ChemComm

Cite this: *Chem. Commun.*, 2011, **47**, 8241–8243

www.rsc.org/chemcomm

COMMUNICATION

Self-sorting self-complementary assemblies of π-conjugated acyclic anion receptors†

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Received 13th April 2011, Accepted 6th June 2011
DOI: 10.1039/c1cc12120k

Pyrrole-based π-conjugated anion-responsive molecules bearing an anionic moiety form self-complementary dimers, which exhibit self-sorting behaviours depending on the substituted positions of anionic sites.

Self-complementary assembly is an essential process for constructing biotic and artificial functional nanoscale architectures.[1] Among all association protocols, anion binding is effective for achieving the formation of molecular assemblies by anion-driven electrostatic hydrogen bonding, and multiple building units can be connected in a fairly compact manner with the help of a small number of noncovalent bonds.[2] Covalent linkages of anionic species with appropriate electronically neutral receptor molecules can facilitate the formation of complementary stimuli-responsive self-assembled dimers and oligomers. Such assemblies possess multiple negative charges, which may develop into various organized structures by combining with appropriate counter cations. However, very few examples of anion-mediated self-assemblies based on electroneutral receptor units have been reported thus far. One example reported by Sessler *et al.* was the formation of self-assembled dimers comprising the calix[4]pyrrole bearing a carboxylate moiety in solution and in the solid state.[3] It is more difficult to prepare self-assemblies of electroneutral receptor units possessing anionic sites than those of zwitterions,[4] presumably because of the electrostatic repulsion exhibited by the former self-assemblies and the absence of suitable anion receptors. As compared to cyclic anion receptors, appropriately designed open-chain structures seem more capable of recognizing themselves as compared to the other units, mainly owing to the geometrical restrictions of cyclic structures. As acyclic π-conjugated anion-responsive molecules, dipyrrolyldiketone boron complexes (*e.g.*, **1a–c**, Fig. 1a), which form planar [1 + 1]-type receptor–anion complexes (Fig. 1b), serve as essential building blocks of anion-responsive supramolecular assemblies and oligomers.[5,6] Therefore, receptors bearing an anionic site would form anion-binding self-assemblies, which would provide useful oligomeric and macromolecular structures. This communication describes the formation of anion-binding self-assembled dimers that exhibit narcissistic self-sorting behaviours.[7]

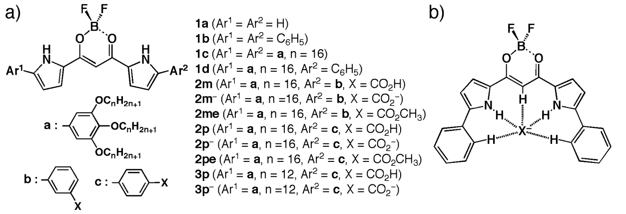

Fig. 1 (a) Acyclic anion receptors **1–3** and (b) anion-binding mode of **1b**.

We have reported the efficient binding behaviours of a series of dipyrrolyldiketone boron complexes with acetate as one of the representative carboxylate anions.[5,6] The binding constants for acetate are higher than those for Cl^- and Br^-, presumably because of the basicity of the anion and the multiple hydrogen bonding interactions between the pyrrole NH and acetate oxygen. The binding modes of anion receptors for carboxylates have been investigated in detail by ^1H NMR and theoretical studies. As a result, we can now elucidate the exact structure of a carboxylate-binding complex by introducing a benzoate instead of an acetate. Single-crystal X-ray analysis of **1a**·benzoate as a tetrapropylammonium (TPA) salt shows that it provides a [1 + 1]-type binding mode (Fig. 2),‡ which is formed through N–H···O and C–H···O hydrogen bonding: the N(–H)···O and C(–H)···O distances are 2.704/2.733 and 3.329 Å, respectively. The benzoate is associated with **1a** in an unsymmetrical fashion, as observed from 163.09° of bridging-C–carboxylate-C–ipso-C; this is a substantial aberration from 180° that we expect in a

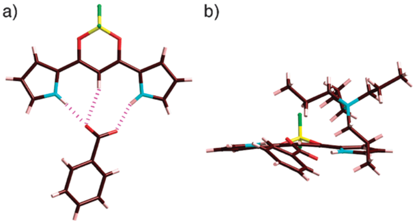

Fig. 2 Single-crystal X-ray structure of **1a**·benzoate as a TPA salt: (a) top and (b) side view. The TPA cation is omitted in (a). Atom colour code: brown, pink, yellow, blue and red indicate carbon, hydrogen, boron, nitrogen and oxygen, respectively.

