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A Bolaamphiphilic Sexithiophene with Liquid Crystalline Triangular Honeycomb Phase

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A new bolaamphiphile comprising a 5,5""-diphenylsexithiophene core with glycerol groups at each end and four lateral decyl chains was synthesized which self-assembles into a liquid crystalline phase representing a nanoscale honeycomb composed of quasi-infinite triangular cylinders of π -conjugated sexithiophenes.

The spatial organization of π -conjugated molecules plays a ¹⁵ crucial role for optoelectronic devices such as OLEDs, TFTs and PVs based on organic semiconducting materials. However, the design of materials with predictable arrangement of the molecules in well defined assemblies, driven by non-covalent interactions that control and direct their self-assembly, still remains a major ²⁰ challenge. In this context it is of interest to consider the possibility of liquid crystalline (LC) phases formed by π conjugated rods, which have the advantage of annealing defects due to their fluidity.^{1,2,3} Sexithiophene and other oligothiophenes⁴ belong to the most intensively investigated π -conjugated rods.^{5,6}

- ²⁵ LC oligothiophenes in most cases form smectic phases^{7,8} and there are only rare cases of columnar and spheroidic cubic phases.⁹ Polar functional end groups have recently been recognized as controlling units for self-assembly of π -conjugated rods in gels and on surfaces.^{10,11} We used polar glycerol end-³⁰ groups in combination with flexible non-polar side groups to
- assemble π -conjugated rods into polygonal honeycombs.^{3,12} In these honeycombs the π -conjugated rods stack parallel and on top of each other, in this way forming walls, and these walls are interconnected by hydrogen bonding networks between the ³⁵ terminal glycerol groups, running along the edges of the resulting
- polygonal cylinders forming the honeycomb. The prismatic cells inside the honeycomb represent channels of different shape and size which are filled with the laterally attached chains.^{12,13} In previous work we have reported T-shaped and X-shaped ⁴⁰ bisthiophenes^{14,15} forming triangular and square cylinders and a
- X-shaped tetrathiophene forming square cylinders.¹⁶



45 Cr 109 °C [34.1 kJmol⁻¹] Col_{hex}/p6mm 148 °C [3.5 kJmol⁻¹] Iso

Fig.1 Compound **6T/10** with transition temperatures with associated enthalpy values as determined by DSC (peak temperatures, 10 K min⁻¹) \ddagger ; abbreviations: Cr = crystalline solid; Col_{hex}/p6mm = hexagonal columnar LC phase with p6mm lattice; Iso = isotropic liquid state.

50 Herein we report the first example of a sexithiophene

bolaamphiphile possessing four lateral decyl chains (see Fig. 1). This compound, which represents the longest oligothiophene based LC bolaamphihpile reported yet, self-assembles into a LC honeycomb composed of regular triangular cylinder cells with a 55 side-length of 4.0 to 4.4 nm.

Scheme 1 describes the synthesis of the target bolaamphipile 6T/10 by using Kumada and Suzuki coupling reactions as key steps. Accordingly, 3-decylthiophene 2,17 was monobrominated with one equivalent NBS in THF at RT.¹⁸ The obtained 2-bromo-60 3-decylthiophene 3 was then transferred to the Grignard reagent 4 with 1.2 equivalent Mg turnings at T < 60 °C, followed by 1h reflux to complete the reaction. Grignard reagent 4 was then coupled with 4-(5-bromothien-2-yl)anisole 6, which was obtained in the monocoupling reaction between 2,5-dibromothiophene and 65 4-methoxybenzene boronic acid¹⁹ under standard Suzuki condition with Pd(PPh₃)₄.²⁰ The resulting dithiophene 7 was monobrominated with one equivalent NBS¹⁸ in THF at 30 °C. The thus obtained bromide 8 was coupled with n-decyl magnesium bromide 4 to give the methoxysubstituted ⁷⁰ terthiophene 9. Demethylation of 9 using BBr₃ at -78 °C²¹ yielded the phenol 10; here it is essential that the reaction is quenched by adding ice water as soon as the reaction was finished (TLC). The obtained phenol 10 was then allylated with allybromide followed by dihydroxylation of the double bonds with catalytic amounts of 75 osmium tetroxide and N-methylmorpholine-N-oxide as reoxydant²² to yield the glycerol ether **12**. Protection of the diol group with 2,2-dimethoxypropane produced the acetonide 13 which was then oxidatively dimerized with n-BuLi and anhydrous $CuCl_2$ to yield the sexithiophene 14. In the final step ⁸⁰ the acetonide protecting groups at both ends were cleaved (10% HCl in CH₃OH) and the obtained bolaamphiphile 6T/10 was purified by repeated crystallization from ethyl acetate/methanol (10:5). Detailed synthetic procedures and analytical data are given in the electronic supporting information (ESI [†]).

