Angewandte Chemie
International Edition

DOI: 10.1002/anie.201006356

Oriented Salts: Dimension-Controlled Charge-by-Charge Assemblies from Planar Receptor–Anion Complexes**

*Yohei Haketa, Sono Sasaki, Noboru Ohta, Hiroyasu Masunaga, Hiroki Ogawa, Nobuhiro Mizuno, Fumito Araoka, Hideo Takezoe, and Hiromitsu Maeda**

Salts, ionic compounds comprising cations (positive ions) and anions (negative ions), are essential materials for biotic activities. They are also utilized as inorganic minerals for industry. The appropriate arrangement of charged species through electrostatic interactions is a significant issue for constructing ordered nanoscale architectures in various states. For example, most inorganic, organic, and inorganic–organic hybrid salts use electrostatic interactions between ions to form organized three-dimensional (3D) crystal structures.[1] The 3D structures defined herein include not only crystals of isomeric space groups in a cubic system but also non-isomeric crystals. Appropriate pairs of cations and anions yield ionic liquids, which are partially ordered but essentially non-dimensional (0D) states.[2] In ionic liquids, bulky geometries of both the cationic and the anionic species effectively prevent crystallization owing to significantly weaker ionic interactions. In contrast to crystals and liquids from ions, soft materials formed by electrostatic interactions between charged components have been reported as liquid crystals on the basis of ionic mesogens.[3,4] For example, Kato et al. reported various ionic liquid crystals comprising alkyl-substituted imidazolium salts, which afford columnar structures and have ionic conduction.[4a,e] Compared to such ionic mesophases, in which the locations of either cations or anions cannot be confirmed, more rigidly organized structures with a certain level of mobility in their building subunits are also useful for various applications such as ferroelectric materials. In contrast to bulky components, planar cationic and anionic molecules effectively interact with each other and form charge-by-charge assemblies composed of alternately stacking charged components. Aided by supplementary van der Waals interactions along with electrostatic and π–π interactions,[5] dimension-controlled charge-by-charge assemblies will form not only crystals but also soft materials such as supramolecular gels, liquid crystals, and other organized structures.

In comparison to π-conjugated cations, which are often based on sp^2-hybridized planar geometries, π-conjugated planar anionic species are required to delocalize their excess electrons, for example by depositing them in aromatic systems, to prevent them from suffering an electrophilic attack. Focusing on these perspectives, one of the strategies for forming planar anions is the complexation of electronically neutral π-conjugated anion receptors and spherical halide anions. As π-conjugated planes for associating with halide anions,[6] BF_2 complexes of 1,3-dipyrrolyl-1,3-propanediones efficiently bind spherical anions with inversion of pyrrole rings (**1** and **2**; Scheme 1 a).[7,8] Receptor **1** affords single crystals, which are composed of 1D columnar structures of alternately stacking chloride and bromide complexes and tetrapropylammonium (TPA) countercations, and are prepared from a hydrocarbon solvent.[8b,c] In contrast to these crystal states, an alkyl-substituted receptor **2** exhibits the formation of anion-responsive supramolecular octane gel, which is temporally transformed into a solution state by the addition of tetrabutylammonium (TBA) salts owing to the formation of soluble ion pairs comprising fairly aliphatic TBA cations and receptor–anion complexes.[8b,9] Therefore, the introduction of planar cations in place of bulky TBA cations may form fine-tuned supramolecular organized structures as soft materials using π–π stacking and electrostatic interactions along with van der Waals forces. Herein, we present the

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[*] Y. Haketa, Prof. Dr. H. Maeda
College of Pharmaceutical Sciences, Institute of Science and Engineering, Ritsumeikan University
Kusatsu 525–8577 (Japan)
Fax: (+81) 77-561-2659
E-mail: maedahir@ph.ritsumei.ac.jp

Prof. Dr. S. Sasaki, Dr. N. Ohta, Dr. H. Masunaga, Dr. H. Ogawa, Dr. N. Mizuno
Japan Synchrotron Radiation Research Institute (JASRI)
Sayo 679–5198 (Japan)

