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Dipyrrolyldiketone Difluoroboron Complexes: Novel Anion Sensors With C-H···X$^-$ Interactions

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Abstract: 1,3-Dipyrrolyl-1,3-propanediones, synthesized from pyrroles and malonyl chloride, form BF$_2$ complexes, which represent a new class of naked-eye sensors for halide and oxoanions. The association mode for the interactions of both the pyrrolyl NH and bridging CH protons with anions was confirmed by ^{1}H NMR chemical shifts in CD$_2$Cl$_2$ and supported by theoretical studies. The binding constants (K_a) were estimated as 8.1×10^4, 2.0×10^3, 3.3×10^2, 1.3×10^4, and $80\,\mathrm{M}^{-1}$ for F$^-$, Cl$^-$, Br$^-$, H$_2$PO$_4$$^-$, and HSO$_4$$^-$ by UV/Vis absorption spectral changes in CH$_2$Cl$_2$. Augmentation of K_a compared with dipyrrolylquinoxaline for H$_2$PO$_4$$^-$ is much larger than those for other anions. Contrary to other anions, F$^-$ quenches the emission almost completely, which was detected by the fluorescence spectrum as well as the naked-eye. In the case of the chloride anion complex, the formation of Cl$^-$-bridged 1D networks, in which anion is associated with two BF$_2$ complexes, is observed in the solid state.

Keywords: anions · fluorescence · oligopyrroles · self-assembly

Introduction

An important class of naked-eye sensors are synthetic receptors that allow anionic guest species to be observed by visual means or by changes in the electronic absorption or fluorescent spectral properties.[1] Among the various artificial host molecules reported to date, pyrroles incorporated into macrocycles are particularly attractive because they behave as essential binding units due to the presence of polarized NH sites.[2] Although studied less well, acyclic pyrrole derivatives often potentially have more advantages. This is because they can form the complexes with anions by synthetic attachment of additional recognition units such as amide NH,[3,4] or simply because they are easily to make their macrocyclic systems. Among open chain anion sensors reported to date are dipyrrolylquinoxalines (dpq), fluorescent dyes directly connected to pyrrole rings. These receptors undergo quenching of emission in the presence of certain anions.[3] We conceived that replacing the aromatic fluorophores by a difluoroboron (BF$_2$) moiety, incorporated between, for example, dipyrrin nitrogens,[5] would provide a new set of dpq analogues that would not only act as efficient sensors but also as energy donating units. In this article, we report a new set of acyclic oligopyrrole receptors, namely the dipyrrolyldiketone BF$_2$ complexes **2a**,**b**, which can act as efficient colorimetric and fluorescent anion sensors.

In the context of these studies, we have found that the supporting interaction between backbone C-H proton and the bound anions is essential and enhances the affinity relative to other systems.[6,7] Strapped calix[4]pyrroles have exhibited enhanced binding affinity for anions by using bridging phenyl CH as well as pyrrole NH.[6b,g] On the other hand, imidazolium CH sites between charged nitrogen atoms associate with anions without the supporting NH.[6a,7] Theoretical studies also support the interaction between CH units and anions or heteroatoms.[8] To the best of our knowledge, this is the first report of anion recognition assisted by *nonaromatic* C-H···anion interactions.

Results and Discussion

Synthesis and initial characterization: 1,3-Dipyrrol-2′-yl-1,3-propanedione (**1a**), α-neopentyl-substituted (**1b**), and N-methyl-substituted (**1c**) derivatives of **1a** were obtained in 33, 17, and 20% yields, respectively, from pyrrole derivatives by reaction with malonyl chloride in CH$_2$Cl$_2$.[9] The

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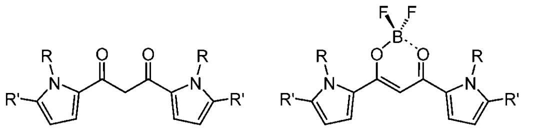
substituents are introduced in order to increase the solubility (→**1b**) and effectively protect the nitrogen site (→**1c**). Accordingly, the ^1H NMR spectra of these diketones in $CDCl_3$ show broad signals for **1a** and relatively sharp signals for **1b** and **1c**. Most likely, this is due to intramolecular aggregation, as well as the low solubility of **1a**. On the other hand, in [D$_6$]DMSO at room temperature, both the keto and enol forms of **1a** were observed in the ratio of 1:0.5, respectively. The enol tautomer can behave as a monoanionic bidentate ligand for metal cations such as acetylacetone. Addition of excess $BF_3 \cdot OEt_2$ in CH_2Cl_2 for 5 min to diketones **1a–c** was found to give rise to the strongly emissive boron difluoride (BF_2) complexes **2a–c** in 82, 80, and 75% yields, respectively (Figure 1). The ^1H NMR spectra of **2a** (**2b**) in $CDCl_3$ revealed resonances at 6.52 (6.38) and 9.50 (9.11) ppm for the methine CH and pyrrolyl NH protons, respectively.



