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Charge-by-charge assemblies based on planar anion receptors*

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Abstract: This critical overview proposes a new concept, a *charge-by-charge assembly*, which consists of alternately stacked positively and negatively charged species, by introducing examples of planar anionic structures in the solid state. The preparation of planar organic anions is not easy; however, complexation of planar anion receptor molecules with inorganic anions is found to be an efficient strategy for constructing them. As suitable motifs, dipyrrolyldiketone boron complexes exhibit various receptor–anion complexes and charge-by-charge assemblies in the solid state. The concept discussed here can be applied to useful soft materials as well as crystals by modifying the anion receptors and cations.

Keywords: anion receptors; cations; π-conjugated molecules; host–guest chemistry; supramolecular assemblies.

INTRODUCTION

The arrangement of charged species is an important issue in the fabrication of nanoscale architectures of functional materials consisting of multiple components [1]. In contrast to inorganic salts, which are usually ordered structures such as crystals, organic and inorganic–organic hybrid salts often form soft materials. For example, the bulky geometries of both cationic and anionic species are effective for producing ionic liquids at room temperature to avoid crystallization by weaker ionic interactions [2]. Moreover, soft materials that use electrostatic interactions between charged components have thus far been limited to liquid crystals comprising ionic mesogens [3]. For example, Kato et al. reported that various ionic liquid crystals composed of alkyl-substituted imidazolium salts, which produce columnar structures, exhibit ion conduction [3b,f]. As such soft materials illustrate, the geometry of charged species is one of the main factors determining the states and properties of ionic compounds. Therefore, interactions between positively and/or negatively charged planar molecules would enable the formation of dimension-controlled assemblies consisting of alternately stacked cationic and anionic components. As compared to cations, planar anionic structures for use as building blocks in supramolecular stacking assemblies are not easy to prepare, presumably because excess electrons must be delocalized to, for example, π-conjugated systems to prevent the anions from suffering electrophilic attacks.

A different protocol for forming planar anions is the complexation of π-conjugated planar receptor molecules and anions [4]. Various electronically neutral receptor molecules can be prepared as platforms for planar structures (Fig. 1). In this case, modification and functionalization of the receptor mol-

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ecules enable the formation of useful materials. This critical overview focuses on solid-state structures from alternately arranged ion pairs, i.e., *charge-by-charge assemblies*, based on planar anion receptors. Although only crystal structures are discussed here, the modification of the receptor molecules and cations yields soft functional materials in which the arrangement of the components is relatively ordered as compared to that in soft materials reported thus far. The concept of charge-by-charge assembly is crucial and is expected to be useful in various fields of chemistry.

Fig. 1 Schematic representation of the formation of a planar anionic structure based on a planar anion receptor.

SOLID-STATE CHARGE-BY-CHARGE ASSEMBLIES FROM π-CONJUGATED HETEROCYCLES

To construct planar anionic structures, it is essential to design and synthesize relatively planar π-conjugated systems that can efficiently bind anions. One way to prepare appropriate receptor molecules is to develop novel synthetic procedures. Click chemistry produces triazole moieties, whose CH site is electropositive and can act as a hydrogen-bonding donor site because of the large dipole moment of triazole. In 2008, Flood and Craig independently reported protocols using click chemistry for the synthesis of triazole-based anion receptors, for example, **1** and **2a**,**b** (Fig. 2a) [5,6]. These receptor molecules bind anions using only CH sites, whose cooperative binding stabilizes the receptor–anion complexes. For example, the binding constant of macrocycle **1** and linear receptor **2a** for Cl^- was estimated to be 1.1×10^7 M^{-1} in CH_2Cl_2 and 1.7×10^4 M^{-1} in acetone-d_6. Among many fascinating triazole-based receptors, Craig et al. reported through single-crystal X-ray analysis the Cl^- complex of **2b** as a tetrabutylammonium (TBA) salt, whose hemi-circular geometry interacts with Cl^- to form a crescent-shaped conformation with a relatively planar geometry [6]. Counter TBA cations are located close to the receptor–anion complex, forming alternately stacked charge-by-charge assembly (Fig. 2b).

