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BF_2 Complexes of β-Tetraethyl-Substituted Dipyrrolyldiketones as Anion Receptors: Potential Building Subunits for Oligomeric Systems

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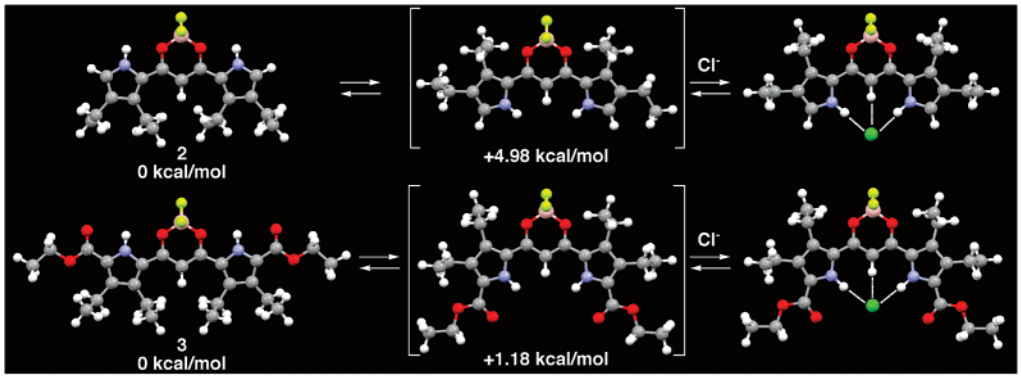

Synthesis and anion binding properties of BF_2 complexes of β-tetraethyl-substituted dipyrrolyldiketones, with and without electron-withdrawing ethoxycarbonyl moieties at pyrrole α-positions, are reported. The substituents at pyrrole rings of these acyclic anion receptors are found to play a key role to control not only the polarization of binding sites (NH and CH) but also the relative stabilities of the preorganized conformations and the degrees of sterical repulsion, both of which notably affect the affinities for anions.

Introduction

Recognition of inorganic and biotic anions such as halide, acetate, and phosphate, ubiquitous in biology, concerns essential aspects like the activity of enzymes, transport of hormones, protein synthesis, and DNA regulation.[1,2] Like natural ion channels, artificial *preorganized* cyclic systems can selectively and tightly associate with anions using cooperative interactions.[3] In contrast, receptors with linear geometry are required to fit with the volume and shape of negatively charged species as targets by conformational changes with significant loss of entropy. Therefore, in these cases, facility of temporal "preorganization" as well as induced effect to polarize association site(s) and sterical and electrostatic repulsion by the peripheral *substituents* would be an essential factor to determine the binding affinities for guest species.

Recently, we have reported a new class of acyclic anion receptors, BF_2 complexes of 1,3-dipyrrolyl-1,3-propanediones (e.g., **1a**−**c**, Figure 1),[4−6] which efficiently bind anions using

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(1) (a) *Supramolecular Chemistry of Anions*; Bianchi, A., Bowman-James, K., Gracía-España, E., Eds.; Wiley-VCH: New York, 1997. (b) *Fundamentals and Applications of Anion Separations*; Singh R. P., Moyer, B. A., Eds.; Kluwer Academic/Plenum Publishers: New York, 2004. (c) *Anion Sensing*; Stibor, I., Ed.; Springer-Verlag: Berlin, Germany, 2005. (d) Sessler, J. L.; Gale, P. A.; Cho, W.-S. *Anion Receptor Chemistry*; RSC: Cambridge, UK, 2006.

(2) (a) Schmidtchen, F. P.; Berger, M. *Chem. Rev.* **1997**, *97*, 1515. (b) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 487. (c) Martínez-Mãnez, R.; Sancenón, F. *Chem. Rev.* **2003**, *103*, 4419.

(3) (a) Gale, P. A.; Sessler, J. L.; Král, V. *Chem. Commun.* **1998**, 1. (b) Sessler, J. L.; Davis, J. *Acc. Chem. Res.* **2001**, *34*, 989.

