Five-fold symmetric penta-substituted corannulene with gelation properties and a liquid-crystalline phase†

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Five-fold symmetric substituted corannulene derivatives that display liquid-crystalline behavior and organogelation properties were prepared by coupling of *N*-azidoethyl long-chain fatty acid amides to *sym*-pentabutynyl corannulenes *via* dipolar cycloaddition chemistry.

Corannulene (**1**) is a bowl-shaped aromatic system that displays physical properties differing from those of planar π-conjugated analogs.[1,2] Its conical symmetry dictates different electron densities on its concave and convex π-faces, the magnitude of which leads to a dipole moment of roughly 5 D;[3] therefore, a material comprising derivatives of **1** ordered in a columnar manner might orient in an electric field and show ferroelectric properties.[4] So far, columnar order of corannulenes has been observed in the solid state for few corannulene derivatives[5] and in the liquid-crystalline mesophase for deca-substituted corannulenes.[6] The recent kilogram scale synthesis of corannulene[7] and the development of a facile procedure for the preparation of several C_5-symmetric penta-substituted corannulenes[8] opened the road to synthesize a family of lipid–corannulene conjugates and to screen their physical and chemical properties.

Three *sym*-pentakislipido-corannulene[9] derivatives (**2**, **3** and **4**) are the focus of this study. Chlorination of **1** leads to the *sym*-pentachlorocorannulene (**5**),[10] which represents the key synthetic intermediate en route to C_5-symmetric substituted corannulenes (Scheme 1).[11] Iron-catalyzed five-fold coupling of the homopropargyl magnesium agent X with **5** followed by base
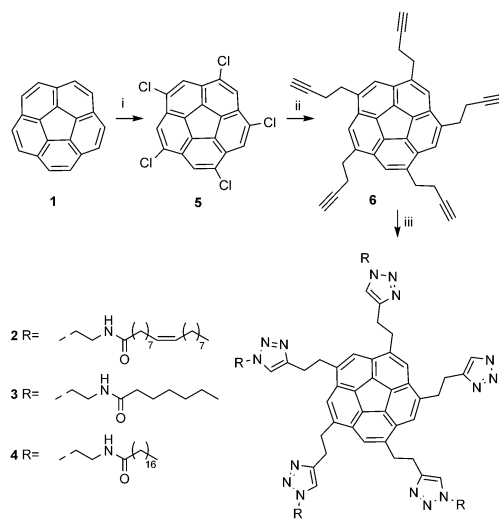
Scheme 1 *Reaction conditions*: (i) ICl, DCM, from −75 °C to r.t., 82 h. (ii) 1. 1-Trimethylsilyl-4-butynyl magnesium bromide, Fe(acac)₃, THF/NMP, r.t., 2.5 h. 2. NaOH, MeOH/THF/H₂O, r.t., 24 h. (iii) RN₃, Cu nanoparticles, DMF, microwave, 60 °C, 2 h.

mediated removal of the terminal TMS groups yields **6**. The desired conjugates, **2**–**4**, are then obtained in high yield and purity by CuAAC activated dipolar cycloaddition between **6** and the respective alkyl azide.[12]

The phase behavior of **2**, **3** and **4** was initially studied by differential scanning calorimetry (DSC) and polarized optical microscopy (POM) (Fig. S1, ESI†). For **2** thermal signatures characteristic of phase transitions were observed at 132 °C and at 99 °C in the DSC cooling scan, and the birefringence texture in the POM images was consistent with the presence of a liquid-crystalline phase. For **3** neither thermal signatures characteristic of phase transition in the DSC scan nor birefringence in the POM images were observed. For **4** DSC cooling scans revealed transitions at 80 °C and 30 °C and again, birefringence of the liquid phases indicated the presence of a liquid-crystalline phase, however only beyond the melting at 30 °C.

