

Solid-state supramolecular assemblies consisting of planar charged species†

Yohei Haketa, Mayumi Takayama and Hiromitsu Maeda*

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Pyrrole-based π -conjugated anion-responsive molecules provided various planar anionic structures by complexation with halide anions, resulting in the formation of solid-state assemblies with planar counter cations and exhibiting various modes of charge-by-charge assembly depending on the substituents of the anion receptors.

Introduction

The arrangement of planar π -conjugated molecules by π - π stacking is an efficient strategy for constructing various supramolecular assemblies in biotic and artificial systems.¹ Both in the solid state and in soft materials, it is essential to precisely control the molecular interactions to fabricate sophisticated stacking objects and tune the electronic properties, such as for the application of electric conductivities or organic light emitting diodes. It is well known that electrostatic interaction between oppositely charged species is fairly strong and can operate in a variety of states.^{2,3} Therefore, incorporation of charges into planar π -conjugated units would result in the formation of highly ordered organised structures using both electrostatic and π - π interactions. In this regard, charge-by-charge assembly, involving the alternate stacking of positively and negatively charged species, is an efficient protocol for fabricating organised structures (Fig. 1a). However, there are significant problems in the preparation of planar anionic species due to their excess electrons, which undergo electrophilic reactions: it is not simple to design planar anions that can delocalize these excess electrons to prevent such transformation. An effective strategy for constructing planar anions is anion binding of electronically neutral π -conjugated molecules.⁴ In this process, various types of negatively charged species can be prepared by combining receptors with anions, which results in the formation of charge-by-charge assemblies with appropriate counter cations.⁵ As for the platforms for such easy preparation method of pseudo-planar anionic species using noncovalent interactions, we have reported dipyrrolyldiketone boron complexes (e.g. **1–4**, Fig. 1b), which bind anions by the inversion of pyrrole rings in the solution state.^{6,7} Planar receptor–anion

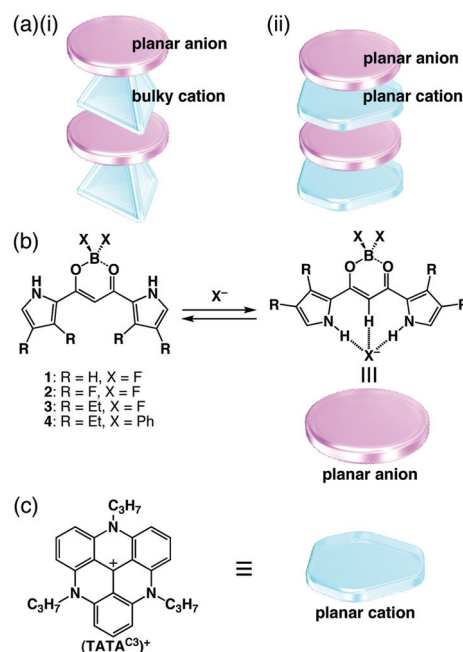


Fig. 1 (a) Charge-by-charge assemblies comprising planar anion and (i) bulky cation and (ii) planar cation; (b) acyclic anion receptors **1–4** and their anion-binding mode; (c) (TATA^{C3})⁺ as a planar cation.

complexes can be incorporated into charge-by-charge assemblies not only as crystals but also as soft materials by combination with counter cations.^{7h} One of the advantages of such charge-based materials is that structures and properties can be tuned by the choice of constituents used as receptor molecules, anions and associated cations.^{7i–k} In particular, the substituents of the receptor molecules and the geometries of the cations, bulky or planar (e.g. Fig. 1c), are essential parameters in preparing functional charge-based materials. This article reports a variety of modes in charge-by-charge assemblies, focusing on the solid state.

College of Pharmaceutical Sciences, Institute of Science and Engineering, Ritsumeikan University, Kusatsu 525-8577, Japan.
E-mail: maedahir@ph.ritsumei.ac.jp; Fax: (+)81-77-561-2659

†Electronic supplementary information (ESI) available: Assembled structures and CIF files for the X-ray structural analysis of **1**·Cl[−]–(TATA^{C3})⁺, **2**·Cl[−]–(TATA^{C3})⁺, **3**·Cl[−]–(TATA^{C3})⁺ and **4**·Cl[−]–(TATA^{C3})⁺. CCDC 845953–845956. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ob07059f

