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Ion-based materials of boron-modified dipyrrolyldiketones as anion receptors⁺

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Cite this: Chem. Commun., 2013, 49, 2506

Received 26th November 2012, Accepted 4th February 2013

DOI: 10.1039/c3cc38494b

www.rsc.org/chemcomm

Boron-modified pyrrole-based anion receptors (catechol-boron and diphenylboron dipyrrolyldiketone derivatives) formed planar receptoranion complexes, leading to charge-by-charge assemblies with planar cations, as in the corresponding difluoroboron derivative.

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Appropriately designed organic ionic species can form highly ordered assembled structures via electrostatic interactions, resulting in the formation of ion-based materials such as crystals and soft materials including liquid crystals.¹⁻³ In contrast to ionbased materials wherein either the cationic or the anionic component plays a predominant role in forming organised structures, the arrangement of both the charged species is especially challenging because very few suitable ionic building subunits are available. Considering the geometries of the charged species, planar π -conjugated ions are suitable for the formation of stacking assemblies via π - π and electrostatic interactions. However, unlike planar cations, planar anions are difficult to prepare because of their excess electrons, which make them susceptible to electrophilic attack. Therefore, anion binding of electronically neutral π -conjugated receptor molecules can be considered an alternative strategy to fabricate planar anionic structures.

As receptor candidates,⁴ dipyrrolyldiketone boron complexes (*e.g.* **1a–d**, Fig. 1a) form planar receptor–anion complexes, which behave as the constituents of ion-based crystals and soft materials in combination with cations.^{5–7} The formation of soft materials requires long-alkyl-chain-substituted aryl moieties at the pyrrole α -positions, as seen in **1b–d**. In particular, the introduction of planar cations such as a 4,8,12-tripropyl-4,8,12-triazatriangulenium (TATA) cation (Fig. 1b)⁸ into the predesigned receptor–anion complexes results in charge-by-charge assemblies comprising alternately stacking positively and negatively charged species as



Fig. 1 (a) Anion-binding mode of boron-modified dipyrrolyldiketone derivatives 1a–d, 2a–d and 3a–d and (b) structure of a TATA cation.

supramolecular gels and thermotropic liquid crystals.^{6*c*,*f*} Bulky cations such as tetrabutylammonium (TBA) are also included in the charge-by-charge assemblies.^{6*d*,*e*} Recently, we found that pyrrole β -substitution is essential for the fabrication of charge-based materials with different assembling modes.^{6*g*} Thus far, the preparation of charge-based materials has been restricted to difluoroboron (BF₂) complexes. With this background, we focused on the introduction of substituents onto boron units for modulating the structures and properties of charge-based materials, as observed in catechol–boron (BO₂) and diphenylboron (BC₂) complexes.⁷

Boron-modified derivatives **2a–d** and **3a–d** (Fig. 1a) were synthesised by reacting the corresponding dipyrrolyldiketone derivatives with BCl₃ and catechol for **2a–d** and with BPh₃ for **3a–d** in dry toluene.⁹ UV/vis absorption spectra of **2a** and **3a** in CH₂Cl₂ (1 × 10⁻⁵ M) showed the maxima (λ_{max}) at 521 and 503 nm, respectively, whereas the fluorescence emission maxima (λ_{em}) and corresponding quantum yields (Φ_F) (in parentheses) of **2a** and **3a** excited at λ_{max} in CH₂Cl₂ were

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 $[\]dagger$ Electronic supplementary information (ESI) available: Synthetic procedures and analytical data, anion-binding behaviour and CIF files for single-crystal X-ray structural analysis of **2a**, **3a** and **2a**·Cl⁻-TBA⁺. CCDC 894126, 921412 and 894127. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc38494b

558 nm (0.02) and 540 nm (0.93), respectively. In contrast, **1a** showed $\lambda_{\text{max}} = 515$ nm and $\lambda_{\text{em}} (\Phi_{\text{F}}) = 552$ nm (0.98). Therefore, the introduction of boron substituents resulted in moderate changes in the absorption and emission wavelengths, while catechol–boron substitution significantly decreased Φ_{F} .‡

