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# Heteroaryl-Substituted $C_3$-Bridged Oligopyrroles: Potential Building Subunits of Anion-Responsive π-Conjugated Oligomers

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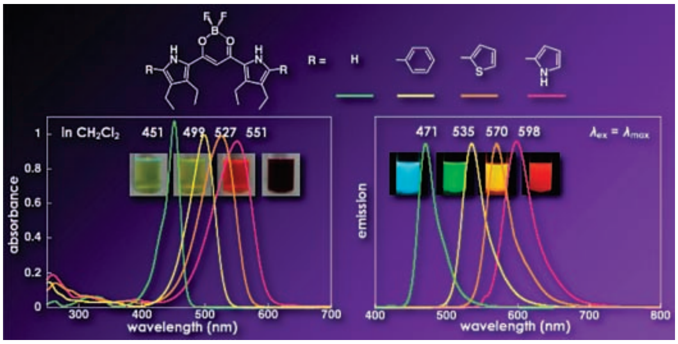
## ABSTRACT



**Acyclic anion receptors ($BF_2$ complexes of dipyrrolyldiketones) with heteroaryl moieties synthesized by using cross-coupling reactions have unique electronic states, as observed in UV/vis absorption spectra. Among heteroaryl-substituted derivatives, a pyrrolyl-substituted receptor exhibits an extremely high affinity for anions in solution.**

π-Conjugated oligomers that are capable of guest binding are fascinating and potentially useful materials because of the possible detection of analytes in solution and in the solid state.[1] The binding sites of most oligomeric systems are the "pendant" units of main-chain backbones. Thus far, there have been some appropriate components that act as building units that constitute π-conjugated oligomers and also function as efficient binding moieties for desired target species. The receptor units incorporated in linear π-conjugated systems would be useful for the fabrication of stimuli-responsive materials. As receptors for anions as external chemical stimuli,[2–4] we have reported novel acyclic π-conjugated systems, $BF_2$ complexes of 1,3-dipyrrolyl-1,3-propanediones (e.g., **1a−d**, Figure 1a), which efficiently bind anions due to the inversion of pyrrole rings (Figure 1b).[5–7] Chemical modifications by cross-coupling reactions that afford aryl-

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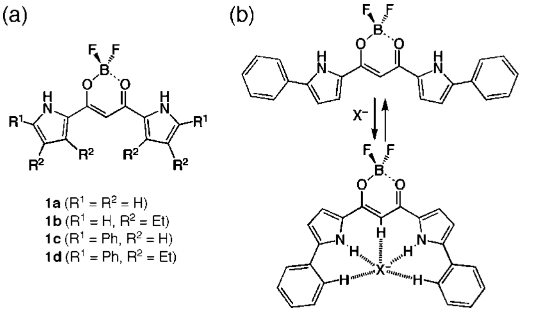
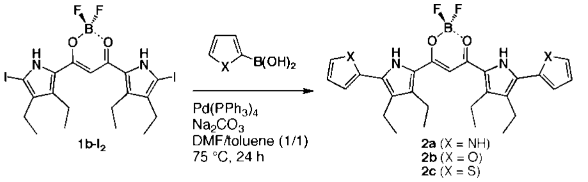


**Figure 1.** (a) $BF_2$ complexes of 1,3-dipyrrolyl-1,3-propanediones as acyclic anion receptors and (b) anion binding mode of **1a**.

substituted receptors such as α-phenyl **1c** and **1d** are crucial steps to introduce various substituents by using terminal aryl units. In fact, α-aryl-substituted derivatives with long alkoxy chains at the terminal units of the receptor systems have exhibited the formation of supramolecular organogels.[7a] In contrast to the assemblies obtained by noncovalent interactions, the oligomerization of these linear building subunits by *covalent* bonds[7b] would also yield anion-responsive polymeric fibers or films. In this paper, the synthesis and efficient anion binding behaviors of heteroaryl-substituted $C_3$-bridged oligopyrroles as potential building subunits of $\pi$-conjugated oligomers are reported. In particular, the pyrrolyl-substituted derivative has reactive terminal α-positions, which are transformed to the connecting sites that will yield higher oligomers by cross-coupling reactions.

