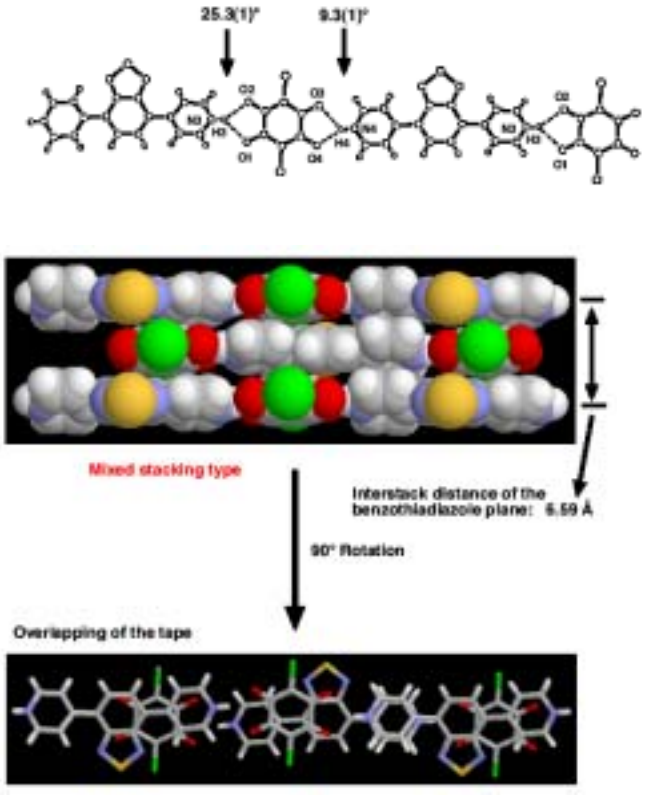
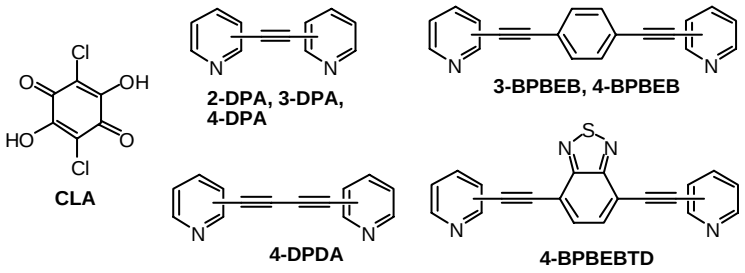


Figure 25. Planar 1-D molecular tapes structures of complex **4**.



Scheme 6

Complex 5: 4-DPDA and CLA **Complex 7:** 4-BPBEB and CLA

Complex 6: 3-BPBEB and CLA **Complex 8:** 4-BPBEBTD and CLA

The author obtained two polymorphic crystals of **4-DPDA-CLA** (**5**) in the different solvents (Scheme 6). One has two crystallographically independent molecules with the triclinic space group $P\bar{1}$, which was obtained from acetone. The other has one independent molecule and 2.5 molecules of solvated water with the monoclinic space group $P2_1/c$, which was obtained from methanol. Very recently, *Zaman et al* showed that the complexes of **DPA-CLA** formed by intermolecular hydrogen bonds allow the different stacking arrangement and ionicity, which depend on the nitrogen position of the pyridyl rings (*Org. Lett*. 2000). For example, in the complex of **4-DPA-CLA**, one pyridine ring of **4-DPA** is protonated and combined with bifurcated N^+-H···O and N^+-H···O^- hydrogen bonding, while the other pyridine ring is not protonated and combined with O-H···N hydrogen-bond interactions. In the complexes of **5**, however, no proton has transferred from **CLA** to **4-DPDA**, and a one-dimensional molecular tape structure via O-H···N hydrogen bonding interactions is observed as shown in Fig. 26. The molecular tapes of the monoclinic crystal have two crossed directions (Fig. 27) where the water molecules are located between the stacking of the tapes, whereas the tapes of the triclinic one run in the single direction in the crystal.

