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Skeletal double gyroid formed by single coaxial bundles of catechol based bolapolyphiles

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A bolapolyphile, derived from a linear *p*-terphenyl core with glycerol groups at each end and two octadecyl chains fixed to the same side of the π-conjugated rod, is synthesized and is found to form a new type of self-assembled cubic LC phase with *Ia*3;¯*d* lattice. Each unit cell involves 16 polar aggregates interconnected by 24 coaxial rod-bundles at single-molecule length, forming two interwoven skeletal networks with three-way junctions, being separated by a continuum of the lateral alkyl chains located around the gyroid minimal surface.

Two-dimensional (2D) and 3D crystal engineering has significantly advanced in the recent decades,[1,2] but the understanding of the molecular self-assembly in soft matter systems, where the individual molecules do not have fixed positions, is still at the infancy.[3] Though a number of fascinating superstructures was observed for amphiphiles in aqueous systems and the reasons forming those were explained by simple geometrical models,[4,5,6] a fundamental knowledge of targeted molecular design towards more complex soft matter structures is still missing. Cubic soft matter phases represent examples of complex 3D structures which have received significant attention.[7] They can be formed by bicontinuous networks with distinct valences of their branchings or by micellar aggregates (bicontinuous and micellar phases,. respectively) and the aggregates can either involve the lipophilic chains or the polar groups and water, leading to normal and inverted types, respectively. The double gyroid[8] is probably the most common cubic phase and is formed by two mutually interwoven networks with three-way junctions and separated by the gyroid minimal surface (Fig. 1a).[9] Though this kind of bicontinuous cubic phases is well known for lyotropic systems and as morphology in block copolymers,[10] only recently it was used for functional materials by inclusion of proper functional building blocks, such as electron-, hole- or ion-conducting units.[11,12] Gyroid phases involving different arrangements of π-conjugated rods are known which are collated in Fig. 1b-d. In the most often observed structure (b), formed by rod-like molecules, having alkyl chains or other bulky groups[13] at the ends of the rods (polycatenar molecules[14]), the rods are arranged perpendicular to the networks and the clashing of the chains leads to a helical organization of the molecules along the networks.[15]

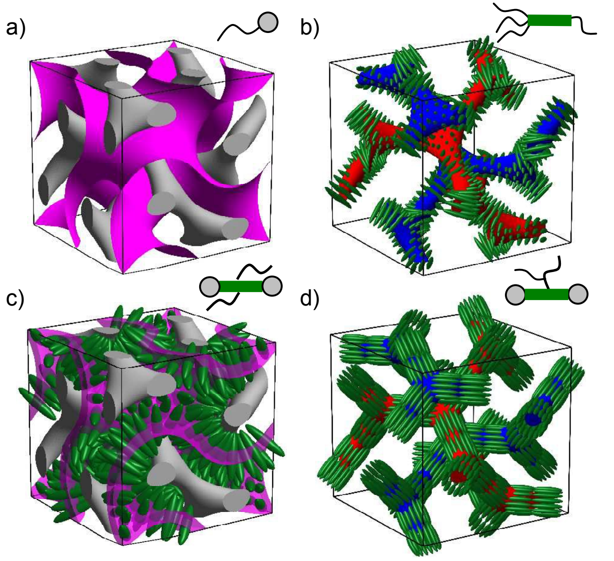

Figure 1: a) The double gyroid cubic phase involving two networks (gray) separated by the gyroid minimal surface (magenta). (b-d) The known arrangements of π-conjugated rods (green) in the LC gyroid phase: b) helical organization of polycatenar molecules (alkyl chains at both ends of the rods) perpendicular to the networks; c) organization of X-shaped molecules (chains in opposite lateral positions) with the π-conjugated rods on the minimal surface and perpendicular to it, and d) coaxial rod-bundle phase formed by T-shaped bolapolyphiles with a branched lateral chain, involving pairs of coaxial rod-bundles forming the skeletal networks; adapted from Ref. 16**.**

More recently two new *Ia*3;¯*d* cubic phases[16,17] were reported for rod-like molecules having bulky chains laterally attached to the rod-like π-conjugated core and hydrogen bonding glycerol groups at the ends. As the lateral chains are incompatible with the rods as well as the glycerols, these

