View Article Online / Journal Homepage / Table of Contents for this issue
ChemComm
Dynamic Article Links

Cite this: *Chem. Commun.*, 2011, **47**, 7620–7622

www.rsc.org/chemcomm

COMMUNICATION

Solvent-dependent supramolecular assemblies of π-conjugated anion-responsive acyclic oligopyrroles†

Hiromitsu Maeda* and Yoshitaka Terashima

Received 13th May 2011, Accepted 1st June 2011
DOI: 10.1039/c1cc12827b

Amide-attached pyrrole-based π-conjugated anion receptors showed solvent-dependent assembled modes such as H-aggregates that were soluble in octane and highly organized structures that provided supramolecular gels in CH_2Cl_2 and 1,4-dioxane in the absence of π–π stacking.

Hydrogen bonding is one of the essential noncovalent interactions that construct functional macromolecular architectures both in the biotic and artificial systems.[1] π-Conjugated molecules provide highly ordered organized structures by the introduction of hydrogen-bonding sites on the basis of π–π stacking interactions.[2] The directional force such as hydrogen bonding can control the strength of the interactions between the π-planes; as a result, the balance between hydrogen bonding and the π–π stacking would tune the electronic and electrooptical properties and the structures of molecular assemblies in soft materials. Among organized structures, the formation of supramolecular gels is significantly influenced by various conditions including the type of solvents.[3] In particular, supramolecular gels that are responsive to anions[4] have attracted considerable attention as an example of a soft material tuned by incorporation of various ionic components that are not only anions but also counter cations.[5] As anion-responsive π-conjugated motifs, dipyrrolyldiketone boron complexes (*e.g.*, **1a–d**, Fig. 1a), which exhibit inversion (flipping) of pyrrole rings by anion binding (Fig. 1b),[6] afford soft materials such as supramolecular gels[6a–c] and liquid crystals.[6b–d] The supramolecular gels comprising anion receptors **1c**,**d** derived from octane were fabricated by interactions between rod-like π-planes with the support of van der Waals interactions of long alkyl chains. Therefore, the introduction of additional hydrogen-bonding sites such as amide moieties would provide supramolecular assemblies that exhibit assembling behaviours and related electronic and electrooptical properties depending on the conditions. Thus far, amide-appended perylene bisimides have been reported to construct solvent-dependent assemblies for soft materials.[7] In addition, amide units can serve as covalent linkages between core π-planes and side alkyl-substituted aryl moieties. In this study, we report solvent-dependent molecular assemblies, including supramolecular gels, of amide-attached pyrrole-based π-conjugated anion receptors.

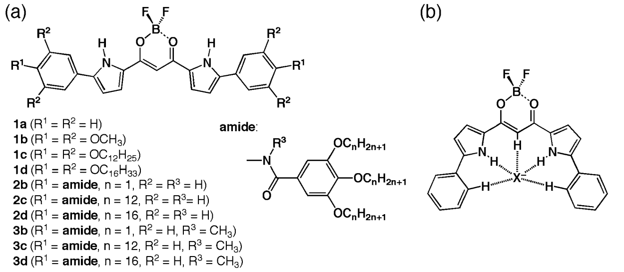

Fig. 1 (a) Structures of anion-responsive dipyrrolyldiketone BF_2 complexes **1a–d**, **2b–d** and **3b–d** and (b) anion-binding mode of **1a**.