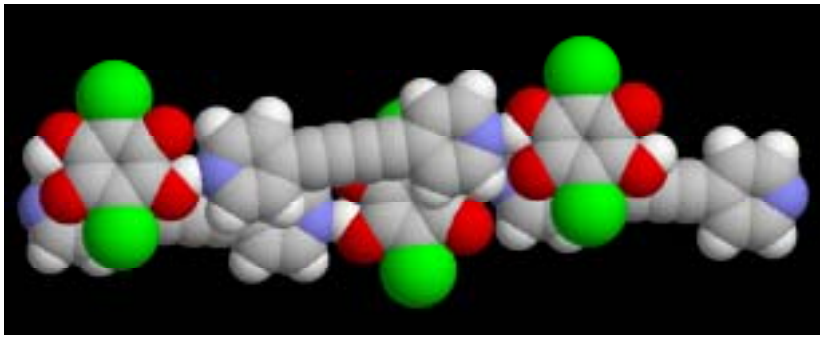


Figure 26. The flat molecular tape structure of triclinic of complex **5**.

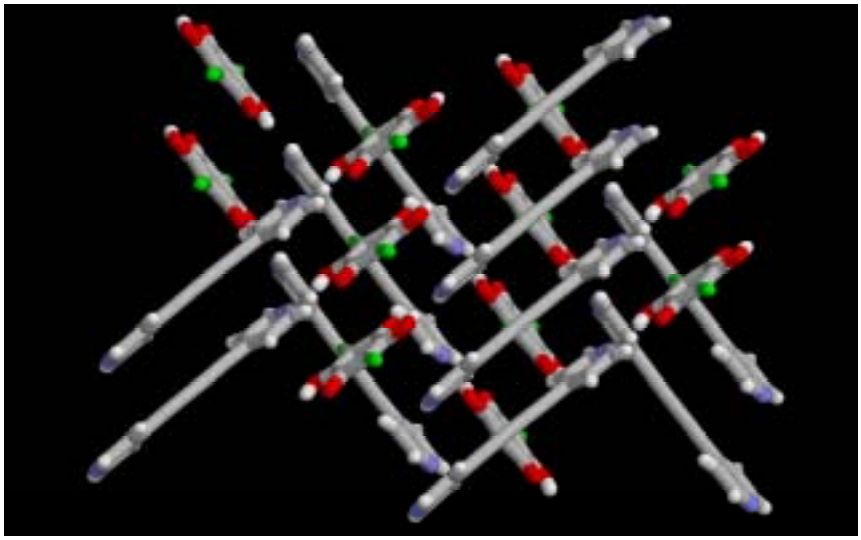
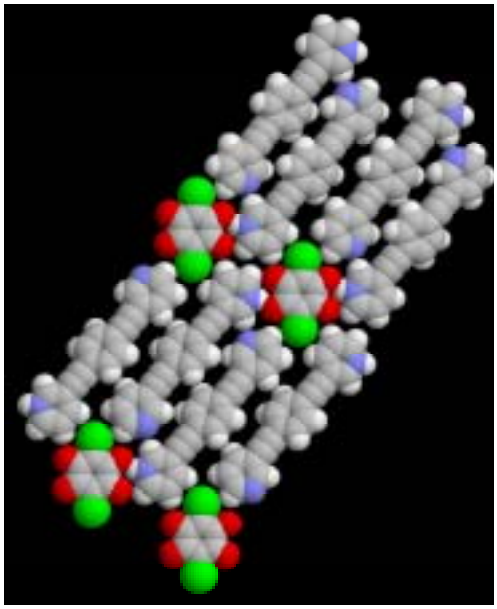


Figure 27. The molecular tapes of the monoclinic complex **5** with two crossed directions.