(4) (a) Maeda, H.; Kusunose, Y. *Chem. Eur. J.* **2005**, *11*, 5661. (b) Fujimoto, C.; Kusunose, Y.; Maeda, H. *J. Org. Chem.* **2006**, *71*, 2389. (c) Maeda, H.; Ito, Y. *Inorg. Chem.* **2006**, *45*, 8205. (d) Maeda, H.; Ito, Y.; Kusunose, Y.; Nakanishi, T. *Chem. Commun.* **2007**, in press (DOI: 10.1039/b615787d). (e) Maeda, H.; Kusunose, Y.; Terasaki, M.; Ito, Y.; Fujimoto, C.; Fujii, R.; Nakanishi, T. *Chem. Asian J.* **2007**, *2*, 350.

(5) Oddo, B.; Dainotti, C. *Gazz. Chim. Ital.* **1912**, *42*, 716.

(6) Stark, W. M.; Baker, M. G.; Leeper, F. J.; Raithby, P. R.; Battersby, A. R. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1187.

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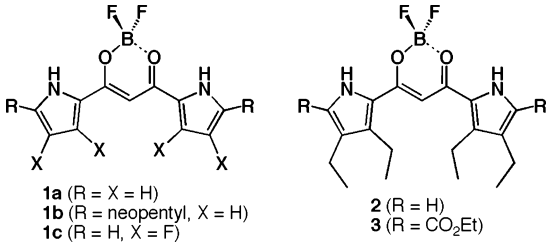

FIGURE 1. BF_2 complexes of dipyrrolyldiketones.

two pyrrole NH groups and bridging CH with the pyrrole rings' *inversion*. Unsubstituted receptor **1a** is less soluble in solvents such as CH_2Cl_2, so substituted receptor **1b** is required in order to investigate anion binding studies in solution.[4a] However, α-substituents, readily introduced to starting pyrrole by acylation and reduction, would prevent the reactions at α-positions to provide π-conjugated oligomers, whose structures could be modulated by anion binding. In contrast, β-fluorinated **1c**,[4c] with free but less reactive α-positions, may be one of the candidates as a subunit in such functional oligomeric systems. On the other hand, introduction of electron-donating alkyl chains in the system may highlight the molecular design of the acyclic π-conjugated oligomers as anion receptors. Herein, synthesis and anion binding properties of BF_2 complexes of β-tetraethyl-substituted dipyrrolylpropanediones (**2**, **3**) are reported. To our surprise, electron-donating and -withdrawing substituents at pyrrole rings of the receptors, possibly to determine the relative stability of preorganized conformation, do not always play a role as "inhibitors" and/or "enhancers" for anion binding, respectively.

Results and Discussion

Synthesis and Initial Characterization. BF_2 complex **2** was synthesized in 38% yield by condensation of β-diethylpyrrole[7] and malonyl chloride followed by treatment with $BF_3{\cdot}OEt_2$ in CH_2Cl_2. Ester-appended **3** was obtained in 19% yield by the similar procedure, using the ethoxycarbonyl-substituted derivative of β-diethylpyrrole as a starting material. The BF_2 complex **3** is the first example of the derivatives with directly linked carbonyl substituents, while introduction of C═O moieties like formyl groups at α-positions of **2** has not been achieved. Chemical identities of **2** and **3** were confirmed by ^{1}H NMR and FAB-MS analyses. UV/vis absorption spectra of **2** and **3** in CH_2Cl_2 show the λ_{max} at 452 and 464 nm, respectively, which are comparable to that of **1b** (457 nm) and red-shifted compared to unsubstituted **1a** (432 nm) and β-fluorinated **1c** (421 nm). The red-shift (12 nm) of **3** compared to **2** is derived from the π-conjugated carbonyl moieties directly attached to pyrrole rings.

Further, the structure of ester-substituted **3** has been elucidated by X-ray single-crystal diffraction analysis (see also the Supporting Information). Like **1a**−**c**, two pyrrole NH groups face the oxygen side possibly due to intramolecular N−H···O hydrogen bonding. In the solid state, crinkled supramolecular assembly with ditopic hydrogen bonding between N−H and O═C (the distances of N(−H)···O: 2.980 and 2.924 Å) is observed (Figure 2),[8] while the BF_2 complexes without ester units at pyrrole rings, like **1a**−**c**, have shown the rather weak association N−H···F−B.[4a−c] The intermolecular dihedral angle between two neighboring planes (consisting of 16 atoms) is estimated to be 37.2°.

