Anion Modules: Building Blocks of Supramolecular Assemblies by Combination with π-Conjugated Anion Receptors

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Ⓢ *Supporting Information*

ABSTRACT: Dipyrrolyldiketone boron complexes, as π-conjugated acyclic anion receptors, act as building sub-units of various assemblies through noncovalent interactions in the form of receptor–anion complexes. Instead of, or in addition to, the modification of receptor structures, the introduction of *anion modules* as building blocks for the assemblies was found to be useful in forming various soft materials. Gallic carboxylate derivatives **3-n** ($n = 16, 18, 20$), as tetrabutylammonium (TBA) salts, form receptor–anion-module complexes that can be used to fabricate supramolecular assemblies. Combinations of aliphatic anion modules **3-n** and receptors **1a,b** along with a TBA cation afforded products with mesophases, which were indicated by differential scanning calorimetry and polarized optical microscopy. X-ray diffraction measurements of the solid states and mesophases of **1a·3-n·TBA** and **1b·3-n·TBA** revealed highly ordered structures including lamellar structures, which could be modulated by the lengths of the alkyl chains of the modules. Functional materials exhibiting electrical conductivity were fabricated by using combinations of anionic building blocks that form assemblies by themselves and π-conjugated acyclic receptors.
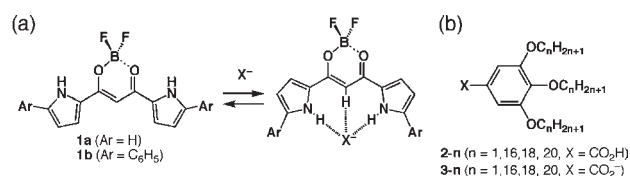
Figure 1. (a) π-Conjugated acyclic anion receptors **1a,b** and their anion-binding mode and (b) gallic acid derivatives **2-n** and **3-n** ($n = 1, 16, 18, 20$).

Interactions between two complementary components are efficient strategies to form various supramolecular organized structures.[1] Among various interactions, anion binding is an effective process for achieving the formation of such assemblies owing to its electrostatic hydrogen bonding, which can tightly connect multiple building units using a small number of non-covalent bonds.[2] Appropriate negatively charged species and open-chain receptors could provide various complexes, which may be suitable for assembled structures when assisted by supplementary interactions. As π-conjugated planar acyclic anion receptors, dipyrrolyldiketone boron complexes (e.g., **1a,b**), which bind anions by the inversion (flipping) of two pyrrole rings (Figure 1a),[3,4] behave as essential building blocks of supramolecular assemblies such as supramolecular gels[4b,d] and thermotropic liquid crystals[4d] based on the core π-planes in the presence of aliphatic side chains. In particular, combinations of the halide anion complexes of receptors bearing long alkyl chains and appropriate cations afford charge-by-charge assemblies consisting of alternately stacking planar charged species.[4f] Instead of the modification of receptor structures or in addition to that, the introduction of

functionalized module anions such as gallic carboxylate derivatives (**3-n**, $n = 1, 16, 18, 20$; Figure 1b) by the replacement of spherical halide anions would result in the fabrication of utility organized structures. This would be possible by complexing with π-conjugated receptors as planar platforms, on the basis of van der Waals interactions between the alkyl chains. In this Communication, the formation and properties of supramolecular assemblies based on anion modules by combinations of the modules with acyclic anion receptors are reported. The assemblies are a new type of soft materials formed by electrostatic interactions between charged components and are different from related materials that have thus far been reported as liquid crystals on the basis of ionic mesogens.[5−7]