Complex **6** has a composition of (monocation of **3-BPBEB**)$_2$·(dianion of **CLA**) and crystallizes in the space group of triclinic $P\bar{1}$. It involves bifurcated N^+-H···O hydrogen bonds on both sides of **CLA** with the pyridine ring to form **3-BPBEB-CLA-3-BPBEB** hydrogen bonding unit. No infinite molecular tape structure is observed. In addition, the hydrogen bonding unit formed a molecular sheet structure with various types of intermolecular interactions such as N-H···O, C-H···O, C-H···N and C-H···Cl (Fig. 28). The molecular sheet structure stacks in a segregated manner.



28. Molecular sheet structure of complex **6**.

Complex **7** has a composition of (dication of **4-BPBEB)** and (dianion of **CLA)**. A one dimensional molecular tape structure is observed in the structure of **7** and the both molecules are located in the inversion centers, as shown in Figure 29. The molecular tape is nearly flat. The angles between the molecular planes of the chloranilate and pyridinium ring, and the pyridinium ring and benzene ring are 7.3 (2) and 11.8 (4)°, respectively. The molecular tapes are connected with two intermolecular N–H····O hydrogen bonds, where both H atoms of chloranilic acid have transferred to the pyridine rings. Overlaps between the chloranilate-pyridinium ring-benzne ring-pyridinium ring-chloranilate are observed in the stacks of molecular taps of **7**. A short C–Cl····π interaction [Cl1····(C7 ≡ C8) 3.440 (7), Cl1····C7 3.503 (4), Cl1····8 3.480 (4), Cl1····C7 ≡ C8 79.1 (3) and Cl1····C8 ≡ C7 81.3 (3)°] exist between the stacks of the molecular tapes (Reddy *et. al*., **1996**, prasanna & Row, **2000**). It is 1.7% shorter than the sum of the van der waals radii of Cl and Csp^2 (Pauling, 1996).

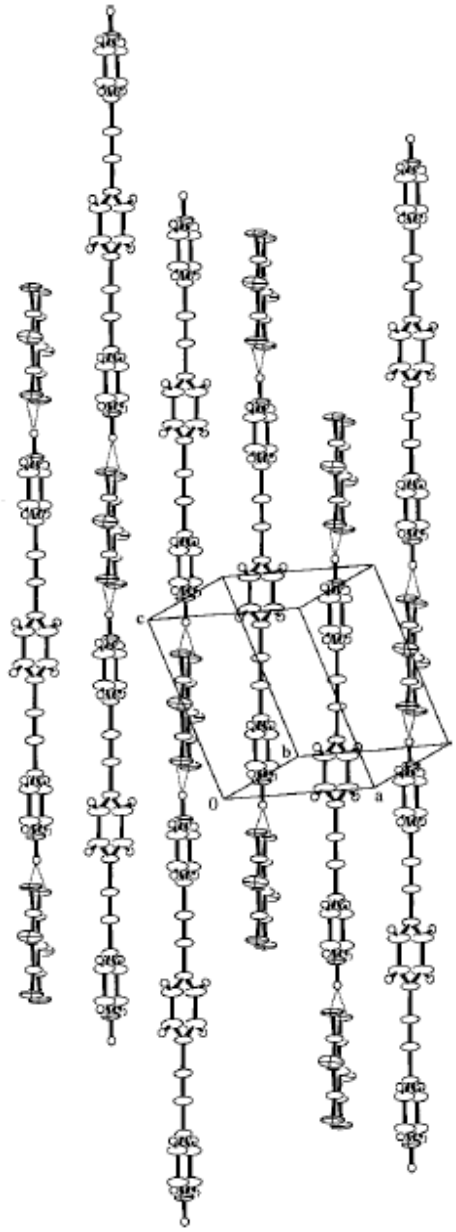
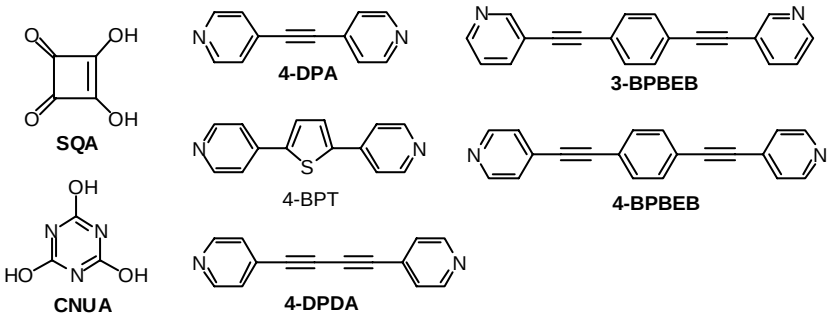