Amide-linked derivatives **2b–d** and **3b–d** were synthesized by the reaction of trialkoxygallic-amide-phenyl-substituted pyrroles[8] with malonyl chloride and following BF_2 complexation. In the ^1H NMR spectra of **2c** and **2d** in $CDCl_3$ (1×10^{-3} M), the signals corresponding to the amide NH were observed at 8.01 and 7.94 ppm, respectively, suggesting that the receptors form no hydrogen bonding with the amide moieties and are dispersed as monomers at rt in this diluted solution. It is noteworthy that methoxy-substituted **2b** was less soluble in $CDCl_3$ (1×10^{-3} M). The UV/vis absorption spectrum of **2b** as a monomer in $CHCl_3$ (1×10^{-5} M) showed a maximum (λ_{max}) at 525 nm; the λ_{max} was slightly red-shifted when compared to those of **1b** (518 nm) and **3b** (515 nm) owing to N-unsubstituted amide units. The fluorescence emission maxima (λ_{em}) and the corresponding quantum yields (Φ_F) of **2b** and **3b** excited at λ_{max} in $CHCl_3$ were 562 ($\Phi_F = 0.98$) and 552 ($\Phi_F = 0.97$) nm, respectively. The binding constants (K_a) of **2b** for Cl^- and $CH_3CO_2^-$ in $CHCl_3$ were estimated as 2200 and 19 000 M^{-1}, respectively, by observing the UV/vis absorption spectral changes upon the addition of anions in the form of tetrabutylammonium (TBA) salts. Further, the solid-state assembled mode of an amide-substituted molecule, which can provide insights into the organized structures of soft materials from analogue derivatives, was examined using single-crystal X-ray analysis of methoxy-substituted **2b** and **3b** (Fig. 2) (for crystal data see ESI†). In a manner similar to **1a**,**b**,[6a] **2b** forms a stacking structure with the distance of 3.88 Å between the plane

---

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: Synthetic procedures and analytical data, anion-binding behaviour and CIF files for single-crystal X-ray structural analysis of **2b** and **3b** and related precursor. CCDC 824850–824852. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc12827b

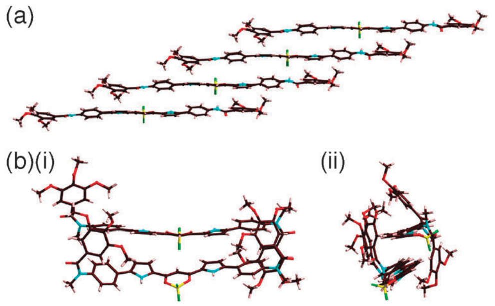

Fig. 2 Single-crystal X-ray structures of (a) **2b** as an assembled structure in side view and (b) **3b** as an interlocked structure in two side views (i) and (ii). Atom colour code: brown, pink, yellow, blue and red refer to carbon, hydrogen, boron, nitrogen and oxygen, respectively.

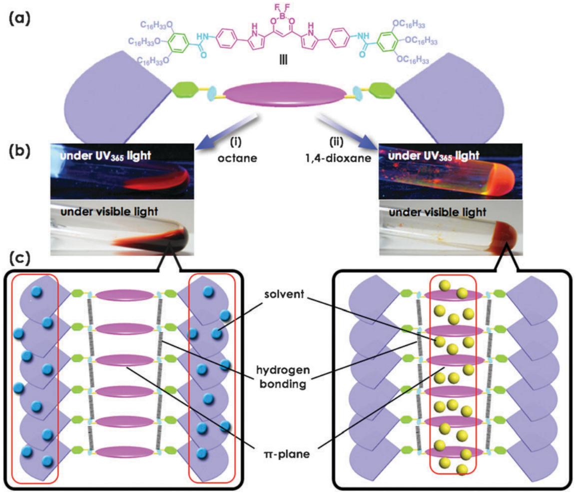

Fig. 3 (a) Graphical representation of **2b**, (b) solution and gel states from (i) octane and (ii) 1,4-dioxane and (c) possible assembled modes from these solvents. Structural colour: magenta, cyan, green and orchid refer to π-receptor unit, amide group, phenyl group and alkoxy chains, respectively. Red boxes at alkoxy chains and π-receptor units for (i) and (ii), respectively, represent the parts that are preferably solvated.

consisting of the core 16 atoms and a phenylpyrrole unit of the neighbouring molecule (Fig. 2a). On the other hand, **3b** possessing the *cis*-conformation of *N*-methyl-amide moieties shows the interlocked dimer structures (Fig. 2b).

