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CH···Anion Interaction in BF_2 Complexes of C_3-Bridged Oligopyrroles

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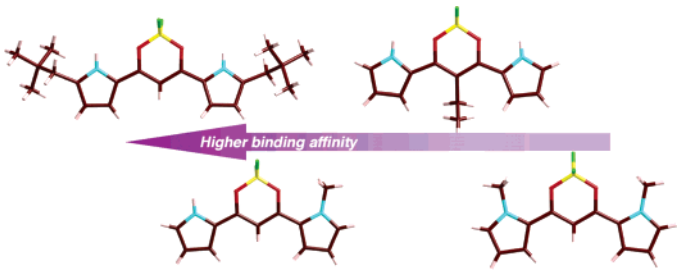

Alkyl-substituted derivatives of 1,3-dipyrrolyl-1,3-propanedione BF_2 complexes, the efficient receptors for halide and oxoanions with use of bridging CH as well as pyrrole NH, are reported. BF_2 complexes with only one pyrrole NH interaction site (**2d**,**e**), which exhibit smaller affinities than the basic structure (**2b**), bind anions tightly, which is inferred by UV/vis absorption spectral changes, compared to the derivatives with an alkyl group at the bridging carbon (**2f**) or two pyrrole nitrogen sites (**2c**). With use of ^{1}H NMR and theoretical studies for anion complexes of **2d** and **2e**, bridging CH (and one β-CH in **2d**) as well as pyrrole NH is found to interact with anions.

Introduction

Among the versatile artificial anion binding receptors,[1] cyclic oligopyrroles such as diprotonated sapphyrins[2] and calixpyrroles[3] show an efficient complexation for F^-, using multiple NH sites. However, there are few examples of acyclic oligopyrroles, such as seen in amidopyrroles[4] and dipyrrolylquinoxalines.[5] Recently, we reported a new class of naked-eye anion sensors, BF_2 complexes (**2a**,**b**) of 1,3-dipyrrolyl-1,3-propanediones (**1a**,**b**), which efficiently bind anions such as halides (F^-, Cl^-, and Br^-) and oxoanions ($H_2PO_4^-$ and HSO_4^-) using two pyrrole NH units and a bridging CH (Figure 1a). *Ring inversion* of pyrroles from the stable geometries was found essential to capturing anions, using these binding sites (Figure 1b). Upon the addition of F^-, the fluorescence of BF_2 complex, rather soluble **2b**, was quenched, and in the case of Cl^-, on the other hand, emission was not completely suppressed. In the solid state, unsubstituted **2a** forms a chloride-bridged 1-D network with N−H···Cl^- and C−H···Cl^- interactions.[6]

Furthermore, totally N-"blocked" derivative **2c** has not exhibited the F^- binding in CH_2Cl_2, which indicated the bridging CH moiety, less polarized than NH, in this acyclic system has not been able to associate with the anion in solution, and also suggested that the NH moieties as the interaction sites are more *essential* to associate with anion than bridging CH.[6] In this new class of anion binding system, when *one* NH site is available for association, which of the interaction sites, the other NH or bridging CH, is more important as a supporting role for an efficient binding? To answer this question, the substituent effect at the NH or the bridging CH site is investigated in detail. If there are no differences in binding affinities of N- and C-substituted derivatives, the positive or negative effect of

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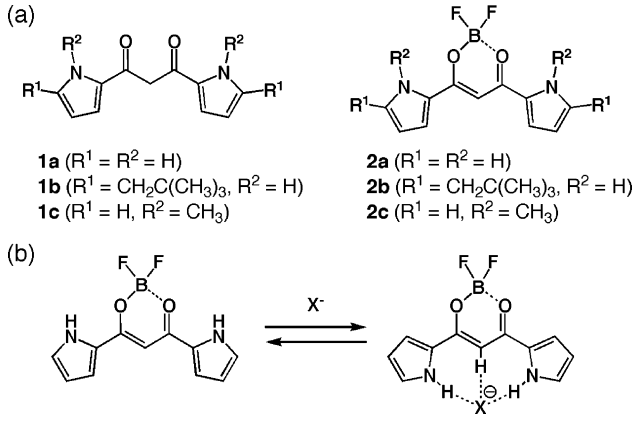