Figure 29. Packing diagram of complex **7**. Dotted lines show the intermolecular N-H···O hydrogen bonds.

To continue the crystal engineering studies, the author has also obtained other four co-crystals **9** (**4-BPT-SQA**), **10** (**3-BPBEB-SQA**), **11** (**4-BPBEB-SQA**) and **12** (**4-DPDA-CNUA**). The co-crystals **9-11** were crystallized from mixture solvents of MeOH-H_2O in an H-tube (Scheme 7).



Scheme 7

Complex 9: 4-BPT and SQA

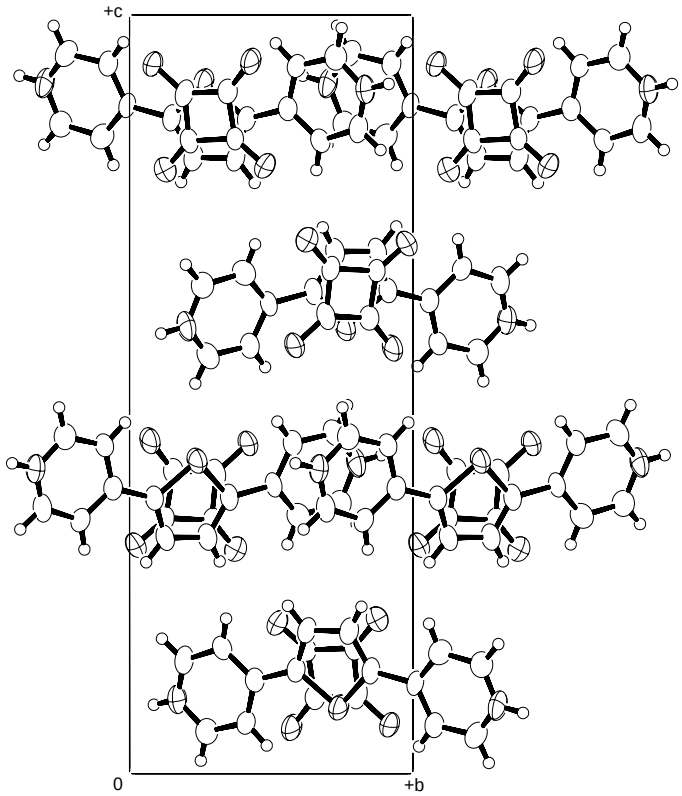
Complex 10: 3-BPBEB and SQA

Complex 11: 4-BPBEB and SQA

Complex 12: 4-DPDA and CNUA

The co-crystal **9** has a composition of (dication of **4-BPT**)·(dianion of **SQA**) (1:1) with the monoclinic space group $P2_1/n$ as shown in Fig. 30a. The molecular tape structure via N-H···O and C-H···O hydrogen bonds is observed and is almost planar (Fig. 30b). The dihedral angles between the squaric acid and pyridine rings are 4.7(6) and 7.3(7)°, and those between the pyridine and the thiophene rings are 6.7(5) and 2.6(6)°. The molecular tapes run in two directions with 45° angle. The distance between the stacking of the molecular tapes is 3.41(1) Å. No ten-membered dimer via hydrogen bonding is formed in this structure.