$\pi$-Conjugated heterocycles such as pyrrole, furan, and thiophene have been introduced in the acyclic anion receptors to yield bispyrrolyl **2a**, bisfuryl **2b**, and bisthienyl **2c** in 71%, 47%, and 48% yields, respectively, by a cross-coupling reaction using α-bisiodo-substituted $BF_2$ complex **1b-I₂**[7b] and the corresponding boronic acid derivatives (Scheme 1). The synthesis procedure using an iodo-receptor affords better yields than those afforded using α-borylated dipyrrolyldiketone.[8] Chemical identifications for **2a−c** are carried out by $^1H$ and $^{13}C$ NMR and ESI-TOF-MS. The modulated electronic states of these anion receptors can be detected by the naked eye on the basis of color and emission properties (figure in abstract). In fact, the UV/vis absorption bands of **2a−c** in $CH_2Cl_2$ (Figure 2a) are observed at 551, 538, and 527 nm, respectively, suggesting red-shifts that are comparable to those of α-unsubstituted **1b** (451 nm)[6d] and α-phenyl **1d** (499 nm).[7b] The order of these $\lambda_{max}$ values is correlated to the HOMO−LUMO gaps (**2a**, 2.814 eV; **2b**, 2.865 eV; **2c**, 2.923 eV; **1d**, 3.154 eV; **1b**, 3.470 eV) estimated by DFT calculations (Figure 2c).[9] Further, fluorescence emissions (and quantum yields, $\Phi_F$) excited at each absorption maximum in $CH_2Cl_2$ (Figure 2b) are observed at 599 (0.42) (**2a**), 572 (0.65) (**2b**), and 570 nm (0.55) (**2c**).

**Scheme 1.** Synthesis of α-Bisaryl-Substituted Receptors **2a−c**



The solid-state structures of **2a−c** have been revealed by single-crystal X-ray analysis (Figure 3).[10] Similar to **1c**,**d**,[7]

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(10) Crystal data for **2a** (from $CH_2Cl_2$/hexane): $C_{27}H_{31}BF_2N_4O_2$, Mw = 492.37, triclinic, $P\bar{1}$ (no. 2), $a = 8.813(5)$, $b = 10.176(5)$, $c = 15.776(9)$ Å, $\alpha = 95.968(18)$, $\beta = 104.752(19)$, $\gamma = 114.023(16)°$, $V = 1214.6(11)$ Å$^3$, $T = 123(2)$ K, $Z = 2$, $D_c = 1.346$ g/cm$^3$, $\mu$(Mo Kα) = 0.096 mm$^{-1}$, $R_1 = 0.0547$, w$R_2 = 0.0873$, GOF = 0.886 ($I > 2\sigma(I)$). CCDC 585533. Crystal data for **2b** (from $CHCl_3$/hexane): $C_{27}H_{29}BF_2N_2O_4$, Mw = 494.34, triclinic, $P\bar{1}$ (no. 2), $a = 10.973(4)$, $b = 14.240(4)$, $c = 16.635(7)$ Å, $\alpha = 77.794(14)$, $\beta = 77.538(15)$, $\gamma = 72.323(14)°$, $V = 2388(15)$ Å$^3$, $T = 123(2)$ K, $Z = 4$, $D_c = 1.375$ g/cm$^3$, $\mu$(Mo Kα) = 0.102 mm$^{-1}$, $R_1 = 0.0483$, w$R_2 = 0.1222$, GOF = 1.006 ($I > 2\sigma(I)$). CCDC 585534. Crystal data for **2c** (from $CH_2ClCH_2Cl$/heptane): $C_{27}H_{29}BF_2N_2O_2S_2$, Mw = 526.45, monoclinic, $C2/c$ (no. 15), $a = 18.575(5)$, $b = 9.0099(18)$, $c = 30.916(9)$ Å, $\beta = 104.860(12)°$, $V = 5001(2)$ Å$^3$, $T = 123(2)$ K, $Z = 8$, $D_c = 1.398$ g/cm$^3$, $\mu$(Mo Kα) = 0.257 mm$^{-1}$, $R_1 = 0.0417$, w$R_2 = 0.0921$, GOF = 1.077 ($I > 2\sigma(I)$). CCDC 585535.