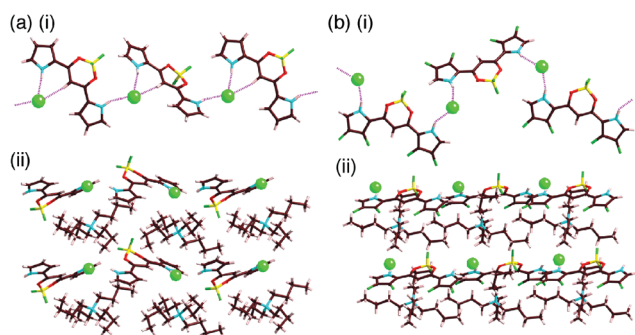


Fig. 2 X-ray crystal structures of (a) $1\text{-Cl}^- \text{-TBA}^{+7a}$ and (b) $2\text{-Cl}^- \text{-TBA}^{+7b}$ ((i) anion-bridged hydrogen-bonding chains and (ii) charge-by-charge layer structures). Atom colour code: brown, pink, yellow, green, yellow-green, blue and red represent carbon, hydrogen, boron, fluorine, chlorine, nitrogen and oxygen, respectively.

Results and discussion

In solution, dipyrrolyldiketone boron complexes **1–4** efficiently bind halide anions by forming [1 + 1]-type receptor–anion complexes. This binding behaviour has been confirmed using NMR, computational modelling and crystallographic studies of receptor–anion complexes.⁷ Although [1 + 1]-type complexes, as described in Fig. 1b, are the predominant species in solution, other binding modes have also been observed in crystal structures. For example, in the crystal structure of $1\text{-Cl}^- \text{-TBA}^+$, only one pyrrole-ring inversion was observed, resulting in the formation of anion-bridged 1D hydrogen-bonding chain structures (Fig. 2a).^{7a} In this case, the TBA counter cations lay beneath the anions, for example, with distances between the TBA-N and Cl^- of 4.58 and 4.63 Å to maintain the charge balance. In the solid state, $1\text{-Cl}^- \text{-TBA}^+$ organised in charge-by-charge layers of TBA cations and receptor–anion complexes as 1D chains. On the other hand, the crystal structure of β -fluorinated receptor **2** with TBACl exhibited a totally uninverted conformation that formed Cl^- -bridged 1D chains with a $\text{Cl}^- \cdots \text{Cl}^-$ distance of 9.67 Å; with TBA cations, it formed a charge-by-charge assembly where distances between TBA-N and Cl^- were 4.21 and 4.71 Å (Fig. 2b).^{7b}

Fascinatingly, in sharp contrast to the bulky TBA cation, introduction of Cl^- as a planar triazatriangulenium ((TATA^{C3})⁺, Fig. 1c) salt⁸ produced different modes of charge-by-charge assembly. X-ray-analysis-quality single crystals of Cl^- complexes of receptors **1–4** as (TATA^{C3})⁺ salts were prepared by vapour diffusion of hexane into CH_2Cl_2 –toluene solutions of 1 : 1 mixtures of the receptors and TATA^{C3}-Cl (Table 1). In contrast to anion-free **1**, which shows three different crystals with different colours,^{7g} crystal polymorphs were not observed in the crystals obtained under these conditions. In the case of the combination of **2**^{7b} and TATA^{C3}-Cl, two of the receptor's pyrrole rings were inverted to provide a [1 + 1]-type complex 2-Cl^- , resulting in the formation of an ion pair of 2-Cl^- and (TATA^{C3})⁺ followed by stacking with another set of ion pairs to produce a charge-by-charge assembly. The distance between two 2-Cl^- planes is 6.74 Å, whereas those between 2-Cl^- and the TATA cations (the mean planes consisting of the core 17 atoms, including Cl^- , of the receptor–anion complex and the centroid of