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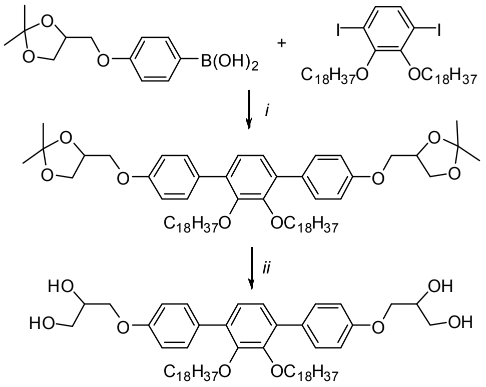
Electronic Supplementary Information (ESI) available: [Methods, syntheses, analytical data, additional XRD and structural data]. See DOI: 10.1039/x0xx00000x molecules involve more than only two incompatible building blocks are considered as polyphiles, more precisely as bolapolyphiles, due to the position of the polar groups at both ends of the lipophilic core.[3,18] Depending on the number and position of the lateral lipophilic chains, T-shaped bolapolyphiles,[19] having only one linear or branched lateral chain, and X-shaped bolapolyphiles,[20] having two chains at opposite sides, can be distinguished. The cubic phases with $Ia\bar{3}d$ symmetry formed by these molecules are shown in Fig. 1c,d.[16,17] In structure (c), found for X-shaped molecules, the rods are organized in layers with saddle-splay curvature, thus forming the minimal surface,[16] whereas in structure (d), found for T-shaped molecules with branched chains, the π-conjugated rods are organized to form the skeletons of the two infinite networks,[17] i.e. orthogonal to case (b). Within this cubic phase the three-way junctions of the two interpenetrating networks are connected by pairs of end-to-end connected bundles, each bundle being one molecule in length and having ~12 molecules in the diameter.[17]



1: Cr 93 °C [77.4 kJmol^{-1}] Cub/$Ia\bar{3}d$ 128 °C [1.1 kJmol^{-1}] Iso

Figure 2: Structure, synthesis and phase transitions of the bolapolyphile **1**. Reagents and conditions: i) $Pd(PPh_3)_4$, sat. $NaHCO_3$, H_2O, THF, reflux, 5h, 43%, ii) HCl (10%), MeOH, THF, reflux, 6 h, 90%. Phase transitions were determined by DSC on the first heating scan with 10 Kmin^{-1} (peak temperatures); abbreviations: Cr = crystalline solid; Cub/$Ia\bar{3}d$ = double gyroid cubic phase with $Ia\bar{3}d$ symmetry, Iso = isotropic liquid.

Herein we report a new type of bolapolyphiles being derived from a catechol based rod-like *p*-terphenyl core, which can be considered as π-shaped. In the reported compound two long identical alkyl chains are fixed at the same side of a *p*-terphenyl rod and this compound exclusively forms a new type of axial rod bundle cubic phase with $Ia\bar{3}d$ lattice (see Fig. 3). In this skeletal cubic phase only a single rod-bundle, instead of two, as observed in all previously known cases,[17] is involved. Compound **1** reported in this work was synthesized as shown in Fig. 2 by a Suzuki cross coupling reaction[21] of 1,4-diiodo-2,3-dioctadecyloxybenzen[22] with two equivalents 4-[(2,2-dimethyl-1,3-dioxolane-4-yl)methoxy] benzene boronic acid,[23] followed by deprotection of the glycerol groups.[24] Details of the synthesis and the analytical data of **1** are described in the Electronic Supporting Information (ESI).