1a: R = H, R' = H
1b: R = H, R' = neopentyl
1c: R = CH_3, R' = H

2a: R = H, R' = H
2b: R = H, R' = neopentyl
2c: R = CH_3, R' = H

Figure 1. Structures of dipyrrolyldiketones **1a–c** and BF_2 complexes **2a–c**.

A single crystal X-ray diffraction analysis of **2a** was performed. It revealed two independent but almost similar structures of the proposed BF_2 complex in the unit cell (Figure 2a). Each structure shows an almost flat framework; the mean plane deviations for the 16 core atoms are 0.022 and 0.056 Å, respectively. In the solid state, the pyrrole nitrogen atoms are twisted to the opposite sides of the molecule due to intramolecular associations with the BF_2-bound oxygen atoms. These latter N-H···O interactions are in the range of 2.696–2.732 Å. Furthermore, two molecules interact to form a dimer structure through two intermolecular N-H···F hydrogen bonds with distances of 2.780 and 2.914 Å (*a* and *b* in Figure 2b). A complex 3D network is also observed, because each dimer has further interactions, such as *c* (2.794 Å) and *d* (2.835 Å) in Figure 2b, with other neighboring dimers. By contrast, the N-alkyl-substituted BF_2 complex **2c** shows the same configuration as the monomer (i.e., absence of assembled structures in the solid state; Figure 2c).

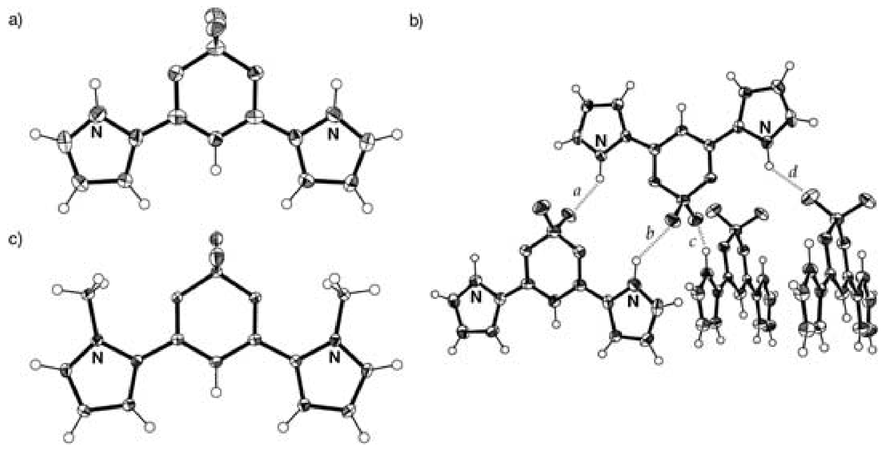


Figure 2. a) X-ray single crystal structure of BF_2 complex **2a** (one of the two independent molecules); b) hydrogen bonding N-H···F interactions (*a–d*) of a molecule with neighboring ones; and c) solid-state structure of **2c**. Thermal ellipsoids are scaled to the 50% probability level.

