Self-Assembly of 3-[4′-(Diethylboryl)phenyl]pyridine and 3-[3′-(Diethylboryl)phenyl]pyridine: Synthesis, Structural Features, and Stability in Solution

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The self-assembly of 3-[4′-(diethylboryl)phenyl]pyridine (**3**) and 3-[3′-(diethylboryl)phenyl]pyridine (**4**) was investigated by ^{1}H and ^{11}B NMR spectroscopies and vapor pressure osmometry. It can be seen that in solution **3** affords an equilibrium mixture of oligomers including a cyclic trimer as a major component via intermolecular boron−nitrogen coordination bonds, which is supported by temperature-, concentration-, and solvent-dependent behaviors of **3**. In contrast, **4** seems to afford a mixture of oligomers including a cyclic dimer in solution. Judging from the low coalescence temperature in variable-temperature NMR in toluene-d_8 and easy scrambling with the corresponding 3-[(diethylboryl)pheny]-5-methoxypyridines at ambient temperature, it is concluded that the intermolecular boron−nitrogen coordination bonds made by **3** or **4** are weaker than those formed by 3-(diethylboryl)pyridine (**1**) or 2-(diethylboryl)-5-methylpyridine (**2**). Poor thermal stability was supported by electrospray mass spectrometry and structural analyses utilizing a semi-empirical molecular orbital calculation AM1. It is noted that in the assembly of **4** there is a tendency to maintain high tetrahedral character at the boron atom in the complex at the expense of strain energy. Thus, these features of **3** and **4** in solution are in marked contrast to those of **1** and **2**.

Introduction

Organoboranes have been widely utilized as versatile reagents in synthetic organic chemistry.[2] 3-(Diethylboryl)pyridine (**1**) synthesized by Terashima[3] in 1983 is commercially available from Aldrich Chemical Co. as a tractable synthetic reagent for the preparation of a variety of arylpyridines.[4] The high stability of **1**, despite little steric hindrance on the boron atom, has been definitively shown by Sugihara in 1994 to be due to the formation of the intermolecular boron−nitrogen (B−N) coordination bonds to form the rigid cyclic tetramer with a cavity,[5] which is contrary to Terashima's interpretation.[3] In contrast, 2-(diethylboryl)-5-methylpyridine (**2**) forms the cyclic dimer, the stability of which is somewhat higher than that of **1**.[6] The stability seems to be correlated not only with the intermolecular B−N bond length (tetramer of **1**, 1.639 Å; dimer of **2**, 1.611 Å), but also with the tetrahedral character (THC: tetramer of **1**, 79.7, 84.2%; dimer of **2**, 96.9%) of the boron atom proposed by Ōki.[7]

It is of great significance to investigate how the self-assembling feature is changed by such a structural modification of the borylpyridines, since this point is crucial to the planned synthesis of more sophisticated systems such as three-dimensional supramolecules.[8] In designing such borylpyridines, we set out to prepare two compounds: 3-[4′-(diethylboryl)phenyl]pyridine (**3**) and 3-[3′-(diethylboryl)phenyl]pyridine (**4**), where a spacer, *p*- and *m*-phenylene unit, respectively, is incorporated into the skeleton of **1** (Chart 1). We report here the synthetic method, structural features, and stability of **3** and **4** in solution. Simple rationalizations for the stability of **3** and **4**, relative to that of **1** and **2**, are provided and supported by semi-empirical molecular orbital calculation AM1.

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Chart 1

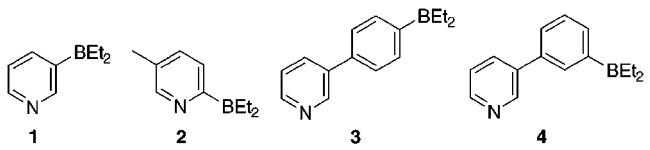
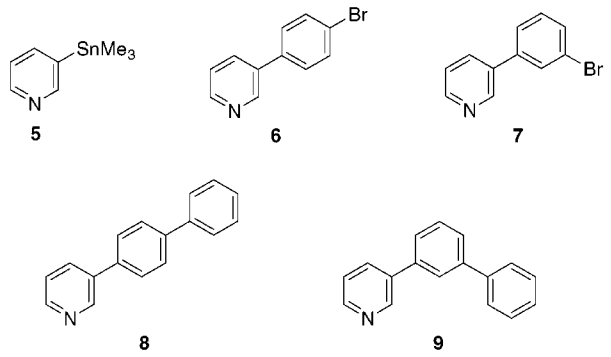


Chart 2



Results and Discussion

Synthesis of 3 and 4. Compounds **3** and **4** were prepared according to the following route via the Stille coupling.[9] 3-(Trimethylstannyl)pyridine (**5**)[10] was treated with 1-bromo-4-iodobenzene in the presence of triphenylarsine, copper(I) iodide, and tris(dibenzylideneacetone)-dipalladium(0) in *N*,*N*-dimethylformamide at 80 °C for 5 h to give 3-(4′-bromophenyl)pyridine (**6**)[11] in 69.7% yield (Chart 2). Subsequently, the reaction of **6** with *n*-butyllithium and tetramethylethylenediamine (TMEDA) followed by diethylmethoxyborane[3b] in ether at −78 °C furnished borane **3** in 61.3% yield. Borane **4** was synthesized in a similar manner: (1) coupling reaction of stannane **5** with 1-bromo-3-iodobenzene, forming 3-(3′-bromophenyl)pyridine (**7**)[12] in 77.5% yield and (2) lithiation of **7** with *n*-butyllithium and TMEDA followed by quenching with diethylmethoxyborane, giving **4** in 61.0% yield.

Compounds **3** and **4** gave satisfactory elemental analyses and spectroscopic data as described in the later section. The structure of **3** was further confirmed by its reaction[4] with bromobenzene in the presence of tetrakis-(triphenylphosphine)palladium(0), tetrabutylammonium bromide, and potassium hydroxide in tetrahydrofuran at 80 °C for 1.5 h to afford 1-phenyl-4-(3′-pyridyl)benzene (**8**)[13] in 80.5% yield. Borane **4** was similarly converted to 1-phenyl-3-(3′-pyridyl)benzene (**9**)[14] in 79.7% yield.

Vapor Pressure Osmometry and Mass Spectrometry. Vapor pressure osmometry (VPO) using a Knauer digital vapor pressure osmometer with benzil as a standard was carried out to estimate the average aggregation value. With various concentrations of **3** in benzene (from 0.0016 to 0.099 mol L^{-1}) at 60 °C and in acetone (from 0.0296 to 0.137 mol L^{-1}) at 40 °C, the respective values 3.40 and 3.16 were obtained, suggesting that ***3*** *forms a trimer on an average in these solvents*. In each experiment, the VPO plots between the concentration and the reading are linear ($r = 0.9999$ in benzene, $r = 0.9981$ in acetone) within the experimental error. Osmometry values in tetrahydrofuran (from 0.018 to 0.148 mol L^{-1}) at 45 °C and in *N*,*N*-dimethylformamide (from 0.0231 to 0.107 mol L^{-1}) at 90 °C were 2.57 ($r = 0.9999$) and 1.52 ($r = 0.9891$), respectively. The VPO plots in *N*,*N*-dimethylformamide are apparently nonlinear and the modal aggregation value is nonintegral, both of which suggest the lack of a discrete aggregate. In contrast, VPO of **4** in benzene (from 0.0016 to 0.098 mol L^{-1}) at 60 °C gave the value of 2.16 ($r = 0.9997$), indicating that ***4*** *forms a dimer on an average*. Although the osmometry of **4** did not, unfortunately, give reproducible data in tetrahydrofuran, the one in *N*,*N*-dimethylformamide (from 0.018 to 0.071 mol L^{-1}) at 90 °C gave the value 1.58 ($r = 0.9972$). We consider that low VPO values of **3** and **4** in *N*,*N*-dimethylformamide show that the boron atom is subjected to the coordination of an oxgen atom of the solvent.