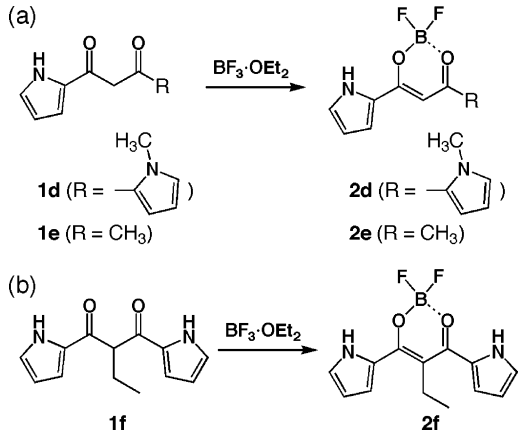
FIGURE 1. (a) Structures of 1,3-dipyrrolyl-1,3-propanediones (**1a**−**c**) and BF_2 complexes (**2a**−**c**) and (b) possible anion binding mode of **2a**.

C−H···anion interaction can be neglected. Here, we report the synthesis and anion binding properties of the derivatives, in which some of the association sites are blocked by an alkyl group or one of the pyrrole rings is removed. In these derivatives, substitutions at pyrrole N and bridging C interfere with the anion binding and the CH site is found to act in a key role to *assist* NH unit(s) to form anion complexes.[4c,7−9] The partially "blocked" receptors also afford the exact anion binding mode, using CH in solution.

Results and Discussion

Synthesis and Characterization. The partially N-"blocked" diketone derivative **1d** was synthesized in 24% from malonyl chloride and a 1:1 mixture of pyrrole and *N*-methylpyrrole.[6,10] BF_2 complexation of diketone **1d** into **2d** was performed in 43% yield by treating with an excess of BF_3·OEt_2 in CH_2Cl_2 (Scheme 1a). The derivative with only one pyrrole, **1e**, was obtained from the reported procedures,[11] also transformed into BF_2 complex **2e** in 88%. Alkyl-substituted diketone **1f**, C-"blocked" diketone, which has an ethyl group at the bridging carbon between two carbonyl moieties, was also synthesized in 7% by condensation of pyrrole and ethyl-substituted malonyl chloride. Further, **1f** was complexed with the BF_2 unit in 74% to afford **2f** under a similar method for **2d,e** (Scheme 1b). Structural determinations of BF_2 complexes **2d**−**f** were performed by ^{1}H NMR and MS analyses.

SCHEME 1. Synthesis of BF_2 Complexes 2d−f from Dipyrrolyldiketones 1d−f



Exact conformations and self-assemblies of the BF_2 complexes **2d**−**f** were revealed by X-ray single-crystal structural analyses (Figure 2a−c). Similar to the BF_2 complexes **2a**−**c** (Figure 2d,e),[6] each pyrrole N of **2d**−**f** points to the carbonyl oxygen side possibly due to intramolecular N−H···O interaction. Both derivatives **2d**,**e**, with one NH site, form a supramolecular network with intermolecular N−H···F(−B) interactions (2.864 and 2.820 Å, respectively). Furthermore, weak association between bridging CH and F(−B) was also observed: 3.287 and 3.343 Å for **2d** and 3.380 and 3.447 Å for **2e**. These short atom distances, within the sum of the van der Waals radii between carbon-hydrogen and fluorine, were also observed in the solid-state structure of **2c**, which fabricate the 1-D chain supramolecular assembly. In the case of C-ethyl-substituted **2f**, on the other hand, only N−H···F(−B) intermolecular interactions (2.890 and 2.844 Å) were observed. These weak interactions were not detected in the solution phase to demonstrate the potential anion binding properties of NH as well as bridging CH.

Anion Binding Properties. Anion binding properties of N-"blocked" (**2d**,**e**) and C-"blocked" derivative **2f** were elucidated by UV/vis absorption spectral changes in CH_2Cl_2 upon the addition of various anions. In the case of F^- binding of **2d**, the absorption maximum at 435 nm was decreased gradually, while a new shoulder around 470 nm emerged (Figure 3a). Similarly, the absorption of **2e** at 370 nm disappeared with the appearance of the band at 383 nm and shoulder around 400 nm (Figure 3b). In **2f**, upon the addition of F^-, λ_{max} at 443 nm declined with the new shoulder around 480 nm. In these cases, isosbestic points were observed at 384 and 445 nm for **2d**, 322 and 377 nm for **2e**, and 406 and 454 nm for **2f**, respectively. Spectral changes of **2d**−**f** by other anions such as Cl^- and $H_2PO_4^-$ were also observed except for the Cl^- complexation of **2f**.