Heterocyclic NH acts as a more polarized hydrogen-bonding site for binding anions than CH. Jeong et al. reported various indole-based linear oligomers, which form anion-driven helical structures, as well as a macrocycle **3** (Fig. 3a) [7]. Macrocycle **3** efficiently binds anions, for example, with a K_a value of 2.1×10^6 M^{-1} for Cl^- in CD_3CN. Jeong et al. constructed single crystals of a Cl^- complex of the macrocycle as a TBA salt. The Cl^- is located in the middle of four indole NH groups and is stabilized by four hydrogen bonds with N(–H)···Cl distances of 3.14 Å. However, the Cl^- is only partially inserted into the cavity of **3**, which implies that the internal size is slightly too small for Cl^-. It is also noteworthy that the TBA cation is located on the plane of the aryl rings, possibly owing to interaction between the cation and the planar anion. Interestingly, **3**·Cl^- forms not a charge-by-charge infinite columnar structure but a [2 + 2]-type discrete assembly, in which the distance between two macrocycle planes and that between Cl^- ions are 8.17 and 5.08 Å, respectively (Fig. 3b). In this case, two macrocycles appear to capture a pair of TBACl between them [7a]. On the other hand, Gale et al. reported indole-appended isophthalamide and 2,6-dicarboxamidopyridine **4a**,**b** (Fig. 3c) as acyclic anion receptors. The solid-state structures of the F^- complexes of **4a**,**b** are similar. They reveal that the receptors have adopted twisted conformations in which one indole is oriented above the central aromatic ring in the receptor and one is below it as a result of the coordination of F^- via four hydrogen bonds. The packing diagram shows distorted F^- complexes arranged in a significantly slipped columnar structure by bridging counter TBA cations (Fig. 3d). The Cl^- complexes of **4a**,**b** exhibit the solid-state structures in

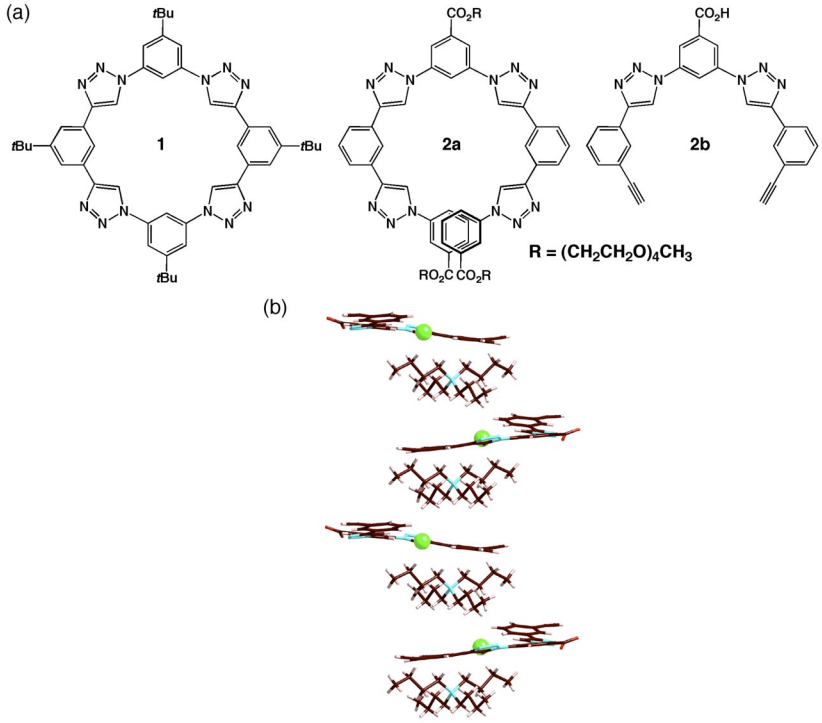

Fig. 2 (a) Triazole-based anion receptors **1** and **2a**,**b** and (b) a selected stacking structure in the single-crystal X-ray analysis of **2b**·TBACl[6] (reproduced from a cif file: CCDC-663329). Solvent water molecules associated with Cl^- are omitted for clarity.

