Design, synthesis, and self-assembly behavior of C_3-symmetry discotic molecules *via* click chemistry

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We prepared a series of C_3-symmetry discogens with three 1,2,3-triazoles and a central benzene ring by a copper-catalyzed “click reaction” between 1,3,5-triethynylbenzene and 3,4,5-trialkoxybenzyl azides. According to the differential scanning calorimetry (DSC) data, compounds with octyl and dodecyl peripheries showed stable liquid crystalline (LC) phases at room temperature, and upon heating underwent an isotropization at 105.3 °C and 92.2 °C, respectively. Compound with octadecyl peripheries melted into a LC phase at 63.5 °C, and changed into a disordered liquid at 84.4 °C. As characterized by optical polarized microscopy (POM) and X-ray scattering techniques, all LC phases revealed hexagonally packed columns, the axes of which are aligned vertically on the glass substrate. Interestingly, the experimentally accessible crystalline phase of the compound with octadecyl chains kept the 2-D hexagonal columnar structure, although the interdisc distance within the columns changed at the transition from the LC to crystalline phase.

Introduction

Discotic liquid crystals, referred as discogens, consisting of a flat aromatic core and flexible peripheral chains are well-known to form columnar mesophases by the stacking of anisotropic disc-like cores. The self-assembling characteristic of discogens has been attracting growing interest because it is able to provide a one-dimensional conducting pathway for electrons, photons or energy *via* the large π-overlap of adjacent aromatic cores.[1] In this regard, it would be interesting to prepare novel discotic liquid crystals, and investigate their mesomorphic behavior.

Click chemistry, *i.e.*, a copper catalyzed [2 + 3] cycloaddition reaction between organic azides and alkynes, has been increasingly used in various chemistry fields, due to its outstanding merits such as high conversion and no side products.[2] Recently, click chemistry has become of great importance to macromolecular chemistry, because a number of research groups have employed this chemistry in the preparation of block copolymers and cyclic, side chain and dendritic polymers.[3]

Meanwhile, click chemistry could be a powerful tool for the design of liquid crystal (LC) molecules, because the formed heterocyclic 1,2,3-triazole has a planar structure and high chemical/thermal stability. Thus, by direct conjugation with other aromatic rings, a molecular anisotropy (a pre-requisite for LC formation) can be achieved. Nevertheless, only a few LC molecules created through the use of click chemistry have been reported, and all of them were calamitic molecules showing smectic or nematic LC phases.[4] Particularly, as far as we know, there is no discotic LC example based upon the efficient click chemistry.

With this in mind, we designed C_3-symmetry discotic molecules **A-C** assisted by click chemistry. As shown in Fig. 1, the discotic molecules consist of the conjugated aromatic core containing three 1,2,3-triazoles connected to the central benzene ring, and to this disc-type mesogen, three 3,4,5-trialkoxybenzyl units are linked. It is interesting note that the three heterocylic triazoles are formed by one-step click chemistry from non-mesogenic azide and alkyne units, thus the extension to the discotic mesogen can be easily accomplished. In this article, we report the synthesis, and self-assembling behavior of discotic molecules **A-C**, as characterized by optical polarized microscopy (POM) and X-ray scattering experiments.

Synthesis

The synthesis began with the alkylation of propyl gallate with octyl, dodecyl, and octadecyl bromides for **2a-c**, respectively. Subsequent reduction, bromination/or chlorination, and azidation reactions yielded azide-terminated precursors (**4a-c**) for a click reaction (Scheme 1(a)).[5] During these reactions, benzyl halide intermediates seemed to be labile during the silica column chromatographies, thus without performing the complete

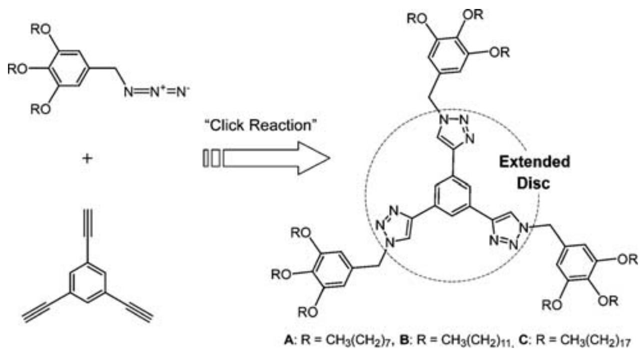

Fig. 1 Design concept *via* click chemistry, and molecular structures of **A-C** with the extended triazole-based disc.