According to the reported procedures,[6] binding constants (K_a, M^{-1}) were estimated by the 1:1 curve fitting for spectral changes (Table 1). Binding stoichiometry (1:1) was confirmed by Job plots, using **2d** and F^- in dry CH_2Cl_2. Affinity orders, $F^- > H_2PO_4^- > Cl^-$, are matched with that of unprotected **2b**.[6] The association constant of **2d** for F^- is comparable (ca. 1/2 times) to that of **2b**, while Cl^- and $H_2PO_4^-$ are ca. 1/10 folds smaller

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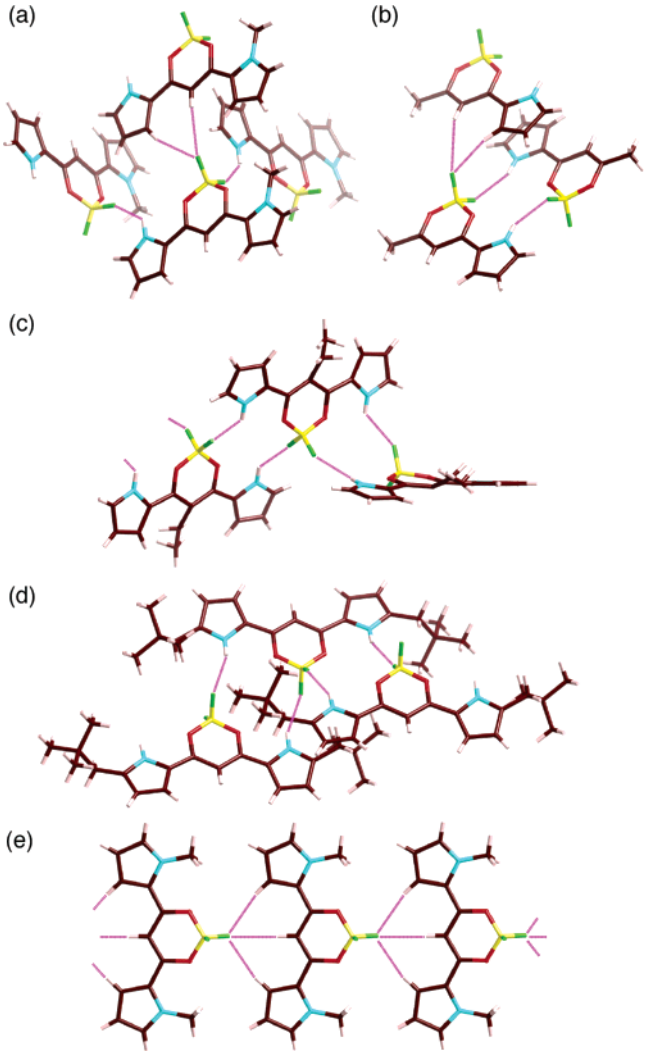

FIGURE 2. Self-assembled structures of BF_2 complexes: (a) **2d**, (b) **2e**, (c) **2f**, (d) **2b**, and (e) **2c**.[6] Atom color code: brown, pink, blue, red, yellow, and green refer to carbon, hydrogen, nitrogen, oxygen, boron, and fluorine, respectively. One of the disordered ethyl substituents is represented in part c.

values than **2b**. A similar trend was observed in **2e**. On the other hand, C-"blocked" derivative **2f** exhibited comparable affinity for F^- and much less K_a for Cl^- and $H_2PO_4^-$ than **2d**,**e**.

