

Anisotropic ionic conductivities in lyotropic supramolecular liquid crystals†

Youju Huang,^a Yuanhua Cong,^a Junjun Li,^a Daoliang Wang,^a Jingtuo Zhang,^a Lu Xu,^a Weili Li,^a Liangbin Li,^{*a} Guoqiang Pan^a and Chuanlu Yang^{*b}

Received (in Cambridge, UK) 24th June 2009, Accepted 22nd October 2009

First published as an Advance Article on the web 10th November 2009

DOI: 10.1039/b912472a

The designed aromatic amide discotic molecule with sulfonic acid groups at its periphery exhibits a hexagonal supramolecular columnar liquid crystalline phase, which leads to the achievement of anisotropic ionic conductivity through macroscopically aligning the ionic channels.

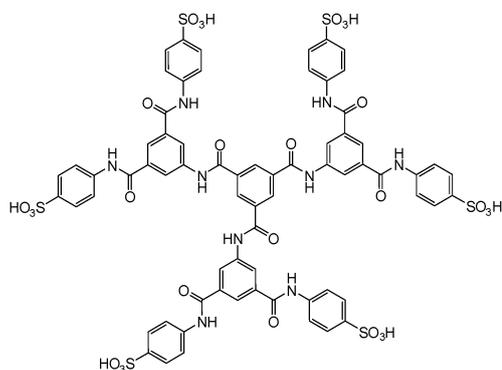
Ion transport through nanochannels or microchannels plays an important role in cell membranes, biosensor/actuator, molecular switches, biomedical materials, and energy materials (proton and Li⁺ transport materials).^{1–7} Intense efforts have been devoted to designing artificial ion channels in the past decades. Combining the intrinsic molecular functions and the anisotropic nature, supramolecular liquid crystals with exquisite control over molecular structure are promising candidates for preparing ordered ionic channels from the molecular to macroscopic scale.^{8–12} For example, a columnar liquid crystal self-organized by discotic molecules through strong π – π stacking interactions is essentially a one-dimensional electron conductor, while supramolecular liquid crystals with dissociable ions are one or two dimensional ionic conductors.^{13–16} The combination of fluidic properties and orientation order of liquid crystals allows easy achievement of macroscopic alignment of these conductive nanochannels. Due to the targeting of technological application in the bulk state, most reports focus on thermotropic rather than lyotropic liquid crystals, though the latter share equal importance.^{17–25} Indeed designing supramolecular lyotropic liquid crystals can be a promising approach to create macroscopically parallel proton nanochannels with superior ionic conductivity like Nafion,^{26,27} whose outstanding performance stems from its parallel cylindrical water nanochannels.

Herein we report a new organic discotic molecule (Scheme 1) consisting of 10 phenyl rings joined symmetrically with amide linkages based upon 1,3,5-benzenetricarbonyl trichloride by a convergent synthetic approach, which is functionalized at the periphery with sulfonic acid groups (synthesis and characterization of the discotic molecule are

shown in Part 1 of the ESI†). The discotic molecule exhibits a hexagonal supramolecular columnar liquid crystalline phase in the aqueous solution with a wide range of concentrations from 0.086 g mL⁻¹ to 0.28 g mL⁻¹ at room temperature.

The textures of the supramolecular liquid crystals were microfibrils as observed by Polarized Light Microscopy (POM) (see S-Fig. 2 in the ESI†). The microfibrils are randomly cured without imposing any flow field (Fig. 1a), but they are extremely easy to be aligned by flow (Fig. 1b). Synchrotron-based small and wide angle X-ray scattering (SAXS/WAXS) data provide essential evidence for the hexagonal columnar phase. Neither birefringence from POM nor a SAXS/WAXS signal was observed from the discotic molecule solution with low concentration (lower than 0.086 g mL⁻¹). When the concentration is higher than 0.28 g mL⁻¹, some discotic molecules precipitate and form a heterogeneous mixture of the hexagonal liquid crystalline phase and crystals of the discotic molecule.