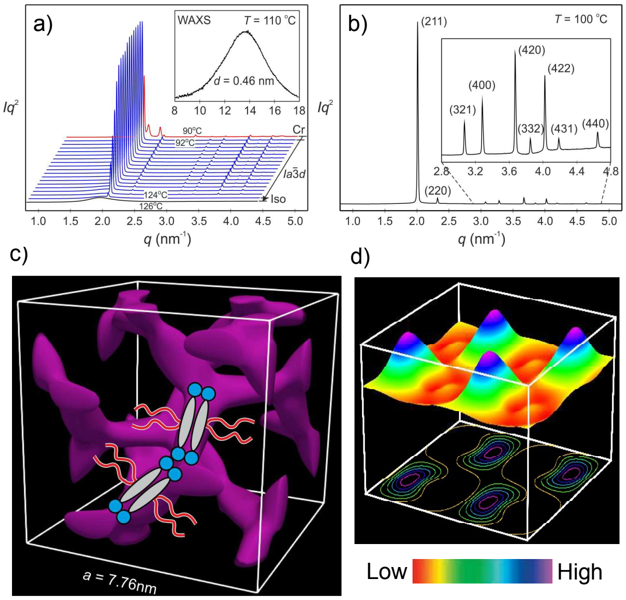


Figure 3: Characterisation of **1**: a) continuous heating scan from crystal to Iso state via Cub/$Ia\bar{3}d$ phase, the inset shows the diffuse wide angle scattering of the Cub/$Ia\bar{3}d$ phase at 110 °C; b) SAXS diffractogram of the Cub/$Ia\bar{3}d$ phase at 100 °C; c) reconstructed electron density map for the Cub/$Ia\bar{3}d$ phase with added schematic molecules, only high-electron-density regions (purple) are shown; d) surface-and-contour plot of electron density distribution of [001] cross section, the continuous colour scale is shown underneath.

Compound **1** was investigated by polarized optical microscopy (POM), differential scanning calorimetry (DSC) and powder X-ray diffraction (XRD) using a synchrotron source. Phase transition temperatures and associated enthalpy values are given in Fig. 2 (see Fig. S1 for DSC traces). The compound shows an optically isotropic mesophase, appearing completely dark between crossed polarizers (see Fig. S2) above the melting point at T = 93 °C until the transition to the isotropic liquid state at T = 128 °C. The transition from this isotropic mesophase to the isotropic liquid is indicated by a relatively small transition enthalpy (1.1 kJmol^{-1}) and a sudden decrease of viscosity, as typically observed for Cub-Iso transitions.

In the temperature range of the isotropic mesophase the XRD wide-angle scattering is completely diffuse, like in the liquid state, with a maximum at d = 0.46 nm (see the inset of Fig. 3a), corresponding to the mean lateral distance between the molecules. This indicates that there is no positional long range order of individual molecules and this phase thus represents an optically isotropic liquid crystalline (LC) mesophase. In the small angle X-ray scattering (SAXS) pattern (Fig. 3a,b) there is a series of sharp Bragg peaks. The d-values of the peaks show a characteristic ratio of $\sqrt{6}$: $\sqrt{8}$: $\sqrt{14}$: $\sqrt{16}$: $\sqrt{20}$: $\sqrt{22}$: $\sqrt{24}$: $\sqrt{26}$: $\sqrt{32}$, which is indexed to the (211), (220), (321), (400), 420), (332), (422), (431) and (440) reflections of a cubic lattice with $Ia\bar{3}d$ symmetry and a lattice parameter a_{cub} = 7.76 nm (see Table S1). Based on this SAXS pattern the electron density (ED) map, shown in Figs. 3c,d and S3, was

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reconstructed. The purple surfaces enclose the high ED regions involving the aromatic cores and the glycerol groups (see Fig. 3c,d), while the low-ED regions around the two networks contain the alkyl chains (see Figs. 3d and S3). The ED histogram of the *Ia* 3;¯ *d* lattice, supporting the chosen phase combination, is shown in Fig. S4. The two electron rich networks of the double gyroid structure are formed by column-like segments connected by three-way junctions. Based on the lattice parameter a_{cub}, which slightly decreases with increasing the temperature (see Fig. S5), the distance between the junctions was always calculated to ~2.7 nm using the equation d_{junct} = a_{cub}/(2·√2). This value is close to the molecular length L_{mol} = 2.5 nm, measured between the ends of the glycerol groups in the most extended conformation. The distance of the two networks is about 3.4 nm, which is much larger than L_{mol}. Therefore, an organization of the rods on the minimal surface with the glycerols forming the networks, as shown in Fig. 1c, can be excluded. Accordingly, we suggest that each columnar network segment is formed by a single bundle of coaxial molecules, aligned with the molecular long axes parallel to the network channels, as shown in Figs. 3c and 4. The number of molecules in each cubic unit cell (n_{cell}) is calculated from the unit cell volume (V_{cell} = a_{cub}^3 = 467 nm^3) and the molecular volume (V_{mol} = 1.44 nm^3; calculated with Immirzis crystal volume increments[25]), and assuming a packing density in the LC state corresponding to the mean value between the solid (0.7) and the liquid (0.55),[26] to be n_{cell} = 290 molecules (n_{cell} = V_{cell}/V_{mol}). As there are 24 rod-like network segments, each bundle contains 12 molecules in cross section on average (see Table S2). This value is equal to that found for other cubic (*Ia*3;¯*d*,[17] *Pn*3;¯*m*[27]) and the hexagonal columnar rod bundle phases.[28]