- ⁸⁵ Compound **6T/10** was investigated by polarizing microscopy (PM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The thermotropic phase sequence and the transition temperatures are collated in Fig. 1. **6T/10** melts at T =109 °C, ‡ forming a LC phase which transforms into an isotropic ⁹⁰ liquid at T = 148 °C. The relatively low enthalpy of the transition to the isotropic liquid state ($\Delta H = 3.5$ kL mol⁻¹) is in line with the
- to the isotropic liquid state ($\Delta H = 3.5$ kJ mol⁻¹) is in line with the presence of a LC phase. On cooling the LC phase is formed from the isotropic liquid at approximately the same temperature, but no crystallization can be observed down to room temperature. At 20 95 °C the LC phase is stable for prolonged periods of time (about
- one hour) before it crystallizes.

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Scheme 1 Synthesis of compound 6T/10; Reagents and conditions: i) C_nH_{2n+1}MgBr, Ni(dppp)Cl₂, THF, reflux, 15 h; ii) NBS, THF, 30 °C, 15 h; iii) Mg, THF, reflux, 1 h; iv) 4-methoxybenzene boronic acid, Pd(PPh₃)₄, NaHCO₃, glyme, H₂O, reflux, 15 h; v) Ni(dppp)Cl₂, THF, reflux, 15 h; vi) BBr₃, -78 °C, CH₂Cl₂, RT, 12 h; vii) K₂CO₃, CH₃CN, allylbromide, reflux, 2 h; viii) OsO₄, NMMNO, H₂O, acetone, RT, 24 h; ix) Me₂C(OMe)₂, PPTS, TosOH, RT, 12 h; x) n-BuLi, THF, CuCl₂, -60 °C, 15 h; xi) 10% HCl, CH₃OH, reflux, 6 h.

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The texture of the LC phase observed by PM between crossed polarizers is characterized by spherulitic domains which indicate the presence of a LC phase with 2D lattice (columnar phase, see Fig. 2b). Some regions appear optically isotropic,§ in these regions the column long axes are perpendicular to the substrate surfaces and the fact that no birefringence is found in these regions indicates that this mesophase is optically uniaxial, as typical for square and hexagonal columnar mesophases. Shearing the sample leads to flow which removes this texture; this confirms the LC state of the material.

- ⁶ Fig. 2a shows the XRD pattern of the LC phase at T = 40 °C (supercooled state) and at T = 140 °C. The diffuse scattering in the wide angle region confirms the fluid liquid crystalline state of the material. The position of the wide angle scattering between d = 0.44 (T = 40 °C) and d = 0.46 nm (T = 140 °C) is typically
- ³⁵ observed as average of the mean distances between the aliphatic chains and the aromatic cores. There is no additional reflection in the wide angle range. The ratio of the positions of the small angle reflections is 1: $3^{1/2}$: 2 at all temperatures, confirming a hexagonal lattice and excluding a square lattice. The lattice ⁴⁰ parameter a_{hex} is strongly temperature dependent and grows from
- $a_{\text{hex}} = 4.03 \text{ nm at } T = 140 \text{ °C}$ to $a_{\text{hex}} = 4.38 \text{ nm at } T = 40 \text{ °C}$. Overall the lattice parameter is in the range of the molecular length L = 4.1 nm and this is in line with a triangular cylinder honeycomb structure of this hexagonal columnar phase. In this
- ⁴⁵ case the position and direction of the rod-like cores coincide with the hexagonal lattice (see Fig. 2c,d), the hydrogen bonding networks incorporating six glycerol units are located at the 6-fold nodes of the (3⁶)-net (blue columns in Fig. 2d) and the triangular prismatic cells are filled with the alkyl chains. Fig 2c indicates ⁵⁰ that satisfactory space filling is achieved in the proposed structure
- if a thickness of the walls corresponding to ~ 1 molecule is

assumed. This number was calculated for a hypothetical unit cell from the experimental 2D lattice parameters and an assumed height of one-molecule thickness of 0.44 - 0.46 nm (average maximum of the diffuse wide angle scattering, see Tab. S1) from the volume of this unit cell (V_{cell}) and the volume of a molecule (V_{mol} , calculated using crystal volume increments²³) according to $n_{cell} = V_{cell}/V_{mol}$ as $n_{cell} \sim 3$ (the density calculated with this value is 1.0 - 1.1 g cm⁻³, see Tab. S1). Since there are three walls per 60 unit cell, the calculated average thickness of the walls ($n_{wall} = n_{cell}/3$) is about one rod-like core.