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† Electronic supplementary information (ESI) available: Synthetic procedures and analytical data, self-assembled behaviours and X-ray structural analysis of **1a**·TPA benzoate. CCDC 809340. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc12120k

symmetrical binding arrangement. Further, the dihedral angle between the receptor plane consisting of 16 atoms and the benzoate plane including the carboxylate unit is estimated to be 30.83°, suggesting that the two π-planes are not arranged in a coplanar fashion.

On the basis of the above observation, *meta*- and *para*-carboxylic-acid-substituted receptors **2m** and **2p** (Fig. 1a) were synthesized from the mixture of two arylpyrroles according to the procedures described in the reference literature.[6a] During the preparation of carboxylate-appended anion receptors, the treatment of **2m** and **2p** with TBAOH afforded the corresponding TBA salts of the carboxylates **2m**$^-$ and **2p**$^-$ after appropriate purification.

Dipyrrolyldiketone boron complexes efficiently bind carboxylate in solution. The binding constants (K_a) of reference molecules—carboxylic-acid-free **1d** and ester-substituted **2me** and **2pe** (Fig. 1a)—for acetate as a tetrabutylammonium (TBA) salt in CH_2Cl_2 were estimated to be 47 000 (±10 000), 2 600 000 (±1 200 000) and 520 000 (±42 000) M^{-1}, respectively, on the basis of UV/vis absorption spectral changes. The difference between the K_a values of **2me** and **2pe** may be derived from the electron-withdrawing effects depending on the substituted positions.

The formation of self-assembled dimers in solution was initially revealed by negative-mode ESI-TOF-MS in CH_3CN, showing the peaks of the dianion species as dimers **2m**$^-{}_2$ and **2p**$^-{}_2$ and excluding the formation of higher discrete oligomers. Self-assembled dimers **2m**$^-{}_2$ and **2p**$^-{}_2$ as TBA salts (5×10^{-4} M as monomers; the following values of concentrations were also for monomers) were also observed in the ^{1}H NMR spectra in $CDCl_3$ at 20–50 °C, wherein monomeric **2m**$^-$ and **2p**$^-$ were not observed (Fig. 3). The fairly low solubilities of **2m**$^-$·TBA and **2p**$^-$·TBA below 10 °C interfered with the measurements recorded at low temperatures. For example, at 20 °C, the signals of NH, bridging CH and *o*-CH of **2p**$^-{}_2$ were observed at 14.4/12.5, 8.9 and 7.3 ppm, respectively, which were in the downfield region as compared to those of **2p** (9.7/9.6, 6.5 and 6.8 ppm, respectively) owing to the hydrogen bonding with a carboxylate unit (Fig. 3i and ii). In the diluted solution of **2m**$^-{}_2$ in $CDCl_3$ (5×10^{-5} M) at 30 °C, equilibrium was observed between the monomer and the dimer, and the dimerization constant (K_{dim}) was estimated to be about 10^4 M^{-1}. On the other hand, under the same conditions, no monomeric state **2p**$^-$ was observed owing to a much higher K_{dim} value of $>10^9$ M^{-1} for **2p**$^-{}_2$.

