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Synthesis and Characterization of Novel Dipyridylbenzothiadiazole and Bisbenzothiadiazole Derivatives

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Novel dipyridyl compounds containing a mono- and bisbenzothiadiazole unit were synthesized using the Stille coupling reaction. Their pyridinium salts, viologen analogues, were also prepared by the *N*-alkylation. The X-ray crystallographic analysis of the compounds containing a benzothiadiazole ring revealed nonplanar molecular structures and unique crystal structures depending on the nitrogen positions. The dipyridyl compounds are efficient fluorophores with high electron affinity. The derivative afforded complexes with chloranilic acid and cyanuric acid composed of hydrogen bonding networks. The methyl viologen analogues showed two-stage one-electron reduction waves.

Recently, much attention has been focused on π-conjugated molecules showing redox-active and/or luminescent properties due to their electronic, optical, and optoelectronic function.[1] Among them, 2,1,3-benzothiadiazole derivatives are outstanding compounds due to the following characteristics: (i) they have electron-withdrawing properties and have been used as units of electron acceptors for conducting materials;[2] (ii) thiadiazole-containing compounds are expected to afford well-ordered crystal structures due to their highly polarized properties leading to intermolecular interactions such as heteroatom contacts or $\pi-\pi$ interactions;[3] and (iii) benzothiadiazole derivatives are known as efficient fluorophores.[4] Highly fluorescent π-conjugated molecules are of interest from application purposes such as EL (electroluminescence) devices[5] and single molecular detection.[6] Polymers containing benzothiadiazole units have been used as luminescent compounds in EL devices.[7] On the other hand, the dipyridyl compounds have been widely used for construction of self-assembling macrocyclic architectures, using the nitrogen atoms of dipyridyl groups for metal coordination and hydrogen bonding.[8] The structure and properties of the dipyridyl compounds can be modified by changing the nitrogen positions.[9] Moreover, they afford viologen analogues which can be used as mediators of electron transfer for molecular devices.[10] With this in mind, we have combined these heterocycles to give novel compounds showing interesting properties derived from both units, and have recently prepared 4,7-bis(pyridylethynyl)-2,1,3-benzothiadiazoles (**1a**−**c**)[11] and the bisbenzothiadiazole derivatives **2b**,**c**.[12] Although they showed efficient fluorescence in solution, the fluorescence in a thin film was weak due to the strong intermolecular interactions. They have not afforded hydrogen-bonding complexes whose structures could be definitely determined. Viologen analogues derived from **1** and **2** showed one-stage two-electron reduction waves for the pyridinium groups, indicating that the interactions between the pyridinium groups are weak or the cation radical states are thermodynamically unstable. To improve these properties, we have now prepared dipyridyl benzothiadiazoles **3** and the bisbenzothiadiazole derivatives **4** without acetylene units and have found that some of them exhibit strong fluorescence in the solid state and cation radical states are more stabilized. We report here their synthesis and unique properties as well as hydrogen-bonding complexes.