Fig. 2A and B show a representative SAXS/WAXS pattern with q as the x -axis from a sample with a concentration of 0.206 g mL⁻¹. Here $q = 4\pi\sin\theta/\lambda$ is the module of the scattering vector; λ and 2θ are the X-ray wavelength and scattering angle, respectively. The major sharp scattering peaks are located in the low q value region with a ratio of $1:3^{1/2}:2:7^{1/2}:13^{1/2}$. In the wide angle region, a single peak with a large width is observed at a q value of 18.08 nm⁻¹, which is orthogonal to the scattering peaks in the low q region in the two-dimensional scattering pattern of the oriented sample (S-Fig. 3, see ESI†). Thus we can conclude that the structure is a lyotropic columnar liquid-crystalline phase with hexagonal symmetry. The columns have a layered structure with an average spacing of about 0.35 nm. Upon decreasing the concentration of discotic molecules, the liquid crystals



Scheme 1 The chemical structure of the discotic molecule.

^a National Synchrotron Radiation Lab and CAS Key Laboratory of Soft Matter Chemistry, University of Science and Technology of China, Hefei, China. E-mail: lbli@ustc.edu.cn; Fax: 0086-551-5141078; Tel: 0086-551-3602081

^b Department of Physics and Electronics, Ludong University, Yantai, China. E-mail: yangchuanlu@263.net

† Electronic supplementary information (ESI) available: Materials, measurements, synthesis of the discotic molecule, SAXS/WAXS pattern, polarized optical photomicrographs of the discotic molecule with different concentrations in water, computational details and the measurement of ionic conductivities. See DOI: 10.1039/b912472a

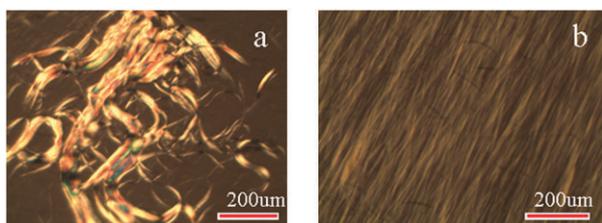


Fig. 1 Polarized optical micrographs of the discotic molecule with a concentration of 0.206 g mL^{-1} (a) randomly cured microfibers and (b) aligned microfibers by flow field.

keep their hexagonal symmetry with an increase in the d spacing calculated from the (100) peak position (see Fig. 2C and D), which covers a range from 9.04 nm to 10.29 nm, corresponding to a concentration range from 0.28 g mL^{-1} to 0.086 g mL^{-1} . Two striking features were observed on the discotic columnar liquid crystals: (i) The spacing of the (100) plane is several times larger than the diameter of the discotic molecule; (ii) The spacing of the (100) plane keeps relatively constant in two concentration regions.

The diameter of the discotic molecule is close to 3 nm (S-Fig. 4a, see ESI[†]), while the intercolumnar distance in the hexagonal supramolecular liquid crystalline phase covers a range from 10.44 nm to 11.88 nm. Evidently the cross section or the layer of the columns is constructed with multiple molecules instead of a single discotic molecule. It is normal for multiple fan-shaped molecules to form one disc, which stacks into columns and further organizes into a liquid crystalline phase. However disc-shaped molecules generally form single molecular stacks. As far as the authors are aware no exceptions have been reported because disc-shaped molecules possess the right symmetry to stack into columns directly. According to the earlier proposed theory^{28,29} of phase equilibrium in the solution of associating polyelectrolyte and charged colloid particles, it is possible for the charged discotic

molecules to form thermodynamically stable clusters with finite size in the solution due to the interplay between the attraction energy among discotic molecules and the Coulomb interaction together with the contribution from the translational entropy of counter ions. The clusters formed by the multiple discotic molecules stack into columns of the hexagonal liquid crystalline phase (S-Fig. 4c and d, see ESI[†]). Based on the layer spacing of 0.35 nm from WAXS data, which is close to the π - π stacking distance, the main driving force for the formation of columnar structures can be π - π interactions between the phenyl rings. This is reasonable as hydrogen bonds can form between water and the amide groups (see Part 5 and S-Fig. 8 of the ESI[†]).