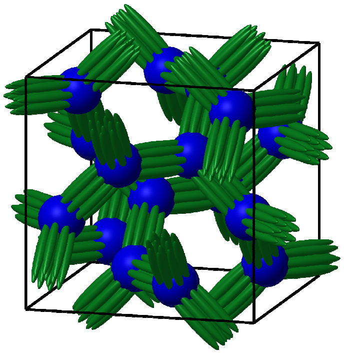

Figure 4: Model showing the two networks at single-molecule length between the junctions, combining spheres formed by the aggregation of the glycerol groups at the junctions (the rod bundles are shown with a time- and space averaged circular cross section).

The main difference to the previously reported cubic cases is that only a single coaxial rod-bundle is connecting each of the junctions. The rod-bundles themselves represent ribbons of six back-to-back packed pairs of terphenyls which are rotationally disordered to give a circular cross section on time and space average. Figure 5 shows the development of the type of coaxial rod-bundle phase depending on the molecular structure. From compound **1** via the biphenyl **2**[17] to the terphenyl **3**[28a] the chain volume to molecular length ratio V_{chain}/L_{mol} increases (see Table S3). Accordingly, the LC phase structure changes from the gyroid involving single rod-bundles via the larger gyroid formed by pairs of rod-bundles to straight columns formed by quasi-infinite chains of rod-bundles. Besides the volume to length ratio, the molecular topology and shape change in this series of compounds too. For compound **3**, having the bulky chains at both ends the formation of hydrogen bonding networks between the glycerol groups is limited and only a linear organization of molecules can be formed. In the case of compound **2**, the lateral group is attached to one end of the molecule, thus making the two ends different. The glycerols adjacent to the lateral chain have a limited capability of hydrogen bonding, thus forming linear junctions between pairs of rod bundles. The glycerol group at the non-substituted end is less shielded and thus allows the formation of junctions with higher valence. In this way the double gyroid cubic phase of the biphenyl compounds **2** is formed by two end-to-end connected longitudinal rod-bundles. But in compound **1**, the lateral chains are attached to the middle of the terphenyl core, the polar glycerol groups at both ends are equal and both are easily accessible and capable of forming multivalent nodes. This leads to a structure formed by single longitudinal rod-bundles connecting each of the three way junctions.

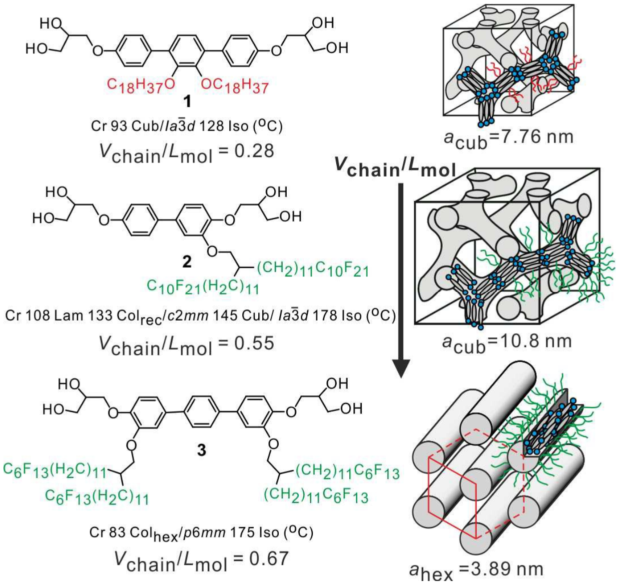

Figure 5: Development of the phase structure of coaxial rod-bundle phases depending on the molecular structure of the bolapolyphile; data for **2** and **3** were taken from refs. 17,28b; for calculation of V_{chain}/L_{mol} and transition enthalpies of **2**, **3**, see Table S3.