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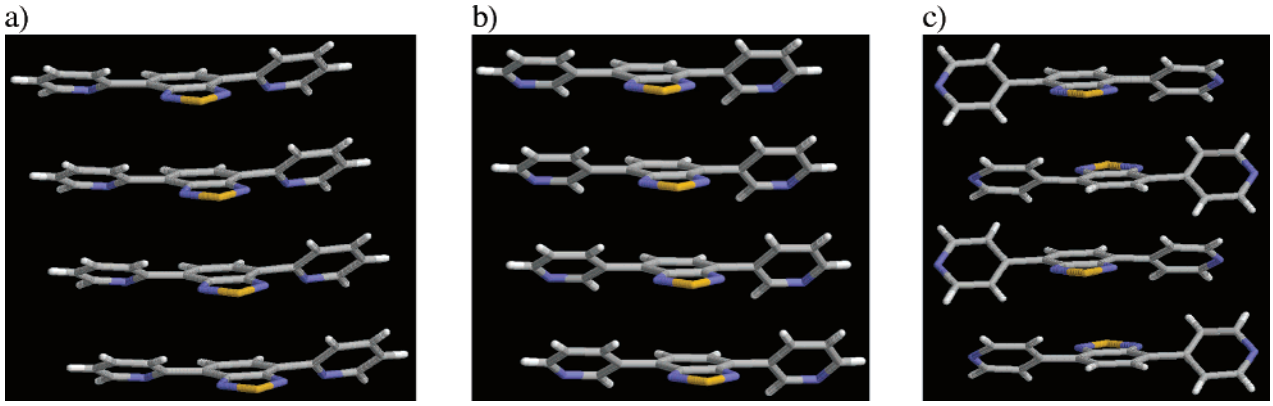
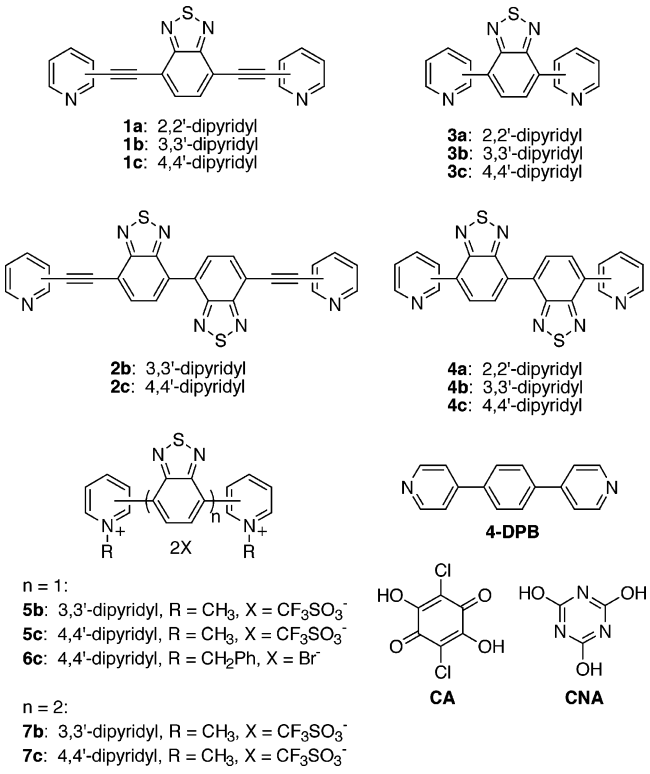


FIGURE 1. Stacking structures for (a) **3a**, (b) **3b**, and (c) **3c**.

Results and Discussion

Preparation. Mono(benzothiadiazole) derivatives **3a**−**c** were synthesized by the Stille coupling reaction of 4,7-dibromo-2,1,3-benzothidiazole[13] with (tributylstanyl)pyridines[14] in dry toluene in 58−80% yields. The bisbenzothiadiazole derivatives **4a**−**c** were also prepared by a similar method from the corresponding dibromo compounds[15] in 59−61% yields. The viologen analogues **5**−**7** were prepared by the reaction with methyl trifluoromethanesulfonate (MeOTf) and benzyl bromide in CH_2Cl_2 in high yields. The methylation reaction of the 2,2′-dipyridyl derivatives has not been successful probably due to their weak basicity as well as the steric interaction. Complexes of **3** were also prepared as single crystals by placing equal molar amounts of **3c** and chloranilic acid (**CA**) or cyanuric acid (**CNA**) in an H-shaped tube filled with acetonitrile as a solvent.



Crystal Structures. The single crystals of **3a**−**c** suitable for X-ray analysis were obtained from recrystallization from a mixed solvent of acetonitrile−chloroform. In contrast to the planar molecular structures of **1a**−**c**, the molecules **3a**−**c** are twisted due to the steric hindrance between the hydrogen atoms. The average dihedral angles between the pyridine and benzothiadiazole rings in **3a**−**c** are 32.4(1)°, 40.4(1)°, and 36.8(5)°, respectively. The molecule **3a** has the smallest dihedral value due to the nitrogen atoms at the ortho position reducing the steric interaction. Although the crystal structures of **1a**−**c** with acetylene units are similar to each other,[11] the nonplanar molecules **3a**−**c** afford different crystal structures depending on the nitrogen positions. The stacking structures are shown in Figure 1. Although the stacking structures are formed, the interactions seem to be weak as judged from the molecular plane distances. The distances between the planes of the benzothiadiazole rings in **3a**−**c** are 3.50, 3.55, and 3.64 Å, respectively. It should be noted that the more planar molecule **3a** has the shortest distance. No short S···N contacts are observed in the crystal structures of **3a**,**b** while the crystal of **3c** bears short S···N contacts [3.003(2) Å] between the sulfur atom of the thiadiazole ring and the nitrogen atom of the pyridine ring as shown in Figure 2.