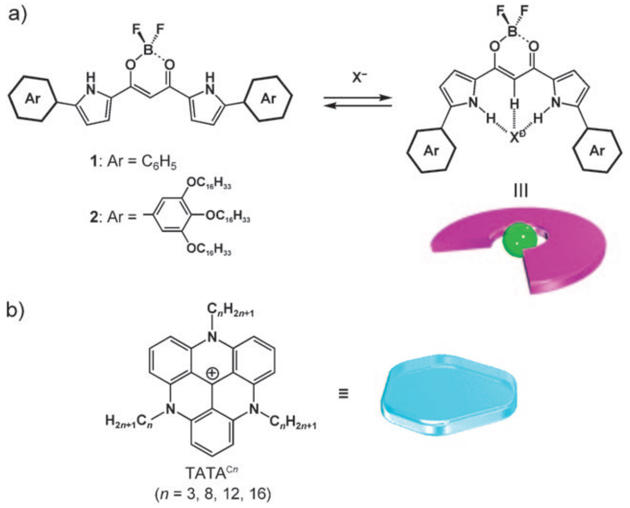
Prof. Dr. S. Sasaki
Department of Biobased Materials Science, Graduate School of Science and Technology, Kyoto Institute of Technology
Kyoto 606–8585 (Japan)

Dr. F. Araoka, Prof. Dr. H. Takezoe
Department of Organic and Polymeric Materials, Institute of Science and Engineering, Tokyo Institute of Technology
Tokyo 152–8522 (Japan)

Prof. Dr. H. Maeda
PRESTO Japan Science and Technology Agency (JST)
Kawaguchi 332–0012 (Japan)

[**] This work was supported by a Grant-in-Aid for Young Scientists (B) (No. 21750155) and for Scientific Research in a Priority Area "Super-Hierarchical Structures" (No. 19022036) from the MEXT and Ritsumeikan R-GIRO project (2008–2013). The authors thank Prof. Atsuhiro Osuka, Dr. Shohei Saito, and Eiji Tsurumaki, Kyoto University, for single-crystal X-ray analysis, Dr. Takashi Nakanishi, National Institute for Materials Science, for SEM measurements, Prof. Kazuchika Ohta and Shohei Shimosugi, Shinshu University, for preliminary examinations on charge-by-charge assemblies, Prof. Tomonori Hanasaki and Shunichi Murayama, Ritsumeikan University, for DSC measurements, SPring-8 (JASRI) for synchrotron radiation experiments at BL40B2 (No. 2009A1985, 2009B1593, 2010A1504, and 2010A1621), and Prof. Hitoshi Tamiaki, Ritsumeikan University, for various measurements. Y.H. thanks JSPS for a Research Fellowship for Young Scientists.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201006356.



Scheme 1. a) Structures and anion-binding mode of π-conjugated acyclic anion receptors **1** and **2**. b) Structure of the TATA^{Cn} cations.