The formation of proton channels in the hexagonal liquid crystalline phase is supported by experimental data (the X-ray data and ionic conductivity) and computer simulation. The SAXS/WAXS data show that the diameter of the columns in the hexagonal liquid crystals is about three times that of the discotic molecule, where each layer of the column contains multiple molecules instead of one. Combining the symmetry of sulfonic acid groups at the periphery of the discotic molecule, it is easy to construct a molecular picture that the sulfonic acid groups in the columns tend to self-organize into two regions. One is at the outer surface of the column, while another locates inside the column. Computer simulation shows that each layer of the column is composed of 7 discotic molecules, which leads us to propose a two-coaxial-proton-nanochannel model. The inner nanochannel is circumambient at the periphery of the interior discotic molecule, while the outer one surrounds the columns of the hexagonal supramolecular liquid crystalline phase (see Part 2 and S-Fig. 4b, c and d, of the ESI[†]). As the outer channels are connected with each other, they are an open ionic channel. Thanks to the novel layer structure of the column with 7 discotic molecules, the inner channels were isolated by the phenyl rings, which are relatively closed ionic nanochannels. This novel structure is expected to have anisotropic ionic conductivity after macroscopic alignment.

The anisotropic ionic conductivities with different concentrations of the discotic molecule are confirmed by the measurements on the samples with macroscopically oriented ionic nanochannels, which are obtained by imposing a simple shear. Illustrations of cells for the measurements of ionic conductivity and the orientation of liquid crystals checked by the POM are shown in S-Fig. 6 of the ESI[†]. The experimental details are provided in S-Fig. 7 and Part 3 of the ESI[†]. Fig. 3 illustrates the anisotropic ionic conductivities of the columnar liquid crystalline phase as a function of concentration. The ionic conductivities in the direction parallel to the columnar axis (σ_{\parallel}) are significantly higher than those in the direction perpendicular to the columnar axis (σ_{\perp}), while the un-aligned samples have ionic conductivities that lie between them. For example, the discotic molecule solution exhibits conductivities of $8.5 \times 10^{-3} \text{ S cm}^{-1}$ and $1.46 \times 10^{-3} \text{ S cm}^{-1}$ in parallel and perpendicular directions, respectively, which lead to a ratio $\sigma_{\parallel}/\sigma_{\perp}$ of 5.8 at a concentration of 0.19 g mL^{-1} . At low concentration where no liquid crystal phase forms, no anisotropic ionic conductivity is observed on the sheared samples, whose ionic conductivity drops sharply. The anisotropic ionic conductivities of the

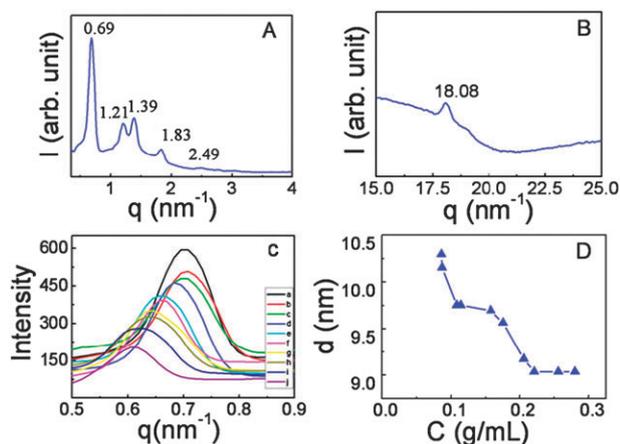


Fig. 2 SAXS (A) and WAXS (B) patterns of the discotic molecule solution with a concentration of 0.206 g mL^{-1} . (C) The first peak of the SAXS/WAXS pattern of the discotic molecule with different concentrations in water: (a) 0.280 g mL^{-1} ; (b) 0.256 g mL^{-1} ; (c) 0.221 g mL^{-1} ; (d) 0.206 g mL^{-1} ; (e) 0.176 g mL^{-1} ; (f) 0.158 g mL^{-1} ; (g) 0.114 g mL^{-1} ; (h) 0.108 g mL^{-1} ; (i) 0.087 g mL^{-1} ; (j) 0.086 g mL^{-1} . (D) The plot of d spacing of the (100) peak of the SAXS pattern vs. concentration.