The X-ray crystallographic analysis of the dication salts **5b** and **6c** was also carried out. The unique stacking structures are shown in Figure 3. The average dihedral angles between the pyridine and benzothiadiazole planes are 33.0(2)° for **5b** and 12.0(6)° for **6c**, which are smaller than those of the corresponding neutral compounds **3b** and **3c**. This result indicates that the molecules become more planar in the dication state. The molecule of **5b** formed a dimeric structure as shown in Figure 3a. The distance between the two molecular planes in the dimer is 3.15 Å, suggesting a strong $\pi-\pi$ interaction. The interdimer distance is 3.39 Å. Within the dimer, the molecules overlap in a head-to-tail fashion, where two thiadiazole rings are directed to the opposite side. The molecules of **6c** are stacked in an unusual manner as shown in Figure 3b, 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-

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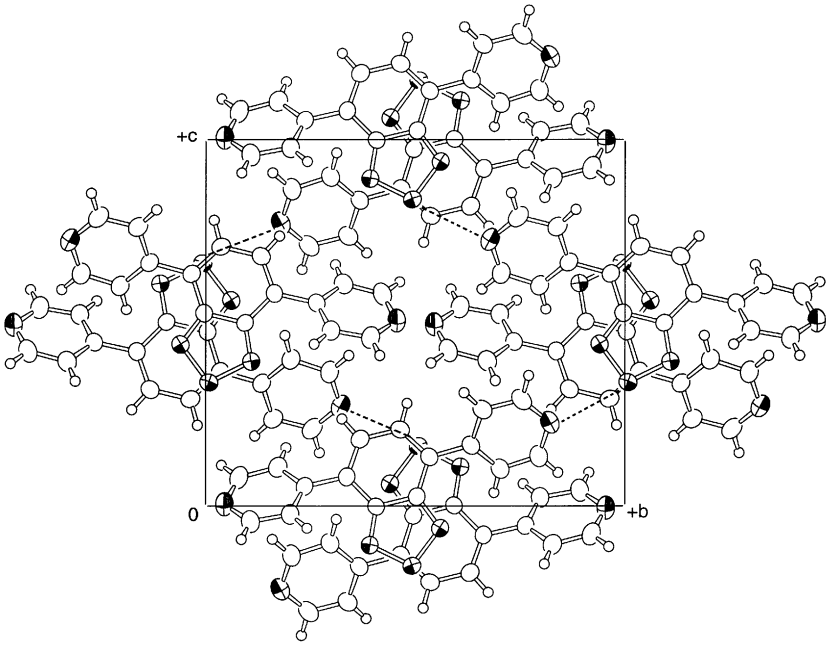

FIGURE 2. Crystal structure of **3c** viewed along the *a* axis. Dotted lines show the short S···N contacts [3.003(2) Å].

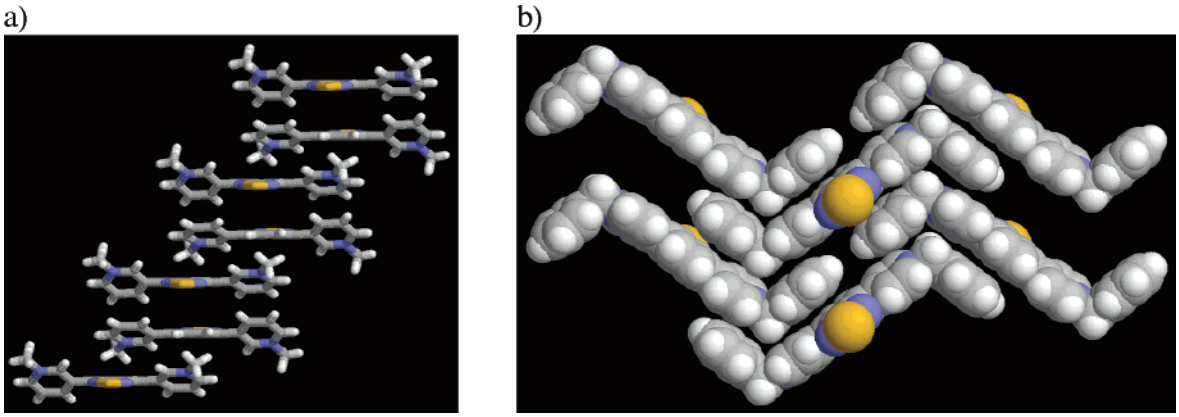

FIGURE 3. Stacking structures for (a) **5b** and (b) **6c**.

dimensional stairs-like stacking. This finding suggests that the benzyl group can be used for construction of unique stacking structures.