The solution-state assembled structure of hexadecyloxy-substituted **2d** (Fig. 3a) was initially suggested by UV/vis and fluorescence spectra in octane at 1.0 × 10^{-5} M. The broad and blue-shifted UV/vis absorption band at 481 nm and the weak and red-shifted fluorescence emission at 699 and 740 nm with Φ_F = 0.003, excited at the λ_{max}, suggest the formation of H-aggregates in octane (Fig. 3b(i)). This is in sharp contrast to the case of **1d**, which exists as a dispersed monomeric form and shows a relatively sharp UV/vis absorption band at 497 nm and a strong fluorescence emission at 533 nm with Φ_F = 0.83 under the identical conditions described for **2d**.[6a] The formation of H-aggregates of **2d** is due to tight π–π stacking with presumably supplementary hydrogen bonding. Surprisingly, even at higher solution concentrations of 10 mg mL^{-1}, **2d** also afforded a solution state by the formation of H-aggregates due to λ_{max} at 478 nm and λ_{em} at 743 nm; however, **2d** did not afford a gel state. This observation strongly suggests that there is an efficient interaction, assisted by hydrogen bonding of amide units, between π-planes; further long alkyl chains in octane enable the formation of smaller aggregates but not larger ones that can provide gels. The hydrogen bonding between amide moieties was evidenced by the IR bands at 3186 and 1655 cm^{-1} for the amide-N–H and C=O bonds, respectively, at 2.5 × 10^{-3} M. Furthermore, the ^1H NMR spectra of **2d** in octane-d_{18} (1 × 10^{-3} M) at variable temperatures from 40 to −40 °C revealed the formation of aggregates; **2d** showed broad signals assignable to aromatic and amide NH protons between 0 and 40 °C, presumably due to the formation of small aggregates, and exhibited no signals below −20 °C owing to the formation of larger structures. In contrast, the ^1H NMR of amide-*N*-methyl-substituted **3d** in octane showed monomeric structures, suggesting that amide-NH is crucial for aggregation.

From the above observations made in octane solution, it is deduced that other factors such as solvents should be examined in order for **2d** to exhibit gelation behaviours. In fact, **2d** formed supramolecular gels from CH_2Cl_2 and 1,4-dioxane (10 mg mL^{-1}) (Fig. 3b(ii)) at their corresponding transition temperatures of 27.0 and 37.0 °C, respectively. On the other hand, **2d** provided a $CHCl_3$ solution at rt; this solution was transformed to a gelated state below 0.5 °C. This is in sharp contrast to **1d** that gave solutions from CH_2Cl_2 and 1,4-dioxane. On the other hand, dodecyloxy-substituted **2c** showed lower transition temperatures at 6.5, −20.5 and 17.5 °C for gelations occurring from CH_2Cl_2, $CHCl_3$ and 1,4-dioxane, respectively. Conversely, derivatives **3c**,**d** in the absence of amide-*N*-methyl substituents provided only solutions, also suggesting the necessity of hydrogen bonding and, possibly, the *trans*-conformation of amide moieties. Gelated material of **2d** in CH_2Cl_2 showed fairly sharp UV/vis absorption and fluorescence emission bands (excited at λ_{max}) with λ_{max} and λ_{em} values at 498 and 567 nm, respectively, which are fairly similar to those at 523 and 562 nm, respectively, of the diluted CH_2Cl_2 solution (1 × 10^{-5} M). This result suggests that there are almost no significant π–π stacking in contrast to the case in octane; however, hydrogen bonding at the amide moieties is essential to the formation of organized structures. Moreover, this is supported by the shifts of the IR band of amide-N–H in solution (2.5 × 10^{-3} M) from 3425 to 3296 cm^{-1} in the case of the gel (10 mg mL^{-1}). In addition, similar trends in UV/vis and IR spectra were observed in 1,4-dioxane. Further, the ^1H NMR spectra of **2d** in CD_2Cl_2 (5 × 10^{-3} M) showed no signals below 10 °C, suggesting the formation of aggregates. On the other hand, the ^1H NMR spectra of **2d** in $CDCl_3$ (5 × 10^{-3} M) exhibited the shifts of amide-NH from 8.05 to 8.31 ppm when the temperature was decreased from 40 to 10 °C, suggesting a stronger intermolecular hydrogen-bonding at lower temperatures. In addition, the broader signals of aromatic protons were observed at 0 °C due to the formation of larger aggregates. This is in contrast to **3d**, for which there are no shifts of signals for variations in temperature.