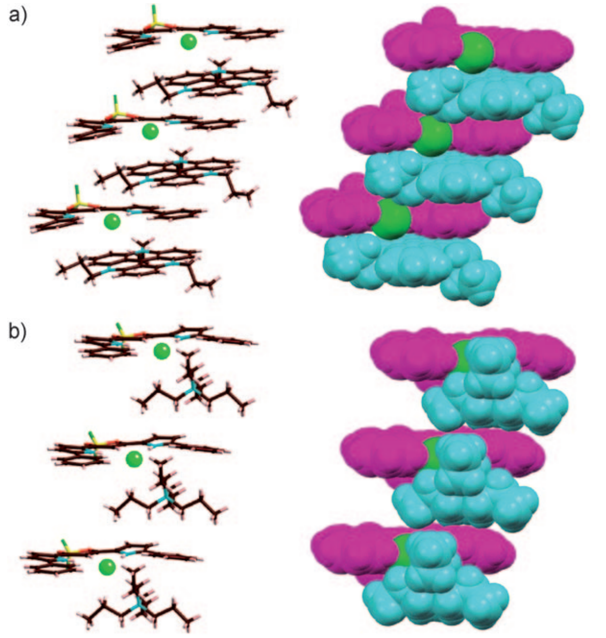


Figure 1. Solid-state stacking structures (left: stick, right: space-filling representations) of a) **1**·Cl$^-$(TATA^{C3})$^+$ and b) **1**·Cl$^-$(TPA)$^+$ (TPA = tetra-*n*-propylammonium).[8b] Atom color code for the stick representations: C brown, H pink, B yellow, F green, Cl green spheres, N blue, O red. Subunit color code for the space-filling representations: **1** magenta, cations cyan, Cl$^-$ yellow-green.

formation and properties of dimension-controlled charge-by-charge assemblies of π-conjugated receptor–anion complexes and planar cations. Compared to the stacking assemblies of electronically neutral heterotopic components,[10] a charge-by-charge assembly is an efficient strategy for gathering multiple π planes in an ordered and desired fashion for the fabrication of functional materials.

To achieve dimension-controlled charge-by-charge stacking assemblies, the introduction of planar cations instead of sterical cations was attempted. In fact, we combined the receptors with Cl$^-$, Br$^-$, and BF$_4^-$ salts of planar 4,8,12-trialkyl-4,8,12-triazatriangulenium (TATA) cations, (TATA^{Cn})Cl ($n = 3$, 8, 12, and 16), (TATA^{C3})Br, and (TATA^{C3})BF$_4$ (Scheme 1b); the core structure of these TATA cations was reported by Laursen et al.[11] Completely flat geometries of TATA cations, which are supported by single-crystal X-ray analysis of (TATA^{C3})X (X = Cl and Br)[12] and theoretical studies at the DFT level,[13] are appropriate for stacking with receptor–halide (Cl$^-$ and Br$^-$) complexes. In fact, single-crystal X-ray analysis of equivalent mixtures of **1** and (TATA^{C3})X (X = Cl and Br) exhibited alternately stacking charge-by-charge structures comprising planar receptor–anion complexes and TATA cations (Figure 1a).[12] The distance between receptor–anion complexes in, for example, **1**·Cl$^-$(TATA^{C3})$^+$ is 6.85 Å, which is 0.44 Å shorter than that of **1**·Cl$^-$(TPA)$^+$ (7.29 Å) (Figure 1b).[8b] The Cl$^-$···Cl$^-$ distance and the distance between proximal receptor–anion complex and planar cation are 7.83 and 3.49/3.49 Å, respectively. The distances between the center of a TATA cation and Cl$^-$ exhibit two unequivalent values: 4.30 and 6.42 Å. These values, which are both more than 3.5 Å, suggest that the columnar structure is not aligned perpendicularly, but is rather inclined at 60° in the crystal state. Similar results were also observed in **1**·Br$^-$(TATA^{C3})$^+$.

Among the various planar cations, the TATA structure was deemed suitable for yielding gel states based on receptor **2**. The ion pairs **2**·Cl$^-$(TATA^{Cn})$^+$ (10 mg mL^{-1} of **2** with 1 equiv of TATA salts) afforded opaque gels from **2**·Cl$^-$(TATA^{C3})$^+$ (inset of Figure 2a) and precipitates from **2**·Cl$^-$(TATA^{Cn})$^+$ ($n = 8$, 12, and 16) in octane at 20 °C after heating to over 40 °C to solution. This observation is in contrast to the observation that the addition of TBACl to an octane gel of **2** (10 mg mL^{-1}) initially affords a solution at room temperature that is followed by the formation of