Gallic acid derivatives **2-n** ($n = 1, 16, 18, 20$) are commercially available for **2-1** and were synthesized for **2-n** ($n = 16, 18, 20$) according to the procedures described in the literature.[8] The corresponding carboxylates **3-n** ($n = 16, 18, 20$) were obtained by treating the carboxylic acids of **2-n** with excess tetrabutylammonium (TBA) hydroxide in CH_2Cl_2, followed by recrystallization from tetradecane for **3-n** ($n = 16, 18, 20$). On the other hand, **3-1** was obtained by mixing **2-1** with 1 equiv of tetrapropylammonium (TPA) hydroxide. Subsequently, **3-n** as TPA or TBA salts were subjected to equivalent amounts of **1a** and **1b** to form complexes. Receptors **1a** and **1b** did not yield soft materials but formed 3D organized crystal structures in the presence of tetraalkylammonium salts of $Cl^−$ and $Br^−$.[4a,b,e] The formation and purification of complexes between **1a,b** and **3-n** ($n = 1, 16, 18, 20$) are performed by recrystallization from CH_2Cl_2/Et_2O ($n = 1$ as a TPA salt) and 1,4-dioxane ($n = 16, 18, 20$ as TBA salts). The identification of **3-n** ($n = 1, 16, 18, 20$) as TPA or TBA salts and their complexes with **1a,b** was performed by ^{1}H NMR and elemental analyses. A carboxylate-binding mode is indicated
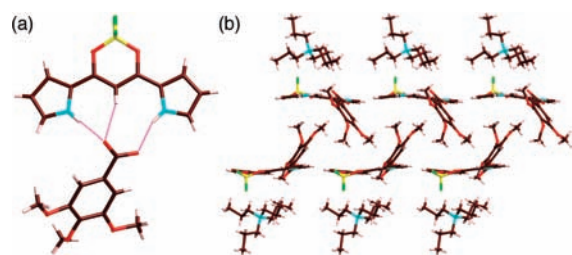
Figure 2. Single-crystal X-ray structure of **1a·3-1** as a TPA salt: (a) top view and (b) side packing view. One chiral conformation is represented. TPA cations are omitted in the top view. Atom color code: brown, pink, yellow, green, blue, and red indicate carbon, hydrogen, boron, fluorine, nitrogen, and oxygen, respectively.

by various spectra[9] along with theoretical studies[10] and the single-crystal X-ray analysis of **1a·3-1** as a TPA salt (Figure 2a).[11] In the solid state, two carboxylate oxygens of **3-1** form hydrogen bonding with two pyrrole NH and bridging CH with $N(-H)\cdots O$ and $C(-H)\cdots O$ distances of 2.707/2.697 and 3.179 Å, respectively. A less symmetrical interaction results in a dihedral angle of 47.19° between the receptor and the aryl moiety of **3-1** to afford chiral conformation in **1a·3-1**. The benzoate is associated with **1a** in an unsymmetrical fashion, as observed from the angle of the bridging-C—carboxylate-C—ipso-C given by 142.65°, which is a substantial aberration from the 180° value in the case of a symmetrical binding arrangement. The same chiral conformations of the receptor—benzoate complexes are aligned and form layers, two of which are located in the alternate stacking with the layers of TPA (Figure 2b). Further, solid-state absorption of **1a·3-16·TBA** at, for example, 450 nm (λ_{max}) is red-shifted to that in solution (430 nm), owing to interactions between the receptor—anion-module complex units in the solid state.

Organized structures of the complexes of **1a,b** and the aliphatic anion modules **3-n** (n = 16, 18, 20) as TBA salts were examined. Differential scanning calorimetry (DSC) of the complexes **1a·3-n·TBA** and **1b·3-n·TBA** (n = 16, 18, 20) exhibited the existence of mesophases with transition temperatures (°C) of 42/56/103 (**1a·3-16·TBA**), 67/73/101 (**1a·3-18·TBA**), 67/81/96 (**1a·3-20·TBA**), 40/61/81 (**1b·3-16·TBA**), 53/64/86 (**1b·3-18·TBA**), and 61/82/89 (**1b·3-20·TBA**) during the second heating (5 °C/min).[12] The tendencies pertaining to melting and clearing seem to be dependent on the alkyl chain lengths of anion modules and the presence or absence of α-phenyl moieties in the receptors. Further, polarized optical microscopy (POM) images of **1a·3-n·TBA** and **1b·3-n·TBA** (n = 16, 18, 20) in the mesophases exhibit a birefringence attributable to liquid crystal properties with, for example, focal conic and mosaic textures (Figure 3). In these mesophases, the emergence of POM textures is significantly dependent on the conditions of formation processes such as heating and cooling paces.

Structures in the solid states and mesophases of **1a·3-n** and **1b·3-n** (n = 16, 18, 20) as TBA salts were examined by synchrotron X-ray diffraction (XRD) analysis at variable temperatures (BL40B2 at SPring-8); the structures exhibited fairly complicated diffraction patterns in many cases. However, the solid states at rt after melting once to isotropic liquids (Iso) had clear and simple XRD patterns, exhibiting the formation of lamellar structures with c = 4.34, 4.56, and 4.76 nm for **1b·3-n·TBA** (n = 16, 18, 20), respectively (Figure 4, left panel).[13] These c values
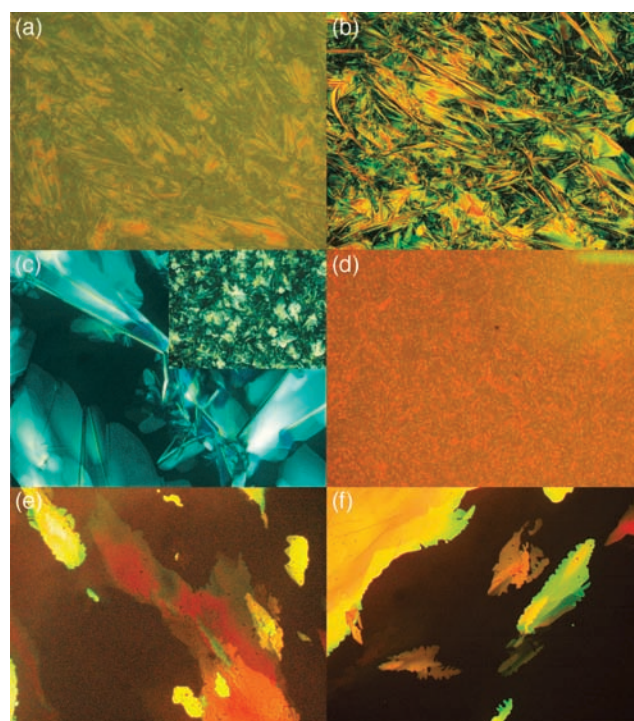