Anion Binding Properties. Next, anion binding properties of **2** and **3** were examined by UV/vis absorption spectral changes upon the addition of anions as tetrabutylammonium salts in CH_2Cl_2. In the case of **2**, a modest shift of absorption maximum from 450 to 452 nm was observed by Cl^- binding. Binding constants (K_a) of **2** are estimated to be, for example, 6 800, 210 000, and 91 000 M^{-1} for Cl^-, $CH_3CO_2^-$, and $H_2PO_4^-$, respectively, which are larger than those of α-neopentyl-substituted **1b** (Table 1). However, the receptor **2** shows the suppressed affinity (42 000 M^{-1}) for smaller F^-, which can be associated with only one NH site,[4b] less polarized due to electron-donating ethyl substituents. In spite of more electron-donating alkyl groups, except for F^-, such augmented anion binding affinities are unexpected and of interest. Binding stoichiometry (1:1) was determined by Job plots of **2** and F^-. In sharp contrast, the Cl^- binding constant of ester-appended **3** is 170 M^{-1}, less than **2** and **1b**, as seen in other anions such as Br^- and $CH_3CO_2^-$. K_a of **3** for F^- is slightly larger than that of **2** due to the more polarized NH site by the ester unit. Here, electron-withdrawing α-substituents such as carbonyl moieties play a role as electrostatic and sterical hindrance, not as an "enhancer" to polarize pyrrole NH as seen in β-fluorinated **1c**.

Anion binding behavior of **2** (5.4×10^{-3} M) was also investigated by ^{1}H NMR at room temperature and at −50 °C upon the addition of Cl^- as a tetrabutylammonium salt. By Cl^- binding (1.6 equiv), the chemical shifts of pyrrole NH and bridging CH at 9.33 and 6.46 ppm were shifted to 11.87 and 8.01 ppm at room temperature in CD_2Cl_2, respectively. The signals derived from receptor (**2**) and complex disappeared by addition of 0.8 equiv of anion at room temperature, suggesting the equilibrium between these species is rather fast in the NMR time scale compared to **1b**,**c**, showing the independent signals.[4a,c] In the case of ester-substituted **3** (5.3×10^{-3} M), the NH and bridging CH signals of anion-free and Cl^- complex are coalesced to a single set of resonances at room temperature, at which the chemical shifts at 9.86 (NH) and 6.69 (CH) ppm were broadened and gradually shifted to 12.26 and 8.75 ppm, respectively, upon the addition of 10 equiv of anion. In both cases (**2** and **3**), the corresponding signals, those of receptor and complex, are independently observed at −50 °C. Various-temperature ^{1}H NMR measurements of **2** (5.8×10^{-3} M) with 0.55 equiv of Cl^- in CD_2Cl_2 gave the coalescence temperature at ca. 30 °C, which are higher than that of **3** (0 °C) with 1.4 equiv of Cl^-. Here, determination of kinetic parameters was not easy from NMR signals due to the association equilibrium of two species, receptor and anion, with the adequate ratios according the respective K_a values. However, the results of **2** and **3**, as well as those of **1b**,**c**, infer that the energy barriers of the anion binding process with pyrrole rings' inversions could not be correlated with the binding constants.

Factors To Determine the Affinities for Anions. The above "unexpected" anion binding observations, (i) augmentation of β-*tetra*alkylated **2** compared to α-*bis*alkylated **1b** in spite of

(7) Sessler, J. L.; Mozaffari, A.; Johnson, M. R. *Org. Synth.* **1992**, *70*, 68.

(8) Sessler, J. L.; Berthon-Gelloz, G.; Gale, P. A.; Camiolo, S.; Anslyn, E. V.; Anzenbacher, P., Jr.; Furuta, H.; Kirkovits, G. J.; Lynch, V. M.; Maeda, H.; Morosini, P.; Scherer, M.; Shriver, J.; Zimmerman, R. S. *Polyhedron* **2003**, *22*, 2963.