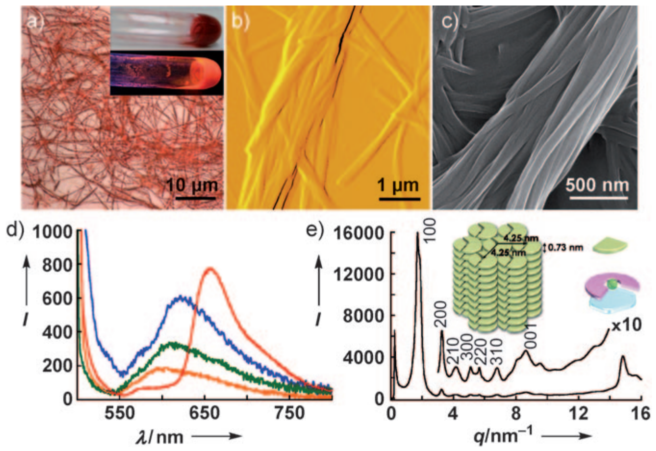


Figure 2. a–c) Surface measurements of an octane xerogel of **2**·Cl$^-$(TATA^{C3})$^+$ at 20 °C: a) optical microscope, b) AFM, and c) SEM images. Inset of (a): photographs of the gel under visible (top) and 365 nm UV light (bottom). d) Fluorescence spectra of gels and precipitates of **2**·Cl$^-$(TATA^{C3})$^+$: $n = 3$ (red), 8 (blue), 12 (green), and 16 (orange). e) XRD pattern of an octane xerogel of **2**·Cl$^-$(TATA^{C3})$^+$ at 25 °C. In-plane spacings: 4.25 nm; between layers: 0.73 nm.

precipitates after several days.[8b] The gel of **2**·Cl$^-$(TATA^{C3})$^+$ is transformed to solution at 35 °C, which is higher at about 8 °C than the gel of **2**, also suggesting that appropriate TATA salts can stabilize gels. Scanning electron microscopy (SEM), optical microscopy (OM), and atomic force microscopy (AFM) analyses showed the submicrometer-scale morphologies of the xerogels or precipitates of **2**·Cl$^-$(TATA^{Cn})$^+$: **2**·Cl$^-$(TATA^{Cn})$^+$ ($n=3$, 8, and 12) formed entangled fibril structures (Figure 2 a–c), whereas **2**·Cl$^-$(TATA^{C16})$^+$ afforded irregular-shaped structures. The diameter and length of the bundled fibers are estimated to be 0.1–2 μm and more than 100 μm, respectively, in, for example, **2**·Cl$^-$(TATA^{C3})$^+$. Receptors bearing methoxy, octyloxy, and dodecyloxy chains as well as **1** provided no gel-like materials when mixed with (TATA^{Cn})Cl ($n=3$, 8, 12, and 16). Longer alkyl chains of receptor–anion complexes help to stabilize the dimension-controlled stacking assemblies, whereas those of the TATA units provide less-ordered morphologies. Thus, the formation of fibril morphologies requires appropriate combinations of receptor–chloride complexes and cations. Furthermore, in contrast to **2**·Br$^-$(TATA^{C3})$^+$, which formed fibers similar to **2**·Cl$^-$(TATA^{C3})$^+$, a mixture of **2** and (TATA^{C3})BF$_4$ afforded TATA^{C3}BF$_4$ crystals, which were insoluble in octane, and a gel of **2** independently, as BF$_4^-$ was unable to form a planar receptor–anion complex and subsequently charge-by-charge assemblies. These results suggest that the size, shape, and polarizability of anions are also essential for constructing gelated materials comprising planar ions. Furthermore, equivalent amounts of receptors and TATA salts are required to form ordered fibril structures, as mixtures of unequivalent amounts of **2** and (TATA^{C3})Cl provide precipitates with nonspecific morphologies from excess components along with the **2**·Cl$^-$(TATA^{C3})$^+$ fibers.