In the EI-MS (20 eV) spectrum of **3**, in addition to the $M^+ - Et$ peak (*m*/*z* 194, relative intensity 100%) and parent peak as a monomer (M^+, 223, 36), extremely weak peaks of $2 \times M^+$ (446, 0.2) and $2 \times M^+ - Et + 1$ (418, 1.9) were observed. This indicates that the energy for ionization was too high to retain the aggregated molecule, after which dissociation occurred. The EI-MS spectrum of **4** displayed the peaks of M^+ (223, 34) and $2 \times M^+ - Et + 1$ (418, 13) as a heaviest ion. The newly developed electrospray mass spectrometry (ES-MS) has proved efficient for the measurement of macromolecular complexes containing noncovalent interactions.[15] Hence, we applied ES-MS to borylpyridines **1**, **3**, and **4**. Upon measuring negative charge accelerating ES-MS of **1** in tetrahydrofuran in the presence of lithium chloride, the charged peaks were observed at *m*/*z* = 181.7 (100), 329.3 (41), 476.2 (20), and 623.4 (15) with moderate intensities, corresponding to the $[M + Cl]^-$, $[2 \times M + Cl]^-$, $[3 \times M + Cl]^-$, and $[4 \times M + Cl]^-$ charge states, respectively, although the molecular ion of the tetramer of **1** was not observed. The observed isotopic distribution of each fragment was in close agreement with the theoretical one. Under the same conditions, however, **3** gave only the charged peak of $[2 \times M + Cl]^-$ (481.0, 7) as the one due to the aggregate fragment, in addition to the peak of [M

(9) (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585. (c) Ciattini, P. G.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1994**, *35*, 2405 and references therein.

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(11) Several methods for the synthesis of **6** have appeared in the literature. (a) *p*-Bromophenylation of pyridine by the Gomberg−Hey reaction: Abramovitch, R. A.; Saha, M. *J. Chem. Soc. B* **1966**, 733. (b) Coupling reaction of 3-(diethylboryl)pyridine and 1,4-dibromobenzene in the presence of palladium catalyst: Dowell, R. I.; Edwards, P. N.; Oldham, K. U.S. Patent 5,225,438, Jul 6, 1993. (c) Coupling reaction of *p*-bromoaniline and pyridine with added sodium nitrite and hydrochloric acid: Mallion, K. B. U.S. Patent 5,554,613, Sep 10, 1996. (d) Coupling reaction of 3-bromopyridine and 4-bromophenylboronic acid in the presence of palladium catalyst: Murugesan, N.; Barrish, J. C.; Stein, P. D. U.S. Patent 5,780,473, Jul 14, 1998. Our approach is different from the method described in the above literature.

(12) The preparation of **7** has been already reported: Guthikonda, R. N.; Schmitt, S. M.; Dininno, F. P. European Patent Application, No. 481,662 A1, Apr 22, 1992. In this patent, **7** was prepared by the reaction of 3-bromopyridine with 3-bromophenylboronic acid in the presence of palladium catalyst in low yield (35%).

(13) McCall, E. B.; Roberts, R. J. Brit. 919,088, Feb 20, 1963.

(14) Bain, P. J.; Blackman, E. J.; Cummings, W.; Hughes, S. A.; Lynch, E. R. *Proc. Chem. Soc.* **1962**, 186.

(15) (a) Fenn, J. B.; Mann, M.; Meng, C. K.; Wong, S. F.; Whitehouse, C. M. *Science* **1989**, *246*, 64. (b) Przybylski, M.; Glocker, M. O. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 806. (c) Brady, P. A.; Sanders, J. K. M. *New J. Chem.* **1998**, 411.

+ Cl]$^-$ (257.9, 100).[16] Borane **4** gave the peaks of [M + Cl]$^-$ (258.1, 100), [2 × M + Cl]$^-$ (480.8, 8), [3 × M + Cl]$^-$ (703.1, 6), and [4 × M + Cl]$^-$ (926.4, 6) with weak intensities. The fact that the intensities of the peaks due to the oligomers of **3** or **4** are very weak, even under the soft ionization conditions such as ES-MS, shows that the B−N coordination bonds made by **3** or **4** are weak and easy to cleave. Since this result is consonant with the one obtained from variable-temperature ^{1}H NMR studies and scrambling experiments as stated later, it could be pointed out that ES-MS is a reliable method for the evaluation of the strength of coordination bonds.

NMR Spectroscopy. In polar solvents such as acetone-d_6 were observed mainly eight proton signals (one set of the signals as a monomer) in the aromatic region of ^{1}H NMR spectrum of **3** at room temperature.[17] Cooling the sample at −80 °C has no effect on the signals in acetone-d_6. This feature strengthens the inference that the main signals observed at room temperature are assigned to a single species and not to a rapidly equilibrating mixture of some species. Upon irradiation of the signals due to the ethyl groups of **3**, the differential NOE spectrum exhibited the distinct and comparable enhancement of the signals due to H_2 (PyH_2), H_6 (PyH_6) of the pyridyl and $H_{3'}$ (Ph$H_{3'}$), $H_{5'}$ (Ph$H_{5'}$) of the phenylene.

In contrast, 16 proton signals (two sets of signals as a monomer) in the aromatic region of the ^{1}H NMR spectrum of **3** were observed in nonpolar solvent like toluene-d_8 at room temperature (for the major component, PyH_2, δ 8.30; PyH_4, δ 7.27; PyH_5, δ 6.63; PyH_6, δ 8.22; Ph$H_{2'}$ and Ph$H_{6'}$, δ 6.96; Ph$H_{3'}$ and Ph$H_{5'}$, δ 7.35; for the minor component in toluene-d_8, PyH_2, δ 8.71; PyH_4, δ 7.35; PyH_5, δ 6.51; PyH_6, δ 8.02; Ph$H_{2'}$ and Ph$H_{6'}$, δ 7.20; Ph$H_{3'}$ and Ph$H_{5'}$, δ 7.27). The ratio of signals of the major component to that of the minor one was 66:34 by NMR integration (0.190 mol L^{-1}). The ^{1}H NMR spectrum in tetrahydrofuran-d_8 displayed some broad signals, together with two sets of signals as a monomer. Furthermore, the ^{11}B NMR spectrum of **3** displayed a strong signal at 3.18 ppm in acetone-d_6 and 2.22 ppm in toluene-d_8, both being accompanied by a weak one at ca. 33 ppm.[18] *These NMR data indicate that (i) at least two different oligomers with highly symmetric structures are formed via the intermolecular B−N coordination bonds in solution as main species*[19] *and (ii) monomer−oligomers equilibrium is exclusively to the side of the oligomers.* Moreover, the observation that all the pyridine and benzene nuclei in each structure are completely equivalent on the basis of NMR in nonpolar solvent is consistent with the explanation that both oligomers should have flexible macrocyclic structures.

To gain further insight into the solution structure of **3**, three experiments were carried out. First, the variable-temperature ^{1}H NMR spectra in toluene-d_8 were measured. When the solution temperature was gradually raised to 105 °C, the NMR signals were simplified to one set of signals as a monomer (Figure 1). The T_c value was ca. 90 °C.[20] Upon cooling to room temperature, the spectrum reverted to the original one. These data indicate that two cyclic oligomers comprising **3** exist in thermal equilibrium. Second, concentration studies by ^{1}H NMR were performed. The NMR analyses in toluene-d_8 provide the equilibrium ratios of major signal to minor one: 66:34, 71:29, 75:25, 83:17, and 86:14 at 0.190, 0.095, 0.040, 0.008, and 0.004 mol L^{-1}, respectively, determined by its integration. That is to say, at higher concentration, the ratio shifted toward the minor component from the major one. Third, when the ^{1}H NMR spectra of **3** were measured in a mixture of toluene-d_8 and acetone-d_6 at room temperature, it proved that both the chemical shifts and relative integrations of the corresponding proton signals of the two sets exhibited a continuous change, showing they were susceptible to the solvent effect (Figure 2).[21]

In the case of **4**, the ^{1}H NMR spectra in the aromatic region displayed 16 proton signals (two sets of the signals as a monomer) both in toluene-d_8 and in acetone-d_6 (for one component, PyH_2, δ 8.57; PyH_4, δ 7.32; PyH_5, δ 6.50; PyH_6, δ 8.07; Ph$H_{2'}$, δ 7.23; Ph$H_{4'}$, δ 6.98; Ph$H_{5'}$, δ 7.21; Ph$H_{6'}$, δ 7.67; for another component in toluene-d_8, PyH_2, δ 8.57; PyH_4, δ 7.44; PyH_5, δ 6.53; PyH_6, δ 7.98; Ph$H_{2'}$, δ 7.28; Ph$H_{4'}$, δ 7.07; Ph$H_{5'}$, δ 7.23; Ph$H_{6'}$, δ 7.50). The ratio of the signals of the two components in toluene-d_8 was nearly equal by NMR integration. Temperature dependence in toluene-d_8 was also observed in the temperature range of 30−100 °C (Figure 3),[20] leading to the conclusion that **4** was self-assembled into at least two thermally equilibrated cyclic oligomers.