Anion-binding properties in solution: In order to examine the anion-binding properties of these complexes **2** in solution, the more soluble derivative **2b** was subject to titration-based analysis. Here, UV/Vis absorption spectral changes seen upon the addition of various anions to CH_2Cl_2 solutions were monitored. Upon the addition of F^- (as its commercially available tetrabutylammonium salt without further dehydration),[10] the absorption maximum at 457 nm was seen to decrease, while a new shoulder around 480 nm was found to increase. Isosbestic points at 420 and 470 nm were observed, and the color was seen to change from pale yellow to dark yellow (Figure 3a). Binding constants (K_a) for F^-, Cl^-, dihydrogenphosphate ($H_2PO_4^-$) in CH_2Cl_2, determined by curve fitting, were estimated at 8.1×10^4, 2.0×10^3, and $1.3 \times 10^4\,\text{M}^{-1}$, respectively, values that are about 4.5-, 40-, and 220-fold higher than those observed in dipyrrolylquinoxaline (dpq) (Table 1).[3a] Receptor **2b** also binds Br^- and HSO_4^- reasonably well ($K_a = 3.3 \times 10^2$ and $80\,\text{M}^{-1}$, respectively), which again stands in contrast to what is seen for dpq. A 1:1 binding stoichiometry was determined for **2b** and F^- by Job plots, since this latter substrate was bound more strongly than the other halide anions. Control experiments with the *unfunctionalized* derivative, **2c**, revealed no absorption spectral changes in the presence of F^-, a finding that supports the assumption that the pyrrolic NH is required for efficient binding. Relative binding constant for **2b** to dpq for $H_2PO_4^-$ is much higher than those for other anions, F^- and Cl^-, which suggests dipyrrolyldiketone derivatives would exhibit selective binding for nucleotides.

The fluorescent emission spectrum of **2b** at 474 nm in CH_2Cl_2, excited at 420 nm, was found to be significantly suppressed and shifted to around 480 nm upon the addition of F^- (Figure 3b). The binding constant estimated from such fluorescence quenching studies was $9.1 \times 10^4\,\text{M}^{-1}$, almost the same as that derived from the absorption spectral changes. In the case of Cl^-, Br^-, $H_2PO_4^-$, and HSO_4^-, although quantitative estimations could not be performed due to the presence of an isosbestic point at 464–466 nm, full quenching was not seen even in the presence of 2000 equiv Cl^-, Br^-, $H_2PO_4^-$, and HSO_4^-.

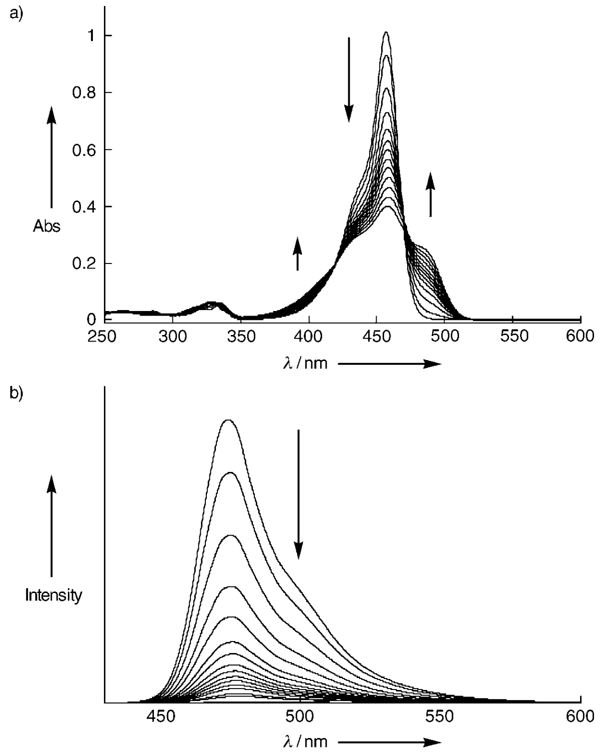


Figure 3. a) UV/Vis absorption and b) fluorescent emission spectral changes (excited at 420 nm) of **2b** (1.5×10^{-5} and 1.8×10^{-6} M, respectively) upon addition of F^- (0–20 and 0–200 equiv each) in CH_2Cl_2.

Table 1. Binding constants [M^{-1}] for dipyrrolylquinoxaline (dpq)[3a] and **2b** for anionic substrates in CH_2Cl_2 at RT.[a]

	dpq	**2b**	$R_{2b/dpq}$[b]
F^-	18200	81000	4.5
Cl^-	50	2000	40
Br^-	–[c]	330	–
$H_2PO_4^-$	60	13000	220
HSO_4^-	–[c]	80	–

[a] Anions used in this assay were in the form of their tetrabutylammonium salts. For a detailed description of titration experiments, see Supporting Information. [b] Relative values for **2b** to dpq. [c] Not measured.