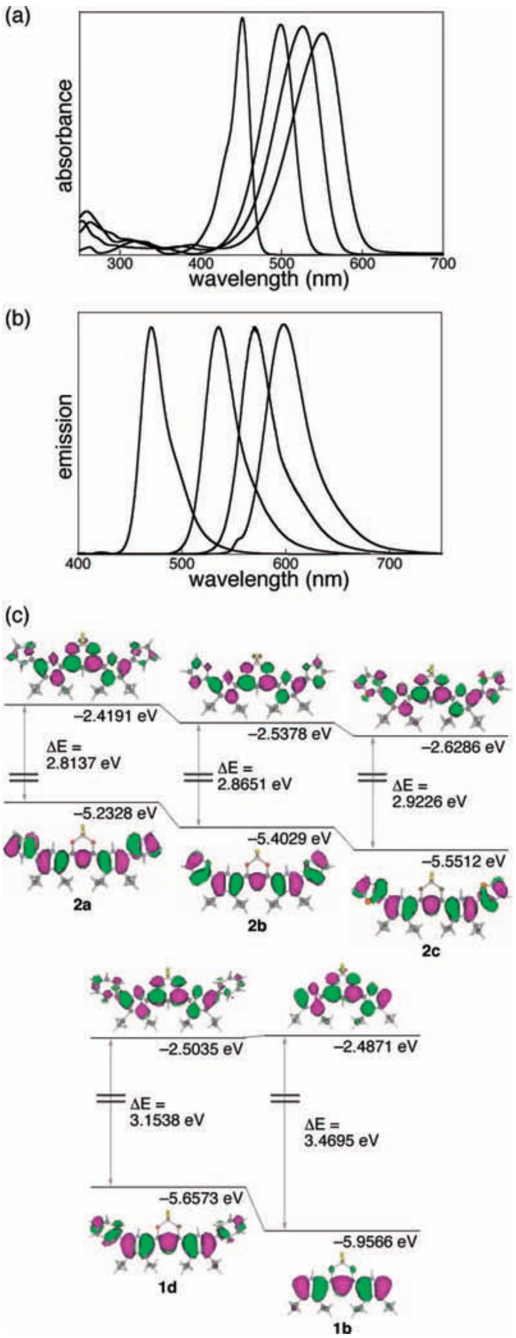

**Figure 2.** (a) UV/vis absorption spectra, (b) fluorescence spectra of **2a**,**c** and **1b**,**d** in $CH_2Cl_2$ (from left to right: **1b**, **1d**, **2c**, and **2a**), and (c) HOMO (upper) and LUMO (lower) of **2a**−**c** and **1b**,**d**.

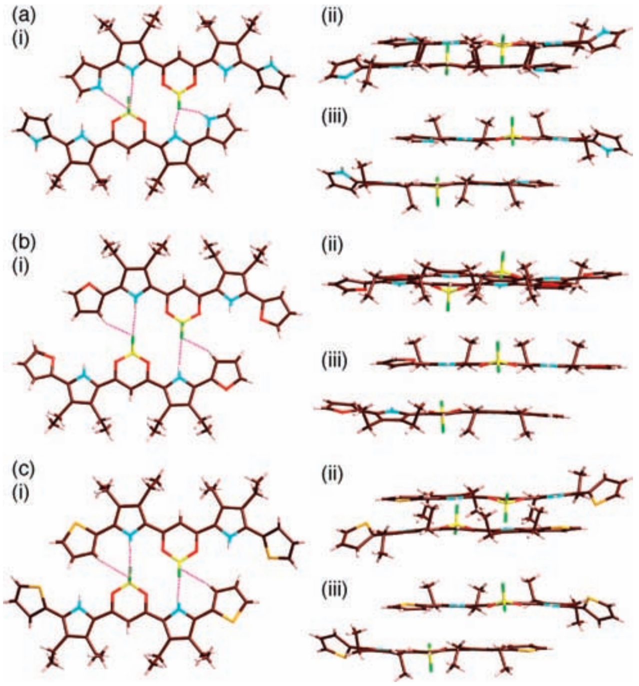

**Figure 3.** Single-crystal X-ray structures of (a) **2a**, (b) **2b** (as a pair of structure-independent molecules), and (c) **2c** (as one of the two disordered conformations) as hydrogen bonding dimeric forms ((i) top and (ii) side view) and (iii) stacking dimer structures. Atom color code: brown, pink, yellow, green, blue, red, and orange refer to carbon, hydrogen, boron, fluorine, nitrogen, oxygen, and sulfur, respectively.