Scrambling Behavior. A scrambling experiment of the constituent molecule **3** or **4** gives further information concerning the solution structures. To this end, two methoxy derivatives of **3** and **4**, 3-[4′-(diethylboryl)-phenyl]-5-methoxypyridine (**10**) and 3-[3′-(diethylboryl)-phenyl]-5-methoxypyridine (**11**), respectively, were prepared in a manner similar to that described for **3** and **4**, starting from 3-bromo-5-methoxypyridine (Chart 3).[22] Examination of the ^{1}H NMR spectra in toluene-d_8 reveals that both **10** and **11** form at least two oligomers in solution, which were in particular characterized by the two singlet signals due to the methoxy proton in both compounds. When a mixture of equimolar amounts of **3** and **10** in toluene-d_8 was allowed to stand at room temperature, new signals were observed within 10 min in the ^{1}H NMR spectrum, together with the signals due to **3** and **10**. The two singlet signals (3.14 and 3.03 ppm) due to the methoxy proton of **10** were split into three and four peaks, respectively. Although isolation was not carried out, the new signals presumably would arise from

(16) Measurements in the absence of salt did not give the peaks due to the oligomers comprised of **3**. Moreover, in acetone either in the presence or absence of lithium chloride, or in toluene in the absence of lithium chloride, **3** also did not give the assignable peaks by means of either positive or negative polarity mode.

(17) A very small amount of proton signals also consists of one set of the signals as a monomer.

(18) Since the intensity of the weak signal at ca. 33 ppm was enhanced from 1−3% in acetone-d_6 or toluene-d_8 to 15% in tetrahydrofuran-d_8, this signal would arise from a small amount of species such as a monomer or acyclic low molecular weight aggregates, which were free from the B−N coordination bond.

(19) As an alternative interpretation, a reviewer made a comment that more than one set of peaks may indicate a cyclic aggregate where the units are inequivalent. However, it appears that the concentration- and solvent-dependent NMR shifts as described in the section on NMR spectroscopy could not be explained by this interpretation.

(20) Since an energy barrier of ca. 17 kcal mol^{-1} could be estimated from T_c, the interconversion should be fast enough to equilibrate them at room temperature.

(21) The signals due to PyH_4, PyH_5, and PyH_6 protons of **3** move markedly upfield with the increase of toluene-d_8 content, whereas the signal for PyH_2 is slightly shifted downfield. Since the shift would be a result of the shielding effect exerted by solvation of toluene around the cyclic cavity, we could assign PyH_4, PyH_5, and PyH_6 protons as being on the outside of the cavity of cyclic oligomers comprised of **3** and PyH_2 proton as being on the inside.

(22) For the synthesis of 3-bromo-5-methoxypyridine, see: Comins, D. L.; Killpack, M. O. *J. Org. Chem.* **1990**, *55*, 69.

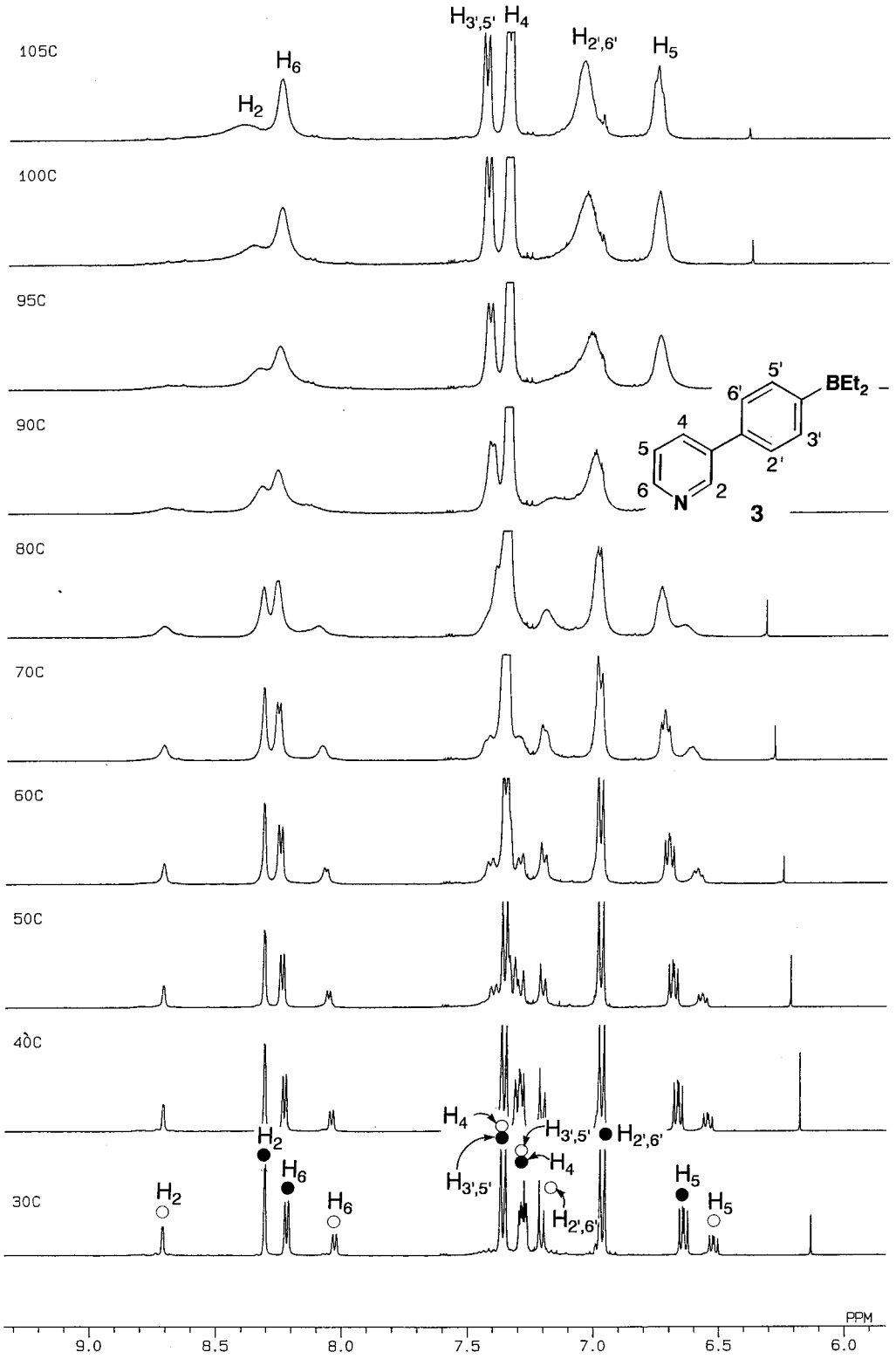


Figure 1. Variable-temperature ^{1}H NMR spectra of **3** (400 MHz, toluene-d_8). ●: major component. ○: minor component.

the scrambling products from the signal patterns in the ^{1}H NMR spectrum. The spectrum remained unchanged even upon heating the mixture to 100 °C for 24 h. The mixture of **4** and **11** exhibited similar behaviors: the two singlet signals (3.02 and 3.04 ppm) of **11** were split into two peaks upon mixing.

Since the scrambling of constituent molecules involves the breaking of the intermolecular B−N coordination bonds as a rate-determining step, these data indicate that the coordination bonds in the oligomers of **3** or **4** are weaker than those in the tetramer of **1**[5] or the dimer of **2**.[6] This result can be satisfactorily explained by the reduced Lewis acidity of the boron atom in **3** and **4**, because the boron atom in **3** and **4** is bonded to the π-electron-donating benzene ring but not directly to the pyridine one.