(a)



(b)

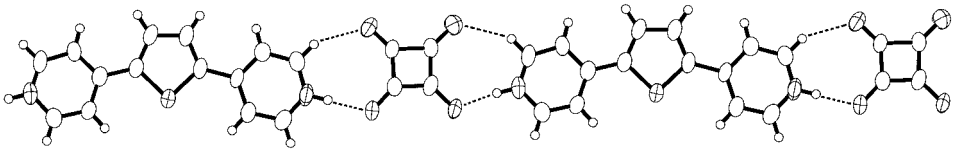


Figure 30. (a) Crystal structure of complex **9** viewed along the a axis. (a) The structure of the planar molecule tape of complex **9** via N-H···O and C-H···O intermolecular interactions.

The co-crystal **10** has a composition of (monocation of **3-BPBEB**)·(monoanion of **SQA**) (1:1) with the triclinic space group $P\bar{1}$. The packing diagram of **10** along the a-axis is shown in Fig. 31a. A zigzag hydrogen bonding unit of **3-BPBEB-SQA-SQA-3-BPBEB** with N-H···O and O-H···O interactions was observed, while no molecular tape structure exists (Fig. 31b). The hydrogen bonding unit is almost planar, where the dihedral angle between the planes for the pyridine and squaric acid is 3.1(1)°. The squarate monoanions form a rare ten-membered dimer linked by intermolecular O-H···O hydrogen bonds.

The co-crystal **11** has a composition of (dication of **4-BPBEB**)·(monoanion of **SQA**)$_2$ (1:2) with the monoclinic space group *C*2/*c*. The packing diagram of **11** along the a-axis is shown in Fig. 32a. The linear molecular tape structure involving a ten-membered dimer of squaric acid via N-H···O and C-H···O hydrogen bonds is observed and is almost planar (Fig. 32b). The dihedral angles between the pyridine and benzene ring, and squaric acid and benzene rings are 2.5(6) and 2.4(6)°, respectively. The tape structures stack in an alternative fashion with the interstack distances of 3.43(7) and 3.72(1) Å.