Next, efforts were made to analyze the binding mode between the BF_2 complex and the halide anions. Upon the addition of F^-, the ^{1}H NMR signals of the methine CH and pyrrole NH protons of **2b** (3×10^{-3} M) in CD_2Cl_2 at room temperature were shifted downfield from 6.44 and 9.23 ppm, respectively (Figure 4a, i). At lower anion concentrations, the signals are broad (Figure 4a, ii), while, upon increasing the concentration, these signals gradually disappear (Figure 4a, iii). At −50 °C, two new broad signals are observed at 6.88 and 14.53 ppm, corresponding to the CH and NH protons, respectively. From this finding, it is inferred that C-H···X^- as well as N-H···X^- interactions are playing an essential role (Figure 4a, iv). At each temperature, the NMR peak of the pyrrole CH resonance is slightly shifted upfield. Upon addition of Cl^- (> 2 equiv), the resonances of these same protons in CD_2Cl_2 shift to 8.57 and 12.18 ppm, respectively, at room temperature. Overall, the strong downfield shifts in the NH signals induced by F^- and Cl^- ($\Delta\delta$: 5.30 and 2.95 ppm, respectively: $\Delta\delta$ is the shift between before and after addition of anions) and CH by these anions ($\Delta\delta$: 0.44 and 2.13 ppm) lead us to suggest that both the NH and CH donor sites are responsible for the strong associations seen for the anions treated in this study. A similar trend was observed in the case of strapped calix[4]pyrrole derivatives.[6b,g] In this latter system, a weak association involving the NH donor sites was inferred for chloride binding, whereas the downfield shift of the CH proton seen in the ^{1}H NMR spectrum was considered to reflect a significant C-H···Cl^- interaction. The bridging nonaromatic sp^2-CH of **2b**, constrained between the pyrrole moieties, is thus thought to act as an association site. This observation and the concerted NH-based binding interactions lead to the proposed binding modes shown in Figure 4b.

Optimization of the proposed F^- and Cl^- complexes of framework **2a** by density functional theory (DFT) calculations at the B3LYP/6-31G** level[11] gives rise to slightly distorted and almost planar structures, respectively, in which the hydrogen-bonding interactions in N-H···X^- (F^-: 2.567–2.569 Å; Cl^-: 3.255 Å) and C-H···X^- (F^-: 2.835 Å; Cl^-: 3.460 Å) are inferred (c.f., Figure 4c and Supporting Information). The geometries of the optimized structures **2a**·F^- and **2a**·Cl^- indicate the presence of "hemi" cavity suitable for anion binding. Consistent with the experimental results, the theoretical calculations also imply that the conformation of **2a** seen in Figure 1 is predominant, being 9.08 kcal mol^{-1} more suitable than one where the two pyrrole NH prorons point toward the methine CH proton. However, upon complexation of an anion (F^- or Cl^-), both pyrrole rings rotate "inward" so as to interact with the anion in a concerted fashion.

Anion-bridged supramolecular network in the solid state: The proposed C-H···anion interaction was also studied by carrying out a single crystal structure analysis of the Cl^- complex of **2a**. In the solid state, the CH proton and one of the two pyrrole NH protons associate with the Cl^- anion at C(N)-H···Cl distances of 3.575 and 3.190 Å, respectively (Figure 5a). These separations are within those expected for hydrogen-bonding interactions.[12] The other NH turns to the opposite side and binds to another Cl^- anion (N-H···Cl: 3.199 Å) to form an anion-bridged 1D chain hydrogen-bonding network (Figure 5b). In this system, the anions are regularly arranged in an almost linear array, wherein the distance between two Cl^- anions and the Cl-Cl-Cl angle are 9.009 Å and 173.44°, respectively. Presumably, the flexibility of the acyclic oligopyrrole framework forms such supramolecular structures.

Fluorescence sensing of anions: The above findings lead to the conclusion that BF_2 complexes of dipyrrolyldiketones and related systems could be made to function as efficient fluoride sensors. This point is emphasized in Figure 6, which