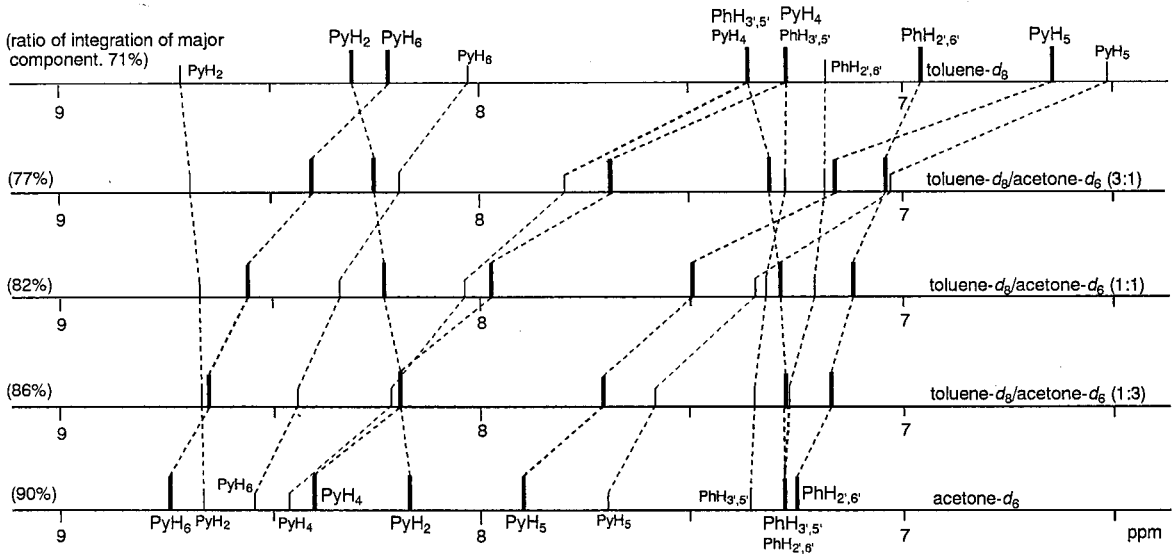
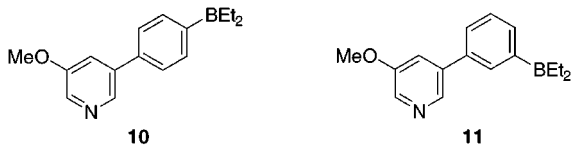


Figure 2. ^{1}H NMR chemical shifts of two oligomers comprised of **3** in a mixture of toluene-d_8 and acetone-d_6. Long wide line: major component. Short narrow line: minor component.

Structure in Solution. From the VPO and NMR studies of **3**, it is obvious that (i) the self-assembly of **3** in solution is critically dependent on solvent, temperature, and concentration, (ii) **3** should form two thermally equilibrated cyclic oligomers in nonpolar solvent,[19] one of which might be assigned as a trimer, (iii) this equilibrium lies predominantly toward the major component in acetone, and (iv) **3** might afford a complex mixture of a monomer and/or cyclic or acyclic low molecular weight aggregates in solvent such as tetrahydrofuran or *N*,*N*-dimethylformamide. Although it is actually difficult to analyze the equilibrium in nonpolar solvent, participation of a cyclic dimer as a minor component would be out of the bounds of possibility, because the formation of a cyclic dimer of **3** is forced unavoidably to suffer from tolerable steric hindrance. Further, the equilibrium between two different cyclic trimers might be ruled out, as pointed out later. Assuming that the minor component is assigned as a cyclic tetramer, the equilibrium ratio of trimer and tetramer would be 72:28 by the NMR analysis in toluene-d_8 (0.190 mol L^{-1}). This gives the estimated value of 3.28 ($= 3 \times 0.72 + 4 \times 0.28$) as the average number of constituent molecules, in good agreement with one (3.40) found by VPO. Since the formation of a pentamer or a hexamer of **3** as the minor component would afford the estimated values of 3.48 and 3.63 close to 3.40, respectively, it is nearly impossible to distinguish these *n*-mers. However, if **3** forms the oligomers larger than a hexamer or a catenane as minor component, the number of constituent molecules would be quite different from VPO value. Thus, both the VPO and NMR data in nonpolar solvent fit well to the equilibrium model of cyclic trimer−tetramer (or pentamer). This model was strongly supported by concentration-dependent NMR shifts as described in the section on NMR spectroscopy. Such a self-reorganization model has been reported for the self-assembled Pd(II) complex by Fujita[23] and Hong,[24] and Fe(II) complex by Romero,[25] where its model was verified by the concentration-dependent NMR spectra and/or VPO, MS data.

Chart 3



10 **11**

In contrast, **4** affords an equilibrium mixture of oligomers most probably assigned as a cyclic dimer from VPO data. The formation of a cyclic dimer is reasonable, from a study of CPK molecular model.

Although our experimental evidence (VPO, NMR) for the structure of assembly of **3** or **4** may not be irrefutable, the above data suggest that self-assembled species comprised of **3** or **4** in nonpolar solvent could be recognized as discrete macrocyclic species despite the fast equilibrium. It should be stressed that the modification of the skeleton of **1** by *p*- or *m*-phenylene led to dramatic changes in the self-assembly process.

Semi-Empirical MO Calculation AM1. Although the recrystallization of **3** and **4** was attempted in order to elucidate the molecular structure in the solid state by a single-crystal X-ray crystallographic study, it was, unfortunately, unsuccessful. It was decided, therefore, to evaluate the stable molecular structures of **3** and **4** using semi-empirical MO (AM1) calculations, on the assumption that **3** forms a cyclic trimer and a cyclic tetramer, and **4** forms two cyclic dimers. Calculations on **1** and **2** were also carried out to compare with the molecular structures determined by X-ray crystallography.[5,6] In Table 1 are listed typical data calculated by AM1 for the constituent molecules **1**−**4** and the oligomers comprised of **1**−**4**. It is found that fully optimized structures of the cyclic tetramer of **1** and the cyclic dimer of **2** are in good agreement with the structures obtained from X-ray analysis in most respects. The lowest energy structures

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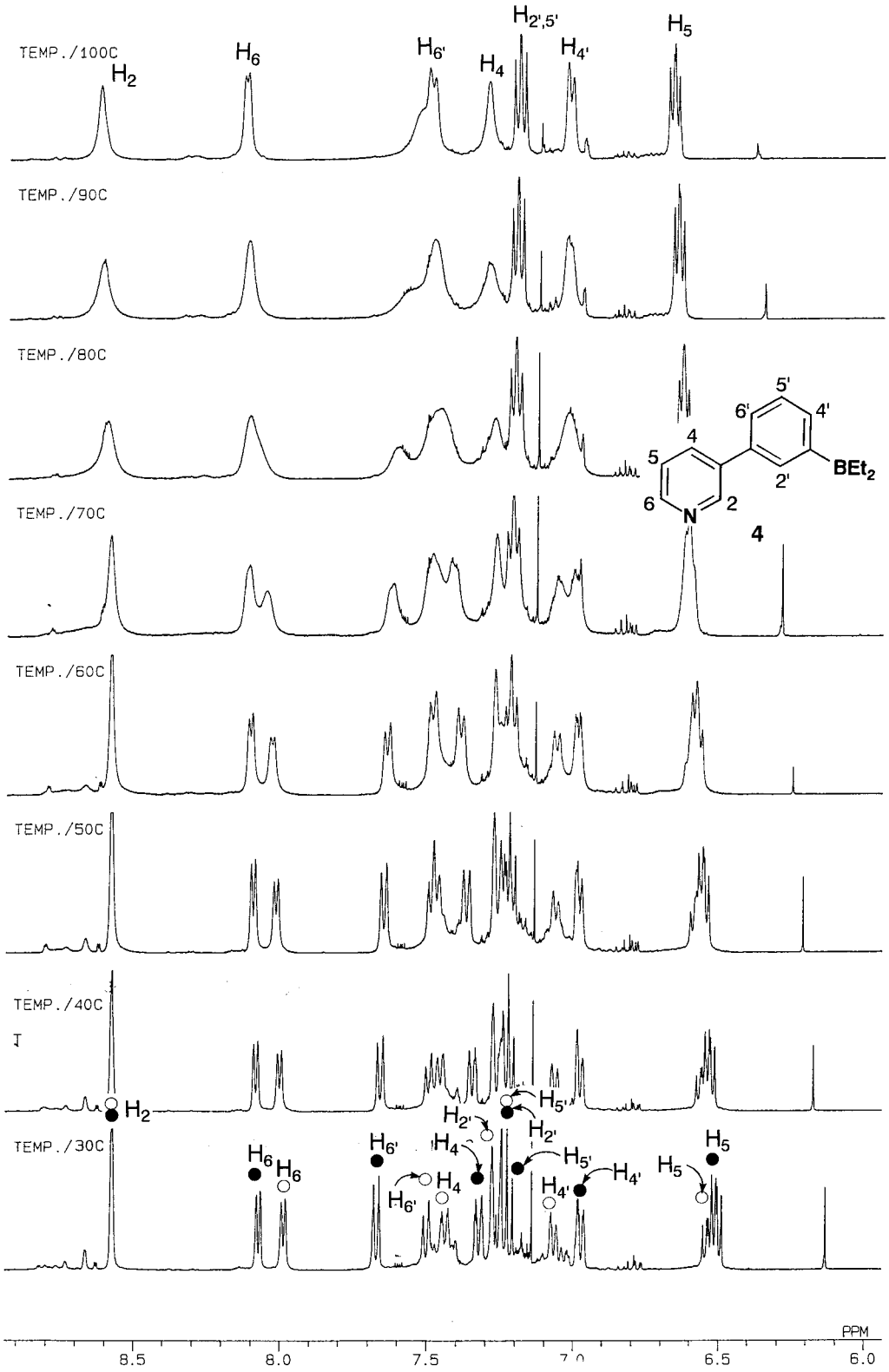

Figure 3. Variable-temperature ^{1}H NMR spectra of **4** (400 MHz, toluene-d_8). ●: one component. ○: another component.

of the cyclic trimer (named as trimer A) and the cyclic tetramer comprised of **3** (Figure 4A,B), and two cyclic dimers (named as dimers A and B) comprising **4** (Figure 4C,D) are found to be symmetric ones. Through a global search of conformations of the cyclic trimer of **3**, another cyclic trimer (named as trimer B) was located within a 4 kcal mol^{-1} window. The conformers are distinguishable by the rotation of the B−C bond in the boron−ethyl group. Since the interconversion between two such cyclic trimers should be extremely fast, two species observed by NMR spectroscopy in toluene-d_8 could not be assigned as two cyclic trimers.