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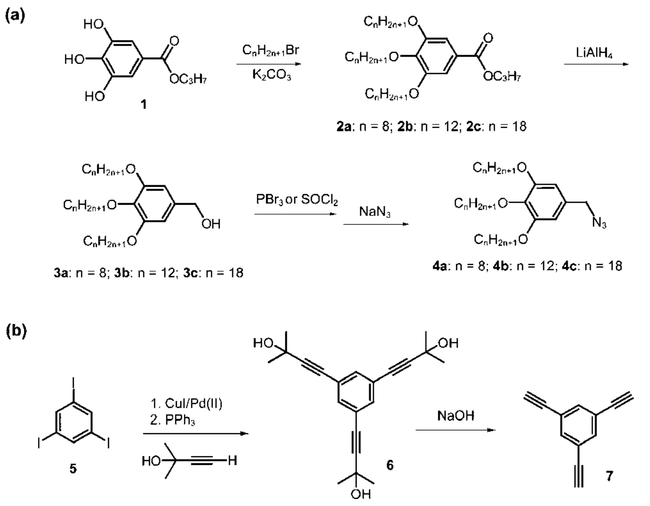

Scheme 1 Synthesis of (a) the azide precursor, and (b) the alkyne precursor for click reaction.

purification of them, the azidation reaction with sodium azide was implemented. The aromatic core precursor, 1,3,5-triethylnylbenzene (**7**), was prepared by the Sonogashira coupling reaction of 1,3,5-triiodobenzene (**5**) with 2-methylbut-3-yn-2-ol, and subsequent deprotection of compound **6** (Scheme 1(b)).[6] The final discotic molecules were obtained by a click reaction of the obtained azide and alkyne precursors using Cu(I)Br and 2,2′-bipyridine as catalysts, as shown in Fig. 1.[7]

The discotic molecules were characterized by ^{1}H- and ^{13}C-NMR spectroscopies, elemental analysis, and gel permeation chromatography. The ^{1}H-NMR spectrum of compound **A** displayed a signal for the protons in the triazoles at 7.86 ppm, and other aromatic protons and benzyl methylene protons could be assigned as might be expected (Fig. 2(a)). In addition, eight distinct carbon signals appeared in the aromatic region of the ^{13}C-NMR spectrum of **A** (Fig. 2(b)), which corroborates the formation of the designed extended aromatic disc. All discotic molecules showed narrow polydispersities (M_w/M_n) of 1.01 in gel permeation chromatography (GPC) data, indicative of high purities (Fig. 2(c)).

Thermotropic behavior

The phase transitions of **A-C** were detected by differential scanning calorimetry (DSC) and POM observations. Fig. 3 represents the second heating and first cooling DSC thermograms of **A-C** in a temperature range of −60 °C–120 °C. Increasing the length of the alkyl peripheries leads to a gradual decrease of the LC-to-liquid phase transition temperature. On the other hand, the crystal (K)-to-LC phase transition temperature steeply increases as the alkyl chain length increases. Compounds **A** and **B** showed stable LC phases at room temperature, and particularly, the former did not crystallize even at −60 °C, and its LC phase persisted to 105.3 °C.

To identify the LC phases, we observed the POM textures of **A-C** in the melt, as represented in Fig. 4(a)–(c). On cooling from the isotropic liquid to the LC phase, they all showed similar optical textures with fan-like or dendritic domains in the dark background. These optical textures are typically found in the hexagonal columnar LC phase of discotic liquid crystals.[8]