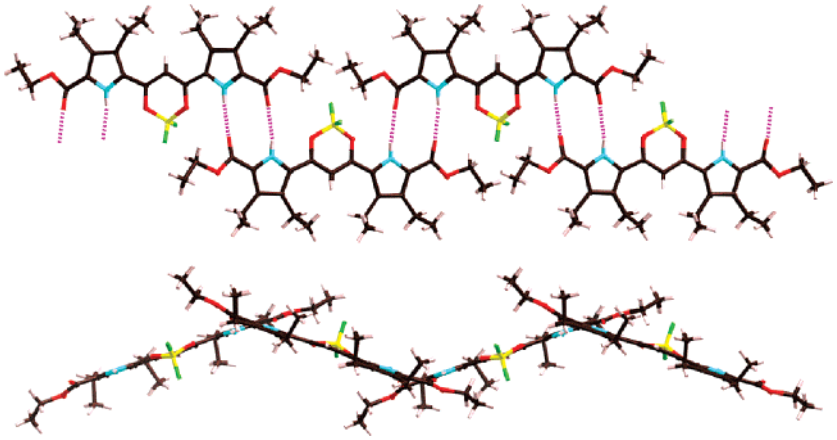

FIGURE 2. Hydrogen bonding assembly of **3** in the solid state (top and side view). Atom color code: brown, pink, yellow, green, blue, and red infer carbon, hydrogen, boron, fluorine, nitrogen, and oxygen, respectively.

TABLE 1. Anion Binding Constants (K_a, M^{-1}) of 2, 3 and 1b,c as References upon the Addition of Anions as Tetrabutylammomium Salts in CH_2Cl_2[a]

anion	K_a(**2**)	K_a(**3**)	K_a(**1b**)	K_a(**1c**)[c]
F^-	42 000 (0.52)	62 000 (0.77)	81 000[b]	160,000[d] (2.0)
Cl^-	6800 (3.4)	170 (0.09)	2000[b]	26 ,000 (13)
Br^-	1200 (3.6)	20 (0.06)	330[b]	1700 (5.2)
$CH_3CO_2^-$	210 000 (1.9)	9100 (0.08)	110 000[c]	960 000 (8.7)
$H_2PO_4^-$	91 000 (7.0)	29 000 (2.2)	13 000[b]	190 000 (15)
HSO_4^-	1200 (15)	490 (6.1)	80[b]	1100 (14)

[a] The values in parentheses are the ratios to K_a of **1b**. [b] Reference 4a. [c] Reference 4c. [d] For 1:1 binding.

more electron-donating groups and (ii) suppression of ester-substituted **3** compared to **2** in spite of more electron-withdrawing moieties, should be further explained by other methods such as DFT calculations at the B3LYP/6-31G(d,p) level.[9] This means that anion binding behaviors of these acyclic receptors cannot always be correlated with the electronic effects of the peripheral substituents. Molecular simulations for the receptors **1a**,**c** so far reported[4a,c] have suggested that the most stable conformations of the free receptors, with intramolecular interactions between pyrrole NH and oxygens, are not suitable for anion recognition and, therefore, the pyrrole inversions are required to bind anions. The ratios of the "preorganized" structures, facing their two NH on the same side of bridging CH, are too small to be detected in solution, so theoretical study of such less stable structures *ideal* for anion binding is crucial.