Table 1 Crystallographic details for anion complexes

	$1_2\text{-Cl}^- \text{-(TATA}^{C3})^+$	$2\text{-Cl}^- \text{-(TATA}^{C3})^+$	$3\text{-Cl}^- \text{-(TATA}^{C3})^+$	$4_2\text{-Cl}^- \text{-(TATA}^{C3})^+$
Formula	$(\text{C}_{11}\text{H}_9\text{BF}_2\text{N}_2\text{O}_2)_2 \cdot \text{C}_{28}\text{H}_{30}\text{N}_3\text{Cl} \cdot \text{CH}_2\text{Cl}_2$	$\text{C}_{22}\text{H}_5\text{BF}_2\text{N}_2\text{O}_2 \cdot \text{C}_{28}\text{H}_{30}\text{N}_3\text{Cl} \cdot 2\text{C}_6\text{H}_{14}$	$\text{C}_{19}\text{H}_{25}\text{BF}_2\text{N}_2\text{O}_2 \cdot \text{C}_{28}\text{H}_{30}\text{N}_3\text{Cl} \cdot \text{CH}_2\text{Cl}_2$	$(\text{C}_{31}\text{H}_{35}\text{BN}_2\text{O}_2)_2 \cdot \text{C}_{28}\text{H}_{30}\text{N}_3\text{Cl}$
Fw	1028.95	852.15	891.15	1400.84
Crystal size, mm	$0.75 \times 0.20 \times 0.20$	$0.40 \times 0.15 \times 0.10$	$0.30 \times 0.25 \times 0.20$	$0.55 \times 0.45 \times 0.40$
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a, Å	8.553(2)	8.341(3)	11.092(4)	15.754(5)
b, Å	13.788(4)	12.445(6)	11.957(4)	17.174(5)
c, Å	20.858(8)	20.303(8)	19.330(6)	17.170(5)
α , °	88.838(14)	79.279(15)	77.243(10)	116.501(12)
β , °	86.545(14)	85.683(13)	82.685(13)	108.051(10)
γ , °	73.382(12)	80.571(15)	63.623(12)	91.068(14)
V, Å ³	2352.7(13)	2040.5(14)	2238.8(13)	3879(2)
ρ_{calcd} , g cm ⁻³	1.452	1.387	1.322	1.199
Z	2	2	2	2
T, K	123(2)	123(2)	123(2)	123(2)
μ , mm ⁻¹ (Mo-K α)	0.267	0.167	0.259	0.106
No. of reflns	22 626	19 971	22 208	36 354
No. of unique reflns	10 176	9212	10 173	17 214
Variables	653	575	557	989
λ , Å (Mo-K α)	0.71075	0.71075	0.71075	0.71075
R_1 ($I > 2\sigma(I)$)	0.0649	0.0662	0.0721	0.0778
w R_2 ($I > 2\sigma(I)$)	0.1725	0.1902	0.1711	0.2066
GO F	1.057	1.109	1.055	1.012

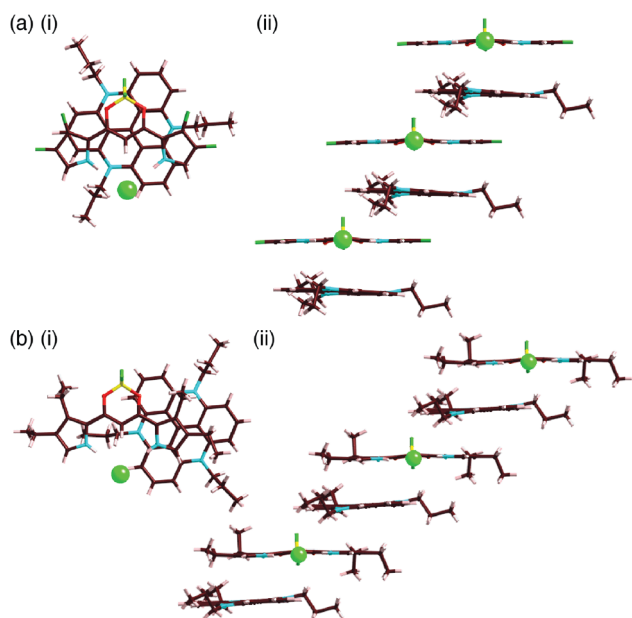


Fig. 3 Charge-by-charge assemblies of (a) $2\cdot\text{Cl}^--(\text{TATA}^{\text{C}3})^+$ and (b) $3\cdot\text{Cl}^--(\text{TATA}^{\text{C}3})^+$ ((i) sets of ion pairs and (ii) charge-by-charge columnar structures).