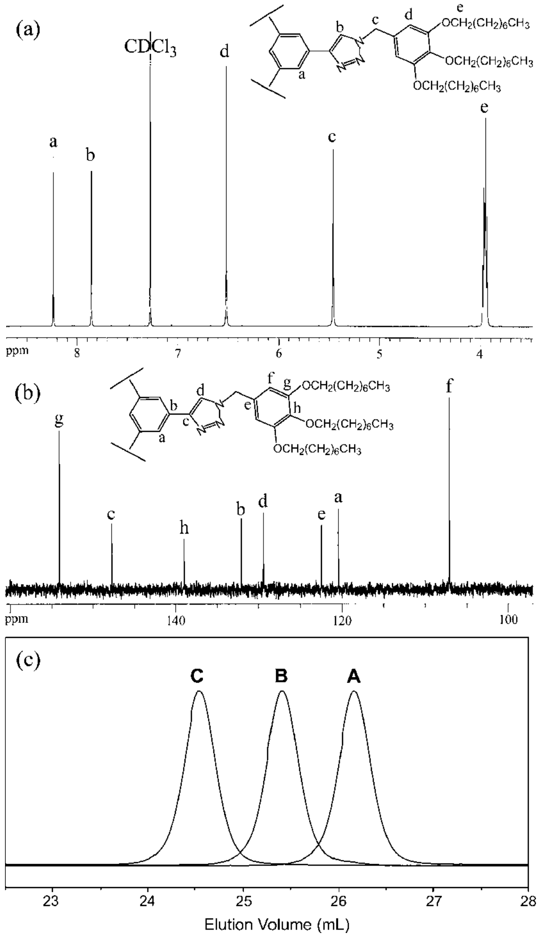

Fig. 2 (a) ^{1}H- and (b) ^{13}C-NMR spectra of **A**, and (c) the GPC elugrams of **A-C**.

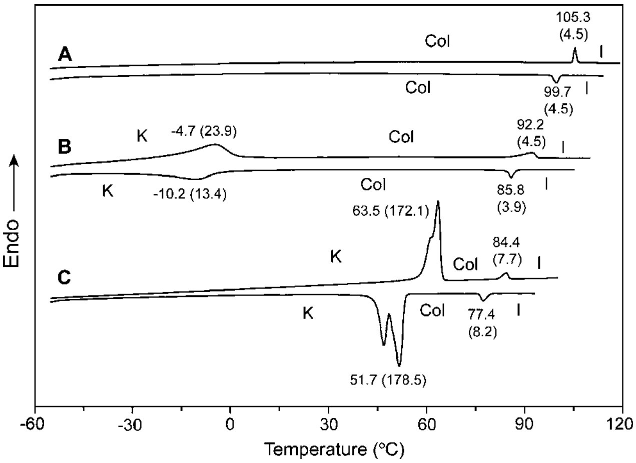

Fig. 3 DSC traces of **A-C**. K = crystalline, Col = hexagonal columnar, I = isotropic liquid. Temperature is given in °C, and the values in the parentheses are the corresponding enthalpy changes (kJ mol^{-1}).

Interestingly, on further cooling, the dark background did not become birefringent in the LC phases, suggesting that the columns occupying the background prefer the orientation perpendicular to the glass substrate.

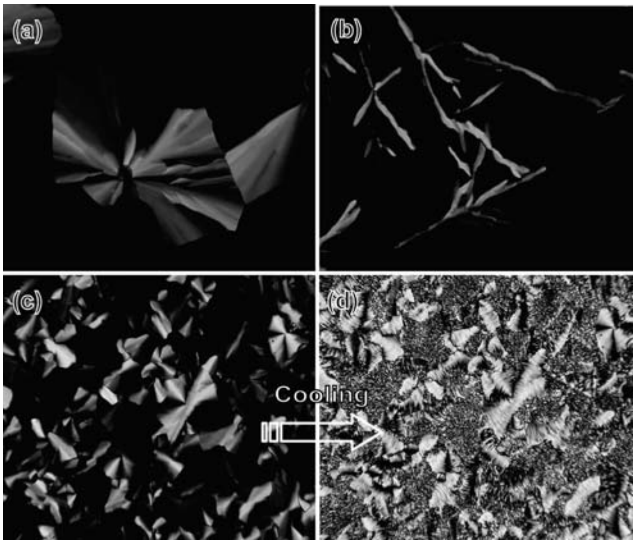

Fig. 4 The optical textures of (a) **A** at 80 °C, (b) **B** at 70 °C, and (c,d) **C** at 70 °C and 40 °C.