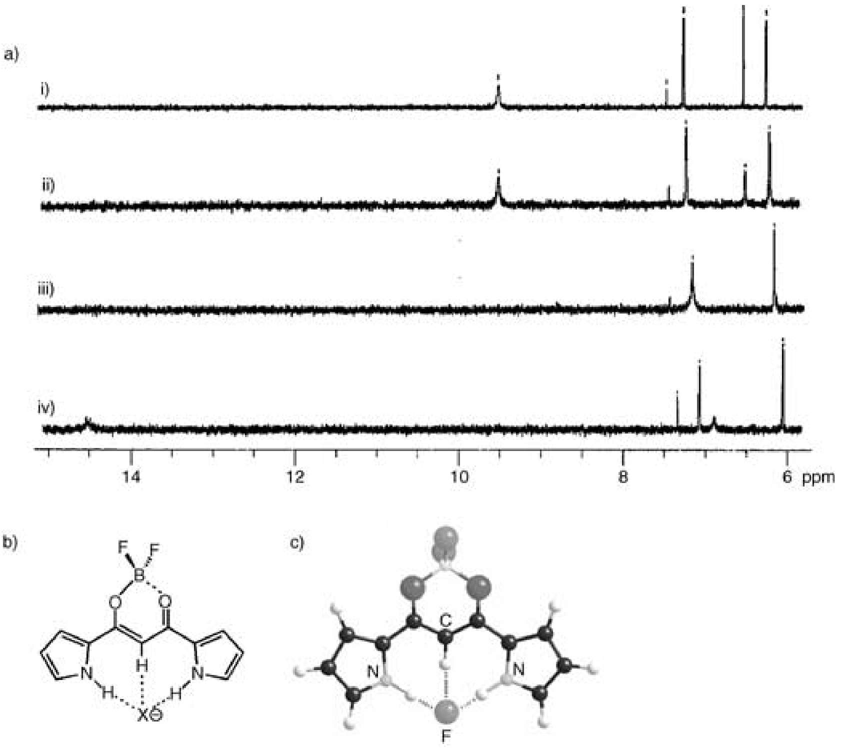


Figure 4. a) ^{1}H NMR spectral changes of **2b** (3×10^{-3} M) upon addition of F$^-$: i) 0 equiv, ii) 0.2 equiv, iii) 5 equiv at RT, and iv) 5 equiv at −50 °C in CD_2Cl_2; b) schematic representation of anion binding mode of structure **2a**, and c) optimized structure of F$^-$-bound **2a** at the B3LYP/6-31G** level.

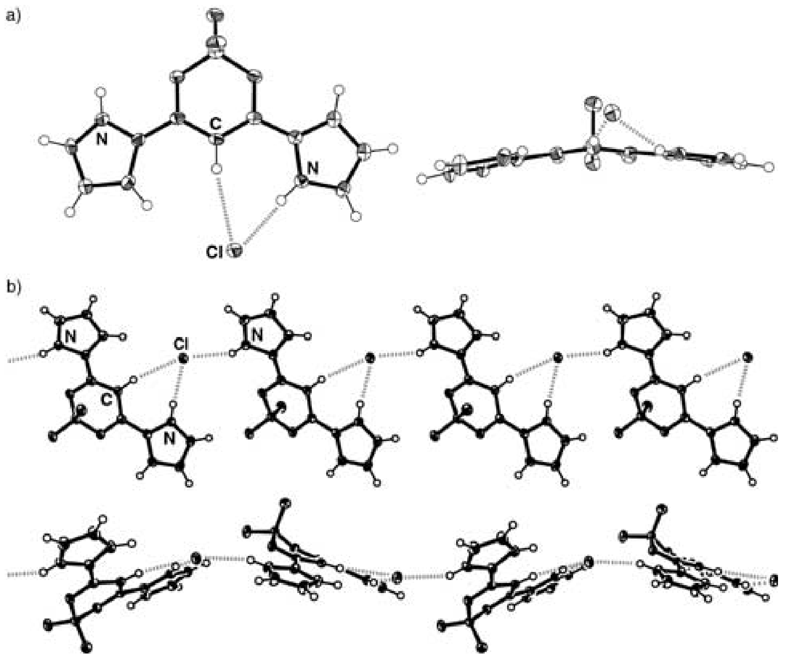


Figure 5. a) X-ray single crystal structure of Cl$^-$ complex of **2a** (top and side view) and b) anion-bridged self-assembly (top and side view). Counter cations, Bu_4N^+, and solvents are omitted for clarity. Thermal ellipsoids are scaled to the 50 % probability level.

shows the changes in color and fluorescence induced by the addition of F$^-$ and Cl$^-$ to a CH_2Cl_2 solution of **2b**. Under conditions where nearly complete association of both anions is assumed, F$^-$ quenches the emission almost completely, whereas Cl$^-$ does not. Addition of other anions such as Br$^-$, $H_2PO_4^-$, and HSO_4^- also maintains the fluorescence. It is essential to point that the fluorescence seen after addition of Cl$^-$ (Figure 6b) reflects not only that of the free **2b** but also emission from the Cl$^-$ complex. In contrast to what must be true in the case of Cl$^-$ binding, the strong interaction of the F$^-$ anion with the NH protons than the central CH proton, as confirmed by the ^{1}H NMR spectral changes, would induce a polarization of the pyrrole–NH bond. This would facilitate intramolecular electron transfer and thus suppress the fluorescence emission.[3a]