75 **Fig. 2** Compound **6T/10**: a) XRD patterns of the Col_{hex}/*p6mm* phase at T = 40 and 140 °C; b) texture between crossed polarizers at T = 140 °C; c)

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CPK models showing the organization of the molecules in the cross section of two adjacent triangular cylinders (one 2D unit cell); d) shows a model of the triangular honeycomb phase and e) (3^6) -net.

An alternative honeycomb formed by hexagonal cylinders can s be excluded as this would provide insufficient space filling of the larger hexagonal cells and would require a lattice parameter of $a_{\text{hex}} = 3^{1/2} L$ which is much larger than the experimental determined value. If the rod-like units would be arranged parallel to the column long axis and surrounded by the fluid alkyl chains as recently proposed for the rod-bundle phases, ²⁴ then a_{hex} should be significantly less than 3.6 nm. ²⁷ This value is much smaller than the experimentally observed lattice parameter and was estimated from twice the length of the lateral chain (1.35 nm in *all-trans* conformation) plus twice the diameter of the aromatic 15 core (0.45 nm).

The shrinkage of the trigonal cylinders with rising temperature can be explained by the increasing mobility of the molecules and especially the alkyl chains with increasing temperature and this is typically observed for columnar phases and especially for ²⁰ polygonal honeycomb phases.^{12,13} The thermal expansion occurs predominately along the cylinder long axis which reduces the core-core packing density along this direction. This is in line with the shift of the position of the diffuse wide angle scattering from d = 0.44 nm at T = 40 °C to d = 0.46 nm at T = 140 °C. Also in ²⁵ line with the enhanced mobility is the significant broadening of

²⁵ line with the enhanced mobility is the significant broadening of the small angle scatterings with rising temperature (Fig. 2a). This indicates a continuously decreasing correlation length of the hexagonal lattice with rising temperature which might be due to the incorporation of a growing number of rhombic cells.¹⁵ These

³⁰ rhombic cells can be formed by fusion of two adjacent triangular cells and hence provide more space for the lateral chains. These cells also allow an enhanced flexibility, as in contrast to triangles the rhombs can more easily change the angles. This leads to a reduced correlation length of the hexagonal lattice. At T = 148 °C ³⁵ the 2D-lattice becomes short range at the phase transition to the

isotropic liquid state which is assumed to be composed of small disordered segments of the previous honeycomb.

In Summary, the first example of a sexithiophene based bolaamphiphile decorated with four lateral decyl chains and two 40 terminal glycerol groups was synthesized. It represents the bolaamphiphilic mesogens with the longest π -conjugated oligothiophene core so far, which self-assembles into a triangular honeycomb-like LC phase over a broad temperature region. This mode of self-assembly is different to all previously reported

⁴⁵ sexithiophenes and opens new possibilities for the directed organization of π -conjugated organic materials into complex superstructures. Further work will be focused on modification of the π -conjugated core to achieve closer π -stacking along the honeycomb walls. Such optimized compounds could be of

50 interest for self-assembled nano-scale organic electronic devices.

Notes and references

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 † Electronic Supplementary Information (ESI) available: [Synthesis, analytical data and XRD data]. See DOI: 10.1039/b000000x/

‡ In the first heating scan here are crystal-crystal transitions at 51 °C and 60 76 °C before the melting point at 109 °C, the given enthalpy is the total of all three transitions.

§ The dark red color of the material is also dominating in the optical isotropic areas.