From the observations described above, it can be safely concluded that the balance of multiple interactions, hydrogen-bonding, π–π stacking and van der Waals interactions is significantly influenced by solvents. Octane appears to prefer aliphatic side chains over core π-planes, resulting in the formation of small H-aggregates with fairly tight π–π stacking and relatively weak interactions between alkyl chains (Fig. 3c(i)). On the other

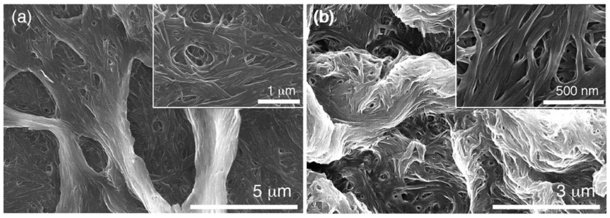

Fig. 4 SEM images of xerogels of **2d** from (a) CH_2Cl_2 (10 mg mL^{-1}) and (b) 1,4-dioxane (10 mg mL^{-1}).

hand, CH_2Cl_2, $CHCl_3$ and 1,4-dioxane prefer π-planes over alkyl chains (Fig. 3c(ii)). While these solvents cause less significant spectral changes as discussed above, they provide highly organized bundled structures based on columnar structures that are suitable for gels.

The organized structures of xerogels of **2d** prepared on silicon substrates from CH_2Cl_2 and 1,4-dioxane were observed using scanning electron microscopy (SEM) (Fig. 4). In the SEM measurements, the CH_2Cl_2 xerogel showed the formation of fibrous structure of widths of *ca.* 50–100 nm (Fig 4a), whereas the xerogel obtained from 1,4-dioxane exhibited similar wire-like structures with widths of 25–75 nm (Fig. 4b). As already reported, **1d** did not form such fibrous structures,[6a] suggesting that the presence of amide units improves the efficiency of the fabrication of stable fibres for supramolecular gels. Further, the packing structure of the CH_2Cl_2 xerogel was examined using synchrotron X-ray diffraction (XRD); the XRD exhibited the diffraction peaks corresponding to d = 6.96 (001), 3.51 (002), 2.34 (003), 1.39 (005) and 1.11 (006) nm. All the peaks were due to the lamellar structure in the xerogel. The diffraction peak value of 6.96 nm is nearly consistent with the AM1-optimized[9] molecular length of 6.61 nm, suggesting the formation of 1D aggregates. Moreover, the 1,4-dioxane xerogel exhibited similar diffraction peaks with a d value of 5.91 (001) nm, presumably due to the interdigitation or tilting of the components. On the other hand, the solid state of nongelated **3d** exhibited diffraction peaks with d values of 2.71 (100), 1.57 (110), 1.35 (200), 1.00 (210) and 0.90 (300) nm, all of which were derived from a hexagonal columnar structure consisting of one molecule (Z = 1) as a circle unit with a lattice constant a = 3.13 nm. These results are consistent with the respective preferred conformations, *trans* for **2d** and *cis* for **3d**, and the presence or absence of hydrogen bonding of amide units.

In a manner similar to an octane gel of **1d**,[6a] the supramolecular gel of **2d** from CH_2Cl_2 was found to be responsive to anions.[5] The addition of TBACl salt as a solid to the gel of **2d** (10 mg mL^{-1}) provided a solution state with λ_{max} and λ_{em} (excited at λ_{max}) values of 529 and 577 nm, respectively. Interestingly, instead of a bulky TBA cation, the introduction of Cl^- as a planar 4,8,12-tripropyl-4,8,12-triazatriangulenium ($TATA^{C3}$) cation salt[10] also afforded a solution state; this was in sharp contrast to the gelated charge-by-charge assemblies observed in **1d**·Cl^-·$(TATA^{C3})^+$.[6c] The introduction of a planar cation appears less efficient for **2d**, presumably because pyrrole inversion by anion binding prevents the effective hydrogen bonding by amide moieties and the size of $(TATA^{C3})^+$ does not match that of **2d**·Cl^-.

In summary, amide-attached pyrrole-based π-conjugated anion receptors showed solvent-dependent assembled modes such as H-aggregates soluble in octane and supramolecular gels in CH_2Cl_2 and 1,4-dioxane. The introduction of hydrogen-bonding interaction sites to the π-conjugated planes enabled the receptors to exhibit tunable stabilities, thereby resulting in the dramatic changes observed in the gels and dispersed solutions in the absence and presence of anions, respectively. Further modifications of receptors could provide various charge-based soft materials by combination with appropriate salts of anions. These detailed 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 the MEXT and Ritsumeikan R-GIRO project (2008–2013). We thank Prof. Atsuhiro Osuka, Dr Naoki Aratani, Mr Taro Koide and Mr Tomohiro Higashino, Kyoto University, for single-crystal X-ray analysis, Dr Takashi Nakanishi, NIMS, for SEM measurements, Dr Noboru Ohta, JASRI/SPring-8, for synchrotron radiation XRD measurements (BL40B2 at SPring-8) and Prof. Hitoshi Tamiaki, Ritsumeikan University, for various measurements.

