Alkoxy-substituted Derivatives of π-Conjugated Acyclic Anion Receptors: Effects of Substituted Positions

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The synthesis, solid-state assemblies, and anion binding affinities of π-conjugated acyclic anion receptors with alkoxyphenyl substituents are discussed. The position of the alkoxy moiety is essential to determining not only the electronic state but also the anion binding affinity.

It is essential to control the binding properties for guest species due to for example, the facile regulation of the conformations of π-conjugated oligomers and their assembled forms.[1] Among the various available targets, inorganic and biotic anions such as halides, acetates, and phosphates, ubiquitous in biology, are essential, as seen in the activity of enzymes, transport of hormones, protein synthesis, and DNA regulation.[2,3] In contrast to cyclic anion receptors with preorganized structures, acyclic receptors must dynamically change their conformations for binding.[3e] We have previously reported the synthesis of π-conjugated acyclic anion receptors ("molecular flippers"), BF_2 complexes of 1,3-dipyrrolyl-1,3-propanediones (e.g., **1a**–**1c** and **2a**–**2c**; Figure 1a),[4–6] which bind anions using two pyrrole NH groups and a bridging CH group with the inversion of the pyrrole rings (Figure 1b). Using cross coupling reactions, various aryl substituents can be introduced at the pyrrole α-positions. In fact, we have reported the synthesis of α-aryl-substituted receptors with long aliphatic chains (e.g., **1b**), which constitute anion-responsive supramolecular organogels from octane solutions and transition to solutions on the addition of appropriate anions,[4b,6a] whereas amphiphilic receptors that possess hydrophilic chains (e.g., **1c**) form solvent-assisted assemblies such as vesicular structures in aqueous solution.[6d] Further, a β-alkyl-substituted receptor **2a**[5b] can be converted into various π-extended receptors **2b** and **2c** via an α-iodinated intermediate.[6b,6c] In order to control the anion binding affinities of acyclic receptors, both the kinds of substituents on the aryl moieties and their positions are essential. Here, we report the synthesis, solid-state assemblies, and anion binding affinities of acyclic anion receptors with alkoxy units at the ortho, meta, and para positions of the side aryl moieties (**3o1**, **3o8**, **3m1**, **3m8**, **3p1**, and **3p8**; Figure 1c).

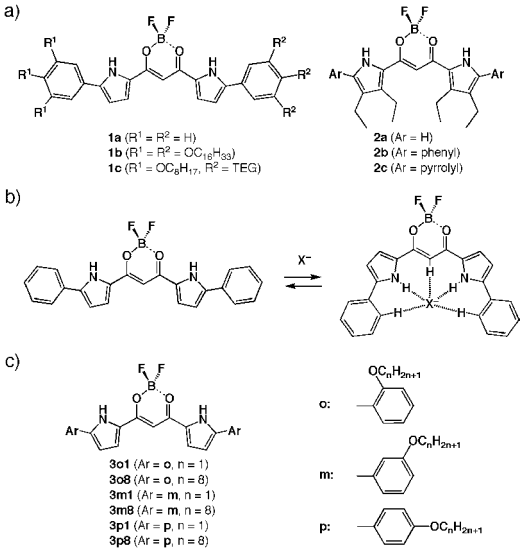

Figure 1. a) BF_2 complexes of dipyrrolyldiketones **1a**–**1c**, **2a**–**2c**; b) anion binding mode of **1a**; c) alkoxy-substituted derivatives (**3o1**, **3o8**, **3m1**, **3m8**, **3p1**, and **3p8**).