Summary

A new class of anion receptors, namely BF_2 complexes of dipyrrolyldiketones, have been shown to interact with anions through interactions involving both pyrrole NH as well as the CH interactions. These latter are considered more efficient for $H_2PO_4^-$ than F$^-$ and Cl$^-$, at least in the case of the present nonaromatic moiety. The key diketone precursor is a potential cation and anion receptor. For instance, it should be possible to modulate its association behavior allowing it via complexation of various metal cations to the carbonyl (keto or enol forms) moieties. Further studies, targeting such complexes, are in progress.

Experimental Section

General procedures: Starting materials were purchased from Wako Chemical Co., Nacalai Chemical Co., and Aldrich Chemical Co. and used without further purification unless otherwise stated. UV-Visible spectra were recorded on a Hitachi U-3500 spectrometer. Fluorescence emission spectra were recorded on a Hitachi F-

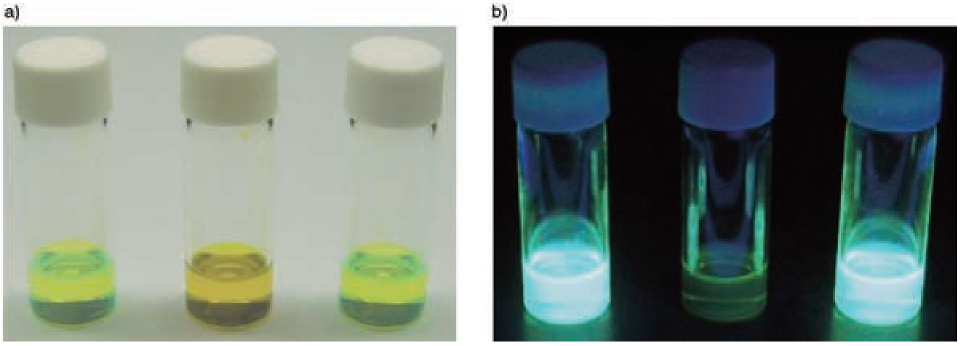


Figure 6. a) Color and b) fluorescent emission changes of **2b** (3×10^{-3} M) in CH_2Cl_2: no anion, F^- (10 equiv), and Cl^- (10 equiv) from left to right in each photograph.

4500 fluorescence spectrometer. NMR spectra used in the characterization of products were recorded on a JEOL AL-400 400 MHz spectrometer. All NMR spectra were referenced to solvent. Fast atom bombardment mass spectrometric studies (FAB-MS) were made using a JEOL-HX110 instrument in the positive ion mode with a 3-nitrobenzylalcohol matrix. TLC analyses were carried out on aluminium sheets coated with silica gel 60 (Merck 5554). Column chromatography was performed on Wakogel C-200, C-300, and Merck silica gel 60 and 60H. Neopentylpyrrole was prepared according to literature procedures.[13,14]

1,3-Dipyrrol-2′-yl-1,3-propanedione (1a): In analogy to a literature procedure,[9] a solution of pyrrole (1.34 g, 20 mmol) in CH_2Cl_2 (60 mL) was treated with malonyl chloride (1.41 g, 10 mmol) at 0 °C and stirred for 3 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 purified by chromatography over silica gel (Wakogel C-200, 2–3 % $MeOH/CH_2Cl_2$) and recrystallized from CH_2Cl_2/hexane to afford **1a** (655 mg, 33 %) as a pale yellow solid. $R_f=0.55$ (5 % $MeOH/CH_2Cl_2$); ^{1}H NMR (400 MHz, $[D_6]$DMSO, 27 °C; diketone **1a** was obtained as a mixture of keto and enol tautomers in the ratio of 1:0.56): keto form $\delta=11.86$ (br s, 2H, NH), 7.10 (m, 2H, pyrrole-H), 7.06 (m, 2H, pyrrole-H), 6.19 (m, 2H, pyrrole-H), 4.22 ppm (s, 2H, CH_2); enol form $\delta=16.75$ (br s, 1H, OH), 11.81 (br s, 2H, NH), 7.10 (m, 2H, pyrrole-H), 6.98 (m, 2H, pyrrole-H), 6.65 (s, 1H, CH), 6.24 ppm (m, 2H, pyrrole-H); FABMS: *m/z* (%): calcd for $C_{11}H_{10}N_2O_2$: 202.07; found: 202.1 (65) $[M^+]$, 203.2 (100) $[M^++H]$.