The heats of formation enable us to estimate the enthalpic contribution to the free energy change associ-

Table 1. Typical Structural Data, Heats of Formation, and Stabilization Energies Calculated by AM1

	1		**2**		**3**				**4**		
						trimer				dimer	
	monomer	tetramer[a]	monomer	dimer[b]	monomer	A[c]	B[d]	tetramer[e]	monomer	A	B
B−N bond length, Å		1.634 1.635		1.595		1.660 1.665 1.678	1.679 1.679 1.679	1.656 1.657 1.657 1.670		1.668 1.677	1.667 1.667
THC, %[f]		80.6 82.3		103.4		60.2 70.7 71.6	59.4 59.4 59.4	68.2 74.4 77.0 77.3		75.7 75.7	83.5 83.5
heat of formation, kcal/mol	12.06	4.68	1.82	−26.99	37.92	96.39	100.04	127.76	37.93	71.22	72.54
stabilization energy, kcal/mol[g]		10.89		15.32		5.79	4.57	5.98		2.32	1.66

[a] C_2 symmetry. [b] C_{2h} symmetry. [c] Dipole moment (μ) = 6.64 D. [d] μ = 6.31 D. [e] μ = 1.36 D. [f] Calculated from the bond angles around a boron atom in the complex.[7] [g] Obtained by subtracting the heat of formation per monomer in oligomers from that of the constituent molecule itself.

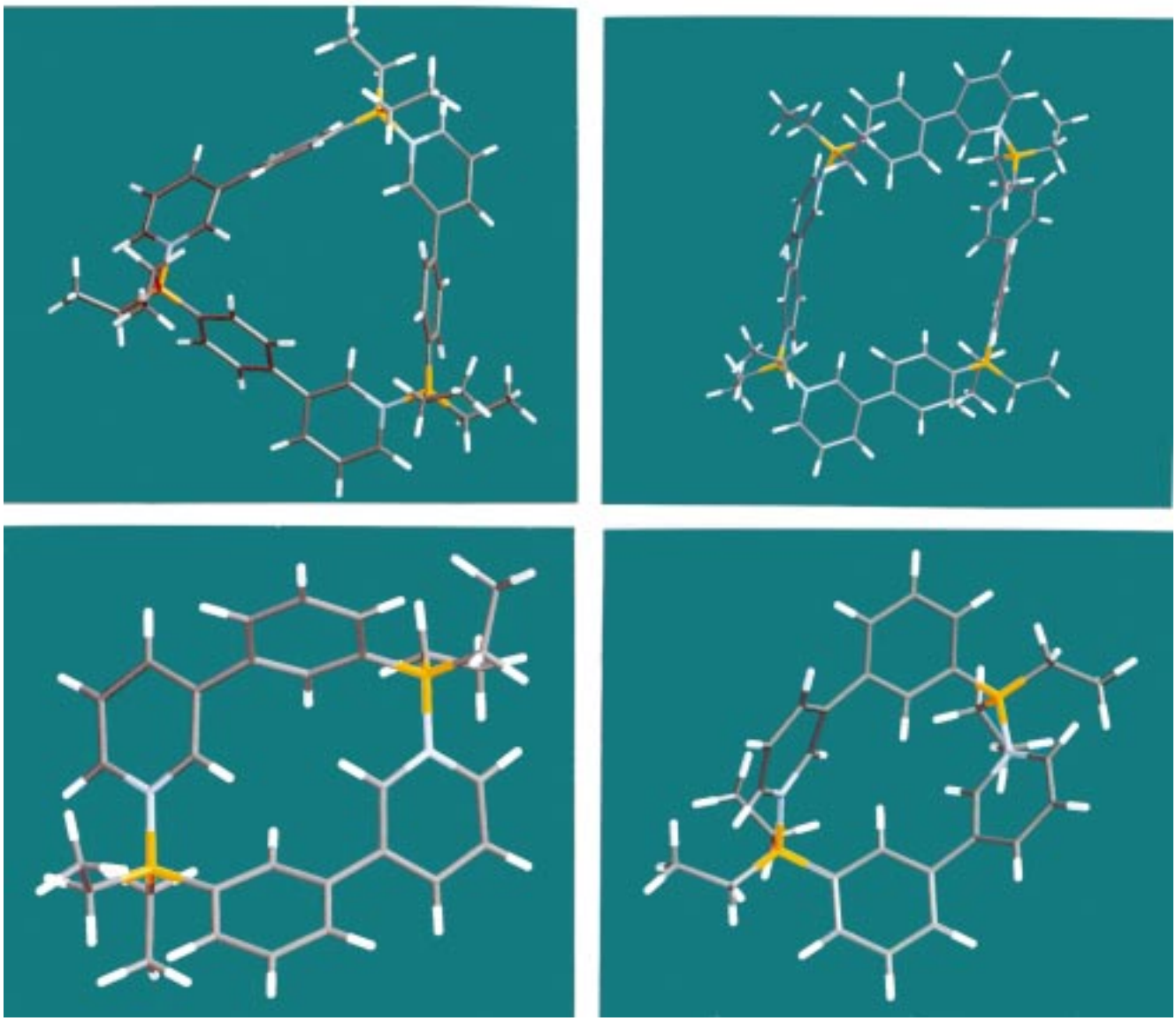

Figure 4. AM1-optimized structures of the oligomers comprised of **3** or **4**. (A, top left) trimer A of **3**. (B, top right) tetramer of **3**. (C, bottom left) dimer A of **4**. (D, bottom right) dimer B of **4**. The tubes are colored according to the type of atom: hydrogen in white, carbon in gray, nitrogen in blue-gray, boron in tan.

ated with self-assembly, namely, stabilization energy, which is calculated by subtracting the heat of formation per monomer in oligomers from that of the constituent molecule itself. The calculated stabilization energies for

1−**4** are 10.89, 15.32, 5.79 (5.98 as cyclic tetramer),[26] and 2.32 (1.66)[26] kcal mol^{-1}, respectively. This order is roughly consistent with that of the strength of intermolecular B−N coordination bonds deduced from the experiments. The equilibrium observed for the oligomers of **3** appears to stem from a thermodynamic balance: the cyclic tetramer of **3** is more stable by only ca. 0.2 kcal mol^{-1} in terms of enthalpy, whereas entropy effects favor the cyclic trimer because of its assembly from fewer components than the cyclic tetramer. Thus, the present equilibrium seems to be governed by the entropy effect.

The length of the B−N coordination bonds in the oligomers of **3** or **4** is longer than that in the tetramer of **1** by ca. 0.02−0.05 Å, making the intermolecular B−N coordination bonds weaker. The bond angles at the boron atom allow the calculation of the THC.[7] As the average THC values, 81%, 103%, 68% (74% as cyclic tetramer),[26] and 76% (84%)[26] were obtained for the oligomers of **1**−**4**, respectively. For compounds **1**−**3**, therefore, both the length of the B−N coordination bond and the magnitude of THC at the boron atom are well correlated with their relative stability. In the case of **4**, however, the correlation between the stability and THC is noteworthy, because THC of the dimer of **4** is close to that of the tetramer of **1** rather than that of the trimer of **3**. According to this calculation, low stability of the dimer of **4** would mainly arise from the additional strain caused by the formation of cyclic dimer. The unfavorable distortion of the dihedral angle between the benzene and pyridine rings (from 39° in the constituent molecule **4** to 69° in dimer A and to 33° in dimer B) would result in the decrease of resonance energy or increase of steric repulsion, both of which destabilize the cyclic dimer of **4**. Therefore, it can be considered that the self-assembly of **4** is strongly governed by the tetrahedral coordination geometry of the boron atom in the complex at the expense of strain energy.