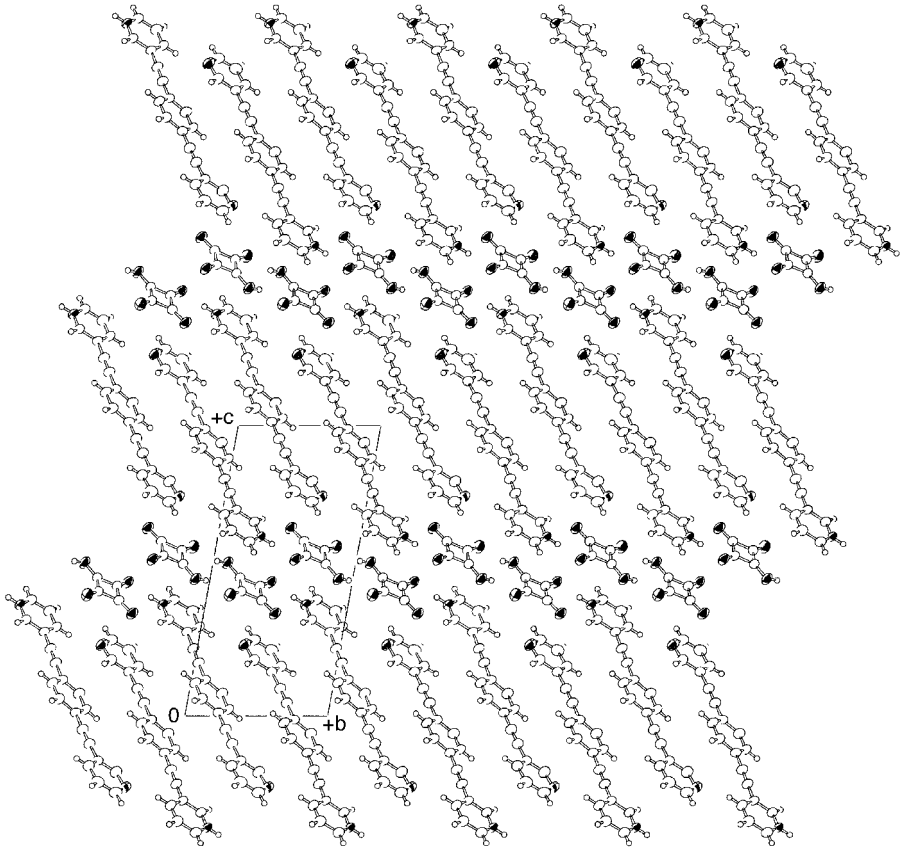


Figure 31a. Crystal structure of complex **10**.

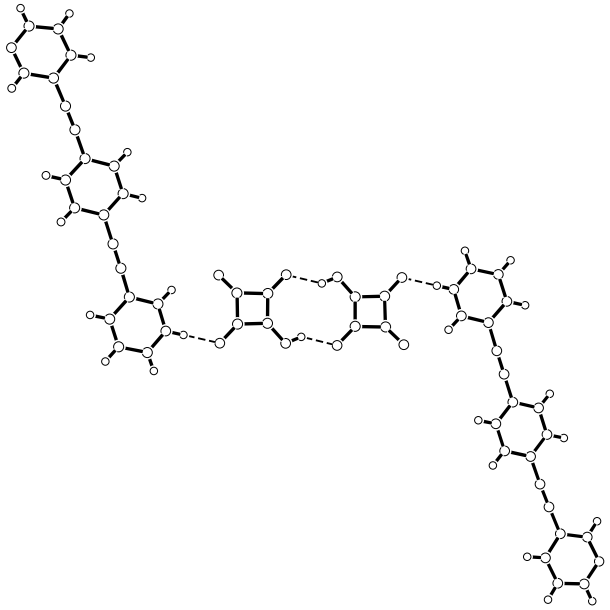


Figure 31(b). The structure of the hydrogen bonding unit including the ten-membered dimer of squaric acid in complex **10**.

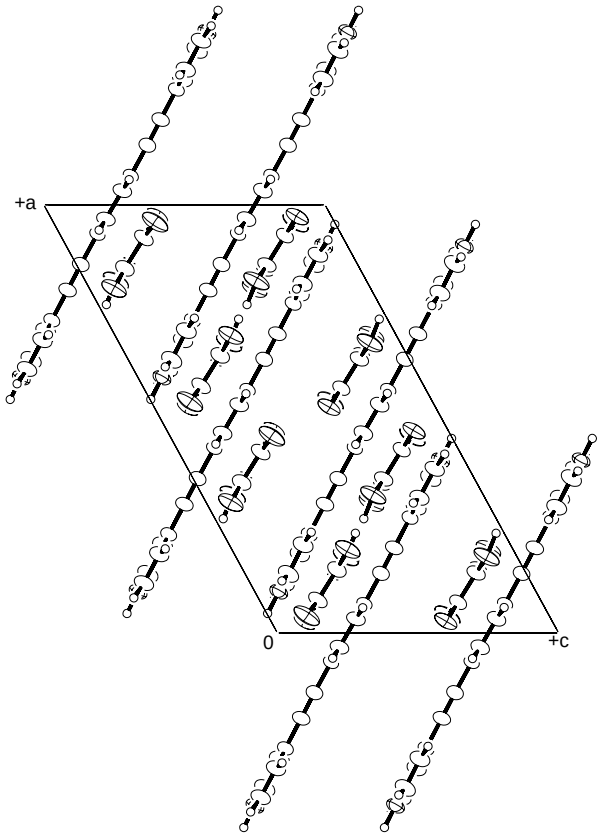


Figure 32a. Crystal structure of complex **11** viewed along a axis.