receptors **2a**−**c** form hydrogen bonding dimers (Figure 3i), wherein the distances of N(−H)···F and the terminal pyrrole N(−H)···F (**2a**) or heteroarene $\beta$-C(−H)···F (**2b**,**c**) are 3.02 and 2.86 Å, respectively, for **2a**, 2.87−2.94 and 3.14−3.17 Å, respectively, for **2b**, and 3.00 and 3.17 Å, respectively, for **2c**. The shorter bond length between the terminal NH and (B−)F as compared to that between the central NH and (B−)F implies the possibility of the former pyrrole NH (in **2a**) as an effective interaction site. The dihedral angles (minimum and maximum values) between heteroarenes and the dipyrrolyl core plane comprising 16 atoms are 9.9° and 35.5°, respectively, for **2a**, in the range of 4.0–12.8° for **2b**, and 8.1° and 39.4°, respectively, for **2c**. These values are slightly smaller than and comparable to those of **1d** (24.3° and 31.9°). The smaller values for each receptor are due to the intermolecular hydrogen bonding with the BF unit. The deviations in the mean plane consisting of 26 atoms are 0.24 Å (**2a**), 0.16 and 0.20 Å (**2b**), and 0.30 Å (**2c**). These values are smaller than that of **1d** (0.34 Å). The $\pi-\pi$ stacking dimers of the receptors **2a**,**c** are also observed (Figure 3ii), and the distances between two mean planes are 3.81 (**2a**) and 3.39 Å (**2c**). These dimers are in contrast to the slipped stacking infinite oligomers observed in $\beta$-free **1a**. Furyl **2b** forms incomplete parallel dimer structures (dihedral angle: 6.74°), with an averaged distance of 3.485 Å between a plane consisting of core 16 atoms and the atoms in another plane formed due to an uneven arrangement (**2b**).

A series of anion receptors with heteroaryl substituents behave as sensors that detect anions in organic solvents. The values of the anion binding constant ($K_a$) of **2a**−**c** are determined by UV/vis absorption spectral changes induced by the addition of appropriate anions as tetrabutylammonium (TBA) salts in $CHCl_3$ containing 0.5% EtOH (Table 1). The $K_a$ values of **2a** in $CH_2Cl_2$ are sufficiently large to be preliminarily estimated by isothermal titration calorimetry (ITC) measurements: e.g., $1.7 \times 10^8$ ($Cl^-$) and $2.2 \times 10^7$ ($CH_3CO_2^-$) $M^{-1}$. Thus, we use 0.5% EtOH/$CHCl_3$ to suppress the binding

**Table 1.** Binding Constants ($K_a$, $M^{-1}$) of **1b**,**d** (as References) and Aryl-Substituted **2a**−**c** with Various Anions in $CHCl_3$ (Containing 0.5% EtOH)[a,b]

| | $K_a$ (**1b**) | $K_a$ (**1d**) | $K_a$ (**2a**) | $K_a$ (**2b**) | $K_a$ (**2c**) |
|---|---|---|---|---|---|
| $Cl^-$ | 990 | 120 (0.12) | 1200000 (1200) | 360 (0.36) | 1,100 (1.1) |
| $Br^-$ | 170 | 30 (0.18) | 180000 (1100) | 68 (0.40) | 150 (0.88) |
| $CH_3CO_2^-$ | 5400 | 410 (0.076) | 3000000 (560) | 500 (0.093) | 1,000 (0.19) |
| $H_2PO_4^-$ | 15000 | 130 (0.0086) | 1800000 (120) | 810 (0.054) | 880 (0.059) |
| $HSO_4^-$ | 210 | 3 (0.014) | 170000 (810) | 180 (0.85) | 15 (0.071) |

[a] The values in the parentheses are the ratios of the $K_a$ values to the $K_a$ value of **1b**. [b] The errors in $K_a$ for anions are within 20%, as observed in the Supporting Information.

affinities by the solvation of EtOH; therefore, the $K_a$ values provided in Table 1 are those of solvated receptors, anion complexes, and solvated anions.[11] For example, pyrrolyl **2a** shows considerably larger $K_a$ values, $> 10^6$ $M^{-1}$ for $Cl^-$, $H_2PO_4^-$, and $CH_3CO_2^-$, than the other heteroaryls **2b**,**c** and α-unsubstituted **1b** as well as α-phenyl analogue **1d**, due to multiple polarized NH sites. The $^1$H NMR spectral changes of **2a**−**c** for anions such as $Cl^-$ in $CDCl_3$ and/or $CD_2Cl_2$ have suggested that the anions are bound to multiple binding sites: pyrrole NH (**2a**), $\beta$-CH of furan (**2b**), and $\beta$-CH of thiophene (**2c**). For example, upon the addition of 1 equiv of $Cl^-$ to $CDCl_3$ solution of **2a** ($1 \times 10^{-3}$ M) at 20 °C, the signals of the "inner" NH and "outer" (terminal) NH are shifted from 9.29 and 8.77 ppm to 11.04 and 11.16 ppm, respectively, suggesting that the anions are bound more tightly to the terminal pyrrole NH. This effective binding site for terminal NH has been speculated by X-ray analysis (vide infra). Similar downfield shifts of $\beta$-CH are observed in **2b** and **2c**. Despite these results, **2b**,**c** and α-phenyl **1d** afford fairly smaller $K_a$ values than **1b**, possibly due to distorted aryl rings formed by the sterical hindrance of proximal $\beta$-ethyl units.