Compound **C** has an experimentally accessible crystalline phase, thus we investigated the variation of the optical texture at the transition from the LC to crystalline phase. Upon the crystallization, the dark areas became birefringent, which confirms the homeotropic alignment of columns in the dark area between two glass, as observed in **A** and **B**. Several discotic LC molecules containing heteroatoms on aromatic cores/or side chains have been reported to have a strong tendency to form such a homeotropic alignment, and the driving force of which might be the polar interaction of the heteroatoms with the glass surface.[9] On the other hand, the fan-like domains in the hexagonal columnar LC phase still persisted in the crystalline phase (Fig. 4(d)). This suggests that the supramolecular hexagonal ordering is kept at the phase transition.[10]

X-Ray scattering characterization

In order to characterize the microstructural details, we carried out X-ray scattering experiments. Fig. 5(a) represents the small angle X-ray scattering (SAXS) data of **A-C**. Compound **A** at 25 °C exhibited three reflections with q-spacing ratios of $1:\sqrt{3}:\sqrt{4}$, which can be interpreted as a 2-dimensional hexagonal columnar structure with the intercolumnar distance (**a**) of 3.05 nm. However, compund **B** displayed only one strong reflection at 2.04 nm^{-1}, with which the structure was not accurately assigned. Thus, to identify it, we plotted the intercolumnar distances (**a**) as a function of [molecular weight]$^{1/2}$. As observed in Fig. 5(b), the plot showed a linear dependence and the extrapolation to $\mathbf{a} = 0$ gave [molecular weight]$^{1/2} = 0$.[11] This suggested that the LC phase of **B** analogous to the hexagonal structure shown in **A**. Together with the pseudo-focal conic texture of **B** from the POM observation, it was concluded that the LC phase of **B** is a hexgaonal columnar structure.

Likewise, compound **C** in the LC phase at 65 °C showed a hexagonal columnar structure, the intercolumnar distance (**a**) of which is estimated to be 4.10 nm. Interestingly, on cooling to the crystalline phase at 25 °C, the SAXS pattern did not alter, indicating that the hexagonal ordering is maintained over the entire ordered state, which is consistent with the POM observations. This supramolecular structural retention in the crystalline phase is particularly important when considering the optical and electrical applications of discotic molecules.[12]

Along with the SAXS investigation in the crystalline and LC phases of compound **C**, we performed wide angle X-ray scattering (WAXS) experiments to examine the interdisc distance in each phase (Fig. 6(a)). According to the WAXS data in the crystalline phase, discs within a column were interpreted to stack with a periodic distance of 4.0 Å which is due to the π–π stacking of aromatic cores. On the other hand, only a diffused halo at 4.5 Å was detected in the LC phase. This dimension is characteristic of the liquid-like aliphatic chains.[13] From these WAXS results, we speculated that this variation of interdisc distance upon melting may significantly influence the intercolumnar distance determined from the SAXS data. In this regard, we examined the principal d-spacing, $d_{(10)}$, of compound **C** as a function of temperature (Fig. 6(b)). In the crystalline phase (K), $d_{(10)}$ increased as temperature increased. This can be elucidated by the fact that upon heating the amorphous region of

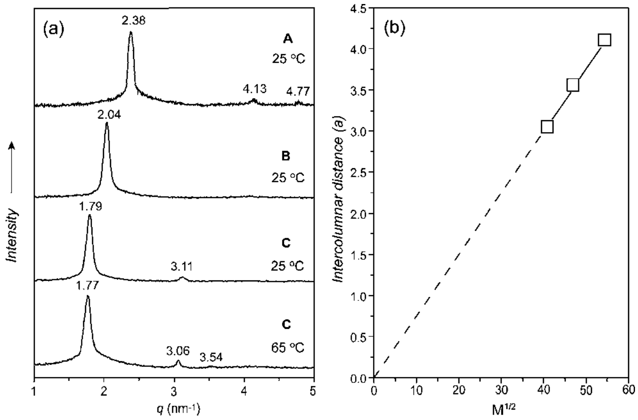

Fig. 5 (a) Small angle X-ray scattering (SAXS) data of **A-C**, and (b) the dependence of the intercolumnar distance (**a**) upon M$^{1/2}$ (M = molecular weight).