1,3-Di-5′-neopentylpyrrol-2′-yl-1,3-propanedione (1b): A solution of neopentylpyrrole (170 mg, 1.24 mmol) in CH_2Cl_2 (5 mL) was treated with malonyl chloride (87 mg, 0.62 mmol) in CH_2Cl_2 (10 mL) and stirred for 2 h at 0 °C. After the similar procedures for **1a**, chromatography over silica gel (Wakogel C-300, 3 % $MeOH/CH_2Cl_2$) and recrystallization from CH_2Cl_2/hexane afforded **1b** (36 mg, 17 %) as a pale yellow solid. $R_f=0.35$ (5 % $MeOH/CH_2Cl_2$); ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C): $\delta=9.06$ (br s, 2H, NH), 7.01 (s, 2H, pyrrole-H), 6.02 (s, 2H, pyrrole-H), 4.13 (s, 2H, CH_2), 2.48 (s, 4H, pyrrole-CH_2), 0.94 ppm (s, 18H, CH_3); FABMS: *m/z* (%): calcd for $C_{21}H_{30}N_2O_2$: 342.23; found: 342.2 (38) $[M^+]$, 343.2 (100) $[M^++H]$.

1,3-Di-1′-methylpyrrol-2′-yl-1,3-propanedione (1c): A solution of 1-methylpyrrole (490 mg, 6.0 mmol) in CH_2Cl_2 (140 mL) was treated with malonyl chloride (420 mg, 3.0 mmol) at 0 °C and stirred for 2 h at room temperature. After the similar procedures for **1a**, chromatography over silica gel (Wakogel C-300, 3 % $MeOH/CH_2Cl_2$) and recrystallization from CH_2Cl_2/hexane afforded **1c** (139 mg, 20 %) as a pale yellow solid. $R_f=0.75$ (5 % $MeOH/CH_2Cl_2$); ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C): $\delta=7.09$ (s, 2H, pyrrole-H), 6.83 (t, $J=2.0$ Hz, 2H, pyrrole-H), 6.15 (dd, $J=4.0$, 2.4 Hz, 2H, pyrrole-H), 4.11 (s, 2H, CH_2), 3.93 ppm (s, 6H, N-CH_3); FABMS: *m/z* (%): calcd for $C_{13}H_{14}N_2O_2$: 230.11; found: 230.2 (60) $[M^+]$, 231.2 (100) $[M^++H]$.

BF_2 complex of 1a: $BF_3{\cdot}OEt_2$ (0.6 mL, 3.8 mmol) was added to a solution of diketone **1a** (31.6 mg, 0.156 mmol) in CH_2Cl_2 (30 mL), and stirred for 5 min at room temperature. After removal of the solvent, silica gel column chromatography and crystallization from CH_2Cl_2/hexane afforded **2a** (32 mg, 82 %) as an orange solid. $R_f=0.55$ (5 % $MeOH/CH_2Cl_2$); ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C): $\delta=9.50$ (br, 1H, NH), 7.21 (s, 2H, pyrrole-H), 7.17 (dd, $J=2.8$, 1.6 Hz, 2H, pyrrole-H), 6.52 (s, 1H, CH) 6.44 ppm (dd, $J=2.8$, 1.6 Hz, 2H, pyrrole-H); UV/Vis (CH_2Cl_2) λ_{max} $(\varepsilon)=432.0$ nm ($83000\,\text{M}^{-1}\text{cm}^{-1}$); FABMS: *m/z* (%): calcd for $C_{11}H_9BF_2N_2O_2$: 250.07; found: 250.1 (100) $[M^+]$, 251.1 (35) $[M^++H]$.