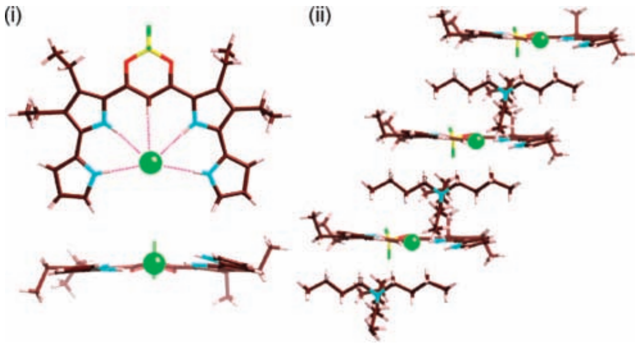

**Figure 4.** Single-crystal X-ray structure of the $Cl^-$ complex of **2a** as (i) monomer structure (top and side views) and (ii) stacking form of **2a**·$Cl^-$ and the TBA cation. Atom color code: yellow green (spherical) refers to chlorine.

Further, X-ray diffraction analysis using a single crystal from an equivalent mixture of **2a** and TBACl has elucidated the solid-state structure of the $Cl^-$ complex of **2a**, wherein a pentacoordinated [1 + 1] complex is observed (Figure 4i).[12] The distances of $N_{inner}$(–H)···Cl and bridging C(–H)···Cl are 3.255, 3.354 ($N_{inner}$(–H)···Cl), and 3.573 (bridging C(–H)···Cl) Å, respectively, while those of $N_{outer}$(–H)···Cl are 3.169 and 3.254 Å. The shorter distance of $N_{outer}$(–H)···Cl as compared to $N_{outer}$(–H)···Cl is correlated to the NMR spectral changes induced by the addition of $Cl^-$. The dihedral angles between the terminal aryl rings and the core planes are estimated as 7.2° and 15.9°, which are smaller than the angle (35.5°) corresponding to the area that is not involved in hydrogen bonding in the anion-free **2a**. The deviation of the mean plane in **2a**·$Cl^-$, consisting of 26 atoms, is 0.16 Å, which is smaller than that of **2a** (0.24 Å). Further, as observed in the anion complex **1c**·$Cl^-$,[7a] the formation of a columnar stacking structure consisting of planar **2a**·$Cl^-$ and a TBA cation is observed (Figure 4ii); the anionic $Cl^-$ complex and TBA are slightly slipped and alternately aligned with the proximal Cl···Cl distance of 8.761 Å.

In summary, we have synthesized heteroaryl-substituted $\pi$-conjugated acyclic anion receptors, e.g., pyrrolyl receptor, which has a distinct electronic state and exhibits extremely efficient anion binding behaviors. By noncovalent interactions, the receptors synthesized in this study can be incorporated in anion-responsive macromolecular systems such as discrete $\pi$-conjugated oligomers, dispersed polymers, and molecular assemblies. This type of incorporation is currently being investigated.

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**Supporting Information Available:** Synthetic procedures and anion binding behaviors (spectral changes and optimized structures) of **2a**−**c** and CIF files for the X-ray structural analysis of **2a**−**c** and **2a**·TBACl. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) The $K_a$ values of **2b**,**c** for anions in $CH_2Cl_2$ are estimated to be 3400 ($Cl^-$), 300 ($Br^-$), 13000 ($CH_3CO_2^-$), 7800 ($H_2PO_4^-$), and 27 ($H_2SO_4^-$) $M^{-1}$ for **2b** and 12000 ($Cl^-$), 1000 ($Br^-$), 55000 ($CH_3CO_2^-$), 11000 ($H_2PO_4^-$), and 40 ($H_2SO_4^-$) $M^{-1}$ for **2c**, which are ca. 10 times greater than those for anions 0.5% EtOH/$CHCl_3$.

(12) Crystal data for **2a**·TBACl (from $CH_2Cl_2$/heptane/toluene (trace)): $C_{27}H_{31}BF_2N_4O_2$·TBACl, Mw = 770.28, monoclinic, $P2_1/n$ (no. 14), $a = 8.761(3)$, $b = 19.396(6)$, $c = 25.376(7)$ Å, $\beta = 104.860(12)°$, $V = 4232(2)$ Å$^3$, $T = 123(2)$ K, $Z = 4$, $D_c = 1.209$ g/cm$^3$, $\mu$(Mo K$\alpha$) = 0.140 mm$^{-1}$, $R_1 = 0.0603$, w$R_2 = 0.1663$, GOF = 1.108 ($I > 2\sigma(I)$). CCDC 585536.