Gels or precipitates of **2**·Cl$^-$(TATA^{Cn})$^+$ ($n=3$, 8, 12, and 16) without solvent removal showed absorption maxima (λ_{max}) at around 510 and 550 nm, in comparison with those of a film cast from CH$_2$Cl$_2$ solutions of receptor **2** at about 480 nm and (TATA^{Cn})Cl salts ($n=3$, 8, 12, and 16) at 547, 544, 546, and 556 nm, respectively. The absorbance ratios at these wavelengths (510 and 550 nm) depend on the alkyl chain lengths of the TATA cations: **2**·Cl$^-$(TATA^{C3})$^+$ had a λ_{max} at 554 nm along with a small shoulder at 513 nm, whereas **2**·Cl$^-$(TATA^{C16})$^+$ had a λ_{max} at 513 nm with a shoulder at 548 nm. This tendency is ascribable to the stacking area and orientation between the core π planes of the receptor–anion complexes and TATA cations as the building subunits of charge-by-charge assemblies. At present, it is not easy to definitively correlate the electronic properties of charge-by-charge assemblies with their stacking structures because of the less symmetrical geometries of receptor–anion complexes and complicated exciton coupling between heterogeneous planar chromophores. Furthermore, emissions from the gels and precipitates of **2**·Cl$^-$(TATA^{Cn})$^+$ ($n=3$, 8, 12, and 16) and **2**·Br$^-$(TATA^{C3})$^+$ ($\lambda_{ex}=497$ nm) were observed at 658, 621, 608, 593, and 672 nm, respectively (Figure 2 d). From these observations, it can be assumed that longer alkyl chains in the TATA cations might loosen the charge-by-charge stacking columns and as a result disturb the column bundling to affect their electronic and optical properties.

The structure of **2**·Cl$^-$(TATA^{C3})$^+$ fibers as a xerogel was revealed through synchrotron radiation X-ray scattering analysis. Peaks with *d* spacings of 3.68, 1.94, 1.51, 1.23, 1.11, 0.92, and 0.73 nm were indexed to (100), (200), (210), (300), (220), and (310); a reflection of (001) was assigned to a periodic stacking distance of the assembled unit of a hexagonal columnar (Col$_{hex}$) phase with $a=4.25$ nm and $c=0.73$ nm based on a trimeric assembly ($Z=3.00$ for a density $\rho=1.0$; Figure 2 e). An interaction between alkyl chains was observed at a 0.42 nm peak. The *c* value (0.73 nm) corresponds to the distance between the stacking structure of both a receptor–anion complex and a TATA cation. An intercolumnar distance of 4.25 nm is derived from a partial interpenetration of the alkyl chains of the proximal columns. The circular trimeric assemblies are also consistent with the fan-like geometry of the pyrrole-inverted receptor–anion complex. Similar to the pattern of **2**·Cl$^-$(TATA^{C3})$^+$, **2**·Br$^-$(TATA^{C3})$^+$ exhibited peaks with *d* spacings of 3.63, 1.95, 1.48, 1.24, 1.16, 0.93, and 0.74 nm, which were indexed to (100), (200), (210), (300), (220), (310), and (001), respectively, of a Col$_{hex}$ phase with $a=4.2$ nm and $c=0.74$ nm based on a trimeric assembly ($Z=2.90$ for $\rho=1.0$). In contrast, a dried sample of **2**·Cl$^-$(TATA^{C16})$^+$ exhibited peaks with *d* spacings of 5.09, 2.55, 1.70, 1.31, 1.09, 1.01, and several small peaks of around 0.8–0.7 nm indexed as (001), (002), (003), (004), (005), (006), and reflections of stacking distances of a discotic lamellar structure. The discotic lamella comprises a planar TATA cation and receptor–anion complex, wherein long alkyl chains of TATA and those of the receptor units are interdigitated, revealing an intercolumnar distance of about 5 nm. In this case, longer alkyl chains at the periphery of a TATA cation may disturb the formation and alignment of a hexagonally ordered stacking columnar structure. From these observations, we can safely conclude that the alkyl chain lengths control the geometries of stacking pairs consisting of receptor–anion complexes and TATA cations and, as a result, their macroscopic states.