TABLE 1. Binding Constants (K_a, M^{-1}) of BF_2 Complexes (2b, 2d−f) for Anions upon the Addition of Tetrabutylammonium Salts in CH_2Cl_2[a]

	2b	2d	2e	2f
F^-	100 000[b]	42 000[b] (0.42)	25 000[b] (0.25)	34 000[b] (0.34)
Cl^-	2 000[c]	240 (0.12)	160 (0.08)	<10 (−)
$H_2PO_4^-$	13 000[c]	1 400 (0.11)	3 200 (0.25)	250 (0.02)

[a] The values in the parentheses are the ratio to K_a of **2b** for each anion. [b] For F^- binding, dry CH_2Cl_2 was used because K_a was drastically affected by the amount of water in solution compared to other anions. [c] Reference 6.

The above observations suggested that only one or two binding sites are efficient for the small anion F^-, while larger anions such as Cl^- and $H_2PO_4^-$ *need a multiple number of interaction NH and CH units*. In addition, the higher association constants in **2b** also confirm the binding mode proposed in Figure 1b.

The anion binding mode was confirmed by NMR study upon the addition of anions as tetrabutylammonium salts to $CDCl_3$ at −50 °C. Before the addition of anions, NH and bridging CH signals of N-blocked derivatives were resonated at 9.49 and 6.54 ppm for **2d** and 9.65 and 6.24 ppm for **2e**, respectively. Upon the addition of the Cl^- anion (11 and 4 equiv for **2d** and **2e**), these signals disappeared and new resonances appeared at 13.38 and 7.97 ppm for **2d** (ca. 1.5×10^{-3} M, Figure 4) and 13.53 and 7.37 ppm for **2e** (ca. 1×10^{-2} M), respectively. In the case of the F^- anion (6.7 and 4.7 equiv), similar signals resonated at 17.14 and 7.96 ppm for **2d** and 17.89 and 7.48 ppm for **2e**, respectively. Compared to Cl^-, F^- can attract the more polarized NH and shift the signal downfield with $\Delta\delta$ values (the shift differences between before and after addition of the anions) of, for example, 7.65 ppm for F^- and 3.89 ppm for Cl^- in **2d**. In contrast, CH resonates in a similar downfield with $\Delta\delta$ values of 1.42 ppm for F^- and 1.43 ppm for Cl^- in **2d**. In addition, one of the β-CH protons at 7.21 ppm was also shifted to 7.60 and 8.05 ppm by F^- and Cl^- binding, respectively. Such downfield shifts infer the weak interaction between the anion and the β-CH site as well. Assignment of the bridging CH and β-CH was achieved by $^1H-^1H$ COSY.[12] On the other hand, in the case of C-blocked **2f** (ca. 3×10^{-3} M), the resonance ascribable to NH was completely eliminated by F^- (9 equiv) and a new peak did not emerge even at −50 °C, and, in contrast, Cl^- complexation of **2f** was not observed. These spectroscopic data infer the anion binding modes, both