Notes and references

1 G. A. Jeffrey and W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer, Berlin, 1991.

2 Examples of hydrogen-bond-based π–π stacking assemblies: (*a*) V. Percec, C.-H. Ahn, T. K. Bera, G. Ungar and D. J. P. Yeardley, *Chem.–Eur. J.*, 1999, **5**, 1070; (*b*) V. Percec, M. R. Imam, T. K. Bera, V. S. K. Balagurusamy, M. Peterca and P. A. Heiney, *Angew. Chem., Int. Ed.*, 2005, **44**, 4739; (*c*) Y. Sagara, S. Yamane, T. Mutai, K. Araki and T. Kato, *Adv. Funct. Mater.*, 2009, **19**, 1869; (*d*) A. Das and S. Ghosh, *Chem.–Eur. J.*, 2010, **16**, 13622.

3 Selected books for further information on supramolecular gels: (*a*) *Low Molecular Mass Gelators*, Topics in Current Chemistry, ed. F. Fages, Springer-Verlag, Berlin, 2005; (*b*) T. Ishi-i and S. Shinkai, *Supramolecular Dye Chemistry*, in *Topics in Current Chemistry*, ed. F. Würthner, Springer-Verlag, Berlin, 2005, p. 119; (*c*) *Molecular Gels*, ed. R. G. Weiss and P. Terech, Springer, Dordrecht, 2006.

4 Selected books for anion binding: (*a*) *Supramolecular Chemistry of Anions*, ed. A. Bianchi, K. Bowman-James and E. García-España, Wiley-VCH, New York, 1997; (*b*) *Anion Sensing*, Topics in Current Chemistry, ed. I. Stibor, Springer-Verlag, Berlin, 2005; (*c*) P. A. J. L. Sessler, P. A. Gale and W.-S. Cho, *Anion Receptor Chemistry*, RSC, Cambridge, 2006; (*d*) *Anion Complexation in Supramolecular Chemistry*, Topics in Heterocyclic Chemistry, ed. P. A. Gale and W. Dehaen, Springer-Verlag, Berlin, 2010, vol. 24.

5 Reviews for anion-responsive supramolecular gels: (*a*) H. Maeda, *Chem.–Eur. J.*, 2008, **14**, 11274; (*b*) G. O. Lloyd and J. W. Steed, *Nat. Chem.*, 2009, **1**, 437; (*c*) M.-O. M. Piepenbrock, G. O. Lloyd, N. Clarke and J. W. Steed, *Chem. Rev.*, 2010, **110**, 1960.

6 (*a*) H. Maeda, Y. Haketa and T. Nakanishi, *J. Am. Chem. Soc.*, 2007, **129**, 13661; (*b*) H. Maeda, Y. Terashima, Y. Haketa, A. Asano, Y. Honsho, S. Seki, M. Shimizu, H. Mukai and K. Ohta, *Chem. Commun.*, 2010, **46**, 4559; (*c*) Y. Haketa, S. Sasaki, N. Ohta, H. Masunaga, H. Ogawa, F. Araoka, H. Takezoe and H. Maeda, *Angew. Chem., Int. Ed.*, 2010, **49**, 10079; (*d*) H. Maeda, K. Naritani, Y. Honsho and S. Seki, *J. Am. Chem. Soc.*, 2011, **133**, 8896.

7 As an example: X.-Q. Li, X. Zhang, S. Ghosh and F. Würthner, *Chem.–Eur. J.*, 2008, **14**, 8074.

8 F. Camerel, G. Ulrich and R. Ziessel, *Org. Lett.*, 2004, **6**, 4171.

9 M. J. Frisch, *et al.*, , *Gaussian 03, Revision C.01*, Gaussian, Inc., Wallingford, CT, 2004.

10 (*a*) B. W. Laursen and F. C. Krebs, *Angew. Chem., Int. Ed.*, 2000, **39**, 3432; (*b*) B. W. Laursen and F. C. Krebs, *Chem.–Eur. J.*, 2001, **7**, 1773.