Single-crystal X-ray analysis of 2a and 2a Cl⁻-TBA⁺ revealed solid-state packing structures, which showed that the assembled structures were similar to 1a and $1a \cdot Cl^{-}-TBA^{+}$, ^{6a} respectively, whereas 3a formed edge-to-edge packing structures because of the bulky diphenylboron moiety.§ In particular, 2a·Cl--TBA+ showed charge-by-charge assemblies comprising alternately stacking two 2a·Cl⁻ planes and two TBA⁺ cations. Introduction of long alkyl chains vielded soft materials both in the absence and presence of anions. In fact, 2d and 3d formed supramolecular gels from octane (10 mg m L^{-1}) at their corresponding transition temperatures, *i.e.* at 27.5 and 22.5 °C, respectively, whereas 2c and 3c were in a gel-like state below 3.5 and -40.5 °C, respectively. Synchrotron X-ray diffraction (XRD) of the xerogels of 2d and 3d showed lamellar and rectangular columnar (Col_r) structures, respectively. In the scanning electron microscopy (SEM) measurements, the xerogel of 3d showed a fibrous structure with a width of ca. 0.5-1.0 µm, whereas that of 2d showed no specific morphology. UV/vis absorption of 2d and 3d as octane gels showed the maxima λ_{max} at *ca.* 538 and 476 nm, respectively, and the fluorescence emission maxima λ_{em} excited at λ_{max} at 667 and 531 nm, respectively. Furthermore, unlike $3\mathbf{d} \cdot \mathbf{Cl}^-$ -TATA⁺, which formed a precipitate, the ion pair 2d·Cl⁻-TATA⁺ formed octane gel at r.t. Similar to that of 2d, the gel of $2d \cdot Cl^-$ -TATA⁺ showed an absorption λ_{max} at *ca.* 530 nm with shoulders at 504 and 566 nm, although 3d·Cl⁻–TATA⁺ showed λ_{max} at *ca.* 512 nm; this observation suggested that the bulky diphenyl substituents in 3d interfere with the efficient stacking of the molecules, although the ion pair of 2d formed an organised structure similar to that of 1d.

The mesophase behaviours of 2b-d and 3a-d were examined by differential scanning calorimetry (DSC) and polarised optical microscopy (POM) (Fig. 2a). DSC measurements of 2b-d revealed reversible mesophases during heating and cooling processes. For example, upon second heating, 2d showed a mesophase over a wider temperature range of 57-208 °C than that in the case of 1d (65–156 °C).^{6b} Longer alkyl chains provided mesophases over narrower temperature ranges, as observed in 1b-d.6b On the other hand, 3b-d showed no mesophase upon cooling and instead showed exothermic first-order crystal-crystal transitions upon heating, e.g. at 59 °C for 3d. In addition, the significantly lower transition temperatures of 3b-d to isotropic liquids (iso), e.g. at 86 °C for 3d, as compared to those of 1b-d and 2b-d suggested that 3b-d formed less effective stacking structures because of the bulky phenyl moieties on boron. Furthermore, POM images of 2b-d showed ribbon-like textures similar to those of **1b-d**^{6b} upon cooling from iso, in contrast to **3b-d**, which showed no textures derived from mesophases.

Synchrotron XRD revealed the organised structures of the mesophases. XRD analysis of **2b–d** revealed the formation of hexagonal columnar (Col_h) mesophases. For example, the XRD pattern of **2d** at 195 °C upon first cooling showed d = 3.63 (100), 2.09 (110), 1.81 (200), 1.39 (210), 1.21 (300), 1.04 (220) and 1.00 (310) nm (Fig. 2b), derived from the Col_h phase of a = 4.19 nm.

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Fig. 2 (a) POM image of (i) 2d at 195 °C and (ii) 3d at 70 °C upon first cooling and second heating and (b) synchrotron XRD analysis of 2d at 195 °C upon first cooling and a possible model of a Col_h structure (inset).

A diffused and broad scattering halo was observed at around 0.44-0.45 nm, corresponding to disordered alkyl chains and the intermolecular stacking distance (c). The average number (Z) of molecules in the assembled unit was estimated to be 2.0 for $\rho = 1$. Moreover, the mesophases of 2b, c exhibited similar diffraction peaks, and the unit parameters of 2b (210 °C) and 2c (205 °C) were a = 3.21 and 3.74 nm, respectively, with c = 0.45 nm (Z = 2.0 for $\rho = 1$). The *a* values of **2b-d** were consistent with the molecular lengths speculated by a theoretical study at the AM1 level.¹⁰ Similar to 1b-d, 2b-d formed organised structures based on the circular units comprising self-assembled dimers (Fig. 2b). On the other hand, the XRD patterns of 3b-d showed various phases; for example, the XRD pattern of 3c as a mesophase at 35 °C upon second heating showed d = 2.82 (200), 2.25 (110), 1.20 (020) and 0.78 (230) nm, derived from the Col_r phase of a = 5.62 nm, b =2.46 nm and c = 0.42 nm (Z = 2.1 for $\rho = 1$) without the formation of a dimer structure. In addition, the XRD pattern of 3c at 55 °C upon second heating exhibited the Col_r phase of a = 4.47 nm, b =2.98 nm and c = 0.42 nm, suggesting the formation of a more condensed packing structure by heating. In contrast, 3d showed a crystal-like diffraction at 70 °C.11 UV/vis absorption and fluorescence emission spectra of 2d in the film after once melting suggested that the stacking mode was similar to that of 1d but different from that of 3d. These observations suggested that aryl substituents on boron prevented the formation of dimensioncontrolled stacking structures based on the core π -planes and instead led to the formation of complicated packing structures in the derivatives possessing long alkyl chains.