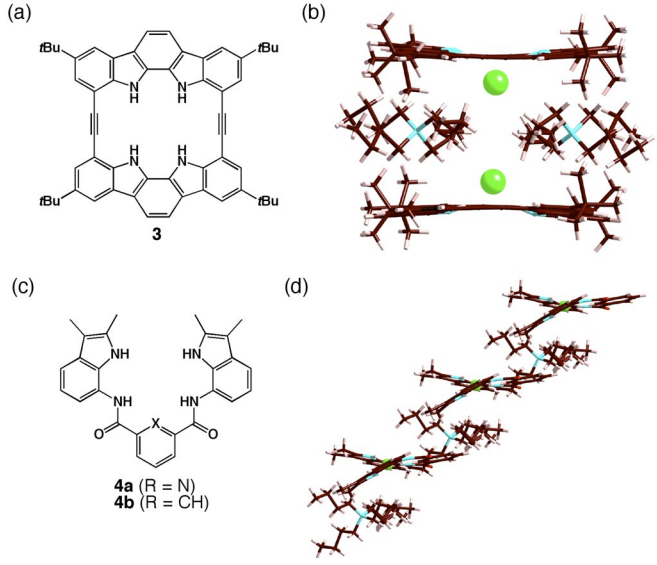

Fig. 3 (a) Indole-based macrocycle **3**, (b) a selected assembled structure observed by single-crystal X-ray analysis of **3**·TBACl[7a] (reproduced from a cif file: CCDC-288190), (c) indole-appended isophthalamide and 2,6-dicarboxamidopyridine **4a**,**b**, and (d) a selected stacking structure observed by single-crystal X-ray analysis of **4b**·TBAF[8] (reproduced from a cif file: CCDC-640967).

which the anion is located above and is bound by four hydrogen-bonding donor groups [8]. Some of the anion complexes of the π-conjugated molecules discussed in this paragraph are not appropriate motifs for forming planar receptor–anion complexes and alternately stacked columnar structures. Therefore, it is necessary to explore more suitable planar complexes for the fabrication of ordered charge-by-charge assemblies.

SOLID-STATE CHARGE-BY-CHARGE ASSEMBLIES FROM π-CONJUGATED ACYLCIC OLIGOPYRROLES

Here, we focus on effective components of planar receptor molecules. Pyrrole, like the analog structure of indole, is a building block for planar anion receptors that is well known as a π-conjugated aromatic heterocyclic molecule [9]. Pyrrole is found not only in biotic dyes such as heme and chlorophyll but also in artificial porphyrin derivatives [10]. Pyrrole rings often appear in preorganized macrocycles such as porphyrins, in which their N sites are located on the inside of fairly rigid closed structures. Consequently, pyrroles cannot achieve all of their potential as interaction sites. Therefore, new aspects of pyrrole rings may be revealed by exploring novel planar oligopyrrolic systems, which may find application in functional supramolecular materials that exploit these new properties and phenomena. In particular, supramolecular assemblies built from planar pyrrole-based anion receptors should exhibit anion-responsive behavior and, under the appropriate conditions, could form functional organized structures consisting of cationic and anionic species. For example, Sessler et al. reported sp^3-bridged cyclic oligopyrroles, calixpyrroles, which form various anion complexes in solution and solid state [11]. In fact, it is remarkable that anion complexes of calixpyrroles form solid-state assemblies with countercations including not only tetraalkylammonium cations but also metal ions. However, the nonplanar structures of calixpyrroles appear unsuitable for stacking structures even if their peripheries are modified. Therefore, in this section, we will discuss recent progress in developing pyrrole-based planar anion receptors that can form solid-state charge-by-charge assemblies.