 \P The orientation of the optical axis can in this case not be determined

- 65 with certainty by observing the birefringence color shift using a lambda retarder plate, due to the color of the material covering the birefringence.
 - (a) I. Mcculloch, M. Heeney, C. Bailey, K. Genevicius, I. Macdonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. M. Zhang, M.
- 70 L. Chabinyc, R. J. Kline, M. D. McGehee and M. F. Toney, *Nat. Mater.*, 2006, **5**, 328-333; (b) M. M. Ling and Z. N. Bao, *Chem. Mater.*, 2004, **16**, 4824-4840.
- 2 M. O'Neill and S. M. Kelly, *Adv. Mater.*, 2011, **23**, 566–584.
- 3 X. 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.
- 4 D. Fichou, J. Mater. Chem., 2000, 10, 571–588; S. Hotta and K.Waragai, Adv. Mater., 1993, 5, 896–908; F. Garnier, A. Yassar, R.
- Hajlaoui, G. Horowitz, F. Deloffre, B. Servet, S. Ries and P. Alnot, J. Am. Chem. Soc., 1993, 115, 8716–8721; M. Halik, H. Klauk, U. Zschieschang, G. Schmid, S. Ponomarenko, S. Kirchmeyer and W. Weber, Adv. Mater., 2003, 15, 917–922.
- 5 (a) G. Horowitz, D. Fichou, X. Peng, Z. Xu and F. Garnier, *Solid State Commun.*, 1989, 72,381-384; (b) H. E. Katz, Z. Bao and S. L. Gilat, *Acc. Chem. Res.*, 2001, 34, 359-369.
- 6 A. Mishra, C.-Q. Ma, and P. Bäuerle, Chem. Rev., 2009, 109, 1141-1276.
- J. Ma, Q. Li, in Self-organized Organic Semiconductors: From Materials to Device Applications, Ed. Q. Li, John Wiley & Sons, Hoboken NJ, 2011.
- 8 A. Dell'Aquila, P. Mastrorilli, C. F. Nobile, G. Romanazzi, G. P. Suranna, L. Torsi, M. C. Tanese, D. Acierno, E. Amendola and P. Morales, J. Mater. Chem., 2006, 16, 1183–1191.
- 95 9 T.Yasuda, H. Ooi, J. Morita, Y. Akama, K. Minoura, M. Funahashi, T. Shimomura and T. Kato, *Adv. Funct. Mater.*, 2009, **19**, 411–419.
- 10 (a) K. Yoosaf, A. R. Ramesh, J. George, C. H. Suresh, and K. G. Thomas, *J. Phys. Chem. C*, 2009, 113, 11836-11843; (b) S. K. Samanata, A. Pal and S. Bhattacharya, *Langmuir*, 2009, 25, 8567-8578.
 - (a) A. Jatsch, E.-K. Schillinger, S. Schmid and P. Bäuerle, *J. Mater. Chem.*, 2010, **20**, 3563–3578; (b) S. Schmid, E. Mena-Osteritz, A. Kopyshev and Peter Bäuerle, Org. Lett., 2009, **11**, 5098-5101.
 - 12 C. Tschierske, *Chem. Soc. Rev.*, 2007, **36**, 1930-1970; C. Tschierske, C. Nürnberger, H. Ebert, B. Glettner, M. Prehm, F. Liu, X. Zeng and G. Ungar, *Interface Focus*, 2012, **2**, 669-680.
 - 13 X. H. 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.
- ¹¹⁰ 14 X. H. Cheng, X. Dong, G. H. Wei, M. Prehm and C. Tschierske, *Angew. Chem.*, 2009, **121**, 8158-8161; *Angew. Chem. Int. Ed.*, 2009, **48**, 8014-8017.
 - 15 H. F. Gao, Y. F. Ye, X. H. Cheng, M. Prehm, H. Ebert and C. Tschierske, *Soft matter* 2012, **8**, 10921-10931
- ¹¹⁵ 16 (a) M. Prehm, G. Götz, P. Bäuerle, F. Liu, X. B. Zeng, G. Ungar and C. Tschierske, *Angew. Chem. Int. Ed.*, 2007, **46**, 7856-7859.
 - 17 C. V. Pham, H. B. Mark, and H. Zimmer, Synth. Commun., 1986, 16, 689-696.
- 18 (a) T.A. Chen, X.M.Wu and R. D.Rieke, J. Am. Chem. Soc., 1995,
 117, 233-244; (b) R. D. McCullough, R. D. Lowe, M. Jayaraman and D. L.Anderson, J. Org. Chem., 1993, 58, 904-912.
 - 19 Y. Huang, X. Dong, T. Zheng, L. J. He and X. H. Cheng, Yunnan Unversity (Natural Science Edition), 2007, 29, 398-400.
 - 20 N. Miyaura and A. Suzuki, Chem. Rev., 1995, 95, 2457-2483.
- 125 21 J. F. W. McOmie, D. E. West, Organic Syntheses, Wiley: New York, 1973, Coll. Vol. V, p. 412.
 - 22 V. Van Rheenen, D. Y. Cha and W. M. Hartley, Org. Synth., 1978, 58, 43-51.
 - 23 A. Immirzi and B. Perini, Acta Cryst. Sect. A., 1977, 33, 216-218.

24 M. Prehm, F. Liu, X. Zeng, G. Ungar and Carsten Tschierske, J. Am. Chem. Soc., 2011, **133**, 4906–4916.