($\text{TATA}^{\text{C}3})^+$, as in the diagrams) are 3.49 and 3.26 Å, suggesting π - π stacking between oppositely charged planes (Fig. 3a). Furthermore, anion-free β -ethyl-substituted 3^{7c} is not a π - π stacking structure owing to the fairly bulky ethyl moieties in the solid state,^{7e} but following anion binding, interaction of **3** with ($\text{TATA}^{\text{C}3})^+$ induces the formation of charge-by-charge assemblies consisting of $3\cdot\text{Cl}^-$ and ($\text{TATA}^{\text{C}3})^+$ (Fig. 3b). In this case, the π - π stacking area of $3\cdot\text{Cl}^-$ and ($\text{TATA}^{\text{C}3})^+$ is smaller than that of $2\cdot\text{Cl}^--(\text{TATA}^{\text{C}3})^+$ due to the more bulky ethyl substituents, but the distance between two $3\cdot\text{Cl}^-$ planes and that between $3\cdot\text{Cl}^-$ and ($\text{TATA}^{\text{C}3})^+$ are 6.88 and 3.43/3.45 Å, respectively, which are comparable to those of $2\cdot\text{Cl}^--(\text{TATA}^{\text{C}3})^+$. Comparison with a single-crystal X-ray structure of a TBACl complex of **3**, which has not yet been obtained, would provide valuable insight into the effects of counter cations.

Another interesting topic in solid-state charge-by-charge assemblies including planar cations is control of the stoichiometry between the receptors and the planar cation salts. The single crystals of the receptors and tetraalkylammonium salts prepared thus far exhibited 1 : 1 stoichiometry, with receptor conformations both with and without pyrrole inversion. In contrast, introduction of the planar TATA cation salt enables the formation of charge-by-charge assemblies with different stoichiometries in the solid state. Even though preparation of single crystals from the 1 : 1 mixtures of receptors and $\text{TATA}^{\text{C}3}\cdot\text{Cl}$ was attempted, two examples of solid-state charge-by-charge assemblies comprising [2 (receptor) + 1 (anion)]-type receptor-anion complexes associated with one TATA cation were observed. The parent receptor **1**^{7a} forms a [2 + 1]-type complex $1_2\cdot\text{Cl}^-$, which stacks on a TATA cation using either of the receptor units (Fig. 4a). The distances between two $1_2\cdot\text{Cl}^-$ planes and that between $1_2\cdot\text{Cl}^-$ and ($\text{TATA}^{\text{C}3})^+$ are 6.89 and 3.50/3.40 Å, respectively. Furthermore, another receptor unit that does not stack with ($\text{TATA}^{\text{C}3})^+$ shows π - π stacking interaction at the pyrrole rings of $1_2\cdot\text{Cl}^-$ in

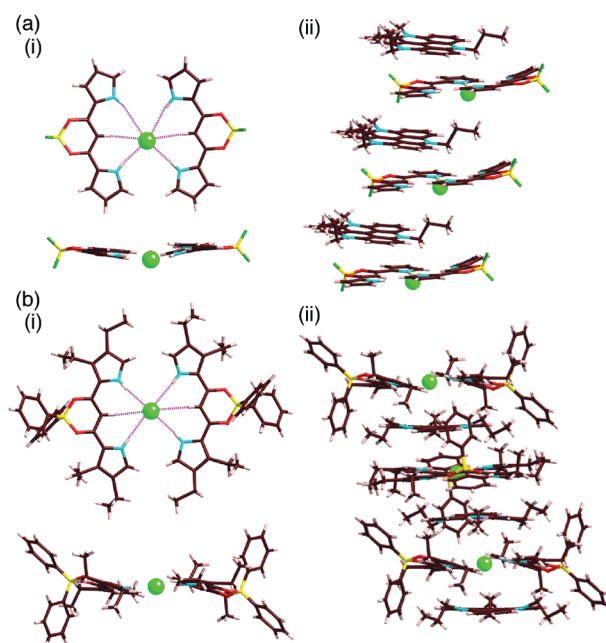


Fig. 4 Charge-by-charge assemblies of (a) $1_2\cdot\text{Cl}^--(\text{TATA}^{\text{C}3})^+$ and (b) $4_2\cdot\text{Cl}^--(\text{TATA}^{\text{C}3})^+$ ((i) receptor-anion [2 + 1]-type complexes and (ii) columnar structures).