Recently, Maeda et al. began focusing on the synthesis of acyclic π-conjugated molecules with hydrogen-bonding donor pyrrole NH site(s) [12–16]. In 2005, Maeda et al. reported the first dipyrrolyldiketone BF_2 complex **5** (Fig. 4) as a candidate π-conjugated acyclic anion receptor with the potential to form stacking structures. This complex consists of two pyrrole rings and a boron-bridged 1,3-propanedione moiety. The pyrrole rings, which exist even in acyclic structures, are stabilized by the neighboring electron-withdrawing carbonyl unit. Therefore, the skeleton structure could be appropriate for various uses such as sensors and functional materials. BF_2 complex **5** does not form a preorganized conformation because the two pyrrole NH units are not located at appropriate positions for anion binding. Upon the addition of anions, receptor **5**, a molecular flipper, exhibits inversion of the two pyrrole rings and binds the anions using the pyrrole NH and bridging CH to form a planar receptor–anion complex (Fig. 4). N–H···X^- and bridging C–H···X^- interactions are implied by the ^{1}H NMR chemical shifts of other molecular flippers upon the addition of anions in the form of TBA salts. Furthermore, the discrete resonances of the two species—the free receptor and the anion complex—suggest that the equilibrium between these states is too slow to be detected on the timescale of NMR, possibly because the pyrrole must invert before anion binding can occur [13a].

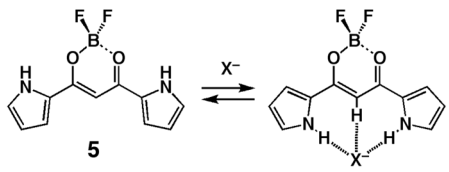

Fig. 4 Pyrrole-based acyclic anion receptor **5** and its anion-binding mode.

The library of available pyrrole derivatives reported thus far shows that the introduction of substituents to the receptor framework of **5** yields a variety of molecular flippers (Figs. 5a–c). Maeda et al. prepared, for example, α-aryl-substituted **6a**,**b** [14a] and β-benzo-fused **7** [14h] along with α-alkyl-substituted **8-n** [13a,e] β-alkyl- and β-fluorine-substituted **9a**, **10a**, and **11a** [13c,d,f], and (partially) binding-site-blocked receptors [13b] from the corresponding pyrrole derivatives. β-Substituted receptors **9a**, **10**, and **11** can act as building blocks for π-extended derivatives and covalently linked oligomers owing to their free α-pyrrole positions. In fact, selective iodination at the α-positions of β-substituted **9a**, **10**, and **11** by treatment with *N*-iodosuccinimide (NIS) in CH_2Cl_2 is found to be a key step in synthesizing iodinated derivatives [14b,k], which are essential starting materials in coupling reactions used for various functional molecules. For example, Suzuki cross-coupling of iodinated derivatives and arylboronic acids afforded bisaryl-substituted **9b**,**c** [14b,c,]. Covalently linked dimers and tetramer **12a**–**c**, prepared by similar procedures, were found to exhibit anion-driven helical structures [14b,i]. Furthermore, catechol and diphenyl substitutions at a boron unit gave boron-modified receptor molecules **13a**–**d** and **14a**–**d** (Fig. 5d) [15]. In addition, receptors bearing long alkyl chains and hydrophilic chains, some of which are building subunits of anion-responsive soft materials [17], were also prepared [14a,e–g,j,k]. The detailed properties of these anion receptors are discussed in reviews [12] and the relevant literature [13–15].

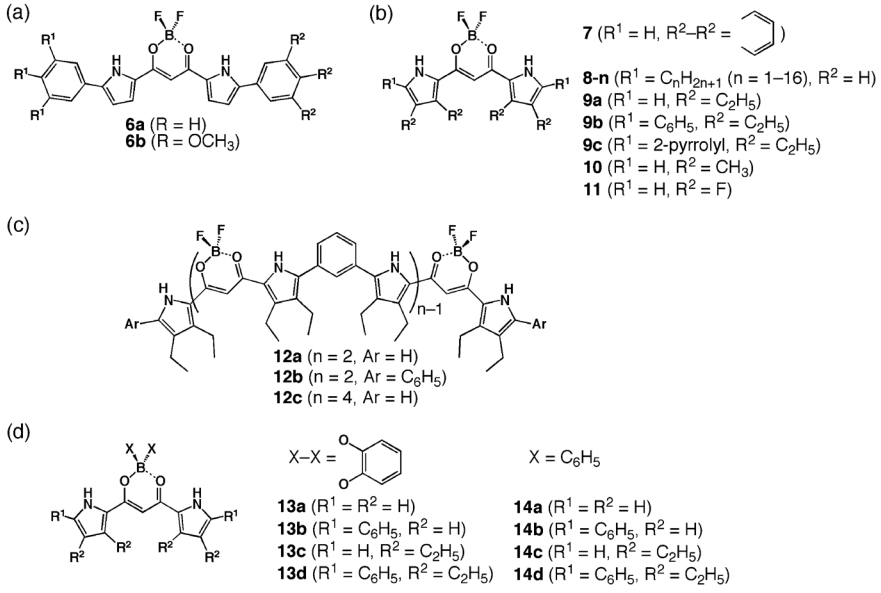

Fig. 5 (a–d) Various derivatives of dipyrrolyldiketone boron complexes **6**–**14**.