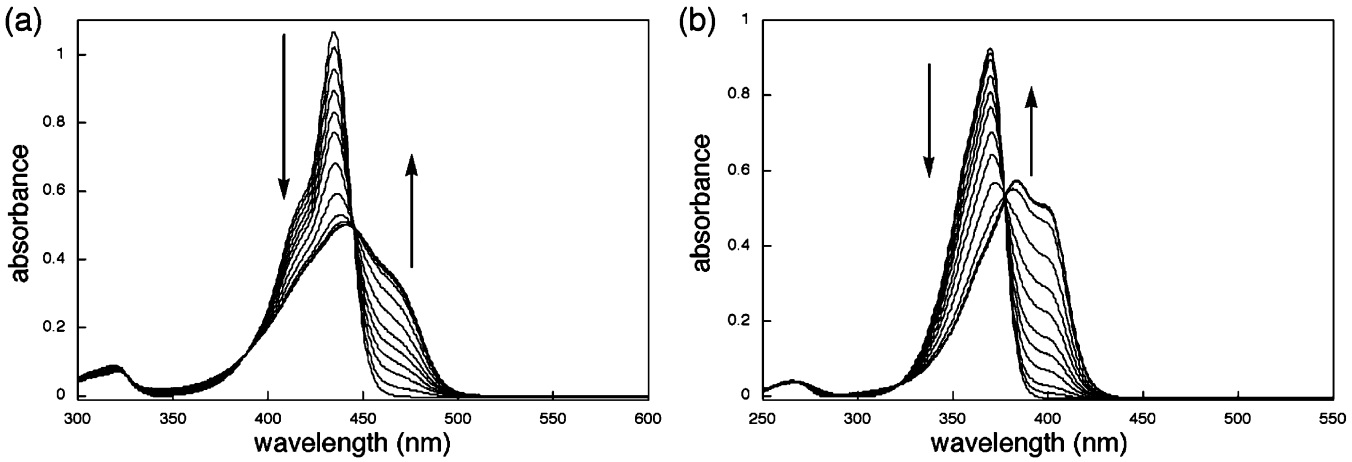

FIGURE 3. UV/vis absorption spectral changes of (a) **2d** (1.5×10^{-5} M) and (b) **2e** (1.5×10^{-5} M) in CH_2Cl_2 upon the addition of F^- (0−4.3 and 0−5.0 equiv, respectively).

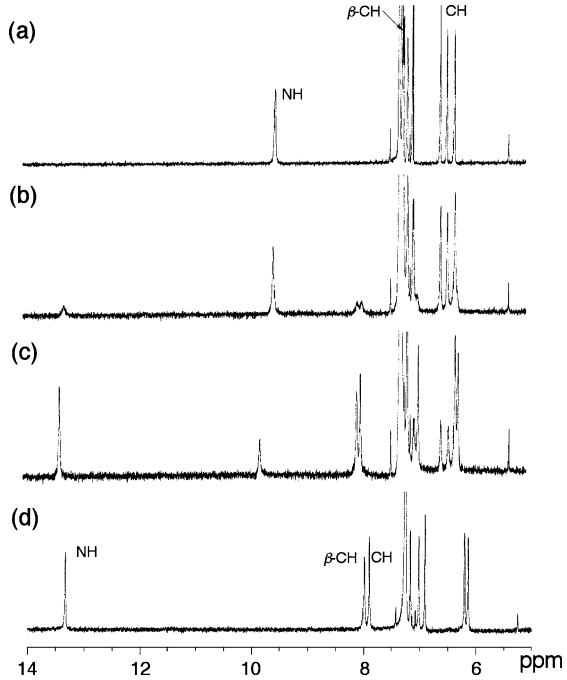

FIGURE 4. ^{1}H NMR spectral changes upon the addition Cl^- as a tetrabutylammonium salt to the $CDCl_3$ solutions of **2d** (1.6×10^{-3} M) at −50 °C: (a) 0, (b) 0.7, (c) 4.7, and (d) 100 equiv of Cl^-.

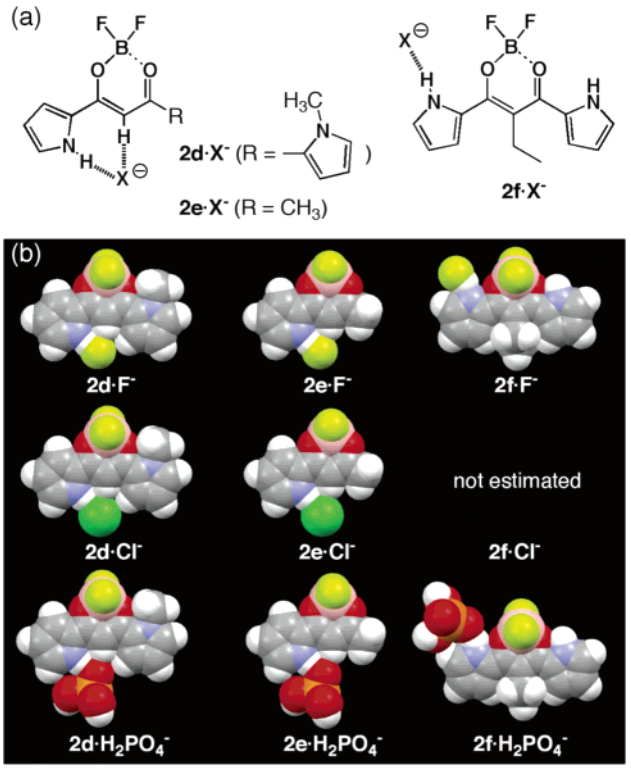

FIGURE 5. (a) Schematic representation and (b) optimized structures of possible anion binding modes of **2d**, **2e**, and **2f** at the B3LYP/6-31G** level.