It is noted that compound **1** is the first example of a non-fluorinated bolapolyphile capable of forming a coaxial rod-bundle phase, meaning that this is a general mode of soft molecular self-assembly of properly designed bolapolyphiles, not requiring semiperfluorinated segments in the lateral chains. The effect of chain fluorination is therefore assumed to be mainly of steric origin. The *Ia*3;¯*d* cubic phase of the

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bolapolyphile **1** belongs to a newly emerging type of cubic phases being bicontinuous as it is formed by two networks. However, as it contains 16 discrete nano-segregated spheroidic aggregates at the nodes of the networks (each involving ~36 glycerol groups) it can simultaneously be considered as a micellar cubic phase (Fig. 4). This hybridization of speroidic and network organization makes the family of coaxial rod-bundle phases more complex and unique among the cubic LC phases.

Conclusions

The first π-shaped bolapolyphiphilic molecule having two lateral alkyl chains fixed at the same side of a rod-like core has been synthesized and investigated. It represents a new type of polyphilic molecules and forms a new kind of double gyroid cubic phase (Cub/*Ia*3;¯*d*) representing a combination of 16 spheres interconnected by 24 longitudinal rod bundles involved in two interwoven networks separated by the continuum of the alkyl chains around the gyroid minimal surface. This is a new mode of soft self-assembly and the formation of this and the other distinct types of these rod-bundle phases can be rationalized based on the molecular structure.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

1 A. Mukherjee, J. Teyssandier, G. Hennrich, S. De Feyter and K. S. Mali, *Chem. Sci*., 2017, 8, 3759–3769; M. J. Zaworotko, *Chem. Commun*., 2001, 1–9.

2 a) G. R. Desiraju, *J. Am. Chem. Soc*., 2013, **135**, 9952−9967; b) L. Brammer, *Chem. Soc. Rev*., 2004, **33**, 476–489.

3 C. Tschierske, *Angew. Chem. Int. Ed*., 2013, **52**, 8828 – 8878.

4 J. N. Israelachvili, *Intermolecular and surface forces*, 3rd ed., Elsevier, Amsterdam, 2011

5 a) K. Borisch, S. Diele, P. Göring, H. Kresse and C. Tschierske, *J. Mater. Chem.*, 1998, **8**, 529–543; b) X. Cheng, M. K. Das, S. Diele and C. Tschierske, *Langmuir,* 2002, **18**, 6521 6529.

6 T. Ichikawa, M. Yoshio, A. Hamasaki, S. Taguchi, F. Liu, X. Zeng, G. Ungar, H. Ohno and T. Kato, *J. Am. Chem. Soc*., 2012, **134**, 2634.

7 a) S. Kutsumizu, *Isr. J. Chem*., 2012, **52**, 844 – 853; b) G. Ungar, F. Liu and X.B. Zeng, *in Handbook of Liquid Crystals*, 2nd Ed., Vol. 5, J.W. Goodby, P.J. Collings, T. Kato, C. Tschierske, H.F. Gleeson and P. Raynes, eds. (Wiley-VCH), 2014, pp. 363–436.

8 V. Luzzati and P. A. Spegt, *Nature,* 1967, **215**, 701-704; D. V. Perroni, C. M. Baez-Cotto, G. P. Sorenson and M. K. Mahanthappa, *J. Phys. Chem. Lett*., 2015, **6**, 993−998.

9 A. H. Schoen, *Nasa technical note NASA TN 015541*, Washington DC, 1970; A. H. Schoen, *Interface Focus,* 2012, **2**, 658-668.

10 M. W. Matsen, *J. Chem. Phys*., **108**, 785-796 (1998).

11 T. Kato, M. Yoshio, T. Ichikawa, B. Soberats, H. Ohno and M. Funahashi, *Nat. Rev. Mater*., 2017, **2**, 17001; D. L. Gin, X. Lu, P. R. Nemade, C. S. Pecinovsky, Y. Xu and M. Zhou, *Adv. Funct. Mater*., 2006, **16**, 865−878.

12 E. J. W. Crossland, M. Kamperman, M. Nedelcu, C. Ducati, U. Wiesner, D.-M. Smilgies, G. E. S. Toombes, M. A. Hillmyer, S. Ludwigs, U. Steiner and H. J. Snaith, *Nano Lett.,* 2009, **9**, 2807-2812.