In addition, the solid-state structures of receptor–anion complexes **5**·Cl^- [13a], **5**·Br^- [14h], **6a**·Cl^- [14a], **6a**·Br^- [14h], **6b**·Cl^- [14a], **7**·Br^- [14h], **8-2**·Cl^- [13e], **9c**·Cl^- [14c], **11**·Cl^- [13c], **14a**·Br^- [15b], **14b**·Br^- [15b], **14c**·Br^- [15b], and **14d**·Cl^- [15b] prepared from TBA or tetrapropylammonium (TPA) salts, as revealed by single-crystal X-ray analyses, exhibit anion-bridged 1D chains (**5**, **7**, and **11**) (Fig. 6) and regular [1 + 1] complexes (**6a**,**b**, **8-2**, **9c**, and **14a**–**d**) (Fig. 7). As the packing diagram shows, receptor–anion complexes behave as building blocks of electrostatically mediated alternately stacked structures consisting of planar anions (receptor–anion complexes) and tetraalkylammonium cations [18]. These charge-by-charge columnar assemblies, which have been observed in the crystal state as 3D organized structures, allow the formation of dimension-controlled organic salts when planar anions are used under appropriate conditions. Only selected views are illustrated here;

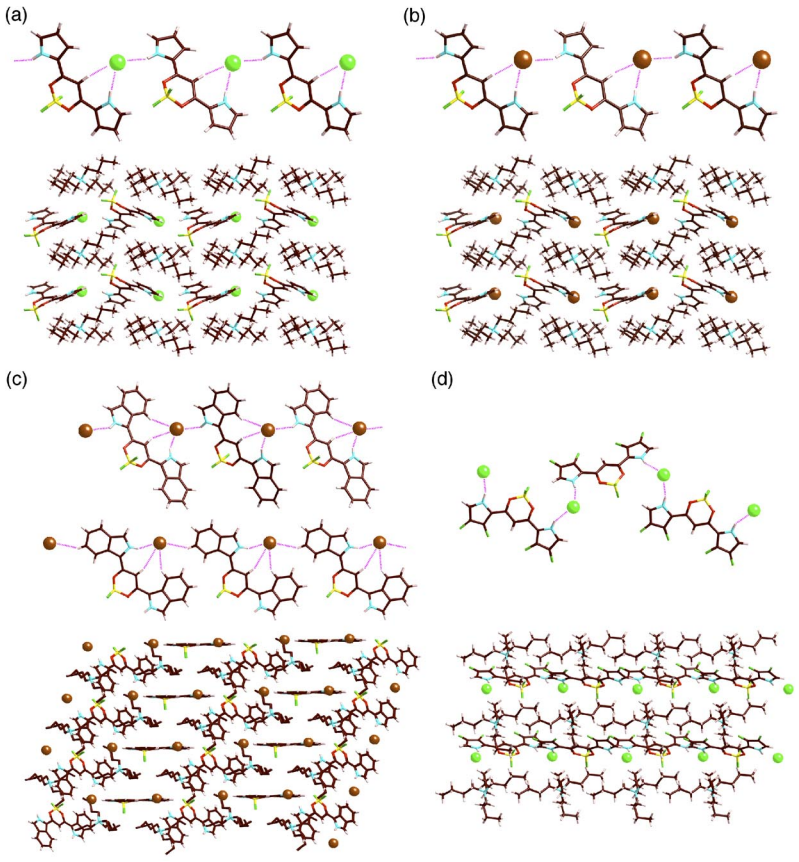

Fig. 6 Selected 1D chain assembled structures and packing diagrams from single-crystal X-ray analyses of (a) **5**·TBACl [13a], (b) **5**·TBABr [14h], (c) **7**·TBABr (two types of 1D chain) [14h], and (d) **11**·TBACl [13c] (reproduced from cif files: CCDC-270297, 760823, 760825, and 290271, respectively).

details such as distances and angles are given in the respective cif files. Of course, the packing diagrams are determined not only by interactions between core moieties, receptor–anion planes and counter-cations, but also by weak interactions at the peripheral substituents that are effective for, for example, C–H···π interactions.