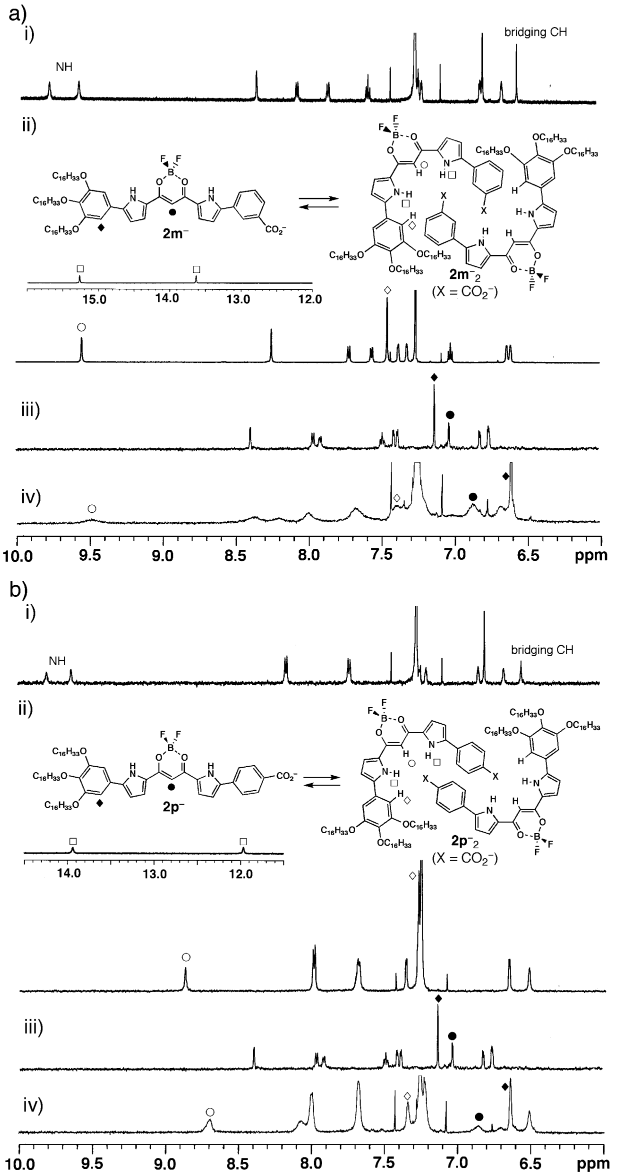

Fig. 3 (a) ^{1}H NMR spectra of (i) **2m** in $CDCl_3$ at 20 °C, (ii) **2m**$^-{}_2$ in $CDCl_3$ at 20 °C, with the scheme showing the equilibrium between **2m**$^-$ and **2m**$^-{}_2$, (iii) **2m**$^-$ in CD_3OD at 50 °C and (iv) **2m**$^-$ and **2m**$^-{}_2$ in equilibrium in 2% $CD_3OD/CDCl_3$ at 20 °C; (b) ^{1}H NMR spectra of (i) **2p** in $CDCl_3$ at 20 °C, (ii) **2p**$^-{}_2$ in $CDCl_3$ at 20 °C, with the scheme showing the equilibrium between **2p**$^-$ and **2p**$^-{}_2$, (iii) **2p**$^-$ in CD_3OD at 50 °C and (iv) **2p**$^-$ and **2p**$^-{}_2$ in equilibrium in 2% $CD_3OD/CDCl_3$ at 20 °C. The concentration of monomers in each case was 5×10^{-4} M. In (a(iv)) and (b(iv)), the signals of hydrogen-bonding NH in the downfield region disappear on account of the exchanges between H and D.

^{1}H NMR DOSY (1×10^{-3} M, 20 °C) was used to obtain the diffusion constants (10^{-10} m^2 s^{-1}) of 3.3, 4.4 and 4.4 for **2p**$^-{}_2$, **2pe** and **1d**, respectively; these values were consistent with those observed during dimer formation in the anionic state. From the UV/vis absorption spectra for **2p**$^-{}_2$ at 1×10^{-5} M, we speculated that the self-assembly existed as a major species. The fluorescence emission for **2p**$^-{}_2$ excited at 513 nm as an absorption maxima was observed at 558 nm. DFT calculations of **2m**$^-{}_2$ and **2p**$^-{}_2$ (as alkoxy-free forms) at the B3LYP/6-31G(d,p) level[8] indicated the formation of complementary self-assembled dimer structures (Fig. 4), wherein the planes of the carboxylate moieties of **2m**$^-{}_2$ and **2p**$^-{}_2$ were tilted at angles of 42.8° and 26.7° with respect to the core receptor plane, respectively. These two values were respectively larger and slightly smaller than the X-ray-based dihedral angle of 31.44° between the receptor **1a** and the benzoate carboxylate moiety. As compared to the fairly planar plate-like dimer of **2p**$^-{}_2$, the dimer **2m**$^-{}_2$ showed a distorted butterfly-like structure. The DFT-based relative stability of **2p**$^-{}_2$, as compared to **2m**$^-{}_2$, was 2.36 kcal mol^{-1}, which was consistent with the value estimated from the dimerization constants, as discussed above.