Detailed properties of **2**·Cl$^-$(TATA^{C3})$^+$, which provided a more stable gel as compared to the others, were also examined in other states as soft materials. Differential scanning calorimetry (DSC) of an octane xerogel of **2**·Cl$^-$(TATA^{C3})$^+$ (5 °C min^{-1}) suggested phase transitions at 75 and 96 °C during the first heating, 88 and 42 °C during the first cooling, and 44 and 96 °C during the second heating. Polarizing optical microscopy (POM) measurements between glass substrates revealed the formation of a focal conic texture around 90 °C on cooling from the isotropic liquid (Iso) phase. Slow cooling at 2 °C min^{-1} afforded larger focal conic domains along with greater areas of dark domains (Figure 3 a) than fast cooling at 5 °C min^{-1}, suggesting that the discotic columnar structures are well-aligned perpendicularly to the substrates. Further, synchrotron radiation X-ray scattering analysis at variable temperatures suggested the phase properties and structures and was consistent with the phase transitions. The measurements at 25, 45, and 65 °C during the first heating were quite similar to that of the xerogel state (Figure 2 e), whereas at 70 °C after cooling from Iso, they showed relatively sharp peaks with *d* spacings of 4.08, 2.35, 2.04, 1.54, 1.36, 1.17, 1.13, and 0.73 nm, which were indexed to (100), (110), (200),

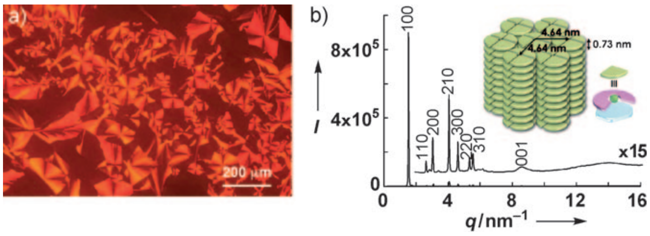


Figure 3. a) Polarizing optical microscope image of **2**$\cdot$Cl$^-$(TATA^{C3})$^+$ at 87 °C by cooling at 2 °C min^{-1} from the isotropic liquid phase (Iso). b) XRD pattern of **2**$\cdot$Cl$^-$(TATA^{C3})$^+$ in the mesophase at 70 °C after cooling from Iso and the proposed assembling model (inset). In-plane spacings: 4.64 nm; between layers: 0.73 nm.

(210), (300), (220), (310), and (001), respectively, of a Col$_{hex}$ phase with $a = 4.64$ nm and $c = 0.73$ nm based on a tetrameric assembly ($Z = 3.58$ for $\rho = 1.0$; Figure 3 b).[14] The style of the molecular assembly in the mesophase is basically identical to that in the xerogel. However, as observed in the differences in peak widths, the organized structure in the mesophase, which shows sharp pattern, is more ordered owing to annealing than those in the xerogels.[15] The intercolumnar distance of 4.64 nm is larger than that of the xerogel (4.25 Å), which is ascribable to the well-aligned columnar structures and moderate interpenetration of alkyl chains. Analysis at 110 °C exhibited only a halo peak, suggesting an isotropic state. Furthermore, the shear-driven alignment of the organized structure, which was prepared by shearing around 90 °C and cooling to room temperature, also suggests the formation of liquid crystal in the mesophase. A diffraction peak corresponding to the interdisc order appeared dominantly along the sheared direction, whereas those corresponding to the intercolumn order appeared strongly along the direction perpendicular to the sheared direction.[16] As no significant decompositions of building components appeared after repeated transitions between the mesophase and the isotropic liquid states, it is worth noting the potential stability of these charge-by-charge assemblies.

In summary, we proposed and demonstrated a charge-by-charge assembly as a new concept and strategy for fabricating stacking structures comprising organic ionic species. Receptor–anion complexes as negatively charged planar components readily assemble with planar cations through electrostatic and π–π interactions. Columnar assemblies based on these charge-by-charge stacking structures were found to form supramolecular organogels consisting of submicrometer-scale fibers. Moreover, the materials exhibited a liquid crystal columnar phase, showing a property to readily form oriented structures owing to the existence of the charge-by-charge columns. Various commercially available or synthesized planar cations[4g,17] may also be fabricated into ordered structures on the basis of a charge-by-charge assembly. The creation of a library of charge-by-charge assemblies, covering various combinations of planar ionic species, would provide promising functional soft materials as oriented salts for future application.

Received: October 10, 2010

Keywords: gels · host–guest systems · ion pairs · nanostructures · supramolecular chemistry

[1] K. Sada, T. Tani, S. Shinkai, *Synlett* **2006**, 2364–2374.