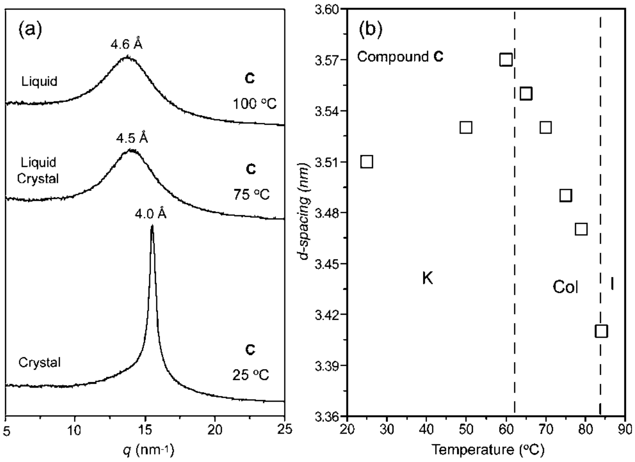

Fig. 6 (a) Wide angle X-ray scattering (WAXS) data of **C** at various temperatures and (b) the dependence of principal d-spacing, $d_{(10)}$, upon temperature for compound **C**.

semi-crystalline octadecyl chains 2-dimensionally expands by keeping the constant interdisc distance of 4.0 Å. In contrast to the crystalline phase, $d_{(10)}$ in the LC phase decreased with increasing temperature. This might be because the interdisc distance is not fixed in the molten state, but it may be increased by flexible alkyl chains which tend to have less stretched conformations at higher temperatures.[14] Consequently, it can be said that in the LC phase, the intercolumnar distance decreases as the interdisc distance increases along the columnar axis.

Conclusions

A series of C_3-symmetry discotic molecules **A-C** with octyl, dodecyl and octadecyl chains, respectively, were synthesized with the aid of an efficient click reaction. By performing the click reaction once, the extension to a conjugate discotic mesogen consisting of three 1,2,3-triazoles and a central benzene ring was easily achieved. Their thermotropic properties were characterized by DSC technique. As the peripheral alkyl chain was elongated, the isotropization temperature decreased, while the crystal melting temperature increased. Discotic molecules **A-C** exhibited stable LC phases on both heating and cooling scans. The observed LC phases were revealed as 2-D hexagonal columnar structures. Interestingly, **A-C** all showed a strong tendency to align homeotropically on the glass substrate, which may be potentially utilized for pattern-applications on distinctly chemically modified surfaces.[15] Unlike **A** and **B**, the crystalline phase of **C** was experimentally accessible, and thus characterized by SAXS and WAXS techniques. Interestingly, the crystalline phase maintained the 2-D hexagonal columnar structure like its LC phase, although the interdisc distance varied at the transition from LC to crystalline phase. It should be noted that the LC molecules in this study, to the best of our knowledge, are the first example to apply the "click chemistry" for the preparation of "discotic LC" materials showing columnar assemblies. Currently, structural modifications using the triazole-based discotic motif shown in this study are in progress for various materials applications.

Experimental

General methods

^{1}H-, and ^{13}C-NMR spectra were recorded from a $CDCl_3$ solution using Varian 200 and Bruker AM 500 spectrometers. The purity of the products was checked by thin-layer chromatography (TLC; Merck, silica gel 60). Gel permeation chromatography (GPC) measurements were conducted in THF and N,N′-dimethylacetamide (99.9%) (98 : 2 volume ratio) using a Waters 401 instrument equipped with Stragel HR 2,3 columns and Shodex AT-8045 at a flow rate of 1.0 mL min^{-1}. X-Ray scattering measurements were performed in transmission mode with synchrotron radiation at the 10C1 beam line of the Pohang Accelerator Laboratory (PAL), Korea. The sample was held in an aluminium sample holder with films on both sides. Microanalyses were performed with a Perkin Elmer 240 elemental analyzer at the Organic Chemistry Research Center, Sogang University, Korea. The compounds were purified by column chromatography (silica gel) and prep-HPLC (Japan Analytical Instrument).