NH and CH interaction in **2d**,**e** and only NH interaction in **2f**, represented in Figure 5a.

DFT calculations at the B3LYP/6-31G** level suggest the optimized geometries of anion complexes.[13] In the case of **2d**·X^- and **2e**·X^-, one pyrrole ring, whose NH orients to the oxygen side in the anion-free optimized structures, is inverted to capture the anion and make a complex (Figure 5b). The estimated atom distance between association sites and anions is 2.524 and 2.526 (N−H···F^-)[14] and 3.088 and 3.158 Å (C−H···F^-) for **2d** and **2e**, respectively. The Cl^- anion also locates near the binding sites of these receptors (**2d**,**e**) at 3.087 and 3.045 (N−H···Cl^-) and 3.570 and 3.594 Å (C−H···Cl^-), respectively, suggesting that, in the optimized structures of **2d**,**e**, anions are captured and shifted to the NH side, in contrast to the "centered" location in the theoretical results of **2a**.[6] Similarly, the complexes with an oxoanion such as $H_2PO_4^-$ are optimized with the distances of 2.720 and 2.659 (N−H···O) and 3.161 and 3.221 Å (C−H···O) for **2d** and **2e**, respectively. Atom distances between anions and the neighboring β-CH of **2d** are estimated as 3.684 (C−H···F^-), 3.853 (C−H···Cl^-), and 3.670 (C−H···O of $H_2PO_4^-$) Å, respectively. In solution, anions associate with CH as a weak interaction site, which augments the association constants for Cl^- and $H_2PO_4^-$ as compared to **2f**. On the other hand, a single pyrrole NH unit is more than enough for F^-, as seen in the similar K_a values among **2d**−**f**. The optimized structures of **2f** locate anions only at the NH site with the distance of 2.540 (N−H···F^-)[14] and 2.616 Å (N−H···O in $H_2PO_4^-$ complex) and show no pyrrole inversion.

Conclusions

In conclusion, BF_2 complexes of alkyl-substituted dipyrrolyldiketones have exhibited the essential role of the CH site for anion binding. The CH site cannot behave as an association unit by itself, and it *assists* the complexation between more polarized NH and anions, especially Cl^- and $H_2PO_4^-$. On the basis of the unique properties seen in C−H···X^- interaction, further investigation to fabricate functional anion receptors of dipyrrolyldiketones is currently going on in our group.

Experimental Section

1-(1′-Methylpyrrol-2′-yl)-3-(pyrrol-2′-yl)-1,3-propanedione, 1d. To a solution of pyrrole (0.509 g, 7.59 mmol) and 1-methylpyrrole (0.333 g, 4.11 mmol) in 80 mL of CH_2Cl_2 was added malonyl

(12) Larger Cl^- (effective ionic radius: 1.81 Å) can be associated with β-CH than F^- (1.33 Å). For the ionic radii, see: Shannon, R. D. *Acta Crystallogr. A* **1976**, *32*, 751.

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(14) (a) F^- associates with NH without removal of proton from the pyrrole ring due to the concerted downfield shifts of bridging CH and β-CH upon the addition of anion. Theoretical studies on F^- binding of **2d**−**f**, however, infer the more stable complexes of deprotonated form and HF. Such deprotonation of pyrrolic NH by halide anion and the formation of an ion pair complex was previously reported; see: (b) Camiolo, S.; Gale, P. A.; Hursthouse, M. B.; Light, M. E.; Shi, A. J. *Chem. Commun.* **2002**, 758. (c) Gale, P. A.; Navakhun, K.; Camiolo, S.; Light, M. E.; Hursthouse, M. B. *J. Am. Chem. Soc.* **2002**, *124*, 11228. (d) Gómez, D. E.; Fabbrizzi, L.; Licchelli, M.; Monzani, E. *Org. Biomol. Chem.* **2005**, *3*, 1495.