Unsubstituted receptor **5** forms anion-bridged 1D chain structures with Cl^- and Br^- from TBA salts by the inversion of only one pyrrole ring (Figs. 6a,b). These 1D chains, in which the anions are located at distances of 9.10 and 9.24 Å, respectively, interact with the layers of TBA cations to produce a charge-by-charge assembly [13a,14h]. Similar but more complicated chain structures are observed in β-benzo-fused **7**, which also forms a singly inverted conformation (Fig. 6c). The Br···Br distances of the chain structures are estimated as 10.14 and 11.72 Å [14h]. Further, β-fluorine **11** exhibits a totally uninverted conformation that forms Cl^--bridged 1D chains with a Cl···Cl distance of 9.67 Å and a charge-by-charge assembly (Fig. 6c) [13c]. As receptors **5**, **7**, and **11** illustrate, the absence of α-substituents of BF_2 complexes provides chain structures quite different from the respective [1 + 1]-type regular complexes in solution (see Fig. 4 for the parent structure). This is presumably due to the additional interaction with the naked binding-site- and solvent-free areas of anions in the solid state.

α-Phenyl-substituted receptor **6a** affords [1 + 1]-type pentacoordinated planar complexes with Cl^- and Br^- from TPA salts (Figs. 7a,b). The corresponding TBA salts do not yield appropriate single crystals. These planar anion structures are stacked with counter TPA cations to form charge-by-charge