BF_2 complex of 1b: $BF_3{\cdot}OEt_2$ (0.35 mL, 2.8 mmol) was added to a CH_2Cl_2 solution (30 mL) of diketone **1b** (30.0 mg, 0.088 mmol), and stirred for 5 min at room temperature. Similar procedures for **2a** afforded **2b** (27 mg, 80 %) as an orange solid. $R_f=0.78$ (5 % $MeOH/CH_2Cl_2$); ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C): $\delta=9.11$ (br, 1H, NH), 7.05 (t, $J=2.0$ Hz, 2H, pyrrole-H), 6.14 (dd, $J=4.0$, 2.4 Hz, 2H, pyrrole-H), 6.38 (s, 2H, CH), 2.54 (s, 4H, pyrrole-CH_2), 0.97 ppm (s, 18H, CH_3); UV/Vis (CH_2Cl_2) λ_{max} $(\varepsilon)=457.0$ nm ($65000\,\text{M}^{-1}\text{cm}^{-1}$); FABMS: *m/z* (%): calcd for $C_{21}H_{29}BF_2N_2O_2$: 390.23; found: 390.2 (100) $[M^+]$, 391.2 (100) $[M^++H]$.

BF_2 complex of 1c: $BF_3{\cdot}OEt_2$ (0.55 mL, 3.9 mmol) was added to a solution of diketone **1c** (30.0 mg, 0.13 mmol) in CH_2Cl_2 (30 mL), and stirred for 5 min at room temperature. Similar procedures for **2a** afforded **2c** (27 mg, 75 %) as an orange solid. $R_f=0.78$ (5 % $MeOH/CH_2Cl_2$); ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C): $\delta=7.12$ (m, 2H, pyrrole-H), 6.96 (m, 2H, pyrrole-H), 6.54 (s, 1H, CH), 6.25 (m, 2H, pyrrole-H), 4.03 ppm (s, 6H, N-CH_3); UV/Vis (CH_2Cl_2) λ_{max} $(\varepsilon)=437.5$ nm ($70000\,\text{M}^{-1}\text{cm}^{-1}$); FABMS: *m/z* (%): calcd for $C_{13}H_{13}BF_2N_2O_2$: 278.10; found: 278.1 (100) $[M^+]$, 279.1 (45) $[M^++H]$.

Ab initio calculations: Ab initio calculations of neutral and protonated forms of **2a** and its anion binding complexes were carried out using Gaussian 03 program[11] and an HPC-alpha UP264 (HIT) computer. The structures were optimized, and the total electronic energies were calculated at the B3LYP level using a 6-31G** basis set.

Single-crystal diffraction analysis: Data was collected on a Rigaku RAXIS-RAPID imaging plate for **2a** and a Bruker SMART CCDC for **2c** and **2a**·Cl^-, 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 **2a** and **2c** were obtained by vapor diffusion of hexane into a $CHCl_3$ solution of **2a** and **2c**, respectively. Crystals of Cl^- complex of **2c** were obtained by vapor diffusion of hexane into a CH_2ClCH_2Cl solution of the mixture of **2c** and 1 equiv Bu_4NCl. Crystallographic details are summarized in Table 2.

CCDC-270295–270297 (**2a**, **2c**, and **2a**·Cl^-) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif/.

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Table 2. Summary of crystallographic data for **2a**, **2c**, and **2a**·Cl⁻.

	2a	**2c**	**2a**·$Bu_4NCl \cdot 0.5\,C_2H_4Cl_2$
formula	$C_{11}H_9BF_2N_2O_2$	$C_{13}H_{13}BF_2N_2O_2$	$C_{28}H_{47}BF_2N_3O_2Cl_2$
F_w	250.01	278.06	577.40
crystal size [mm]	0.45 × 0.20 × 0.20	0.40 × 0.40 × 0.05	0.60 × 0.20 × 0.10
crystal system	orthorhombic	monoclinic	orthorhombic
space group	*Pbca* (no. 61)	$P2_1/c$ (no. 14)	$Pca2_1$ (no. 29)
a [Å]	9.527(10)	7.3205(15)	18.168(3)
b [Å]	18.291(16)	18.715(4)	8.5938(14)
c [Å]	24.666(16)	9.501(2)	39.917(7)
α [°]	90	90	90
β [°]	90	106.466(3)	90
γ [°]	90	90	90
V [Å^3]	4298(6)	1248.3(4)	6232.3(18)
ρ_{calcd} [g cm^{-3}]	1.545	1.480	1.231
Z	16	4	8
T [K]	123(2)	90(2)	123(2)
no. reflns	38207	7432	41864
no. unique reflns	36208	2799	7367
variables	326	183	693
λ (Mo$_{K\alpha}$) [Å]	0.71075	0.71073	0.71073
R_1 [$I > 2\sigma(I)$]	0.0484	0.0524	0.0534
wR_2 [$I > 2\sigma(I)$]	0.1494	0.1146	0.1332
GOF	1.075	1.174	1.162

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