The solvent effect observed for oligomers of **3** might be well explained by calculated dipole moments of the cyclic trimer A and the cyclic tetramer (6.64 and 1.36 D, respectively). Better stabilization of the polar ground state due to greater solvation in more polar solvent than in less polar solvent may favor the trimer.

In conclusion, borylpyridines **3** and **4** in nonpolar solvent were spontaneously self-assembled via B−N coordination bonds to form the well-defined aggregate whose structure and stability were quite different from those of **1** and **2**. The structure of the assembly of **3** or **4** is characterized by weak coordination bonds. These weak interactions facilitate the interconversion between the cyclic oligomers comprised of **3** or **4** at ambient temperature.[20] We believe that this investigation demonstrates how the structural modification of borylpyridines can affect the features of self-assembly in solution and would be helpful in construction of artificial self-assembly molecular systems.[27]

Experimental Section

General Methods. Melting points (mp) were determined on a Shibata MEL-270 melting point apparatus and are uncorrected. ^{1}H, ^{13}C, and ^{11}B nuclear magnetic resonance (NMR) spectra were recorded on JEOL JNM-A400, A500, or GSX-400 or Varian UNITY plus 600 instruments. The chemical shifts are described as values in ppm relative to a $Si(CH_3)_4$ standard for ^{1}H NMR. ^{11}B NMR chemical shifts quoted are downfield from $BF_3{\cdot}OEt_2$ as an external standard. Infrared (IR) spectra were measured with a Shimadzu FT IR-8100 Fourier transform infrared spectrophotometer. Electron impact mass spectra (EI-MS) were measured using a Shimadzu GCMS-QP 1000EX gas chromatograph−mass spectrometer. Analytical thin-layer chromatography (TLC) was conducted on a plate coated with E. Merck Kieselgel 60 F_{254} (0.25-mm thickness). Most reactions were carried out in serum-capped, oven-dried, and argon-purged flasks. Measurement of the variable-temperature NMR spectra was carried out at 30−105 °C after the solution containing **3** or **4** was degassed and sealed in an NMR tube. Scrambling experiments were carried out according to ref 5b. The MO calculations were performed using Spartan programs (Release 4.0.1a) on SGI workstation computer.

3-(Trimethylstannyl)pyridine (5). Stannane **5** was synthesized by a modified method of ref 10a. To a solution of 3-bromopyridine (4.0 mL, 41.5 mmol) in ether (90 mL) was added 1.55 M *n*-butyllithium hexane solution (28.1 mL, 43.6 mmol) at −65 to −55 °C for 4 min. After 0.5 h of stirring at −50 °C, to this suspension was added dropwise a solution of trimethylstannyl chloride (8.3 g, 41.7 mmol) in ether (40 mL). The mixture was gradually warmed to room temperature over 0.5 h. The mixture was poured into a saturated NH_4Cl solution (100 mL) and a mixture of ether and hexane (1:1) (500 mL). The aqueous layer was extracted with a 1:1 mixture of ether and hexane (100 mL × 2). The combined organic extracts were washed with brine (100 mL × 2) and dried over $MgSO_4$. The dried solution was concentrated, and the residue was distilled to afford **5** (8.146 g, 81.2%): colorless oil; bp 66−69 °C/1 Torr (lit.[10a] bp 72−73 °C/10 Torr). Although a small discrepancy was found in bp, the bp (116−118 °C/16 Torr) reported in ref 10b was comparable with our observed bp. The ^{1}H NMR and IR spectra are consistent with previously reported ones:[10a,b] ^{13}C NMR (100 MHz, $CDCl_3$) −9.6, 123.8, 137.1, 143.4, 149.3, 155.5. Anal. Calcd for $C_8H_{13}NSn$: C, 39.72; H, 5.42; N, 5.79. Found: C, 40.07; H, 5.44; N, 5.96.

3-(4′-Bromophenyl)pyridine (6). To a solution of **5** (1.188 g, 4.911 mmol) and 1-bromo-4-iodobenzene (98%, 1.460 g, 5.059 mmol) in DMF (20 mL) were added successively Pd_2dba_3 (118 mg, 0.128 mmol), $AsPh_3$ (97%, 185 mg, 0.584 mmol), and CuI (110 mg, 0.575 mmol). The mixture was stirred at 80 °C for 5 h. After cooling, to this were added ether (100 mL) and water (30 mL), and the mixture was extracted with ether (30 mL × 3). The combined organic layer was washed with water, 1 M KF solution (30 mL), and brine (30 mL × 2), dried over $MgSO_4$, and concentrated. The crude product was subjected to silica gel (30 g) column chromatography and eluted with a mixture of benzene and ether (4:1) to afford **6** (801 mg, 69.7%) as an oil, which became a faint yellow solid on cooling in the freezer, mp 37.0−39.5 °C (lit.[11] colorless oil). The ^{1}H NMR data matched that previously reported:[11] IR (KBr) 1576, 1468, 1424, 1385 cm^{-1}; EI-MS (70 eV) *m*/*z* 235 (93%), 233 (93, M^+), 154 (97, M^+ − Br), 127 (100); ^{13}C NMR (126 MHz, $CDCl_3$) 122.5, 123.6, 128.3, 128.7, 132.2, 134.1, 135.5, 136.8, 148.06, 148.11, 148.9. Anal. Calcd for $C_{11}H_8NBr$: C, 56.44; H, 3.44; N, 5.98. Found: C, 56.72; H, 3.39; N, 5.99.

3-(3′-Bromophenyl)pyridine (7). To a solution of **5** (1.231 g, 5.091 mmol) and 1-bromo-3-iodobenzene (98%, 1.531 g, 5.302 mmol) in DMF (20 mL) were added successively $Pd_2dba_3{\cdot}CHCl_3$ (141 mg, 0.136 mmol), $AsPh_3$ (97%, 190 mg, 0.601 mmol), and CuI (140 mg, 0.732 mmol). The mixture was stirred at 80 °C for 5 h. After cooling, to this were added ether (100 mL) and water (30 mL), and the mixture was extracted with ether (30 mL × 3). The combined organic layer was washed with water (30 mL), 1 M KF aqueous solution (30 mL), and brine (30 mL), dried over $MgSO_4$, and concentrated. The crude product was subjected to silica gel (30 g) column chromatography and eluted with a mixture of benzene and ether (4:1) to afford **7** (880 mg, 77.5%): faint yellow oil; bp 110−120 °C (bath

(26) In parentheses were shown the stabilization energy or THC value of another cyclic oligomer of two stable ones.

(27) For recent reviews, see: (a) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89. (b) Whitesides, G. M.; Mathias, J. P.; Seto, C. T. *Science* **1991**, *254*, 1312. (c) Lawrence, D. S.; Jiang, T.; Levett, M. *Chem. Rev.* **1995**, *95*, 2229. (d) Philip, D.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1154. (e) MacGillivray, L. R.; Atwood, J. L. *Ibid.* **1999**, *38*, 1018.

temperature)/1 Torr (lit.[12] bp 140−142 °C/2 Torr). The ^{1}H NMR and MS spectra are consistent with previously reported data: [12] IR (neat) 1593, 1576, 1559, 1468, 1190 cm^{-1}; ^{13}C NMR (100 MHz, $CDCl_3$) 122.9, 123.4, 125.5, 129.9, 130.3, 130.8, 134.0, 134.9, 139.6, 147.9, 148.8. Anal. Calcd for $C_{11}H_8NBr$: C, 56.44; H, 3.44; N, 5.98. Found: C, 56.49; H, 3.40; N, 6.13.