In Figure 3, two optimized conformations of **2**, **3**, and **1b** as well as their Cl^- complexes are illustrated. To explain issue i, the calculated relative energy of **2-B**, with two *inverted* pyrrole rings, to **2-A** is 4.98 kcal/mol, which is about half of that between **1b-A** and **1b-B** (8.93 kcal/mol). This means that the preorganized geometry of **2** (**2-B**) is rather preferable to bind anions more efficiently than **1b**. In addition, the less sterically binding pocket of **2** due to substituent-free α-positions may be the essential factor. However, a theoretical study of **3** also gives a similar tendency: the inverted structure of **3** (**3-B**) is only 1.18 kcal/mol less stable than the normal one (**3-A**), which may exclude issue ii. Here, the ester-substituted **3** has shown binding constants (K_a) *smaller* than those of **2** and comparable to those of **1b**, possibly because of the electrostatic repulsion between carbonyl oxygens and anions as well as the steric effect and intramolecular interaction between ester CO and pyrrole NH, which may cancel the positive factor speculated by DFT. Similar *compensation* has been observed in *β*-fluorinated **1c**, which has polarized NH by electron-withdrawing groups but no favorable preorganized conformation (ca. 15 kcal/mol less stable than normal one) estimated by calculations.[4c]

Fluorescence Controlled by Anions. Like **1b**,**c**,[4a,c] BF_2 complexes **2** and **3** exhibit fluorescence emission at 471 and 480 nm, respectively, by excitation at 420 and 411 nm. Upon the addition of anions, emission of **2** is almost quenched by F^- and modestly suppressed by oxoanions ($CH_3CO_2^-$, $H_2PO_4^-$, HSO_4^-), possibly due to the intramolecular electron-transfer process. In contrast, binding with Cl^- and Br^-, which may be weakly associated at pyrrole NH compared to F^-, hardly affects the intensity of fluorescence. The quantum yield of **2** in CH_2Cl_2 is almost quantitative and estimated to be 0.98, which is comparable to that of **1b** (0.98) and much higher than that of **1c** (0.26). Such high efficiency of these anion receptors would be useful for anion sensing in the case of potential higher homologues. A similar trend was observed in the fluorescent emission studies of **3** in CH_2Cl_2.

Summary

In summary, we have synthesized the BF_2 complex of *β*-tetraethyl-substituted dipyrrolylpropanedione, showing the higher anion binding affinity than the α-bisalkyl-derivative possibly due to the relatively stable inverted conformation. In

(9) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, (Revision C.01); Gaussian, Inc.: Wallingford, CT, 2004.

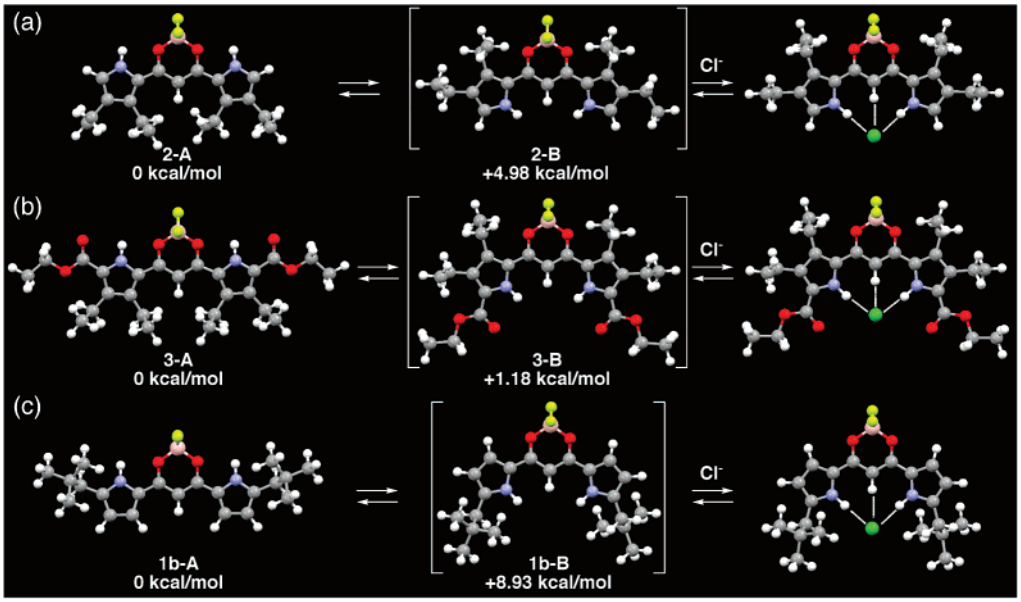

FIGURE 3. Optimized structures and proposed anion (Cl^-) binding mode of (a) β-tetraethyl-**2**, (b) **3**, and (c) α-neopentyl-substituted derivative **1b**.

sharp contrast, a smaller K_a of the α-ester-substituted derivative is derived from the electrostatic and steric repulsions with anions. Further modification, such as borylation,[10,11] of the diketone of the precursor of **2** at the α-position(s) would drive us to form oligomeric systems by coupling reactions. Syntheses of higher homologues and further investigations are now in progress.