Further, in acetone-d_6 (5×10^{-4} M) at 20 °C, only the dimers of **2m**$^-{}_2$ and **2p**$^-{}_2$ were stabilized, whereas, in CD_3OD (5×10^{-4} M) at 20–50 °C, only monomeric **2m**$^-$ and **2p**$^-$ were observed (Fig. 3iii). These results suggest that the protic solvents interfered with dimerization because of their hydrogen-bonding solvation at the carboxylate unit of **2m**$^-$ and **2p**$^-$ and that they

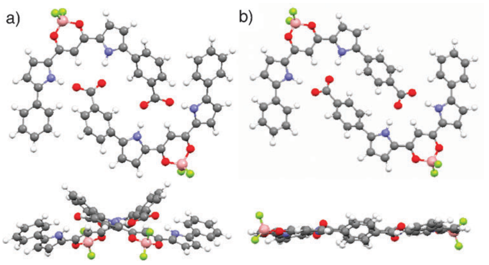

Fig. 4 Optimized structures (top and side views) of (a) $\mathbf{2m}^{-}_{2}$ and (b) $\mathbf{2p}^{-}_{2}$ at the B3LYP/6-31G(d,p) level. Hexadecyloxy substituents are omitted for concise calculations. Atom colour code: gray, white, pink, yellow-green, blue and red represent carbon, hydrogen, boron, fluorine, nitrogen and oxygen, respectively.

can be used as chemical stimuli to induce the dissociation of self-assembled dimers. In 2% $CD_3OD/CDCl_3$ (1×10^{-3} M), the equilibrium between $\mathbf{2m}^{-}$ and $\mathbf{2m}^{-}_{2}$ and that between $\mathbf{2p}^{-}$ and $\mathbf{2p}^{-}_{2}$ were observed in the ^{1}H NMR spectra at 20–40 °C (Fig. 3iv). Van't Hoff plots were obtained using the following K_{dim} values (10^3 M^{-1}) of $\mathbf{2m}^{-}$ and $\mathbf{2p}^{-}$: 0.53 and 1.7 (at 20 °C), 3.2 and 13 (at 30 °C) and 55 and 210 (at 40 °C), respectively. The plots provided the thermodynamic parameters $\Delta H^0 = 17$ and 17 kJ mol^{-1} and $\Delta S^0 = 0.65$ and 0.68 kJ mol^{-1} K^{-1}, respectively. For both the receptors, the positive ΔH^0 values suggest the occurrence of an endothermic process, owing to the more favourable solvation of methanol for carboxylate moieties than for hydrogen bonding between the carboxylate and the receptor binding sites. However, the positive ΔS^0 values were derived from the release of CD_3OD molecules that were entropically predominant over the self-dimerization.