Small- and wide-angle X-ray scattering experiments (SAXS and WAXS) were performed in order to obtain more information

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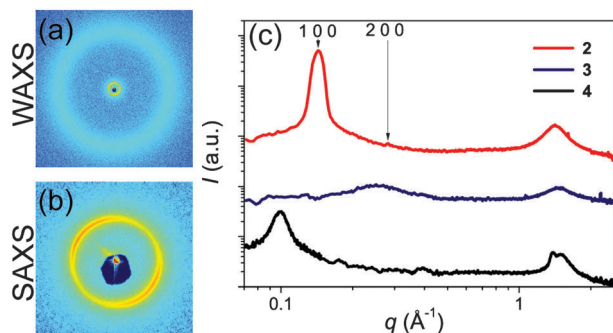
Fig. 1 (a) 2D wide and (b) small angle X-ray scattering (WAXS, SAXS) patterns of **2** and (c) the 1D scattering intensity distribution of **2**, **3** and **4** after annealing.

about the supramolecular organization of **2** at room temperature (Fig. 1). In the wide-angle region, an isotropic halo indicates the liquid-like behavior of the component without a specific π-interaction peak (Fig. 1a). In the small angle region, the appearance of a strong reflection followed by a weak second order reflection at $q_2 : q_1 = 2 : 1$ suggests a lamellar phase (Fig. 1b). The azimuthally integrated X-ray scattered intensity shows the Bragg reflection of lamellae with a layer-to-layer distance of 4.4 nm after sample annealing (Fig. 1c). Transmission electron microscopy (TEM) images of **2** were acquired to visualize the lamellar structure (Fig. 2a) and a very long-range ordered lamellar phase was observed, with a *d*-spacing of 4.1–4.3 nm measured after Fourier transformation, in good agreement with the X-ray analysis.

The gelation properties of **2** in organic solvent, IPA–water and ethanol–water mixtures were screened in order to study its propensity for molecular aggregation.[13,14] In cyclohexane (1 w/w%) and methylcyclohexane (2 w/w%), **2** forms gels with fully thermoreversible behavior upon cooling after being heated to 60 °C. Analysis by POM and SWAXS of the gel in cyclohexane did not show any birefringent phase or ordered structure.

To get further information about the orientation of corannulene cores with respect to each other UV-vis and emission spectroscopies[14] were performed (Fig. S2 and S3, ESI†). Quenching of

the fluorescence was found with increasing concentration of **2**. However, the absorption spectra do not show any hypsochromic or bathochromic shift, which augurs poorly for the existence of π-stacked structures in the gel as well as *H*- and *J*-aggregates.

To study the influence of hydrogen bonding on the formation of the gel, IR spectra were measured as a function of concentration of **2** in cyclohexane.[13] Upon increasing concentration of **2** and gelation, neither of the amide bands (C=O, N–H) were shifted (Table S4, ESI†). Thus, no evidence for the formation of hydrogen bonds in the gelation process was found. These findings for **2** suggest a molecular model in which the microphase separation of the corannulene core and the symmetric substituents drive the molecule into a lamellar structure with partially interdigitated alkyl chains (Fig. 2b) and reduced symmetry compared to the molecule itself. In the presence of solvent, the microstructure of **2** is lost in the gel.

SAXS and WAXS studies on **3**, bearing a short saturated tail, reveal only a diffuse peak, indicative of a correlation hole at 2.5 nm and corresponding to chemical heterogeneities on the scale of the molecule.[15] Furthermore, **3** does not show any gelation behavior and is solely observed as an isotropic liquid.

The SAXS and WAXS studies on **4**, the direct saturated analog of **2**, reveal the presence of a partially crystallized phase at room temperature (Fig. 1c). In cyclohexane (1 w/w%) **4** forms gels with fully thermoreversible behavior upon cooling after being heated to 60 °C. Similar to compound **2**, FTIR, UV-vis and emission spectra of gels of **4** in cyclohexane suggest the absence of any ordered supramolecular organization or H-bonding network in the gel phase.[13]

In summary, these results show that the nature of the hydrocarbon chains influences the phase behavior and the gelation properties of C_5-symmetric pentakislipido-corannulene derivatives. Specifically, **2**, functionalized with oleyl chains, forms gels in cyclohexane and, as a neat substance, exhibits a room temperature liquid-crystalline phase, with lamellar order and a 4.4 nm layer-to-layer spacing. In contrast, **3**, with short saturated chains showed no appreciable LC or gelation properties, and **4** appears in a partially crystallized phase and forms gel only in cyclohexane. The promising results for **2** and the versatility of the synthetic strategy provoke one to consider a wide library of molecularly engineered *sym*-penta-substituted corannulenes suitable for numerous materials applications.