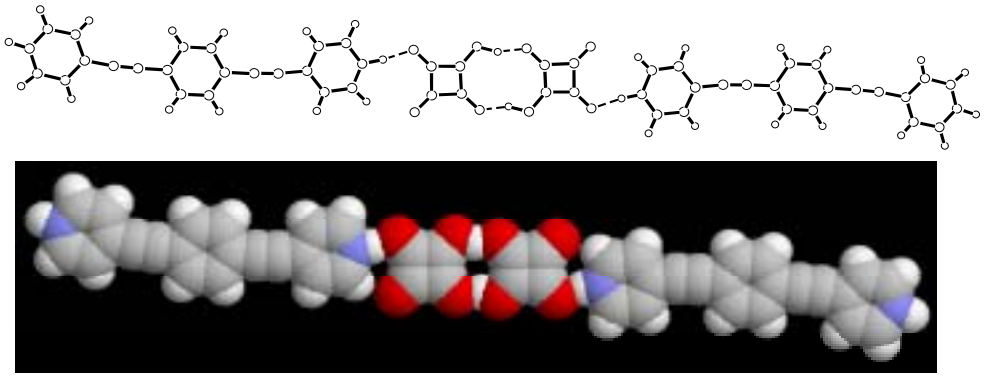


Figure 32b. The molecular tape structure of complex**11**.

The crystal structure of the complex of 1,4-di(4-pyridyl)-1,3-butadiyne (**4-DPDA**) with cyanuric acid (**CNUA**) and solvated water (**complex12**) contains a planar 2D-molecular sheet structure with mult-intermolecular hydrogen bonds such as N-H···N, N-H···O, O-H···N, O-H···O and C-H···O as shown in Figure 33. The didehral angles between the pyridine ring and cyanuric acid are 12.8(1) and 14.3(1)°. Each molecule in the molecular sheet overlaps in a segregated manner, and the intersheet distances are 3.24 and 3.40 Å. Three N-H bonds in cyanuric acid connect with the N atom of the pyridine ring, the O atoms of water molecule and the carbonyl O atom of cyanuric acid, respectively. There are two crystallographically independent half molecules of **DPDA** in the cell.

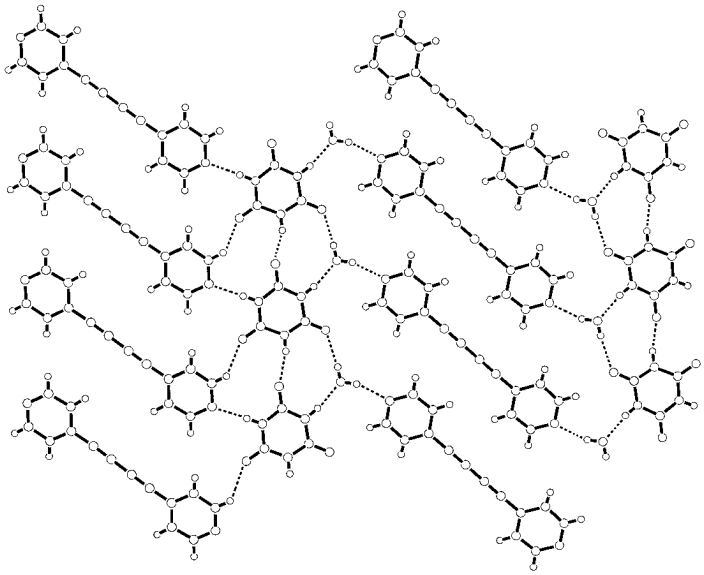


Figure 33. 2D-Molecular sheet structure of complex 12 via multi-intermolecular hydrogen bonds.

4.4 Summary

As describe above, the author has found that unusual crystal structures have been constructed using π-extended dipyridyl compounds. The crystal structures are strongly dependent on the spacer group. Although the details of relationship between the crystal structures and the spacer group are still ambiguous, it should be noted that the twisted molecule affords the completely different structure from the planar molecule. We believe that more elaborated crystal engineering would be possible by changing the spacer group and/or substituents of anilic acid. These works would be also important for exploring novel properties induced by proton and/or electron transfer.