Figure 3. POM images of (a) **1a·3-16·TBA** at 90 °C, (b) **1a·3-18·TBA** at 95 °C, (c) **1a·3-20·TBA** at 92 and 80 °C (inset), (d) **1b·3-16·TBA** at 80.5 °C, (e) **1b·3-18·TBA** at 83 °C, and (f) **1b·3-20·TBA** at 86 °C. All the measurements were conducted during cooling processes. Like **1a·3-20·TBA**, multiple mesophases were often observed by POM.
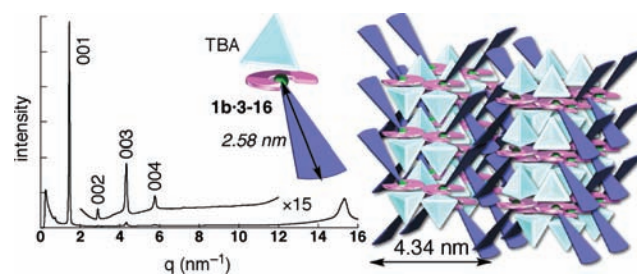

Figure 4. XRD pattern (left) and an assembled model (right) of **1b·3-16·TBA** as the solid state at rt prepared after melting. The assembled structure indicated by XRD seems more disordered than the proposed model. The value of 2.58 nm was estimated by theoretical study.

in **1b·3-n·TBA** are consistent with the approximately summed lengths of the two receptor—anion-module complexes, as supported by molecular modeling. Further, there are no clear diffractions assignable to the repeated distances of the receptor—anion-module complexes, suggesting that more disordered structures are constructed around the anionic components (receptor—anion-module complexes) and cations (TBA), which can form charge-by-charge assemblies. Under the consideration of the solid-state assembled mode of **1a·3-1·TPA**, the anion modules **3-n** may be located with distorted angles to the receptor plane and can predominantly control the assembled modes through van der Waals interactions of aliphatic chains (Figure 4, right panel). This is one of the characteristic points of assemblies comprising

anion modules. Similarly, the solid state of $1a \cdot 3$-$20 \cdot$ TBA forms a lamellar structure with $c = 4.64$ nm, in comparison with the broad peaks of $1a \cdot 3$-$16 \cdot$ TBA and $1a \cdot 3$-$18 \cdot$ TBA. On the other hand, mesophases of $1a \cdot 3$-$n \cdot$ TBA and $1b \cdot 3$-$n \cdot$ TBA ($n = 16$, 18, 20) exhibited complicated and relatively sharp XRD patterns, which were presumably derived from soft crystals as significantly ordered states of liquid crystals.[6b,14] Although the exact packing structures cannot be determined at present, mesophases are basically constructed by lamellar and related structures in highly ordered modes as can be speculated from the patterns obtained from the solid states. Among various conditions and combinations of receptors and modules, $1a \cdot 3$-$16 \cdot$ TBA at 93 °C and $1a \cdot 3$-$18 \cdot$ TBA at 90 °C during the second heating exhibit lamellar structures with $c = 5.53$ and 5.89 nm, respectively. Further, diffractions possibly assignable to repeated distances of charge-by-charge assemblies (ca. 7−8 Å) were also observed, for example, at 7.61 and 7.49 Å at 53 and 93 °C, respectively, for $1a \cdot 3$-$16 \cdot$ TBA and at 7.68 and 7.62 Å at 70 and 90 °C, respectively, for $1a \cdot 3$-$18 \cdot$ TBA during the second heating. This suggests that the interaction between the anionic planes of the receptor−anion-module complex and the TBA cations is weak but contributes to the construction of assembled structures.