[2] Selected reviews on ionic liquids: a) T. Welton, *Chem. Rev.* **1999**, *99*, 2071–2084; b) P. Wasserscheid, W. Keim, *Angew. Chem.* **2000**, *112*, 3926–3945; *Angew. Chem. Int. Ed.* **2000**, *39*, 3772–3789; c) H. Ohno, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1665–1680.

[3] K. Binnemans, *Chem. Rev.* **2005**, *105*, 4148–4204.

[4] Selected examples of ionic liquid crystals can be found in a) M. Yoshio, T. Kagata, K. Hoshino, T. Mukai, H. Ohno, T. Kato, *J. Am. Chem. Soc.* **2006**, *128*, 5570–5577; b) P. H. J. Kouwer, T. M. Swager, *J. Am. Chem. Soc.* **2007**, *129*, 14042–14052; c) T. Ichikawa, M. Yoshio, T. Mukai, H. Ohno, T. Kato, *J. Am. Chem. Soc.* **2007**, *129*, 10662–10663; d) K. Tanabe, T. Yasuda, M. Yoshio, T. Kato, *Org. Lett.* **2007**, *9*, 4271–4274; e) H. Shimura, M. Yoshio, K. Hoshino, T. Mukai, H. Ohno, T. Kato, *J. Am. Chem. Soc.* **2008**, *130*, 1759–1765; f) M. Wathier, M.-W. Grinstaff, *J. Am. Chem. Soc.* **2008**, *130*, 9648–9649; g) D. Wu, W. Pisula, V. Enkelmann, X. Feng, K. Müllen, *J. Am. Chem. Soc.* **2009**, *131*, 9620–9621; h) Md.-A. Alam, J. Motoyanagi, Y. Yamamoto, T. Fukushima, J. Kim, K. Kato, M. Takata, A. Saeki, S. Seki, S. Tagawa, T. Aida, *J. Am. Chem. Soc.* **2009**, *131*, 17722–17723.

[5] Selected reviews of π-plane-based assemblies: a) A. P. H. J. Schenning, E. W. Meijer, *Chem. Commun.* **2005**, 3245–3258; b) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning, *Chem. Rev.* **2005**, *105*, 1491–1546; c) T. Kato, N. Mizoshita, K. Kishimoto, *Angew. Chem.* **2006**, *118*, 44–74; *Angew. Chem. Int. Ed.* **2006**, *45*, 38–68; d) J. Wu, W. Pisula, K. Müllen, *Chem. Rev.* **2007**, *107*, 718–747; e) A. Ajayaghosh, V. K. Praveen, *Acc. Chem. Res.* **2007**, *40*, 644–656; f) A. R. A. Palmans, E. W. Meijer, *Angew. Chem.* **2007**, *119*, 9106–9126; *Angew. Chem. Int. Ed.* **2007**, *46*, 8948–8968; g) T. Kato, T. Yasuda, Y. Kamikawa, M. Yoshio, *Chem. Commun.* **2009**, 729–739; h) C. C. Lee, C. Grenier, E. W. Meijer, A. P. H. J. Schenning, *Chem. Soc. Rev.* **2009**, *38*, 671–683.

[6] Selected books on anion binding: a) *Supramolecular Chemistry of Anions* (Eds.: A. Bianchi, K. Bowman-James, E. García-España), Wiley-VCH, New York, **1997**; b) *Fundamentals and Applications of Anion Separations* (Eds.: R. P. Singh, B. A. Moyer), Kluwer Academic/Plenum Publishers, New York, **2004**; c) *Anion Sensing, Topics in Current Chemistry, Vol. 255* (Ed.: I. Stibor), Springer, Berlin, **2005**, p. 238; d) J. L. Sessler, P. A. Gale, W.-S. Cho, *Anion Receptor Chemistry*, RSC, Cambridge, **2006**; e) *Recognition of Anions, Structure and Bonding* (Ed.: R. Vilar), Springer, Berlin, **2008**.