Physical Properties. The physical properties of all new compounds **3a**−**c**, **4a**−**c**, **5b**,**c**, **6c**, and **7b**,**c** along with mono(benzothiadiazole) derivatives **1a**−**c** and 1,4-di(4-pyridyl)benzene (**4-DPB**) are summarized in Table 1. The absorption maxima of **3a**−**c** are observed in a longer wavelength region compared to that of **4-DPB** (Table 1) due to the small HOMO−LUMO gap of the benzothiadiazole unit. These absorption maxima are blue-shifted compared to those of **1a**−**c**. This is explained by the reduced conjugation in **3** caused by the nonplanar structures as well as loss of acetylene units. In the series of **3**, **3a** shows the longest absorption maximum due to the more planar structure as revealed by X-ray analysis. The molecules **3a**−**c** exhibit efficient fluorescence in solution similar to **1a**−**c**. There is no significant effect of the nitrogen positions on the fluorescence quantum yields. The Stokes shifts of **3** are larger than those of **1**, suggesting that a large conformational change occurs upon photoexcitation in **3**. In thin films and even in single crystals, the fluorescence emission was observed, which

TABLE 1. Absorption Maxima,[a] Fluorescence Maxima,[b] Quantum Yields,[b] and Reduction Potentials[c] for Dipyridyl Compounds

compds	λ_{max} (log ϵ)	$\lambda_{ex,max}$ (nm)	Φ_{em} (nm)	E_{red} (V)
1a[d]	393 (4.48)	473	0.87	−1.18
1b[d]	396 (4.45)	479	0.80	−1.08
1c[d]	388 (4.43)	464	0.87	−1.00
3a	377 (4.51)	469	0.80	−1.25
3b	366 (4.06)	467	0.90	−1.30
3c	356 (5.03)	448	0.68	−1.19
4a[i]	401[e]	484	0.26	−1.28, −1.48
4b[i]	397[e]	481	0.21	*f*
4c[i]	389[e]	469	0.24	*f*
5b	350 (4.08)	441	0.24	−0.84, −1.12[g]
5c	362 (4.71)	427	0.11	−0.51, −0.63
6c	366[e]	432	0.08	−0.35[h]
7b	387[e]	493	0.10	−0.53, −0.86
7c	397[e]	480	0.15	−0.40, −0.86
4-DPB[j]	278 (4.51)			−1.98, −2.14

[a] In MeCN. [b] In MeCN. $\lambda_{ex} = 299$ nm. The fluorescent quantum yields were obtained by using 2-phenylbenzoxazole ($\Phi_{em} = 0.75$) as a standard.[18] [c] 0.1 mol dm^{-3} of *n*-Bu_4NPF_6 in MeCN, Pt electrode, scan rate 100 mV s^{-1}, V vs SCE. [d] Reference 11. [e] The absorption coefficients could not be measured due to its low solubility in solvents. [f] Not measured due to the low solubility. [g] Irreversible. [h] In DMSO, broad peak. [i] The absorption and fluorescence spectra of **4a**−**c** were measured in $CHCl_3$, and the reduction potential of **4a** was measured in CH_2Cl_2. [j] **4-DPB**: 1,4-bis(4-pyridyl)benzene.[17]

is interesting from the viewpoint of application to EL devices. In the single crystal of **3c**, anisotropy in fluorescence was observed.

The absorption maxima of derivatives **4** are further red-shifted compared to **3** due to the more extended conjugation. The compounds **4** also show strong fluorescence emission with large stokes shifts although the quantum yields decrease compared to those of the mono(benzothiadiazole) derivatives. The absorption maxima of dications **5**, **6**, and **7** are similar to those of the corresponding neutral compounds, indicating that the HOMO−LUMO energy gaps are not so much affected by the alkylation. The 4,4′-dipyridinium compounds **5c** and **7c** show the absorption maxima at a little longer wavelength than the corresponding 3,3′-isomers **5b** and **7b**. This is ascribed to the resonance effect. The fluorescence quantum yields of the dications decrease probably due to the stronger intermolecular interactions as revealed by the X-ray analysis.