the neighbouring column. Similarly, β -ethyl-substituted diphenylboron complex **4**^{7f} constructs a [2 + 1]-type complex $4_2\cdot\text{Cl}^-$, which alternately stacks with ($\text{TATA}^{\text{C}3})^+$, with distances of 7.27 and 3.68/3.62 Å to another $4_2\cdot\text{Cl}^-$ and a neighbouring ($\text{TATA}^{\text{C}3})^+$, respectively (Fig. 4b). In contrast with the charge-by-charge assembly of $1_2\cdot\text{Cl}^--(\text{TATA}^{\text{C}3})^+$, the TATA cation in $4_2\cdot\text{Cl}^--(\text{TATA}^{\text{C}3})^+$ is located in the centre of $4_2\cdot\text{Cl}^-$, resulting in the formation of a more perpendicularly aligned columnar structure. The formation of $4_2\cdot\text{Cl}^-$ is in contrast to the solid-state structure of a [1 + 1]-type Br^- complex **4** $\cdot\text{Br}^-$ as a TBA salt.^{7f} At present, it is not easy to explain the exact reason why such planar [2 + 1]-type receptor-anion complexes can be formed by the introduction of a planar cation. Theoretical optimization at AM1 level⁹ also reveals that orthogonally arranged [2 + 1]-type complexes are more stable (5.22 and 5.08 kcal mol⁻¹ for $1_2\cdot\text{Cl}^-$ and $4_2\cdot\text{Cl}^-$, respectively) compared to the corresponding planar [2 + 1]-type complexes, possibly due to steric repulsions at the pyrrole units. Formation of [2 + 1]-type complexes in solution state has been observed only for the receptors with α -aryl substituents in the concentrated solutions (1 mM) at low temperature.^{7d} Therefore, it is a great surprise that a planar TATA cation induces the formation of fairly unstable planar [2 + 1]-type complexes as suitable geometries for charge-by-charge assemblies. The effects of crystal packing should also be taken into consideration in the formation of such unstable complexes. From the single-crystal X-ray structures, the stoichiometries and conformations of the receptors are found to be significantly dependent on stable packing modes, which are influenced by the geometries of the cations and the substituents of the receptors.

Conclusions

In summary, we have reported on solid-state charge-by-charge assemblies. Introduction of the anion to pyrrole-based

π -conjugated anion receptors as a planar TATA cation salt, instead of a bulky cation salt, leads to the fabrication of assemblies which can be verified by controlling the conformation of receptors and the stoichiometry of the receptor–anion complexes. These new findings will help us to understand the principles of charge-by-charge assemblies, and can be useful in the design of functional materials. Investigations into soft materials comprising planar charged species and their fascinating properties are currently underway.

Experimental

Method for single-crystal X-ray analysis

Crystallographic details of the data crystals are summarized in Table 1. All the single crystals were obtained from vapor diffusion of hexane into 1.5 mL (*ca.* 5 mM) CH_2Cl_2 (10% toluene) solution of each receptor and $\text{TATA}^{\text{C}3}\text{-Cl}$ with a 1:1 stoichiometry as an initial condition. Compositions and purities of the single crystals for each complex were uniform under the crystallisation conditions described above, as estimated by ^1H NMR for the compositions. A single crystal of $1_2\text{-Cl}^--(\text{TATA}^{\text{C}3})^+$ was a red prism of approximate dimensions 0.75 mm \times 0.20 mm \times 0.20 mm. A single crystal of $2\text{-Cl}^--(\text{TATA}^{\text{C}3})^+$ was a red prism of approximate dimensions 0.40 mm \times 0.15 mm \times 0.10 mm. A single crystal of $3\text{-Cl}^--(\text{TATA}^{\text{C}3})^+$ was a red prism of approximate dimensions 0.3 mm \times 0.25 mm \times 0.2 mm. A single crystal of $4_2\text{-Cl}^--(\text{TATA}^{\text{C}3})^+$ was an orange prism of approximate dimensions 0.55 mm \times 0.45 mm \times 0.40 mm. All the data were collected at 123 K on a Rigaku RAXIS-RAPID diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71075 \text{ \AA}$); the structure was solved by the direct method. In each case, the non-hydrogen atoms were refined anisotropically. The calculations were performed using the Crystal Structure crystallographic software package of Molecular Structure Corporation.¹⁰

AM1 calculation

AM1 calculations of 1_2-Cl^- and 4_2-Cl^- in different anion-binding modes were carried out using the Gaussian 03 program⁹ and a DELL OPTIPLEX960 computer. The structures were optimized, and the total electronic energies were calculated.

Acknowledgements

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