TABLE 2. Crystallographic Details for 2b,d−f

parameter	2b	2d	2e	2f
empirical formula	$C_{21}H_{29}BF_2N_2O_2$	$C_{12}H_{11}BF_2N_2O_2$	$C_8H_8BF_2NO_2$	$C_{13}H_{13}BF_2N_2O_2$
MW	390.27	264.04	198.96	278.06
space group (no.)	*Pbcn* (no. 60)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
a, Å	18.193(5)	7.2512(15)	8.4650(11)	13.2822(17)
b, Å	11.808(3)	10.180(2)	15.953(2)	10.0025(13)
c, Å	9.980(3)	15.873(3)	7.1898(10)	19.084(2)
β, deg	90	91.287(4)	112.498(2)	93.460(2)
V, Å^3	2143.9(10)	1171.4(4)	897.0(2)	2530.7(6)
T, °C	90(2)	90(2)	90(2)	90(2)
Z	8	4	4	8
D_{calcd}, g cm^{-3}	1.209	1.497	1.473	1.460
crystal size, mm^3	0.40 × 0.15 × 0.10	0.20 × 0.10 × 0.05	0.35 × 0.20 × 0.10	0.45 × 0.20 × 0.15
no. of reflectns measd	9704	6937	5339	7567
no. of reflectns obsd	1887	2667	2003	2874
μ(Mo Kα), mm^{-1}	0.088	0.122	0.130	0.117
GOF on F^2	1.331	1.261	1.143	1.030
$R(I>2\sigma(I))$	0.1095	0.0802	0.0508	0.0487
$R_w(I>2\sigma(I))$	0.1916	0.1531	0.1126	0.1176
R(all data)	0.1235	0.0949	0.0575	0.0548
R_w(all data)	0.1972	0.1593	0.1158	0.1220

chloride (0.507 g, 6.25 mmol) in CH_2Cl_2 (20 mL) dropwise over 15 min with stirring for 2 h. The mixture was washed with Na_2CO_3 aq, water, and brain. The solvent was removed by evaporation, and the residue was purified by silica gel column chromatography (Wakogel C-300, 2%MeOH/CH_2Cl_2) to give **1d** in 25% yield. R_f 0.72 (5%MeOH/CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 9.54 (sb, 1H), 7.12 (dd, J = 1.6 and 4.0 Hz, 1H), 7.04 (m, 2H), 6.83 (m, 1H), 6.28 (m, 1H), 6.14 (dd, J = 2.4 and 4.0 Hz, 1H), 4.21 (s, 2H), 3.92 (s, 3H). FABMS *m*/*z* (% intensity) 216.2 (52, M^+), 217.2 (100, $M^+ + 1$). Calcd for $C_{12}H_{12}N_2O_2$, 216.09.

2-Ethyl-1,3-(dipyrrol-2′-yl)-1,3-propanedione, 1f. A mixture of distilled thionyl chloride (2.81 g, 23.6 mmol) and ethylmalonic acid (1.00 g, 7.49 mmol) was stirred at reflux temperature for 6 h. The reaction mixture was purified by distillation under reduced pressure (54−55 °C/23.0−24.7 mmHg) to give 2-ethylmalonyl chloride in 53% yield. To a solution of pyrrole (0.537 g, 8.00 mmol) and $AlCl_3$ (0.638 g, 4.78 mmol) in 160 mL of CH_2Cl_2 was added 2-ethylmalonyl chloride (0.665 g, 3.93 mmol) in CH_2Cl_2 (10 mL) dropwise over 10 min and the resulting solution was stirred for 16 h at room temperature. After monitoring the consumption of the pyrrole on TLC, the mixture was poured into ice and extracted with CH_2Cl_2. The organic layer was washed with brine and the solvent was removed by evaporation. The residue was purified by silica gel column chromatography (Merck silica gel 60, 4%MeOH/CH_2Cl_2) and recrystallized from CH_2Cl_2/hexane to give **1f** in 7% yield. R_f 0.37 (5%MeOH/CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 9.33 (sb, 2H), 7.03 (m, 4H), 6.26 (m, 2H), 4.54 (t, J = 7.2 Hz, 1H), 2.15 (qui, J = 7.2 Hz, 2H), 0.99 (t, J = 7.2 Hz, 3H). ESI-MS *m*/*z* (% intensity) 229.1 (100, $M^+ - 1$), 230.1 (15, M^+). Calcd for $C_{13}H_{14}N_2O_2$, 230.11.