Next, the assemblies comprising receptor–anion complexes, $2\mathbf{d} \cdot \mathbf{Cl}^-$ and $3\mathbf{d} \cdot \mathbf{Cl}^-$, and a planar cation were examined. The assembly $2\mathbf{d} \cdot \mathbf{Cl}^-$ –TATA⁺, which was prepared by reprecipitation from 1,4-dioxane, showed the formation of mesophases with three transition temperatures of 74, 59 and 44 °C during first cooling. In addition, similar to $1\mathbf{d}$, ^{6b,c} the transition temperature of $2\mathbf{d} \cdot \mathbf{Cl}^-$ –TATA⁺ to Iso was significantly lower (94 °C) than that of $2\mathbf{d}$ (208 °C). On the other hand, $3\mathbf{d} \cdot \mathbf{Cl}^-$ –TATA⁺ showed no mesophase upon cooling but underwent exothermic second-order crystal–crystal



Fig. 3 (a) POM images of (i) $2d \cdot Cl^--TATA^+$ at 64 °C upon first cooling and (ii) $3d \cdot Cl^--TATA^+$ at 70 °C upon second heating and (b) corresponding synchrotron XRD pattern of $2d \cdot Cl^--TATA^+$.

transitions at, for example, 51 °C upon heating. Furthermore, the POM image of $2d \cdot Cl^-$ -TATA⁺ exhibited a broken-fan-like texture at 64 °C upon first cooling (Fig. 3a(i)), whereas $3d \cdot Cl^-$ -TATA⁺ showed a crystal-like texture at 70 °C upon second heating (Fig. 3a(ii)).

XRD analysis of $2\mathbf{d} \cdot \mathrm{Cl}^-$ -TATA⁺ at 64 °C upon first cooling suggested the formation of a Col_r phase of a = 7.34 nm, b =2.84 nm and c = 0.80 nm (Z = 4.3 for $\rho = 1$) consisting of the dimeric disk unit on the basis of d = 3.67 (200), 2.65 (110), 1.92 (310), 1.83 (400), 1.71 (410), 1.33 (220) and 0.80 (001) nm. In addition, the XRD pattern at 53 °C upon second heating exhibited a Col_r phase of a =7.76 nm, b = 3.99 nm and c = 0.80 nm (Z = 6.1 for $\rho = 1$), suggesting the increasing number of constituent ion pairs in an ellipsoidal disk in the expanded unit lattice. In this case, the introduction of a catechol-boron moiety instead of BF2 changed the phase from Colh in $1d \cdot Cl^-$ -TATA^{+6c} to Col_r in $2d \cdot Cl^-$ -TATA⁺, because of the stacking of charged planes with parallel displacement. On the other hand, the XRD pattern of 3d Cl⁻-TATA⁺ exhibited various phases such as a Col_h phase of a = 5.02 nm and c = 0.85 nm (Z = 4.2 for $\rho = 0.9$) at 40 °C upon second heating, on the basis of d = 4.35 (100), 2.62 (110), 2.16 (200), 1.45 (300) and 0.85 (001) nm. In addition, XRD analysis at 72 °C upon second heating revealed a crystal-like diffraction pattern, which was found to be well correlated with an exothermic transition in the DSC profile. The bulky diphenylboron moiety leads to weak stacking between the charged components, resulting in low transition temperatures and complicated structures in the mesophases.

In summary, boron-modified pyrrole-based π -conjugated anion receptors formed supramolecular assemblies such as mesophases based on charge-by-charge assembled structures. The substituents on a boron affected the assembled structures both in the absence and presence of anions as a planar cation salt. In particular, catechol-boron complexes formed mesophases based on charge-by-charge assemblies, similar to the BF₂ complexes, whereas diphenylboron complexes formed crystal-like mesophases upon heating. Further modified boron substituents can change the mode of assembly and afford various ionic materials based on charge-segregated assemblies, which comprise stacking structures of identical charged species.^{6g,h} Detailed investigations on the formation of such assemblies are currently under way.

This work was supported by PRESTO/JST (2007–2011), Grant-in-Aid for Young Scientists (A) (No. 23685032) from the MEXT and Ritsumeikan R-GIRO project (2008–2013). We thank Prof. Atsuhiro Osuka, Dr Naoki Aratani, Dr Taro Koide, Mr Tomohiro Higashino and Mr Hirotaka Mori, Kyoto University, for single-crystal X-ray analysis, Prof. Kazuchika Ohta and Mr Masahiro Shimizu, Shinshu University, for preliminary examinations on mesophases, Dr Takashi Nakanishi, NIMS, for SEM measurements, Prof. Tomonori Hanasaki, Ritsumeikan University, for POM and DSC measurements, Dr Noboru Ohta, JASRI/SPring-8, for synchrotron radiation XRD measurements (BL40B2 at SPring-8), Prof. Hikaru Takaya, Kyoto University, for XRD measurements carried out in the Joint Usage/Research Center (JURC) at ICR and Prof. Hitoshi Tamiaki, Ritsumeikan University, for various measurements.

Notes and references

[‡] **2a** and **3a** exhibited anion-binding behaviour as evident from the K_a values of 250 000 and 170 000 M⁻¹ for Cl⁻, 25 000 and 15 000 M⁻¹ for Br⁻, 520 000 and 110 000 M⁻¹ for CH₃CO₂⁻ and 77 000 and 50 000 M⁻¹ for H₂PO₄⁻, respectively, in CH₂Cl₂; these values were estimated by the changes in UV/vis absorption spectra upon the addition of anions as TBA salts. § Crystal data are summarised in the ESI.

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