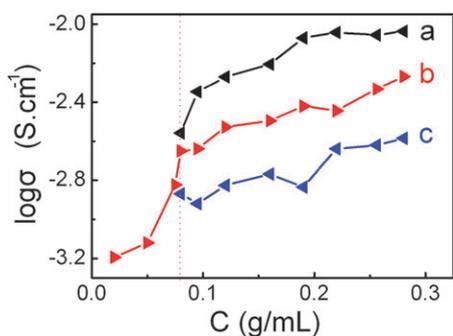


Fig. 3 Ionic conductivities of the liquid crystal phase (to the right of the dashed line) with different discotic molecular concentration. (a) Parallel and (c) perpendicular to the axis of the column, (b) un-aligned sample.

aligned columnar liquid crystals further confirm the existence of the ionic nanochannels.

Another unexpected structural finding is that the d spacing keeps relatively constant in two sub-ranges of concentrations, which indicates a nonlinear correlation between the concentration and the d spacing. This can not be explained with the mean-field approaches of Debye–Hückel or Poisson–Boltzmann theory,³⁰ though it can account for the increase in d spacing with the decrease in concentration. Clearly an attraction force should exist in the system, which prevents the d spacing from continuously decreasing. Attraction between like-charged rods has been observed in a variety of systems especially in biological materials like actins. In the past 30 years, a great effort has been dedicated to interpret this phenomenon and different models are proposed, which, however, do not reach a full agreement yet.^{31,32} The basic idea of like-charged rods may explain our observation (see Part 4 and S-Fig. 8 of the ESI†). Nevertheless, as the discotic molecules in the water contain nearly all secondary interactions such as hydrogen bonding, π – π interactions, hydrophobic and hydrophilic, electrostatic and van de Waals forces, a quantitative interpretation on this phenomenon is still a challenge.

In conclusion, we have designed and synthesized a new organic discotic molecule consisting of 10 phenyl rings joined symmetrically with sulfonic acid groups at the periphery, which exhibits a hexagonal supramolecular columnar liquid crystalline phase in aqueous solution. Unexpectedly the diameter of the columns in the hexagonal liquid crystals is about three times that of the discotic molecule. The spacing of the hexagonal phase keeps relatively constant in two sub-concentration ranges. The combination of ionic channels and liquid crystalline properties leads to the achievement of anisotropic ionic conductivity through macroscopic alignment of the ionic nanochannels.

LB Li would like to thank Prof. Wim de Jeu (AMOLF) and Prof. Stephen. J. Picken (Delft) for their great help in building the soft matter group in Hefei. This work is supported by the

NNSFC (20774091), Fund for one hundred talent scientist, the ‘NCET’ program, 973 program from MOST and the experimental fund of NSRL.