[7] a) H. Maeda in *Handbook of Porphyrin Science, Vol. 8* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), World Scientific, New Jersey, **2010**, chap. 38; b) H. Maeda in *Anion Complexation in Supramolecular Chemistry, Topics in Heterocyclic Chemistry, Vol. 24* (Eds.: P. A. Gale, W. Dehaen), Springer, Berlin, **2010**, pp. 103–144.

[8] a) H. Maeda, Y. Kusunose, *Chem. Eur. J.* **2005**, *11*, 5661–5666; b) H. Maeda, Y. Haketa, T. Nakanishi, *J. Am. Chem. Soc.* **2007**, *129*, 13661–13674; c) H. Maeda, Y. Bando, Y. Haketa, Y. Honsho, S. Seki, H. Nakajima, N. Tohnai, *Chem. Eur. J.* **2010**, *16*, 10994–11002; d) Y. Haketa, H. Maeda, *Chem. Eur. J.* **2010**, DOI: 10.1002/chem.201002748.

[9] a) H. Maeda, *Chem. Eur. J.* **2008**, *14*, 11274–11282; b) G. O. Lloyd, J. W. Steed, *Nat. Chem.* **2009**, *1*, 437–442; c) M.-O. M. Piepenbrock, G. O. Lloyd, N. Clarke, J. W. Steed, *Chem. Rev.* **2010**, *110*, 1960–2004.

[10] For pyrrole-based systems see: a) R. Custelcean, L. H. Delmau, B. A. Moyer, J. L. Sessler, W. S. Cho, D. Gross, G. W. Bates, S. J. Brooks, M. E. Light, P. A. Gale, *Angew. Chem.* **2005**, *117*, 2593–

2598; *Angew. Chem. Int. Ed.* **2005**, *44*, 2537–2542; b) M. Stępień, B. Donnio, J. L. Sessler, *Angew. Chem.* **2007**, *119*, 1453–1457; *Angew. Chem. Int. Ed.* **2007**, *46*, 1431–1435.

[11] a) B. W. Laursen, F. C. Krebs, *Angew. Chem.* **2000**, *112*, 3574–3576; *Angew. Chem. Int. Ed.* **2000**, *39*, 3432–3434; b) B. W. Laursen, F. C. Krebs, *Chem. Eur. J.* **2001**, *7*, 1773–1783.

[12] Crystallographic data are summarized in the Supporting Information.

[13] *Gaussian 03* (Revision C.01), M. J. Frisch, et al., Gaussian, Inc., Wallingford CT, **2004**.

[14] Packing structure of a metastable mesophase at 88–94 °C, which was observed by DSC during only cooling process, could not be identified in detail, whereas that of the solid state obtained below ca. 40 °C was found to be almost identical structure to the stable mesophase.

[15] a) Some unidentified diffractions in the xerogel and precipitates are due to their fairly disordered structures; b) A similar $\mathrm{Col_{hex}}$ phase was preliminarily observed in the XRD of mesophase of **2**$\cdot\mathrm{Br^-}$-$(\mathrm{TATA^{C3}})^+$.

[16] An optical response in POM images was preliminarily observed upon application of an electric field. When the sample was maintained in an alternating rectangular field (50 Vpp, 2 Hz), the initial fan texture in only the region sandwiched between the transparent electrodes with oriented polyimide films gradually turned into a dark state with less light scattering in optical isotropy. The existence of material in the dark region was confirmed by an observation made after removing the analyzer. These facts imply that charged stacks are highly polarized by the field and respond to form a homeotropic alignment. It is also noteworthy that this optical isotropy retained itself even after terminating the field application. Details on the formation of macroscopic polar order will be reported in the near future.

[17] For example see: a) B. W. Laursen, F. C. Krebs, M. F. Nielsen, K. Bechgaard, J. B. Christensen, N. Harrit, *J. Am. Chem. Soc.* **1998**, *120*, 12255–12263; b) S. Lovell, B. J. Marquardt, B. Kahr, *J. Chem. Soc. Perkin Trans. 2* **1999**, 2241–2247.