Synthesis

Analogous/or idendtical compounds to **2a-c**, **3a-c**, **6** and 7 were synthesized previously, and the related experimental data were described elsewhere.[5d,6b] Here, we presented the synthetic procedures and spectroscopic data of **4a-c** and the final compounds (**A-C**).

Synthesis of 3,4,5-trialkoxybenzyl-N_3 (4a-c)

Although **4a** and **4b-c** were mediated *via* bromination and chlorination, respectively, the synthesis procedures for **4a-c** were almost identical, thus **4a** is described here as a representative example. To a stirred solution of 3,4,5-trioctyloxybenzyl alcohol (**3a**) (5.3 g, 10.8 mmol) in dichloromethane (20 mL) was added a solution of PBr_3 (5.8 g, 21.5 mmol) in dichloromethane (21.5 mL) at 0 °C. The reaction mixture was stirred 3 h at room temperature, and then quenched with water. The mixture was extracted with dichloromethane and deionized water three times, and then dried over $MgSO_4$. Without further purification, the brominated compound (2.7 g, 4.9 mmol) and sodium azide (1.6 g, 24.3 mmol) were dissolved in 5 mL of anhydrous DMF. The reaction mixture was heated at 100 °C for 3 days under N_2 atmosphere. The reaction mixture was extracted with dichloromethane and deionized water three times, and then dried over $MgSO_4$. After removing dichloromethane in a rotary evaporator, the resulting mixture was purified by a silica gel column chromatography to hexane–ethyl acetate = 20 : 1 as the eluent, to yield 1.84 g (73.1%). ^{1}H-NMR ($CDCl_3$, δ, ppm): 6.48 (s, Ar–*H*), 4.24 (s, CH_2N_3), 3.91–4.00 (m, CH_2OAr), 1.70–1.84 (m, CH_2CH_2OAr), 1.29–1.46 (m, $CH_3(CH_2)_5CH_3$), 0.88 (t, J = 6.2 Hz, $(CH_2)_7CH_3$).

3,4,5-Tridodecyloxybenzyl-N_3 (4b). Yield: 75.1% ^{1}H-NMR ($CDCl_3$, δ, ppm): 6.48 (s, Ar–*H*), 4.24 (s, CH_2N_3), 3.91–4.00 (m, CH_2OAr), 1.67–1.83 (m, CH_2CH_2OAr), 1.26–1.46 (m, $CH_3(CH_2)_5CH_3$), 0.88 (t, J = 6.4 Hz, $(CH_2)_7CH_3$).

3,4,5-Trioctadecyloxybenzyl-N_3 (4c). Yield: 69.7% ^{1}H-NMR ($CDCl_3$, δ, ppm): 6.48 (s, Ar–*H*), 4.24 (s, CH_2N_3), 3.91–4.00 (m, CH_2OAr), 1.67–1.83 (m, CH_2CH_2OAr), 1.26–1.46 (m, $CH_3(CH_2)_5CH_3$), 0.88 (t, J = 6.6 Hz, $(CH_2)_7CH_3$).

Synthesis of dicotic molecules (A-C)

B and **C** were prepared in a similar manner, thus **A** is described here as a representative example. 1,3,5-Triethynylbenzene (**7**) (0.12 g, 0.8 mmol), azide-functionalized compound (**4**) (1.32 g, 2.56 mmol), 2,2′-dipyridyl (1.25 g, 7.99 mmol) and copper(I)-bromide (0.92 g, 6.39 mmol) were dissolved in 5 mL of anhydrous THF. The reaction mixture was degassed three times by freeze-pump-thaw cycles. The mixture was heated at 50 °C for two days with stirring. The mixture was extracted with deionized water and dichloromethane. The solvent was removed by a rotary evaporator, and the remaining azide-functionalized compound (**4**) was removed by the silica gel column chromatography using dichloromethane–ethyl acetate = 8 : 1 as the eluent, and the crude product was then purified by a HPLC (Japan Analytical Industry), to yield 0.88 g (64.7%). ^{1}H-NMR (500 MHz, $CDCl_3$, δ, ppm): 8.24 (s, Ar-*H*), 7.86 (s, *H*-triazole), 6.52 (s, benzyl-*H*), 5.46