The reduction potentials listed in Table 1 indicate that the thiadiazole-containing compounds **3** and **4** have stronger electron affinities compared to those of the reference compound **4-DPB** due to the electron-withdrawing thiadiazole ring. Compound **4a** shows stepwise one-electron reduction waves in contrast to **3** since **4a** contains two units of benzothiadiazole. The reduction potentials of **4b**,**c** could not be measured due to the low solubility. The dications **5**, **6**, and **7** showed higher reduction potentials than the corresponding neutral compounds. Interestingly, the methyl viologen analogue **5c** showed stepwise one-electron reduction waves in contrast to the dication derived from **1c**, which undergoes one-stage two-electron reduction.[11] This result indicates that the pyridyl groups in **5c** interact with each other and the cation radical is stabilized. This fact suggests that **5c** is a promising mediator for electron-transfer reactions.

Complexation with Choranilic Acid (CA) and Cyanuric Acid (CNA). The dipyridyl compound **3c** afforded a hydrogen-bonding complex with **CA** whose composition is $(\mathbf{3c})^{2+}\cdot(\mathbf{CA})^{2-}\cdot(H_2O)_3$. The one-dimensional (1D) molecular tape-like structure is formed through a hydrogen-bonding network as shown in Figure 4. In the complex, the two protons of **CA** are transferred to the pyridine ring and the tape-like structure is stacked with the interaction between the pyridinium ring and the chloranilate ring. This suggests the presence of charge-transfer interaction between them. The tape-like structure is a little twisted. Thus, the angles between the pyridine ring and the benzothiadiazole ring are 15.3(1)° and 31.0(1)° and those between the pyridine ring and the plane of the chloranilate in the tapes are 9.3(1)° and 25.3(1)°. The lengths of the $N^+-H\cdots O^-$ hydrogen bonds between the pyridinium ring and the chloranilate are 2.742(5), 2.761(5), 2.793(5), and 2.858(5) Å. The tape structure stacks in an alternate fashion to give a mixed stacking, where the interstack distance of the tape is 3.3 Å. On the other hand, water molecules are included in the crystal, and the chloranilate dianion and three water molecules form a two-dimensional hydrogen-bonding network (molecular sheet) with a large number of O−H···O and O−H···Cl contacts. The average 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 4b).

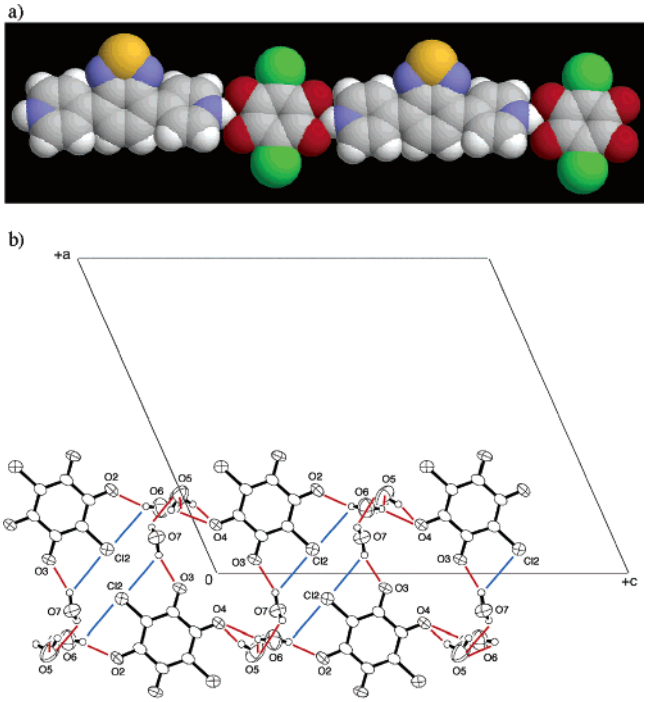

FIGURE 4. (a) Planar 1D molecular tape-like structure of the complex $(\mathbf{3c})^{2+}\cdot(\mathbf{CA})^{2-}\cdot(H_2O)_3$; (b) hydrogen bonding networks between chloranilic acid and water in the complex $(\mathbf{3c})^{2+}\cdot(\mathbf{CA})^{2-}\cdot(H_2O)_3$. Red and blue lines show O−H···O and O−H···Cl hydrogen bondings, respectively.