Experimental Section

General Procedures. The ^{1}H NMR spectra were recorded at 600 MHz, while ^{13}C NMR spectra were recorded at 151 MHz. All NMR spectra were referenced to solvent. Purification of reaction products was carried out by silica gel chromatography. Commercial grade reagents and solvents were used without further purification unless otherwise stated.

BF_2 Complex of 1,3-Bis(3′,4′-diethylpyrrol-2′-yl)-1,3-propanedione, 2. In analogy to a literature procedure,[4−6] a CH_2Cl_2 solution (200 mL) of 3,4-diethylpyrrole[7] (1.24 g, 10.0 mmol) was treated with malonyl chloride (705 mg, 5.0 mmol) at 0 °C and stirred for 1 h at the same temperature. After confirming the consumption of the starting pyrrole by TLC analysis, the mixture was washed with saturated Na_2CO_3 aq and water, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was then chromatographed over flash silica gel column chromatography (eluent: 2%MeOH/CH_2Cl_2) and recrystallized from CH_2Cl_2/hexane to afford diketone (750 mg, 48%) as a pale yellow solid. R_f 0.67 (3%MeOH/CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C; diketone is obtained as a mixture of keto and enol tautomers in the ratio of 1:0.66): δ (ppm) keto form 9.73 (s, br, 2H, NH), 6.79 (d, J = 3.0 Hz, 2H, pyrrole-H), 4.20 (s, 2H, keto-CH_2), 2.81 (s, J = 7.2 Hz, 4H, CH_2), 2.44 (s, J = 7.8 Hz, 4H, CH_2), 1.17 (t, J = 7.8 Hz, 6H, CH_3), 1.14 (t, J = 7.8 Hz, 6H, CH_3); enol form 17.53 (s, 1H, enol-OH), 9.04 (s, br, 2H, NH), 6.77 (d, J = 3.0 Hz, 2H, pyrrole-H), 6.28 (s, 1H, enol-CH), 2.79 (q, J = 7.8 Hz, 4H, CH_2), 2.48 (q, J = 7.8 Hz, 4H, CH_2), 1.25 (t, J = 7.8 Hz, 6H, CH_3), 1.21 (t, J = 7.8 Hz, 6H, CH_3). FABMS: m/z (% intensity) 314.3 (100, M^+), calcd for $C_{19}H_{26}N_2O_2$ 314.20. This compound was further characterized by X-ray diffraction analysis.[4e] To a CH_2Cl_2 solution (100 mL) of diketone (300 mg, 0.95 mmol) was addedBF_3·OEt_2 (2.3 mL, 19 mmol) with stirring for 15 min at room temperature. After removal of the solvent, silica gel column chromatography (Wakogel C-300, eluent: 1%MeOH/CH_2Cl_2) and crystallization from CH_2Cl_2/hexane afforded **2** (302 mg, 80%) as a yellow solid. R_f 0.55 (3%MeOH/CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 9.31 (br, 2H, NH), 6.94 (d, J = 3.0 Hz, 2H, pyrrole-H), 6.48 (s, 1H, CH), 2.78 (q, J = 7.8 Hz, 4H, CH_2), 2.48 (q, J = 7.8 Hz, 4H, CH_2), 1.25 (t, J = 7.8 Hz, 6H, CH_3), 1.21 (t, J = 7.8 Hz, 6H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$, 20 °C) δ (ppm) 168.0, 135.0, 129.4, 124.0, 123.1, 90.3, 19.0, 17.8, 15.0, 14.7. UV/vis (CH_2Cl_2, λ_{max}[nm] (ϵ, 10^5 M^{-1} cm^{-1})): 452.0 (1.2). FABMS: m/z (% intensity) 362.2 (100, M^+), calcd for $C_{19}H_{25}BF_2N_2O_2$ 362.20.