(s, ArCH_2), 3.94–3.98 (m, CH_2OAr), 1.74–1.82 (m, CH_2CH$_2$OAr), 1.44–1.50 (m, CH_2(CH$_2$)$_4$CH$_3$), 1.28–1.34 (m, CH$_2$(CH_2)$_4$CH$_3$), 0.88 (t, J = 11.5 Hz, (CH$_2$)$_7$CH_3). ^{13}C-NMR (125 MHz, CDCl$_3$, δ, ppm): 153.96, 147.6, 138.9, 132.0, 129.3, 122.4, 120.3, 107.0, 73.7, 69.5, 55.0, 32.1, 32.0, 30.6, 29.8, 29.6, 29.5, 26.3, 22.9, 22.9, 14.3. Anal. Calcd for $C_{105}H_{171}N_9O_9$: C, 74.03; H, 10.12; N, 7.40, Found: C, 73.97; H, 10.17; N, 7.60. M_w/M_n = 1.01 (GPC).

Discotic molecule B. Yield: 48.0%. ^{1}H-NMR (500 MHz, CDCl$_3$, δ, ppm): 8.26 (s, Ar–H), 7.88 (s, H-triazole), 6.52 (s, benzyl-H), 5.46 (s, ArCH_2), 3.94–3.98 (m, CH_2OAr), 1.72–1.82 (m, CH_2CH$_2$OAr), 1.44–1.50 (m, CH_2(CH$_2$)$_8$CH$_3$), 1.26–1.34 (m, CH$_2$(CH_2)$_8$CH$_3$), 0.88 (t, J = 7.0 Hz, (CH$_2$)$_7$CH_3). ^{13}C-NMR (125 MHz, CDCl$_3$, δ, ppm): 153.7, 147.4, 138.6, 131.5, 129.0, 122.3, 120.3, 106.7, 73.5, 69.2, 54.9, 32.0, 31.9, 30.4, 29.78, 29.76, 29.71, 29.68, 29.66, 29.47, 29.41, 29.38, 26.14, 26.11, 22.7, 14.12. Anal. Calcd for $C_{141}H_{243}N_9O_9$: C, 76.68; H, 11.09; N, 5.71, Found: C, 76.76; H, 10.99; N, 5.40. M_w/M_n = 1.01 (GPC).

Discotic molecules C. Yield: 38.0%. ^{1}H-NMR (500 MHz, CDCl$_3$, δ, ppm): 8.24 (s, Ar–H), 7.86 (s, H-triazole), 6.52 (s, benzyl-H), 5.46 (s, ArCH_2), 3.94–3.98 (m, CH_2OAr), 1.74–1.82 (m, CH_2CH$_2$OAr), 1.44–1.50 (m, CH_2(CH$_2$)$_8$CH$_3$), 1.26–1.32 (m, CH$_2$(CH_2)$_{14}$CH$_3$), 0.89 (t, J = 7.0 Hz, (CH$_2$)$_7$CH_3). ^{13}C-NMR (125 MHz, CDCl$_3$, δ, ppm): 153.7, 147.4, 138.6, 131.7, 129.0, 122.2, 120.1, 106.7, 73.5, 69.2, 54.8, 31.9, 30.4, 29.80, 29.78, 29.74, 29.68, 29.67, 29.48, 29.41, 29.38, 26.14, 26.12, 22.7, 14.1. Anal. Calcd for $C_{195}H_{351}N_9O_9$: C, 78.97; H, 11.93; N, 4.25, Found: C, 78.98; H, 12.23; N, 4.13. M_w/M_n = 1.01 (GPC).

Acknowledgements

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References

1 S. Sergeyev, W. Pisula and Y. H. Geerts, *Chem. Soc. Rev.*, 2007, **36**, 1902.

2 V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2002, **41**, 2596.

3 (*a*) G. Franc and A. Kakkar, *Chem. Commun.*, 2008, 5267; (*b*) D. Fournier, R. Hoogenboom and U. S. Schubert, *Chem. Soc. Rev.*, 2007, **36**, 1369; (*c*) B. A. Laurent and S. M. Grayson, *J. Am. Chem. Soc.*, 2006, **128**, 4238; (*d*) J. Geng, J. Lindqvist, G. Mantovani and D. M. Haddleton, *Angew. Chem., Int. Ed.*, 2008, **47**, 4180; (*e*) C. N. Urbani, C. A. Bell, M. R. Whittaker and M. J. Monteiro, *Macromolecules*, 2008, **41**, 1057; (*f*) P. Wu, A. K. Feldman, A. K. Nugent, C. J. Hawker, A. Scheel, B. Voit, J. Pyun, J. M. J. Fréchet, K. B. Sharpless and V. V. Fokin, *Angew. Chem., Int. Ed.*, 2004, **43**, 3928.