Fascinatingly, the narcissistic self-sorting behaviour[7] of the self-assembled dimers was observed in $CDCl_3$ by mixing equivalent amounts of $\mathbf{2m}^{-}_{2}$ and $\mathbf{2p}^{-}_{2}$ (Fig. 5). There were no signals derived from $\mathbf{2m}^{-}\cdot\mathbf{2p}^{-}$ except the independent signals of $\mathbf{2m}^{-}_{2}$ and $\mathbf{2p}^{-}_{2}$. Dodecyloxy-substituted $\mathbf{3p}^{-}$ was used with a negative-mode ESI-TOF-MS in CH_3CN, which elucidated the major peaks of $\mathbf{2m}^{-}_{2}$ and $\mathbf{3p}^{-}_{2}$ along with a smaller peak corresponding to $\mathbf{2m}^{-}\cdot\mathbf{3p}^{-}$. These results suggest that each carboxylate-substituted anion receptor seemed to bind itself instead of the other receptor, depending on the positions of anionic moieties. This is because of the preferential formation of the relatively stable $\mathbf{2p}^{-}_{2}$ over $\mathbf{2m}^{-}\cdot\mathbf{2p}^{-}$ (+2.26 kcal mol^{-1}) and $\mathbf{2m}^{-}_{2}$, presumably owing to a more appropriate hydrogen-bonding direction and less sterical hindrance in $\mathbf{2p}^{-}_{2}$, as estimated by DFT calculations for alkoxy-free forms. In other words, the self-sorting phenomenon discussed in this report occurred mainly because of the difference in the self-dimerization ability of the anion-appended receptor molecules.

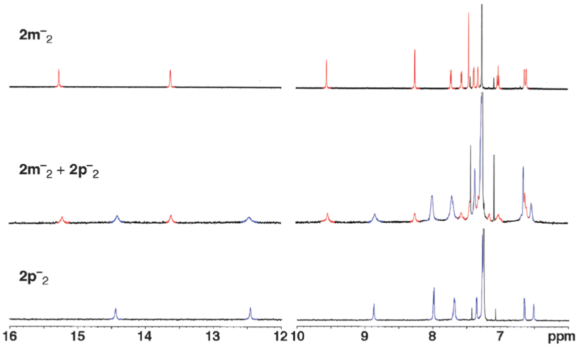

Fig. 5 ^{1}H NMR spectra of $\mathbf{2m}^{-}_{2}$ (red, top), $\mathbf{2p}^{-}_{2}$ (blue, bottom) and the mixture of equivalent amounts of $\mathbf{2m}^{-}_{2}$ and $\mathbf{2p}^{-}_{2}$ (middle) in $CDCl_3$ (1×10^{-3} M for each species, 20 °C).

In summary, we have found carboxylate-appended pyrrole-based π-conjugated anion-responsive molecules that form self-assembled dimers and exhibit self-sorting behaviours depending on the substituted positions of anionic sites. Such assemblies are constructed on the basis of the binding abilities of the anion receptor moieties, even though efficient anion binding is restricted in less polar solvents. Anion-binding self-assembly can be applied to supramolecular polymers and various macromolecular systems such as thermotropic liquid crystals, which were preliminarily observed. Relevant investigations are currently underway.

This work was supported by PRESTO/JST (2007–2011), Grants-in-Aid for Young Scientists (B) (No. 21750155) and (A) (No. 23685032) from MEXT and the Ritsumeikan R-GIRO project (2008–2013). The authors thank Prof. Atsuhiro Osuka and Mr Tomohiro Higashino, Kyoto University, for the single-crystal X-ray analysis, Prof. Hiroshi Shinokubo and Dr Satoru Hiroto, Nagoya University, and Dr Naoki Aratani, Kyoto University, for their help with ESI-MS and Prof. Hitoshi Tamiaki, Ritsumeikan University, for various measurements.

Notes and references

‡ Crystal data for **1a**·benzoate·TPA (from EtOAc/*i*-propyl ether): $C_{30}H_{42}N_3O_4BF_2$, Mw = 557.48, monoclinic, $P2_1/a$ (no. 14), $a = 18.0991(3)$, $b = 10.0405(2)$, $c = 18.2608(3)$ Å, $\beta = 113.7402(10)°$, $V = 3037.62(9)$ Å^3, $T = 93(2)$ K, $Z = 4$, $D_c = 1.219$ g cm^{-3}, μ(Cu-Kα) = 0.724 mm^{-1}, 29 033 reflections measured, 5521 unique ($R_{\mathrm{int}} = 0.0658$), $R_1 = 0.0720$, w$R_2 = 0.1867$, GOF = 1.219 ($I > 2\sigma(I)$ for R_1, wR_2 and GOF). CCDC 809340.

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