Ordered assembled structures, as observed in the receptor−anion-module complexes, are suitable for use as charge-conductive materials. Therefore, we conducted flash-photolysis time-resolved microwave conductivity (FP-TRMC) measurements,[15] which allow the estimation of the behavior of mobile charge carriers. Receptor−anion-module complexes $1a \cdot 3$-$16 \cdot$ TBA and $1b \cdot 3$-$16 \cdot$ TBA as solid states after once melting showed the mobility of the charge carriers of 0.02 and 0.05 cm^2/V·s, respectively, at 40 °C and of 0.007 and 0.003 cm^2/V·s for mesophases of the respective compounds at 46 and 50 °C. In the mesophase of $1a \cdot 3$-$16 \cdot$ TBA at a higher temperature of 70 °C, the value of mobility drops drastically to 9×10^{-4} cm^2/V·s; however, surprisingly, the mobility recovers to 0.04 cm^2/V·s in the mesophase of $1b \cdot 3$-$16 \cdot$ TBA at 70 °C. These changes in the mobility of charge carriers may be ascribable to the transitions among solid states and several mesophases, even though it is not easy to describe the detailed structures of mesophases as mentioned previously.

The conductivity measurement of $1b \cdot 3$-$16 \cdot$ TBA was also performed under dark conditions, showing a drastic increase in the electrical conductivity of $1b \cdot 3$-$16 \cdot$ TBA from 5×10^{-11} to 3×10^{-8} S/m, with an increase in temperature from 28 to 67 °C. This strongly suggests that the population of thermally activated charge carriers with equivalent mobility increases considerably in the mesophase of $1b \cdot 3$-$16 \cdot$ TBA, causing a dramatic transition in the electrical conductivity of the materials.

In summary, we have described the formation of various supramolecular assemblies based on anionic modules and π-conjugated acyclic receptors. The assemblies in the solid states and mesophases suggest that the combination of appropriate modules and π-conjugated receptor molecules affords fairly ordered organized structures, which can be influenced by the platform receptor geometries along with the properties of the modules, such as alkyl chain lengths. Assemblies of multiple components, receptors, and anionic species, in this case, can be achieved with the help of the characteristic features of the linear geometries of the receptors. Further, an introduction of the functional properties to anion modules is currently under preparation.

■ ASSOCIATED CONTENT

S **Supporting Information.** Synthetic procedures and analytical data, anion-binding properties, a CIF file for the X-ray structural analysis of $1a \cdot 3$-$1 \cdot$ TPA, and complete ref 10b. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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(9) ^{1}H NMR analysis indicated the formation of carboxylate complexes in the solution state. Binding constants (K_a) of **1a** and **1b** for **3-16** as a TBA salt were estimated as 600 000 and 380 000 M^{-1}, respectively, by UV/vis absorption spectral changes in CH_2Cl_2.

(10) (a) Complexes of **1a,b** with acetate, benzoate, and **3-1** were optimized at the DFT level, whereas those with **3-*n*** (*n* = 16, 18, 20) were optimized at AM1. (b) Frisch, M. J., et al. *Gaussian 03*, revision C.01; Gaussian, Inc.: Wallingford, CT, 2004.

(11) Crystal data for **1a·3-1·TPA** (from acetone/^{i}Pr$_2$O): $C_{33}H_{48}$-BF$_2$N$_3$O$_7$, M_w = 647.55, orthorhombic, $P2_12_12_1$ (no. 19), a = 9.686(2) Å, b = 16.213(5) Å, c = 21.630(5) Å, V = 3396.9(14) Å^3, T = 123(2) K, Z = 4, D_c = 1.266 g/cm^3, μ(Mo Kα) = 0.095 mm^{-1}, R_1 = 0.0427, wR_2 = 0.0869, GOF = 1.039 ($I > 2\sigma(I)$). CCDC 810681.

(12) (a) Modules **3-*n*** (*n* = 16, 18, 20) as TBA salts exhibit the mesophases with transitions at 47/71, 56/76, and 67/71/81 °C (on second heating), respectively, which were determined by DSC, POM, and XRD analyses. (b) The DSC analysis suggested that the transitions of **1a·3-*n*·TBA** and **1b·3-*n*·TBA** (*n* = 16, 18, 20) in the cooling process were at 55/40, 64, 69, 36/32, 50, and 59 °C, respectively, but the POM analysis showed that the transitions were at higher temperatures, presumably because of the existence of supercooling properties, which may occur because of the existence of multiple components forming mesophases.

(13) Modules **3-*n*** (*n* = 16, 18, 20) as TBA salts, as the solid states after melting, also form lamellar structures with c = 3.20, 3.49, and 3.75 nm, respectively, which are consistent with the optimized structures at the AM1 level.

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