The dipyridyl compounds **3c** also afforded a complex $(\mathbf{3c})_2\cdot(\mathbf{CNA})$ with **CNA** containing three hydroxyl groups. The hydrogen-bonding assembly of **CNA** with **3c** possesses an interesting structural unit like meshed combs with $\pi-\pi$ interactions as shown in Figure 5. The molecules **3c** are stacked with 3.49 Å of the distances between the benzothiadiazole and pyridine rings. The **CNA** molecule combines the two molecules of **3c** by N−H···N hydrogen bonds to give the **3c**−**CNA**−**3c** molecular unit. The **CNA** itself forms a 1D molecular tape structure with N−H···O hydrogen bonding. No protons of **CNA** are transferred to the pyridine ring in contrast to the **CA** complex. This is attributed to the weaker acidity of **CNA** than that of **CA**. These results indicate the usefulness of dipyridyl compound **3c** for construction of supramolecular architectures using hydrogen bonding.

In the bis(benzothiadiazole) derivatives **4**, formation of a tape-like network by S···N contacts between the thiadiazole rings is expected.[12] Studies on complex formation of other dipyridyl compounds **3** and **4** are currently underway.

Conclusion

In conclusion, we have explored novel dipyridyl compounds containing electron-withdrawing benzothiadaizole groups as spacer units, which show efficient fluorescence with high electron affinity. The twisted structures are favorable for fluorescence in the solid state. They can also be used as hydrogen-bonding acceptors for supramolecular architectures. The 4,4′-dipyridyl derivative can afford a viologen analogue that shows stepwise redox behavior.

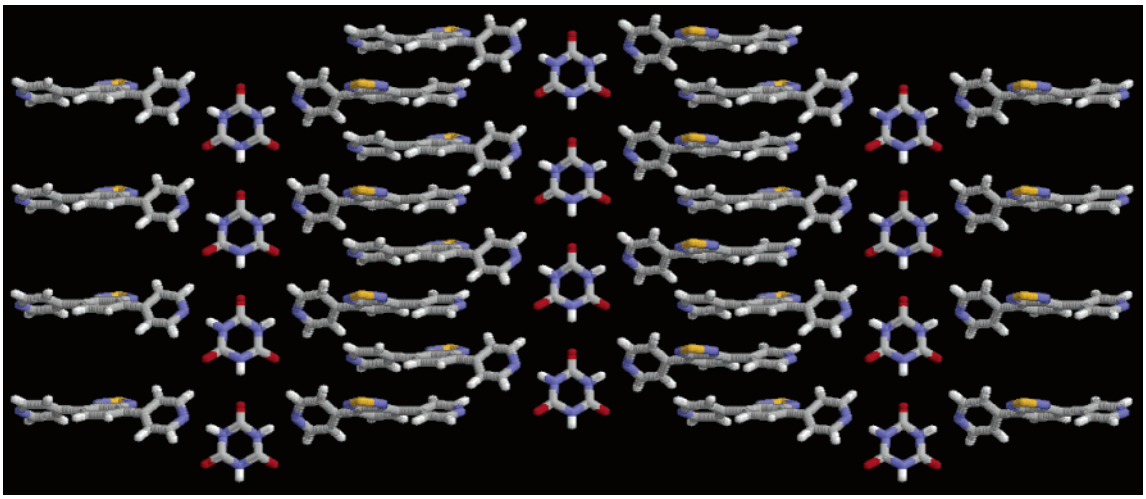

FIGURE 5. Hydrogen bonding meshed combs-like structure of the complex (**3c**)$_2$·(**CNA**).

Experimental Section

All reactions were performed under argon. Diethylamine was purified under argon by passing through aluminum oxide (neutral, activity I). All other reagents and solvents commercially available were used without further purification unless otherwise noted. 2-, 3-, and 4-(tributylstanylyl)pyridine[14] and 4,7-dibromo-2,1,3-benzothiadiazole[13] were prepared according to the literature methods.

Preparation of 4,7-Di(2-pyridyl)-2,1,3-benzothiadiazole (3a). To a solution of 4,7-dibromo-2,1,3-benzothiadiazole (300 mg, 1.04 mmol) in dry toluene (10 mL) were added 2-stannylpyridine (950 mg, 2.58 mmol) and tetrakis(triphenylphosphine)palladium [Pd(PPh$_3$)$_4$, 235 mg, 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 extract was 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 to afford **3a**. 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} (log ϵ) 289 (4.28), 314 (4.02), 323 (4.04), 377 nm (4.12); ^{1}H 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 123.1, 125.2, 129.7, 132.3, 136.6, 149.8, 153.8, 154.1; 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 (3b). Following the same procedure as that for **3a**, compound **3b** 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} (log ϵ) 237 (4.23), 268 (4.32), 307 (4.07), 316 (4.12), 366 nm (4.06); ^{1}H 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 123.4, 128.2, 130.8, 132.9, 136.6, 149.6, 149.8, 153.8; 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 (3c). Following the same procedure as that for **3a**, compound **3c** 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} (log ϵ) 272 (5.23), 318 (5.08), 356 nm (5.03); ^{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 ($CDCl_3$, 75 MHz) δ 123.6, 123.6, 128.5, 132.0, 144.2, 150.3, 153.5, 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.