13 Y. Maeda, H. Yokoyama, A. Yoshizawa and T. Kusumoto, *Liq. Cryst*., 2007, **34**, 9 18; E. Nishikawa, J. Yamamoto and H. Yokoyama, *Liq. Cryst*., 2003, **30**, 785 798.

14 a) J. Malthete, A. M. Levelut and H. L. Nguyen, *J. Phys. Lett*. A, 1985, **46**, 875 880; b) H. L. Nguyen, C. Destrade and J. Malthete, *Adv. Mater*., 1997, **9**, 375 388; c) D. W. Bruce, *Acc. Chem. Res*., 2000, **33**, 831 840; A. M. Levelut and M. Clerc, *Liq. Cryst*., 1998, **24**, 105-115.

15 a) C. Dressel, F. Liu, M. Prehm, X.-B. Zeng, G. Ungar and C. Tschierske, *Angew. Chem. Int. Ed*., 2014, **53**, 13115−13120; b) C. Tschierske and G. Ungar, *ChemPhysChem,* 2016, **17**, 9-26.

16 M. Poppe, C. Chen, F. Liu, S. Poppe and C. Tschierske, *Chem. Eur. J.,* 2017, **23**, 7196-7200.

17 F. Liu, M. Prehm, X. Zeng, C. Tschierske and G. Ungar, *J. Am. Soc. Chem*., 2014, **136**, 6846–6849.

18 a) C. Tschierske, *Chem. Soc. Rev*., 2007, **36**, 1930-1970; b) X.-B. Zeng, R. Kieffer, B. Glettner, C. Nürnberger, F. Liu, K. Pelz, M. Prehm, U. Baumeister, H. Hahn, H. Lang, G. A. Gehring, C. H. M. Weber, J. K. Hobbs, C. Tschierske and G. Ungar, *Science,* 2011, **331**, 1302 1306; c) F. Liu, R. Kieffer, X.-B. Zeng, K. Pelz, M. Prehm, G. Ungar and C. Tschierske, *Nat. Commun*., 2012, **3**, 1104; d) S. Poppe, A. Lehmann, A. Scholte, M. Prehm, X.-B. Zeng, G. Ungar and C. Tschierske, *Nat. Commun.,* 2015, **6**, 8637.

19 X. Cheng, M. Prehm, M. K. Das, J. Kain, U. Baumeister, S. Diele, D. Leine, A. Blume, and C. Tschierske, *J. Am. Chem. Soc.* **2003**, 125, 10977-10996.

20 R. Kieffer, M. Prehm, B. Glettner, K. Pelz, U. Baumeister, F. Liu, X. Zeng, G. Ungar and C. Tschierske, *Chem. Commun*., 2008, 3861–3863.

21 a) N. Miyaura, T. Yanagi and A. Suzuki, *Synth. Commun*., 1981, **11**, 513; b) N. Miyaura, and A. Suzuki, *Chem. Rev*., 1995, **95**, 2457-2483.

22 Z. Zhu and T. M. Swager, *Org. Lett*., **2001**, **3**, 3471–3474.

23 M. Kölbel, T. Beyersdorff, X. Cheng, C. Tschierske, J. Kain and S. Diele, *J. Am. Chem. Soc.*, 2001, **123**, 6809-6818.

24 R. van Rijsbergen, M.-J. Anteunis and A. de Bruyn, *J. Carbohydr. Chem.,* 2006, **2**, 395–404.

25 A. Immirzi and B. Perini, *Acta Cryst*., 1977, **A33**, 216–218.

26 A. I. Kitaigorodski, in "Molekülkristalle", Akademieverlag Berlin, 1979.

27 X. Zeng, M. Prehm, G. Ungar, C. Tschierske and F. Liu, *Angew. Chem. Int. Ed*., 2016, **55**, 8324–8327.

28 a) M. Prehm, F. Liu, X. Zeng, G. Ungar and C. Tschierske*, J. Am. Chem. Soc*., 2008, **130**, 14922–14923; b) M. Prehm, F. Liu, X. Zeng, G. Ungar and C. Tschierske, *J. Am Chem. Soc.,* 2011, **133**, 4906–4916; c) F. Liu, M. Prehm, X. Zeng, G. Ungar and C. Tschierske*, Angew. Chem. Int. Ed.,* 2011, **50**, 10599 –10602.