BF_2 Complex of 1,3-Bis(5′-ethoxycarbonyl-3′,4′-diethylpyrrol-2′-yl)-1,3-propanedione, 3. A CH_2Cl_2 solution (40 mL) of ethyl 3,4-diethylpyrrole-2-carboxylate (780 mg, 4.0 mmol) was added to the mixture of malonyl chloride (282 mg, 2.0 mmol) and BF_3·OEt_2 (0.75 mL, 6.0 mmol) in CH_2Cl_2 solution (120 mL) at room temperature with stirring at reflux temperature for 20 h at the same temperature. After removal of the solvent, flash silica gel column chromatography (eluent: CH_2Cl_2) and crystallization from CH_2Cl_2/hexane afforded **3** (191 mg, 19%) as a yellow solid. R_f 0.22 (CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 9.85 (br, 2H, NH), 6.69 (s, 1H, CH), 4.41 (q, J = 7.2 Hz, 4H, CH_2), 2.79 (m, 8H, CH_2), 1.42 (t, J = 7.2 Hz, 6H, CH_3), 1.28 (t, J = 7.8 Hz, 6H, CH_3), 1.16 (t, J = 7.8 Hz, 6H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$, 20 °C): δ (ppm) 169.8, 159.8, 135.8, 134.6, 125.3, 124.4, 93.6, 61.2, 18.7, 17.6, 15.6, 15.5, 14.4. UV/vis (CH_2Cl_2, λ_{max}[nm] (ϵ, 10^5 M^{-1} cm^{-1})): 464.0 (1.3). FABMS: m/z (% intensity) 506.2 (100, M^+), calcd for $C_{25}H_{33}BF_2N_2O_2$ 506.24. This compound was further characterized by X-ray diffraction analysis.

Fluorescence Quantum Yields. Fluorescence emission and excitation spectra were recorded on a PTI QM4-2003 fluorescence spectrometer and are corrected against photomultiplier and lamp intensity. A long wavelength range emission corrected photomultiplier R928 was used. The given quantum yields are averaged from

(10) (a) Ishiyama, T.; Miyaura, N. *J. Organomet. Chem.* **2003**, *680*, 3. (b) Ishiyama, T.; Takagi, J.; Yonekawa, Y.; Hartwig, H, F.; Miyaura, N. *Adv. Synth. Catal.* **2003**, *345*, 1103. (c) Ishiyama, T.; Miyaura, N. *Pure Appl. Chem.* **2006**, *78*, 1369.

(11) (a) Hata, H.; Shinokubo, H.; Osuka, A. *J. Am. Chem. Soc.* **2005**, *127*, 8264. (b) Hiroto, S.; Hisaki, I.; Shinokubo, H.; Osuka, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 6763.

values measured at three different excitation wavelengths with OD 0.02−0.05 in the absorption maximum.

Method for X-ray Analysis. A single crystal of **3** was obtained by vapor diffusion of hexane into a $CHCl_3$ solution. The data crystal was an orange prism of approximate dimensions 0.55 × 0.30 × 0.15 mm^3. Data were collected at 123 K on a Rigaku RAXIS-RAPID diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71075 Å), and structure was solved by direct method. The non-hydrogen atoms were refined anisotropically. The calculations were performed with use of the Crystal Structure crystallographic software package of Molecular Structure Corporation. A CIF file (CCDC-625998) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Methods. Ab initio calculations of **1b**, **2**, **3**, and F^- and Cl^- binding complexes were carried out with the Gaussian 03 program[9] and an HP Compaq dc5100 SFF computer. The structures were optimized, and the total electronic energies were calculated at the B3LYP level, using a 6-31G** basis set.

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Supporting Information Available: Spectroscopic data, optimized structures, ^1H NMR, UV/vis absorption, fluorescence spectral changes by anion binding of dipyrrolyldiketone derivatives, and a CIF file for the X-ray structural analysis of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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