Preparation of 7,7′-Di(2-pyridyl)-4,4′-bis(2,1,3-benzothiadiazole) (4a). To a solution of 7,7′-dibromo-4,4′-bis(2,1,3-benzothiadiazole)[13] (600 mg, 1.40 mmol) in dry toluene (70 mL) were added 2-stannylpyridine (1500 mg, 4.0 mmol) and tetrakis(triphenylphosphine)palladium [Pd(PPh$_3$)$_4$, 440 mg, 0.38 mmol] under an argon atmosphere. The resulting mixture was heated under reflux overnight. After the solution was 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 °C; IR (KBr) ν_{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 $C_{22}H_{12}N_6S_2$: 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.

Preparation of 7,7′-Di(3-pyridyl)-4,4′-bis(2,1,3-benzothiadiazole) (4b). Following the same procedure as that for **4a**, compound **4b** was obtained as a yellow solid (61%): mp 343−345 °C; IR (KBr) ν_{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.

Preparation of 7,7′-Di(4-pyridyl)-4,4′-bis(2,1,3-benzothiadiazole) (4c). Following the same procedure as that for **4a**, compound **4c** was obtained as a yellow solid (61%): mp 444−446 °C; IR (KBr) ν_{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 4,7-Di(3-pyridyl)-2,1,3-benzothiadiazole (3b). Methyl trifluoromethanesulfonate (360 mg, 2.2 mmol) was added to a solution of **3b** (100 mg, 0.35 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for 3 h at room temperature. The resulting solid was filtered and washed with CH_2Cl_2 to give **5b** as a yellow solid (80% yield): mp 145−147 °C; UV (MeCN) λ_{max} (log ϵ) 246 (4.16), 277 (3.98), 319 (4.13), 350 nm (4.08); ^{1}H 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 (3c). Following the same procedure as above, the dimethylated compound **5c** was obtained as a yellow solid (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} (log ϵ) 303 (3.46), 362 nm (4.71); ^{1}H 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 49.0, 128.5, 130.8, 132.2, 146.5, 152.8, 153.9. 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 (3c). Benzyl bromide (360 mg, 2.11 mmol) was added to a solution of **3c** (50 mg, 0.17 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for 2 d at room temperature. The resulting solid was filtered and washed with CH_2Cl_2−ether to give **6c** as a yellow solid (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 cm^{-1}; ^{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, 75 MHz) δ 62.9, 127.7, 128.8, 129.3, 129.4, 131.3, 134.3, 144.8, 151.2, 147.6, 152.3.

Methylation of 7,7′-Di(3-pyridyl)-4,4′-bis(2,1,3-benzothiadiazole) (4b). Tetrafluromethane sulfonic acid (70 mg, 0.43 mmol) was added to a solution of **4b** (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 **7b** as a yellow solid (90% yield): mp 145−147 °C; IR (KBr) ν_{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(4-pyridyl)-4,4′-bis(2,1,3-benzothiadiazole) (4c). Following the same procedure as above, dimethylated **7c** was obtained as a yellow solid (92%): mp 145−147 °C; IR (KBr) ν_{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).

General Procedure for the Complexation of 3c. An equivalent molar amount (0.05 mmol) of chloranilic acid (**CA**) or cyanuric acid (**CNA**) and **3c** was placed at the bottom of the H-shaped tube and the tube was filled with distilled acetonitrile (10−25 mL) as a solvent. After 3−7 days, single crystals suitable for X-ray analysis were obtained at room temperature.