BF_2 Complex of Diketone 1d, **2d.** To a CH_2Cl_2 (200 mL) solution of diketone **1d** (0.226 g, 1.05 mmol) was added BF_3·OEt_2 (2.6 mL, 21 mmol) and the resulting solution was stirred at room temperature for 20 min. The solvent was removed, and the residue was purified by silica gel column chromatography (Wakogel C-300, 0.5%MeOH/CH_2Cl_2). Recrystallization from CH_2Cl_2/hexane gave BF_2 complex **2d** in 43% yield. R_f 0.72 (5%MeOH/CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 9.48 (sb, 1H), 7.17 (m, 2H), 7.11 (m, 1H), 7.00 (sb, 1H), 6.53 (s, 1H), 6.42 (m, 1H), 6.28 (m, 1H), 4.04(s, 3H). UV/vis (CH_2Cl_2, λ_{max}[nm] (ϵ, 10^4 M^{-1} cm^{-1})) 435.0 (7.0). FABMS *m*/*z* (% intensity) 264.2 (100, M^+). Calcd for $C_{12}H_{11}BF_2N_2O_2$: 264.09. This compound was further characterized by X-ray diffraction analysis.

BF_2 Complex of 2-(1′,3′-Dioxobutyl)pyrrole 1e, 2e. The 2-(1′,3′-dioxobutyl)pyrrole **1e** as a starting material was prepared by the previous reported procedure.[15] To a CH_2Cl_2 (160 mL) solution of **1e** (0.098 g, 0.648 mmol) was added BF_3·OEt_2 (2.0 mL, 15 mmol) with stirring at room temperature for 5 min. The solvent was removed, and the residue was purified by silica gel column chromatography (Wakogel C-300, 4%MeOH/CH_2Cl_2). Recrystallization from CH_2Cl_2/hexane gave **2e** in 88% yield. R_f 0.65 (5%MeOH/CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 9.65 (sb, 1H), 7.27 (m, 1H), 7.19 (m, 1H), 6.45 (m, 1H), 6.19 (s, 1H), 2.30 (s, 3H). UV/vis (CH_2Cl_2, λ_{max}[nm] (ϵ, 10^4 M^{-1} cm^{-1})) 369.5 (6.1). FABMS *m*/*z* (% intensity) 198.8 (100, M^+). Calcd for $C_8H_8BF_2NO_2$, 199.06. This compound was further characterized by X-ray diffraction analysis.

BF_2 Complex of 1f, 2f. To a CH_2Cl_2 (20 mL) solution of **1f** (0.020 g, 0.087 mmol) was added BF_3·OEt_2 (0.32 mL, 2.5 mmol) and the resulting solution was stirred at room temperature for 5 min. The solvent was removed, and the residue was purified by silica gel column chromatography (Wakogel C-300, CH_2Cl_2). Recrystallization from CH_2Cl_2/hexane gave **2f** in 74% yield. R_f 0.59 (5%MeOH/CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 9.83 (sb, 2H), 7.22 (m, 2H), 7.20 (m, 2H), 6.50 (m, 2H), 2.97 (q, J = 7.6 Hz, 2H), 1.39 (t, J = 7.6 Hz, 3H). UV/vis (CH_2Cl_2, λ_{max}[nm] (ϵ, 10^4 M^{-1} cm^{-1})) 443.0 (9.2). FABMS 278.2 (100, M^+). Calcd for $C_{13}H_{13}BF_2N_2O_2$, 278.10. This compound was further characterized by X-ray diffraction analysis.

X-ray Crystallography. Data were collected on a Bruker SMART CCDC for **2b**, **2d**, **2e**, and **2f**, refined by full-matrix least-squares procedures with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were calculated in ideal positions. Solutions of the structures were performed by using the Crystal Structure crystallographic software package (Molecular Structure Corporation). Crystals of **2b**,**d**−**f** were obtained by vapor diffusion of hexane into a CH_2Cl_2 solution of **2b**,**d**−**f**, respectively. CIF files (CCDC-288404-288407 for **2b**, **2d**, **2e**, and **2f**) 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 **2d**−**f** and its F^-, Cl^-, and $H_2PO_4^-$ binding complexes were carried out by using the Gaussian 03 program[13] 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: Details of optimized structural data, spectral changes on anion binding, and X-ray crystal analyses data (**2b**,**d**−**f**), as well as CIF files for **2b**, **2d**, **2e**, and **2f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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