Notes and references

- F. I. Valiyaveetil, M. Leonetti, T. W. Muir and R. MacKinnon, *Science*, 2006, **314**, 1004–1007.
- S. Liu, Q. Pu, L. Gao, C. Korzeniewski and C. Matzke, *Nano Lett.*, 2005, **5**, 1389–1393.
- Q. Pu, J. Yun, H. Temkin and S. Liu, *Nano Lett.*, 2004, **4**, 1099–1103.
- L. Husaru, R. Schulze, G. Steiner, T. Wolff, W. D. Habicher and R. Salzer, *Anal. Bioanal. Chem.*, 2005, **382**, 1882–1888.
- M. Yoshio, T. Mukai, H. Ohno and T. Kato, *J. Am. Chem. Soc.*, 2004, **126**, 994–995.
- M. A. Hickner, H. Ghassemi, Y. S. Kim, B. R. Einsla and J. E. McGrath, *Chem. Rev.*, 2004, **104**, 4587–4612.
- T. Kato, T. Yasuda, Y. Kamikawa and M. Yoshio, *Chem. Commun.*, 2009, 729–739.
- L. Brunsveld, B. J. B. Folmer, E. W. Meijer and R. P. Sijbesma, *Chem. Rev.*, 2001, **101**, 4071–4098.
- T. M. Fyles, *Chem. Soc. Rev.*, 2007, **36**, 335–347.
- D. Pijper, M. G. M. Jongejan, A. Meetsma and B. L. Feringa, *J. Am. Chem. Soc.*, 2008, **130**, 4541–4552.
- D. A. Tomalia, *Nat. Mater.*, 2003, **2**, 711–712.
- J. Ruokolainen, R. Mäkinen, M. Torkkeli, T. Mäkelä, R. Serimaa, G. ten Brinke and O. Ikkala, *Science*, 1998, **280**, 557–560.
- B. Chen, X. B. Zeng, U. Baumeister, S. Diele, G. Ungar and C. Tschierske, *Angew. Chem., Int. Ed.*, 2004, **43**, 4621–4625.
- R. Mezzenga, J. Ruokolainen, N. Canilho, E. Kasëmi, D. A. Schlüter, W. B. Lee and G. H. Fredrickson, *Soft Matter*, 2009, **5**, 92–97.
- M. Suárez, J. M. Lehn, S. C. Zimmerman, A. Skoulios and B. Heinrich, *J. Am. Chem. Soc.*, 1998, **120**, 9526–9532.
- G. Kestemont, V. de Halleux, M. Lehmann, D. A. Ivanov, M. Watson and Y. H. Geerts, *Chem. Commun.*, 2001, 2074–2075.
- C. T. Imrie, Z. Lu, S. J. Picken and Z. Yildirim, *Chem. Commun.*, 2007, 1245–1247.
- S. Viale, A. S. Best, E. Mendes and S. J. Picken, *Chem. Commun.*, 2005, 1528–1530.
- J. Wu, M. Baumgarten, M. G. Debije, J. M. Warman and K. Müllen, *Angew. Chem., Int. Ed.*, 2004, **43**, 5331–5335.
- H. Shimura, M. Yoshio, K. Hoshino, T. Mukai, H. Ohno and T. Kato, *J. Am. Chem. Soc.*, 2008, **130**, 1759–1765.
- J. O. Rädler, I. Koltover, T. Salditt and C. R. Safinya, *Science*, 1997, **275**, 810–814.
- K. R. Purdy, J. R. Bartles and G. C. L. Wong, *Phys. Rev. Lett.*, 2007, **98**, 058105.
- G. C. L. Wong, J. X. Tang, A. Lin, Y. Li, P. A. Janmey and C. R. Safinya, *Science*, 2000, **288**, 2035–2039.
- G. C. L. Wong, A. Lin, J. X. Tang, Y. Li, P. A. Janmey and C. R. Safinya, *Phys. Rev. Lett.*, 2003, **91**, 018103.
- T. Kato, N. Mizoshita and K. Kishimoto, *Angew. Chem., Int. Ed.*, 2006, **45**, 38–68.
- S. Schmidt-Rohr and Q. Chen, *Nat. Mater.*, 2008, **7**, 75–83.
- B. Yameen, A. Kaltbeitzel, A. Langner, H. Duran, F. Müller, U. Gösele, O. Azzaroni and W. Knoll, *J. Am. Chem. Soc.*, 2008, **130**, 13140–13144.
- I. I. Potemkin, V. V. Vasilevskaya and A. R. Khokhlov, *J. Chem. Phys.*, 1999, **111**, 2809–2817.
- J. Groenewold and W. K. Kegel, *J. Phys. Chem. B*, 2001, **105**, 11702–11709.
- N. G. Jensen, R. J. Mashl, R. F. Bruinsma and W. M. Gelbart, *Phys. Rev. Lett.*, 1997, **78**, 2477.
- A. A. Kornyshev, D. J. Lee, S. Leikin and A. Wynveen, *Rev. Mod. Phys.*, 2007, **79**, 943.
- R. Golestanian, M. Kardar and T. B. Liverpool, *Phys. Rev. Lett.*, 1999, **82**, 4456.