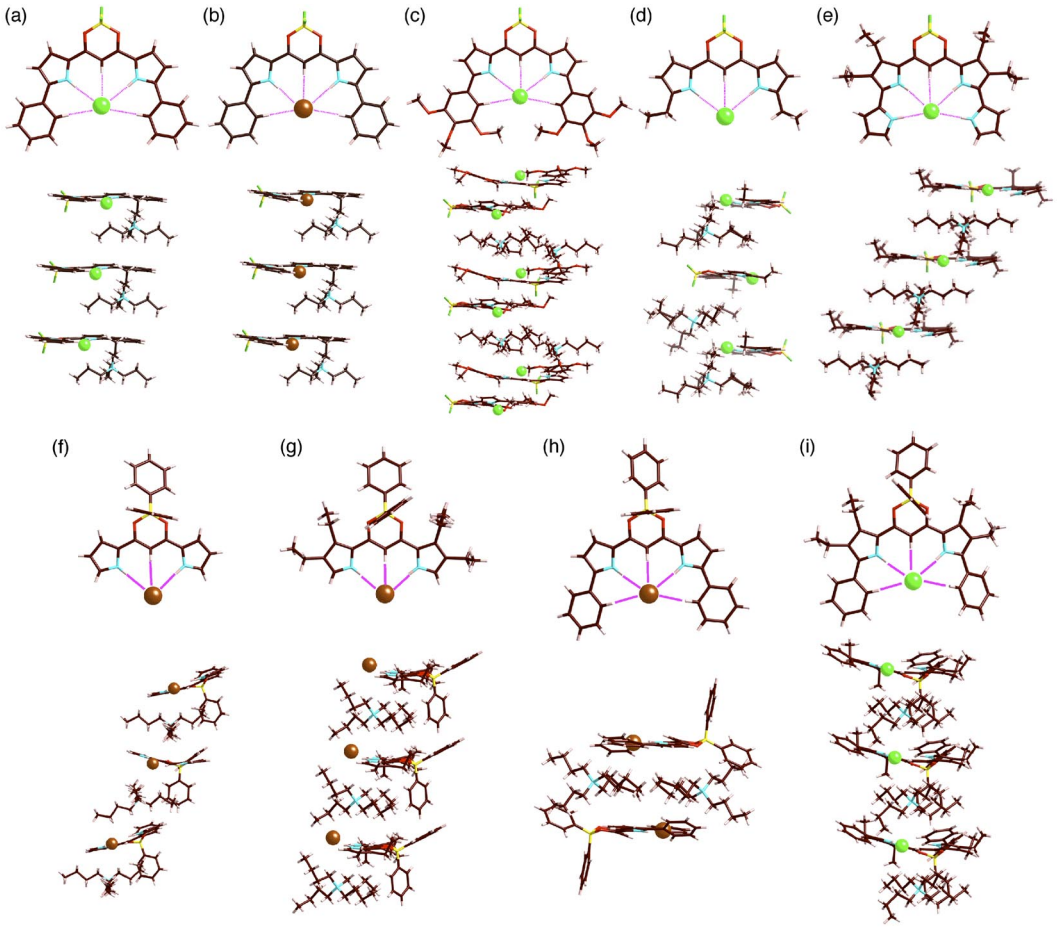

Fig. 7 Top views and selected assembled structures from single-crystal X-ray analyses of (a) **6a**·TPACl [14a], (b) **6a**·TPABr [14h], (c) **6b**·TBACl [14a], (d) **8-2**·TBACl [13e], (e) **9c**·TBACl [14c], (f) **14a**·TBABr [15b], (g) **14b**·TBABr [15b], (h) **14c**·TBABr [15b], and (i) **14d**·TBACl [15b] (reproduced from cif files: CCDC-646480, 760824, 639771, 666250, 585536, 759624, 759625, 759626, and 759627, respectively).

columnar structures consisting of alternately stacked receptor–anion complexes and cations. The distances between anions are 8.54 and 8.67 Å, respectively, whereas the plane distances between the receptor–anion complexes are estimated to be 7.29 and 7.44 Å, respectively [14a,h]. A similar [1 + 1]-type Cl^- complex is observed in trimethoxyphenyl-substituted **6b**, which forms charge-by-charge assemblies by stacking two complexes and two TBA cations (Fig. 7c). The distances between two neighboring Cl^- ions along the column are 5.71 and 8.26 Å [14a]. α-Ethyl-substituted **8-2** also forms a planar anion consisting of a [1 + 1]-type complex that forms a columnar structure in which neighboring Cl^- anions are separated by a distance of 5.88 Å (Fig. 7d) [13e]. β-Alkyl-substituted receptors afford [1 + 1]-type relatively planar Cl^- complexes upon introduction of aryl moieties at α-positions, as seen in the case of **9c** (Fig. 7e). In this case, the neighboring Cl···Cl distance in charge-by-charge assembly is 8.76 Å [14c]. As compared to the crystal structures of BF_2 complexes as discussed above, diphenylboron complexes exhibit quite distinct packing modes owing to the effects of bulky phenyl moieties. For example, in contrast to **5**, which forms Br^--bridged 1D chains [14h], pyrrole-unsubstituted **14a** provides a [1 + 1]-type complex to yield columnar stacking structures with TBA cations, in which neighboring receptor–anion complexes are not arranged in parallel (Fig. 7f). A similar structure is observed for β-ethyl **14b**, which

has no substituents at α-positions (Fig. 7g). In these cases, the Br···Br distances in the column are 9.53 and 11.43 Å for **14a** and 9.03 Å for **14b**. Interestingly, α-phenyl **14c** forms a [1 + 1]-type Br^- complex and [2 + 2]-type assemblies with TBA cations (Fig. 7h), rather than infinite columnar structures, like **3**·TBACl. In this discrete assembly, the distance between receptor–anion complexes is 7.33 Å and that between two Br^- is 8.50 Å. On the other hand, α-phenyl-β-ethyl **14d** forms charge-by-charge assemblies with a Cl···Cl distance of 8.47 Å based on [1 + 1]-type Cl^- complexes (Fig. 7i) [15b]. Among the receptors discussed in this paragraph, **14d** exhibits a distorted and bowl-shaped anion complex owing to sterical hindrance between the α-phenyl and the β-ethyl moieties.