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15. The solvated methanol is disordered over two sites with 0.592(6) and 0.408(6) of occupancies, respectively. The carbon and oxygen atoms of the disordered methanol were localized in the Fourier map and refined isotropically.
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Conclusion

The author explored novel dipyridyl compounds with electron-withdrawing properties and high fluorescence of quantum yields. The violgen analogues have been found to be easily obtained and show high electron affinities and high fluorescence quantum yields.

The compounds **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 angles between the benzothiadiazole and pyridyl rings. The quantum yields of fluorescence depend on the torsion angle between the benzothiadiazole and pyridine rings. The compounds **1a-c** have stacked structures 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 salts are lower than those of the corresponding neutral compounds due to decrease of the torsion angles between the benzothidiazole and pyridine rings. The compounds **4a-c** also show high electron affinities and high quantum yields of fluorescence. The absolute quantum yield of **4c** is 0.87±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 structure analysis revealed that the torsion angles between the benzothiadiazole and pyridine rings are smaller than those of the compounds **1a-c**. So the intermolecular interaction becomes stronger and the solid-state fluorescence decreases. The molecules are stacked to afford unusual two-dimensional columns with

45°. No short heteroatom contacts such as S···N are observed. The crystal structures of **4a,b** 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 those of the corresponding neutral compounds. They include π···π staking of long molecules. A number of intermolecular O-H···O, C-H···O, and C-H···F interactions are also found in the methyalted structures. The analogous compounds containing benzothiadiazole group are of interest from the application purposes such as electroluminescence (EL) devices due to the high quantum yield of fluorescence, electron carriers due to the electron-withdrawing property and supramolecular devices. The polarized heteroatoms containing compounds are also interest in the field of crystal engineering through the intermolecular interactions.

The absorption maxima of bis(benzothiadiazole) compounds (**8-11**) are observed at longer wavelength than those of mono(benzothiadiazole) compounds due to the longer conjugation in these compounds. The fluorescence 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 wave 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 rings. X-ray structure analysis

reveals that the bis(benzothidiazole) derivatives are nonplanar structure due to the repulsion between the pyridine and benzothidiazole ring. There are short S···N contacts observed, leading to the molecular tape structures. It is noteworthy that the dihedral angles of their methyalted compounds are drastically decreased, and the dihedral angle between the pyridine and benzothidiazole rings is nearly zero degree in **11c**. They are expected to afford unique molecular assemblies by heteroatom contacts and/or hydrogen bonding. Studies on construction of host-guest chemistry in supramolecular architecture of these molecules are also of interest due to the longer π-conjugation, high electron affinities and high quantum yields of fluorescence.

Finally, the author used dipyridyl compounds containing π-conjugated groups as proton acceptor, and investigated their complexation with chloranilic (**CLA**), squaric acid (**SQA**) and cyanuric acid (**CNUA**) by hydrogen-bonding interactions which are very important in the field of crystal engineering and supramolecular chemistry. The introduction of a π-conjugated spacer to dipyridyl compounds has been considered to increase intermolecular π-π interactions and decrease Coulomb 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 structures of the complexes of the twisted molecules are completely different from the planar molecules. The author believes that more elaborated crystal engineering would be possible by changing the spacer group and/or substituents of anilic acid.

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LIST OF PUBLICATIONS

Chapter 2.

1. Md. Akhtaruzzaman, Masaaki Tomura, Md. Badruz Zaman, Jun-ichi Nishida and Yoshiro Yamashita "Synthesis and Characterization of New Linear π–Conjugated Molecules Containing Bis(ethynylpyridine) Units with a Benzothiadiazole Spacer" *J. Org. Chem*., **2002**, 67, 7813-7818

2. Md. Akhtaruzzaman, Masaaki Tomura, and Yoshiro Yamashita, "4,7-Bis(4-pyridylethynyl)-2,1,3-benzothiadiazole and its dipyridinium diperchlorate" *Acta Cryst*. **2001**, C57, 751.

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