X-ray Analysis. Reflection data for **3b**, **5b**, and (**3c**)$^{2+}$·(**CA**)$^{2-}$·$(H_2O)_3$ were collected on a Rigaku Mercury CCD area detector, using Mo Kα radiation (λ = 0.71070 Å) at 296 K. Reflection data for (**3c**)$_2$·(**CNA**) were collected on a Rigaku RAXIS-RAPID imaging plate area detector, using Mo Kα radiation (λ = 0.71070 Å) at 296 K. Reflection data for **3a**,**c** and **6c** were collected on an Enraf-Nonius CAD4 diffractometer, using Cu Kα radiation (λ = 1.54178 Å) at 296 K. No absorption correction was applied for **3b**, **5b**, and (**3c**)$^{2+}$·(**CA**)$^{2-}$·$(H_2O)_3$. Absorption correction for **3a**,**c**, **6c**, and (**3c**)$_2$·(**CNA**) was applied using the ψ scan method and empirical procedure based on reflection intensities, respectively. All structures were solved by direct methods and refined by full-matrix least squares on F^2 with SHELX-97.[16] All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed in geometrically calculated positions and refined by using a riding model except for (**3c**)$^{2+}$·(**CA**)$^{2-}$·$(H_2O)_3$. All hydrogen atoms of (**3c**)$^{2+}$·(**CA**)$^{2-}$·$(H_2O)_3$ were located in the Fourier map and were refined isotropically.

Crystal data for 3a: $C_{16}H_{10}N_4S$, MW = 290.34, monoclinic, space group $P2_1/n$, a = 3.7763(2) Å, b = 27.0492(11) Å, c = 12.9087(4) Å, β = 94.877(3)°, V = 1313.80(10) Å^3, Z = 4, R_1 = 0.0441 and wR_2 = 0.1109 for 1834 reflections with $I > 2\sigma(I)$.

Crystal data for 3b: $C_{16}H_{10}N_4S$, MW = 290.34, monoclinic, space group $P2_1/c$, a = 3.8113(13) Å, b = 24.552(6) Å, c = 14.056(5) Å, β = 94.123(11)°, V = 1311.9(7) Å^3, Z = 4, R_1 = 0.1071 and wR_2 = 0.2485 for 2146 reflections with $I > 2\sigma(I)$.

Crystal data for 3c: $C_{16}H_{10}N_4S$, MW = 290.34, monoclinic, space group $P2_1/c$, a = 7.3213(3) Å, b = 14.3519(5) Å, c = 12.4801(6) Å, β = 90.206(3)°, V = 1311.33(9) Å^3, Z = 4, R_1 = 0.0338 and wR_2 = 0.0921 for 2100 reflections with $I > 2\sigma(I)$.

Crystal data for 5b: $(C_{18}H_{16}N_4S)$·$(CF_3SO_3)_2$·(H_2O), MW = 634.55, triclinic, space group $P1$, a = 8.7475(13) Å, b = 11.3927(15) Å, c = 14.991(2) Å, α = 67.544(17)°, β = 77.59(2)°, γ = 67.938(18)°, V = 1275.2(3) Å^3, Z = 2, R_1 = 0.1030 and wR_2 = 0.2673 for 3765 reflections with $I > 2\sigma(I)$.

Crystal data for 6c: $(C_{30}H_{24}N_4S)$·Br_2·$(H_2O)_3$, MW = 680.41, orthorhombic, space group $Pbcn$, a = 22.3292(18) Å, b = 15.1543(10) Å, c = 8.8149(8) Å, V = 2982.8(4) Å^3, Z = 4, R_1 = 0.0872 and wR_2 = 0.2603 for 2003 reflections with $I > 2\sigma(I)$.

Crystal data for (3c)$^{2+}$·(CA)$^{2-}$·(H$_2$O)$_3$: $(C_{16}H_{12}N_4S)$·$(C_6Cl_2O_4)$·$(H_2O)_3$, MW = 553.36, monoclinic, space group $P2_1/c$, a = 17.386(10) Å, b = 6.908(3) Å, c = 20.683(12) Å, β = 113.937(7)°, V = 2270(2) Å^3, Z = 4, R_1 = 0.0914 and wR_2 = 0.1597 for 3864 reflections with $I > 2\sigma(I)$.

Crystal data for (3c)$_2$·(CNA): $(C_{16}H_{10}N_4S)_2$·$(C_3H_3N_3O_3)$, MW = 709.76, monoclinic, space group $C2/c$, a = 20.374(12) Å, b = 7.055(3) Å, c = 21.396(10) Å, α = 90° β = 96.54(4)°, V = 3056(3) Å^3, Z = 4, R_1 = 0.0371 and wR_2 = 0.1033 for 3166 reflections with $I > 2\sigma(I)$.

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Supporting Information Available: The absorption and fluorescence spectra of **3a**−**c**, and X-ray crystallographic data for **3a**−**c**, **5b**, **6c**, (**3c**)$^{2+}$·(**CA**)$^{2-}$·$(H_2O)_3$, and (**3c**)$_2$·(**CNA**) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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