α-Alkoxy-substituted anion receptors (**3o1**, **3o8**, **3m1**, **3m8**, **3p1**, and **3p8**) were synthesized in good yields by previously reported procedures[6a] using the corresponding arylpyrroles as starting materials. Chemical identifications for **3o1**, **3o8**, **3m1**, **3m8**, **3p1**, and **3p8** were carried out by ^{1}H NMR and MALDI-TOFMS. The UV–vis absorption maxima (λ_{max}) of **3o1**, **3m1**, and **3p1** in CH_2Cl_2 were observed at 513, 501, and 518 nm, respectively, suggesting that alkoxy-substitution at the ortho and para positions affords a red-shift while that at the meta position has almost no effect in comparison with the λ_{max} value of α-unsubstituted **1a** (500 nm).[6a] Lengths of the alkoxy chains give almost no effects on the electronic states. The order of these λ_{max} values is correlated to the order of the HOMO–LUMO gaps (**3o1**, 3.007 eV; **3m1**, 3.040 eV; **3p1**, 2.969 eV) estimated by DFT calculations.[7] Further, **3o1**, **3m1**, and **3p1** are highly emissive in CH_2Cl_2; the fluorescence wavelengths (and quantum yields, Φ_F) for excitation at the corresponding λ_{max} are 542 (0.97), 533 (0.98), and 558 (0.95) nm, respectively.

Single-crystal X-ray analyses of methoxy-substituted **3o1**, **3m1**, and **3p1** elucidated the molecular structures along with the formation of hydrogen-bonding dimers and π–π stacking assemblies in the solid state (Figure 2).[8] Ortho substituted **3o1** has the methoxy units facing the pyrrole NH, thus forming intramolecular N–H···O hydrogen bonds as observed in solution, whereas the other receptors exhibit N–H···F–B interactions with N(–H)···F distances of 3.04 and 3.38 (**3m1**), and 3.15 and 3.16 (**3p1**) Å. Further, these methoxy-substituted receptors have slightly distorted side aryl rings: the dihedral angles (minimum and maximum values) between the aryl rings and the dipyrrolyl core plane comprising 16 atoms are 12.1 and 18.5° for **3o1**, 21.3 and 28.4° for **3m1**, and 18.9 and 25.9° for **3p1**. These values are slightly smaller (**3o1**) than and comparable (**3m1** and **3p1**) to those of **1a** (20.0 and 28.6°). The smaller values for **3o1** are due to the intramolecular hydrogen bonding between NH and the oxygen atom from the methoxy group. The deviations in the mean plane consisting of 16 atoms are 0.11 Å (**3o1**), 0.042 Å (**3m1**), and 0.043 Å (**3p1**); these values are larger than that of **1a** (0.035 Å). Compared with **3m1** and **3p1**, **3o1** has edge-to-edge-like stacking assemblies.

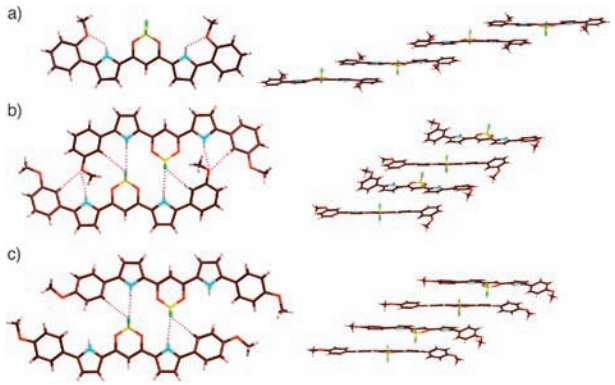

Figure 2. Single-crystal X-ray structures (left, monomer or hydrogen-bonded dimers; right, stacking structures) of a) **3o1**, b) **3m1**, and c) **3p1**. Atom color code: brown, pink, yellow, green, blue, and red refer to carbon, hydrogen, boron, fluorine, nitrogen, and oxygen, respectively.

Table 1. Binding constants (K_a, M^{-1}) of **1a** (as a reference), **3m1**, **3m8**, **3p1**, and **3p8** with various anions in the form of TBA salts in CH_2Cl_2[a]

	K_a (**1a**)[b]	K_a (**3m1**)	K_a (**3m8**)	K_a (**3p1**)	K_a (**3p8**)
Cl^-	30000	57000 (1.9)	25000 (0.83)	26000 (0.67)	24000 (0.80)
Br^-	2800	5100 (1.8)	2100 (0.75)	2600 (0.82)	2400 (0.86)
$CH_3CO_2^-$	210000	490000 (2.3)	420000 (2.0)	140000 (0.67)	330000 (1.6)
$H_2PO_4^-$	72000	38000 (0.53)	38000 (0.53)	27000 (0.38)	28000 (0.39)
HSO_4^-	540	270 (0.50)	150 (0.28)	240 (0.44)	180 (0.33)

[a]The values in the parentheses are the ratios of the K_a values to the K_a value of **1a**. [b]Ref. 6a.