3-[4′-(Diethylboryl)phenyl]pyridine (3). To an ethereal solution (10 mL) of **6** (630 mg, 2.692 mmol) and TMEDA (410 μL, 2.70 mmol) was added dropwise a hexane solution of *n*-butyllithium (1.55 M, 1.91 mL, 2.961 mmol) at −78 °C over 2 min, and the whole was stirred for 1 h. To this was added a THF solution of diethylmethoxyborane (1.0 M, 8.1 mL, 8.1 mmol) at −78 °C, and the mixture was stirred for 1 h. After being warmed to 0 °C, the mixture was stirred for additional 0.5 h, diluted with ethyl acetate (100 mL), washed with water (30 mL) and brine (10 mL × 2), and dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on deactivated (5% H_2O) silica gel (10 g) with a mixture of benzene and hexane (1:1) as an eluent to give **3** (368 mg, 61.3%): faint yellow solid; mp 125−141 °C; IR (KBr) 2864, 1582, 1478, 1429, 1387, 1259 cm^{-1}; EI-MS (20 eV) 446 (0.2, 2M$^+$), 418 (1.9, 2M$^+$ − Et + 1), 223 (36, M$^+$), 194 (100, M$^+$ − Et); ES-MS (LiCl in THF, negative mode) 481.0 (7, [2M + Cl]$^-$), 257.9 (100, [M + Cl]$^-$); ^{1}H NMR (500 MHz, acetone-d_6) 0.61 [t, 6 H, J = 7.6 Hz, −B(CH$_2$C*H*$_3$)$_2$], 0.82−0.94 [m, 4 H, −B(C*H*$_2$CH$_3$)$_2$], 7.25 (d, 2 H, J = 8.6 Hz, H-2′, -6′ of phenylene), 7.28 (d, 2 H, J = 8.6 Hz, H-3′, -5′ of phenylene), 7.90 (dd, 1 H, J = 5.8, 7.9 Hz, H-5 of pyridyl), 8.17 (s, 1 H, H-2 of pyridyl), 8.39 (dd, 1 H, J = 1.2, 7.9 Hz, H-4 of pyridyl), 8.73 (d, 1 H, J = 5.8 Hz, H-6 of pyridyl); ^{1}H NMR (600 MHz, toluene-d_8) major component 0.99 [t, J = 7.6 Hz, −B(CH$_2$C*H*$_3$)$_2$], 1.03−1.18 [m, −B(C*H*$_2$CH$_3$)$_2$], 6.63 (dd, J = 5.8, 7.7 Hz, H-5 of pyridyl), 6.96 (d, J = 8.2 Hz, H-2′, -6′ of phenylene), 7.27 (H-4 of pyridyl), 7.35 (d, J = 8.2 Hz, H-3′, -5′ of phenylene), 8.22 (d, J = 5.5 Hz, H-6 of pyridyl), 8.30 (d, J = 1.9 Hz, H-2 of pyridyl); minor component 0.94 [t, J = 7.7 Hz, −B(CH$_2$C*H*$_3$)$_2$], 1.03−1.18 [m, −B(C*H*$_2$CH$_3$)$_2$], 6.51 (dd, J = 5.6, 8.1 Hz, H-5 of pyridyl), 7.20 (d, J = 8.2 Hz, H-2′, -6′ of phenylene), 7.27 (d, J = 8.2 Hz, H-3′, -5′ of phenylene), 7.35 (H-4 of pyridyl), 8.02 (d, J = 5.5 Hz, H-6 of pyridyl), 8.71 (d, J = 1.8 Hz, H-2 of pyridyl); ^{13}C NMR (100 MHz, acetone-d_6) 10.1, 15.9, 125.9, 126.2, 126.4, 126.5, 129.1, 132.4, 134.2, 134.4, 138.8, 140.3, 144.1, 144.5, 145.9; ^{11}B NMR (128 MHz, $CDCl_3$) 2.50 (strong), 31.41 (weak), 32.36 (w); ^{11}B NMR (160 MHz, acetone-d_6) 3.18 (s), 33.48 (w); ^{11}B NMR (160 MHz, toluene-d_8) −4.56 (s), 2.22 (s), 31.83 (medium), 32.64 (m); ^{11}B NMR (128 MHz, THF-d_8) 2.81 (s), 20.39 (w), 29.25 (w), 32.66 (m). Anal. Calcd for $C_{15}H_{18}NB$: C, 80.75; H, 8.13; N, 6.28. Found: C, 80.94; H, 8.24; N, 5.61.

3-[3′-(Diethylboryl)phenyl]pyridine (4). To an ethereal solution (4 mL) of **7** (406 mg, 1.736 mmol) and TMEDA (260 μL, 1.723 mmol) was added dropwise a hexane solution of *n*-butyllithium (1.55 M, 1.23 mL, 1.907 mmol) at −78 °C over 2 min, and the whole was stirred for 1 h. To this was added a THF solution of diethylmethoxyborane (1.0 M, 5.3 mL, 5.3 mmol) at −78 °C, and the mixture was stirred for 1 h. After being warmed to 0 °C, the mixture was stirred for additional 0.5 h, diluted with ethyl acetate (40 mL), washed with water (15 mL) and brine (5 mL × 2), and dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on deactivated (5% H_2O) silica gel (4 g) with a mixture of benzene and hexane (1:1) as an eluent to give **4** (248 mg, 61.0%): faint yellow solid; mp 66−74 °C; IR (KBr) 2864, 1615, 1582, 1470, 1429, 1383, 1262 cm^{-1}; EI-MS (20 eV) 418 (13%, 2M$^+$ − Et + 1), 223 (34, M$^+$), 194 (100, M$^+$ − Et), 166 (95); ES-MS (LiCl in THF, negative mode) 926.4 (6, [4M + Cl]$^-$), 703.1 (6, [3M + Cl]$^-$), 480.8 (8, [2M + Cl]$^-$), 258.1 (100, [M + Cl]$^-$); ^{1}H NMR (500 MHz, acetone-d_6) major component 0.60 [t, J = 7.5 Hz, −B(CH$_2$C*H*$_3$)$_2$], 0.73−0.87 [m, −B(C*H*$_2$CH$_3$)$_2$], 7.29−7.49 (m, 4H), 7.80 (dd, J = 5.8, 7.6 Hz, H-5 of pyridyl), 8.34 (d, J = 7.4 Hz, H-4 of pyridyl), 8.43 (s, H-2 of pyridyl), 8.61 (d, J = 5.5 Hz, H-6 of pyridyl); minor componemt 0.49−0.56 [m, −B(CH$_2$-C*H*$_3$)$_2$], 0.73−0.87 [m, −B(C*H*$_2$CH$_3$)$_2$], 7.29−7.49 (m, 4 H), 7.77 (dd, J = 5.8, 7.6 Hz, H-5 of pyridyl), 8.32 (d, J = 7.4 Hz, H-4 of pyridyl), 8.43 (s, H-2 of pyridyl), 8.49 (d, J = 5.9 Hz, H-6 of pyridyl); ^{1}H NMR (toluene-d_8, 600 MHz) one component 0.93 [t, J = 7.6 Hz, -B(CH$_2$C*H*$_3$)$_2$], 1.00−1.15 [m, −B(C*H*$_2$CH$_3$)$_2$], 6.50 (dd, J = 5.8, 8.0 Hz, H-5 of pyridyl), 6.98 (d, J = 7.7 Hz, H-4′ of phenylene), 7.21 (H-5′ of phenylene), 7.23 (d, J = 7.5 Hz, H-2′ of phenylene), 7.32 (dt, J = 1.6, 8.0 Hz, H-4 of pyridyl), 7.67 (d, J = 7.4 Hz, H-6′ of phenylene), 8.07 (d, J = 5.5 Hz, H-6 of pyridyl), 8.57 (s, H-2 of pyridyl); another component 0.83 [t, J = 7.6 Hz, −B(CH$_2$C*H*$_3$)$_2$], 1.00−1.15 [m, −B(C*H*$_2$-CH$_3$)$_2$], 6.53 (dd, J = 5.8, 8.0 Hz, H-5 of pyridyl), 7.07 (d, J = 7.5 Hz, H-4′ of phenylene), 7.23 (d, J = 7.5 Hz, H-5′ of phenylene), 7.28 (s, H-2′ of phenylene), 7.44 (dd, J = 1.5, 8.0 Hz, H-4 of pyridyl), 7.50 (d, J = 7.3 Hz, H-6′ of phenylene), 7.98 (d, J = 5.5 Hz, H-6 of pyridyl), 8.57 (s, H-2 of pyridyl); ^{13}C NMR (126 MHz, acetone-d_6) 10.0, 15.2, 15.7, 124.0, 124.2, 126.2, 126.3, 126.4, 128.67, 128.75, 129.1, 131.3, 131.8, 134.2, 134.3, 134.5, 134.6, 138.8, 140.6, 144.4, 144.6, 145.0, 145.1, 145.3; ^{11}B NMR (128 MHz, $CDCl_3$,) 2.09 (s), 32.35 (m), 33.31 (m), 55.21 (w); ^{11}B NMR (128 MHz, THF-d_8) 2.27 (s), 19.84 (w), 29.11 (w), 31.99 (m), 32.54 (m); Anal. Calcd for $C_{15}H_{18}$-NB: C, 80.75; H, 8.13; N, 6.28. Found: C, 80.93; H, 8.32; N, 5.40.