Notes and references

1 For review, see: Y.-T. Wu and J. S. Siegel, *Chem. Rev.*, 2006, **106**, 4843.
2 T. J. Sieders, K. K. Baldridge, G. H. Grube and J. S. Siegel, *J. Am. Chem. Soc.*, 2001, **123**, 517.
3 K. K. Baldridge and J. S. Siegel, *Theor. Chem. Acc.*, 1997, **97**, 67.
4 L. M. Blinov, *Liq. Cryst.*, 1998, **24**, 143; J. L. Atwood, L. J. Barbour, M. J. Hardie and C. Raston, *Coord. Chem. Rev.*, 2001, **222**, 3; B. Xu and T. M. Swager, *J. Am. Chem. Soc.*, 1993, **115**, 1159; D. Mizajima, F. Araoka, H. Takezoe, J. Kim, K. Kato, M. Takata and T. Aida, *Science*, 2012, **336**, 209.
5 Y.-T. Wu, T. Hayama, K. K. Baldrige, A. Linden and J. S. Siegel, *J. Am. Chem. Soc.*, 2006, **128**, 6870; A. Sygula, H. E. Folsom, R. Sygula, A. H. Abdourazak, Z. Marcinow, F. R. Fronczek and P. W. Rabideau, *J. Chem. Soc., Chem. Commun.*, 1994, 2571; Y.-T. Wu, D. Bandera, R. Maag, A. Linden, K. K. Baldridge and J. S. Siegel, *J. Am. Chem. Soc.*, 2008, **130**, 10729; B. M. Schmidt, S. Seki, B. Topolinski, K. Ohkubo, S. Fukuzumi, H. Sakurai and D. Lentz, *Angew. Chem., Int. Ed.*, 2012, **51**, 11385; I. V. Kuvychko, S. N. Spisak, Y.-S. Chen, A. A. Popov,
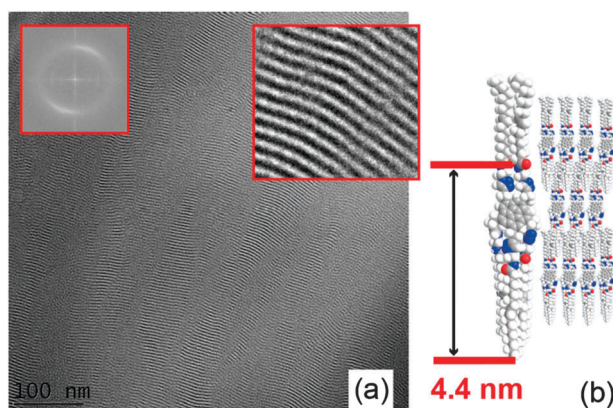
Fig. 2 (a) Transmission electron microscopy (TEM) image of compound **2** with a lamellar structure. The insets show the Fourier transformation (FFT) and a zoom-up of a lamellar domain (edge size of 50 × 45 nm). (b) A possible molecular model of the molecular organization in the lamellar structure.

M. A. Petrukhina, S. H. Strauss and O. V. Boltalina, *Angew. Chem., Int. Ed.*, 2012, **51**, 4939.

6 D. Miyajima, K. Tashiro, F. Araoka, H. Takezoe, J. Kim, K. Kato, M. Takata and T. Aida, *J. Am. Chem. Soc.*, 2009, **131**, 44.

7 A. M. Butterfield, B. Gilomen and J. S. Siegel, *Org. Process Res. Dev.*, 2012, **16**, 664.

8 M. Mattarella and J. S. Siegel, *Org. Biomol. Chem.*, 2012, **10**, 5799.

9 Prefix *sym* is used here to indicate the C_5-symmetric-substituted corannulene corresponding to 1,3,5,7,9-pentasubstitution.

10 T. J. Seiders, E. L. Elliot, G. H. Grube and J. S. Siegel, *J. Am. Chem. Soc.*, 1999, **121**, 7804.

11 A new candidate as a starting point for the synthesis of *sym*-penta-substituted corannulenes has been recently reported: M. N. Eliseeva and L. T. Scott, *J. Am. Chem. Soc.*, 2012, **134**, 15169.

12 H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2001, **40**, 2004; J. E. Moses and A. D. Moorhouse, *Chem. Soc. Rev.*, 2007, **36**, 1249.

13 ESI†.

14 M. Wang, G. L. Silva and B. A. Armitage, *J. Am. Chem. Soc.*, 2000, **122**, 9977; E. G. McRae, *Aust. J. Chem.*, 1961, **14**, 229; E. Jelley, *Nature*, 1936, **138**, 1009; E. Jelley, *Nature*, 1937, **139**, 631.

15 L. Leibler, *Macromolecules*, 1980, **13**, 1602.