The anion binding properties of the alkoxy-substituted receptors have been examined by ^{1}H NMR and UV–vis spectroscopy upon the addition of anions in the form of tetrabutylammonium (TBA) salts. The binding constants (K_a) of **3m1**, **3m8**, **3p1**, and **3p8** for anions, as determined by UV–vis absorption spectral changes (Table 1), in CH_2Cl_2 are almost comparable to those of **1a**. There are no significant differences between methoxy- and octyloxy-substituted receptors. The binding mode of for example, **3p8** for anions has been deduced from the ^{1}H NMR spectral changes in CD_2Cl_2 (1×10^{-3} M) at 20 °C in the presence of 2.0 equiv of TBACl: ^{1}H NMR revealed downfield shifts for the pyrrole NH, bridging CH, and *o*-CH from 9.57, 6.54, and 7.57 ppm to 12.26, 8.94, and 8.14 ppm, respectively. Further, both *o*-CH sites of **3m1** and **3m8** associate with anions.[9] In contrast, the intramolecular hydrogen bonding in ortho substituted **3o1** and **3o8** affords complicated binding modes in ^{1}H NMR along with low affinities for anions. This suggests that ortho substituents can interfere with anion binding.

In summary, the positions of the substituent influences the structures and properties, such as the organized structures and anion binding behavior, of π-conjugated acyclic anion receptors with alkoxyphenyl substituents. The introduction of a single-alkoxy-substituted aryl moiety to the subunits of supramolecular assemblies is currently underway.

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8 Crystal data for **3o1** (from CH_2Cl_2/hexane): $C_{25}H_{21}BF_2N_2O_4$, $M_r = 462.25$, triclinic, $P\bar{1}$ (no. 2), $a = 7.961(6)$, $b = 8.167(5)$, $c = 18.427(10)$ Å, $\alpha = 89.90(3)$, $\beta = 81.04(2)$, $\gamma = 63.71(3)°$, $V = 1058.0(12)$ Å^3, $T = 123(2)$ K, $Z = 2$, $D_c = 1.451$ g/cm^3, μ(Mo Kα) = 0.110 mm^{-1}, 10356 reflections measured, 4803 unique ($R_{int} = 0.0684$), $R_1 = 0.0630$, $wR_2 = 0.1286$, GOF = 1.026 ($I > 2\sigma(I)$). Crystal data for **3m1** (from CH_2Cl_2/hexane): $C_{25}H_{21}BF_2N_2O_4 \cdot CH_2Cl_2$, $M_r = 547.17$, monoclinic, $P2_1/a$ (no. 14), $a = 12.524(5)$, $b = 12.858(4)$, $c = 16.237(8)$ Å, $\beta = 106.788(18)°$, $V = 2503.1(18)$ Å^3, $T = 123(2)$ K, $Z = 4$, $D_c = 1.452$ g/cm^3, μ(Mo Kα) = 0.311 mm^{-1}, 23253 reflections measured, 5699 unique ($R_{int} = 0.0822$), $R_1 = 0.0585$, $wR_2 = 0.1218$, GOF = 1.049 ($I > 2\sigma(I)$). Crystal data for **3p1** (from CH_2ClCH_2Cl/hexane): $C_{25}H_{21}BF_2N_2O_4$, $M_r = 462.25$, orthorhombic, *Pbca* (no. 61), $a = 12.808(3)$, $b = 25.217(6)$, $c = 13.176(2)$ Å, $V = 4255.6(15)$ Å^3, $T = 123(2)$ K, $Z = 8$, $D_c = 1.443$ g/cm^3, μ(Mo Kα) = 0.109 mm^{-1}, 34899 reflections measured, 4868 unique ($R_{int} = 0.1020$), $R_1 = 0.0420$, $wR_2 = 0.0939$, GOF = 0.960 ($I > 2\sigma(I)$). Crystallographic data for **3o1**, **3m1**, and **3p1** have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-712987–712989. Copy of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.uk).

9 Optimized structures of the receptors and anion binding complexes are presented in the Supporting Information Ref 10.

10 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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