1-Phenyl-4-(3′-pyridyl)benzene (8). A mixture of **3** (96 mg, 0.430 mmol), bromobenzene (70 μL, 0.665 mmol), powdered KOH (73 mg, 1.301 mmol), Bu_4NBr (70 mg, 0.217 mmol), and $Pd(Ph_3P)_4$ (25 mg, 0.022 mmol) in THF (5 mL) was stirred at 80 °C for 1.5 h. The mixture was diluted with AcOEt (40 mL), washed with brine (10 mL × 2), and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography (SiO_2, 4 g) with a mixture of benzene and ether (4:1 v/v) to afford **8** (80 mg, 80.5%): faint yellow crystals; mp 147.0−148.5 °C (lit.[13] mp: 152−153 °C); IR (KBr) 1582, 1474, 1397 cm^{-1}; EI-MS (70 eV) 231 (M$^+$, 100), 202 (12), 152 (6); ^{1}H NMR (500 MHz, $CDCl_3$) 7.36−7.39 (m, 2 H, H-5′ of pyridyl and H-4″ of phenyl), 7.47 (t, 1 H, J = 7.6 Hz, H-3″, -5″ of phenyl), 7.64 (d, 2 H, J = 7.0 Hz, H-2″, -6″ of phenyl), 7.66 (dt, 2 H, J = 2.1, 8.5 Hz, H-3, -5 of phenylene or H-2, -6 of phenylene), 7.71 (dt, 2 H, J = 2.1, 8.5 Hz, H-2, -6 of phenylene or H-3, -5 of phenylene), 7.91 (dt, 1 H, J = 2.0, 7.9 Hz, H-4′ of pyridyl), 8.60 (d, 1 H, J = 3.4 Hz, H-6′ of pyridyl), 8.90 (d, 1 H, J = 2.1 Hz, H-2′ of pyridyl); ^{13}C NMR (126 MHz, $CDCl_3$) 123.5, 127.0, 127.4, 127.5, 127.7, 128.3, 128.8, 134.1, 136.1, 136.6, 140.3, 140.9, 148.2, 148.5. Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.67; N, 6.06. Found: C, 87.48; H, 5.58; N, 5.93.

1-Phenyl-3-(3′-pyridyl)benzene (9). A mixture of **4** (94 mg, 0.420 mmol), bromobenzene (70 μL, 0.665 mmol), powdered KOH (76 mg, 1.360 mmol), Bu_4NBr (73 mg, 0.226 mmol), and $Pd(Ph_3P)_4$ (26 mg, 0.023 mmol) in THF (5 mL) was stirred at 80 °C for 2.5 h. The mixture was diluted with AcOEt (50 mL), washed with brine (10 mL × 2), and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography (SiO_2, 3.5 g) with a mixture of benzene and ether (4:1 v/v) to afford **9** (77 mg, 79.7%) as a yellow oil, bp 130−140 °C (bath temperature)/1 Torr (lit.[14] mp 151−152 °C). We could not induce crystallization in **9** even by cooling in the freezer: IR (neat) 3032, 1599, 1586, 1574, 1474, 1422, 1393 cm^{-1}; EI-MS (70 eV) 231 (M$^+$, 100), 202 (12), 152 (6); ^{1}H NMR (400 MHz, $CDCl_3$) 7.37−7.41 (m, 2 H, H-5′ of pyridyl and H-4″ of phenyl), 7.45−7.50 (m, 2 H, H-3″, -5″ of phenyl), 7.55−7.57 (m, 2 H, H-5, -6 of phenylene), 7.62−7.66 (m, 3 H, H-4 of phenylene and H-2″, -6″ of phenyl), 7.79 (s, 1 H, H-2 of phenylene), 7.93 (d, 1 H, J = 8.0 Hz, H-4′ of pyridyl), 8.62 (dd, 1 H, J = 1.2, 4.9 Hz, H-6′ of pyridyl), 8.91 (d, 1 H, J = 1.9 Hz, H-2′ of pyridyl); ^{13}C NMR (100 MHz, $CDCl_3$) 123.6, 126.05, 126.08, 126.9, 127.2, 127.6, 128.3, 128.9, 129.5, 134.4, 136.6, 138.4, 140.8, 142.2, 148.4, 148.6. Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.44; H, 5.67; N, 6.21.

3-[4′-(Diethylboryl)phenyl]-5-methoxypyridine (10): IR (KBr) 2865, 1590, 1456, 1331, 1223 cm^{-1}; ^{1}H NMR (400 MHz, toluene-d_8) major component 0.74−1.22 [m, −B(C*H*$_2$CH$_3$)$_2$], 3.14 (s, −OC*H*$_3$), 7.01 (s, H-4 of pyridyl), 7.04 (d, J = 8.1 Hz, H-2′, -6′ of phenylene), 7.44 (d, J = 8.1 Hz, H-3′, -5′ of phenylene), 8.02 (s, H-2 of pyridyl), 8.30 (d, J = 2.7 Hz, H-6 of pyridyl); minor component 0.74−1.28 [m, -B(C*H*$_2$CH$_3$)$_2$], 3.03 (s, −OC*H*$_3$), 7.10 (s, H-4 of pyridyl), 7.25 (d, J = 8.1 Hz, H-2′,

-6′ of phenylene), 7.35 (d, J = 8.1 Hz, H-3′, -5′ of phenylene), 8.08 (d, J = 2.4 Hz, H-6 of pyridyl), 8.42 (s, H-2 of pyridyl).

3-[3′-(Diethylboryl)phenyl]-5-methoxypyridine (11): IR (KBr) 1595, 1559, 1466, 1401, 1312, 1219 cm^{-1}; ^1H NMR (400 MHz, toluene-d_8) major component 0.93−1.40 [m, $-B(CH_2CH_3)_2$], 3.02 (s, $-OCH_3$), 7.00−7.73 (m), 8.16 (s, J = 2.7 Hz, H-6 of pyridyl), 8.31 (d, J = 1.2 Hz, H-2 of pyridyl); minor component 0.93−1.40 [m, $-B(CH_2CH_3)_2$], 3.04 (s, $-OCH_3$), 7.00−7.73 (m), 8.06 (d, J = 2.7 Hz, H-6 of pyridyl), 8.31 (d, J = 1.2 Hz, H-2 of pyridyl).

Vapor Pressure Osmometry Results. 3: 3.40 in benzene at 60 °C [benzil (2.0, 16.6, 71.4, 174.0 for 0.0011, 0.0107, 0.0408, 0.1000 mol L^{-1}, respectively), **3** (2.0, 6.1, 21.4, 52.5 for 0.0016, 0.0079, 0.039, 0.099 mol L^{-1}, respectively)]; 3.16 in acetone at 40 °C [benzil (9.3, 33.6, 64.6, 114.2 for 0.0052, 0.0197, 0.0398, 0.0703 mol L^{-1}, respectively), **3** (17.9, 31.4, 46.8, 73.6 for 0.0296, 0.0493, 0.0822, 0.137 mol L^{-1}, respectively)]; 2.57 in tetrahydrofuran at 45 °C [benzil (10.3, 17.5, 81.9, 158.8 for 0.005, 0.010, 0.050, 0.100 mol L^{-1}, respectively), **3** (14.9, 59.3, 94.2 for 0.0178, 0.0889, 0.148 mol L^{-1}, respectively)]; 1.52 in *N*,*N*-dimethylformamide at 90 °C [benzil (10.5, 23.9, 41.5, 92.3 for 0.0054, 0.0201, 0.0404, 0.1005 mol L^{-1}, respectively), **3** (17.4, 30.6, 47.4, 65.9 for 0.0231, 0.0386, 0.0644, 0.1073 mol L^{-1}, respectively)]; **4**: 2.16 in benzene at 60 °C [benzil (2.0, 16.6, 71.4, 174.0 for 0.0011, 0.0107, 0.0408, 0.1000 mol L^{-1}, respectively), **4** (1.7, 7.7, 33.9, 80.0 for 0.0016, 0.0078, 0.039, 0.098 mol L^{-1}, respectively)]; 1.58 in *N*,*N*-dimethylformamide at 90 °C [benzil (7.8, 23.1, 41.8, 99.7 for 0.0054, 0.0201, 0.0404, 0.1005 mol L^{-1}, respectively), **4** (20.7, 32.0, 49.1, 71.5 for 0.0230, 0.0383, 0.0638, 0.106 mol L^{-1}, respectively)].

Electrospray Mass Spectrometry. Electrospray ionization mass spectra of **1**, **3**, and **4** were recorded on an API 300 triple quadrupole LC/MS/MS mass spectrometer (Perkin-Elmer Sciex Instruments) with an *m*/*z* range of 1000. A sample solution was introduced to the spectrometer at a flow rate of 4 μL min^{-1} using a syringe pump (Harvard Apparatus). The electrospray probe capillary was maintained at a potential of −3.5 kV, and the orifice to the skimmer potential (cone voltage) was −60 V.

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