Maeda et al. also investigated the solid-state electronic and optical properties of the Br^- complexes of **5**, **6a**, and **7** and discovered their unique properties based on the ordered assembly of π-conjugated molecules. The excitation and emission maxima of the crystalline Br^--binding complexes are observed at 380, 450, and 468 nm (λ_{max}) and 484 and 583 nm (λ_{em}) (**5**·Br^--TBA^+), 406 and 560 nm (λ_{max}) and 580 nm (λ_{em}) (**6a**·Br^--TPA^+), and 581 nm (λ_{max}) and 612 nm (λ_{em}) (**7**·Br^--TBA^+). These properties are distinct from those of the crystals of anion-free receptors **5** (including three polymorphs **5r**, **5y**, and **5v**), **6a**, and **7**: the excitation maxima (λ_{max}) are distinct for **5r** (522 nm), **5y** (340 and 494 nm), **5v** (540 nm), **6a** (579 nm), and **7** (589 nm), and the emission maxima reflect these values: λ_{em} = 630 nm (**5r**), 524 nm (**5y**), 604 nm (**5v**), 610 nm (**6a**), and 685 nm (**7**) when excited at 500 nm (**5r**, **5v**, **6a**, and **7**) or 400 nm (**5y**). The results for these Br^- complexes suggest that TBA or TPA cations are located between receptor–anion complexes, and therefore interfere with the π–π interactions of the π-plane chromophores. Blue shifts, which are moderate as compared to those of the free receptors, are derived from the insertion of aliphatic cations between the chromophores (receptor–anion complexes), which weakens their exciton coupling. However, red shifts as compared to the solution state are presumably due to edge-to-edge interactions of the receptor–anion complexes. Ordered stacking structures of π-conjugated molecules, such as those observed in the crystal structures of the anion receptors and their anion complexes, are suitable for use as charge-conductive materials. Flash photolysis time-resolved microwave conductivity (FP-TRMC) measurements [19] allow the behavior of mobile charge carriers along all the axes of the crystals to be estimated. When a 355-nm laser pulse was applied at 25 °C, Br^- complexes exhibited smaller conductivities of 7×10^{-3}, 8×10^{-3}, and 3×10^{-4} $cm^2/V{\cdot}s$ (**5**·Br^--TBA^+) and 4×10^{-3}, 4×10^{-3}, and 7×10^{-4} $cm^2/V{\cdot}s$ (**6a**·Br^--TPA^+) for the *a*, *b*, and *c* axes of the crystals, and 8×10^{-3} and 7×10^{-3} $cm^2/V{\cdot}s$ (**7**·Br^--TBA^+) for the *a* and *c* axes of the crystal, respectively. Conversely, in the crystals of anion-free receptors, higher mobilities were observed in **5r** (0.05, 0.02, and 0.03 $cm^2/V{\cdot}s$ for the *a*, *b*, and *c* axes), **5y** (0.8, 0.2, and 0.07 $cm^2/V{\cdot}s$), **5v** (0.7, 0.8, and 0.6 $cm^2/V{\cdot}s$), **6a** (0.02, 0.03, and 0.05 $cm^2/V{\cdot}s$), and **7** (1, 0.2, and 0.06 $cm^2/V{\cdot}s$). Apparently, slipped parallel stacking of π-planes leads to high hole mobility and anistropic properties along the stacking direction. Owing to the presence of tetraalkylammonium cations, the crystals of Br^- complexes exhibit smaller conductivities than those of anion-free crystals [14h].

CONCLUDING REMARKS

In this critical overview, we have shown some examples of solid-state charge-by-charge assemblies based on planar anion receptors. Such solid-state structures are the basis of functional soft materials including liquid crystals and supramolecular gels, which will be reported in the near future. We found that, among various anion receptor molecules, the pyrrole-based acyclic anion receptors that we reported behave as efficient building blocks of charge-by-charge assemblies through combination with anions. This is presumably because the linear oligopyrrole receptors form stable receptor–anion complexes with planar geometries that are suitable for interaction with countercations. Of course, the structures of the countercations are essential in determining the states of the assembled structures. Therefore, the choice of both receptors and cations dominates the properties and functionalities of mixtures con-

sisting of the receptors and the anion source salts [20]. The concept of charge-by-charge assemblies is expected to become widespread through future reports of soft materials as well as the crystal structures seen here.

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