4 (*a*) H. Gallardo, F. Ely, A. J. Bortoluzzi and G. Conte, *Liq. Cryst.*, 2005, **32**, 667; (*b*) Z. Cui, Y. Zhang and S. He, *Colloid Polym. Sci.*, 2008, **286**, 1553; (*c*) Y. Xia, R. Verduzco, R. H. Grubbs and J. A. Kornfield, *J. Am. Chem. Soc.*, 2008, **130**, 1735; (*d*) C. Saravanan, S. Senthil and P. Kannan, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 7843; (*e*) D. Srividhya, S. Manjunathan, S. Thirumaran, C. Saravanan and S. Senthil, *J. Mol. Struct.*, 2009, **927**, 7.

5 (*a*) V. S. K. Balagurusamy, G. Ungar, V. Percec and G. Johansson, *J. Am. Chem. Soc.*, 1997, **119**, 1539; (*b*) Y.-W. Chung, J.-K. Lee, W.-C. Zin and B.-K. Cho, *J. Am. Chem. Soc.*, 2008, **130**, 7139; (*c*) M. Yoshio, T. Mukai, H. Ohno and T. Kato, *J. Am. Chem. Soc.*, 2004, **126**, 994; (*d*) K. Tanabe, T. Yasuda, M. Yoshio and T. Kato, *Org. Lett.*, 2007, **9**, 4271.

6 (*a*) C. Mechtler, M. Zirngast, W. Gaderbauer, A. Wallner, J. Baumgartner and C. Marschner, *J. Organomet. Chem.*, 2006, **691**, 150; (*b*) J. G. Rodríguez, J. Esquivias, A. Lafuente and C. Díaz, *J. Org. Chem.*, 2003, **68**, 8120.

7 L. Mespouille, M. Vachaudez, F. Suriano, P. Gerbaux, O. Coulembier, P. Degee, R. Flammang and P. Dubois, *Macromol. Rapid Commun.*, 2007, **28**, 2151.

8 (*a*) J. J. van Gorp, J. A. J. M. Vekemans and E. W. Meijer, *J. Am. Chem. Soc.*, 2002, **124**, 14759; (*b*) V. Percec, W.-D. Cho, P. E. Mosier, G. Ungar and D. J. P. Yeardley, *J. Am. Chem. Soc.*, 1998, **120**, 11061; (*c*) M. Kölbel, T. Beyersdorff, C. Tschierske, S. Diele and J. Kain, *Chem.–Eur.J.*, 2000, **6**, 3821.

9 (*a*) J. M. Kroon, R. B. M. Koehorst, M. van Dijk, G. M. Sanders and E. J. R. Sudhölter, *J. Mater. Chem.*, 1997, **7**, 615; (*b*) H. Bock, A. Babeau, I. Seguy, P. Jolinat and P. Destruel, *ChemPhysChem*, 2002, **3**, 532; (*c*) A. N. Cammidge and H. Gopee, *J. Mater. Chem.*, 2001, **11**, 2773.

10 (*a*) M. Lee, D.-W. Jang, Y.-S. Kang and W.-C. Zin, *Adv. Mater.*, 1999, **11**, 1018; (*b*) L. Y. Jin, J.-H. Ahn and M. Lee, *J. Am. Chem. Soc.*, 2004, **126**, 12208.

11 (*a*) H. C. Holst, T. Pakula and H. Meier, *Tetrahedron*, 2004, **60**, 6765; (*b*) B.-K. Cho, A. Jain, J. Nieberle, S. Mahajan, U. Wiesner, S. M. Gruner, S. Türk and H. J. Räder, *Macromolecules*, 2004, **37**, 4227.

12 H. Eichhorn, D. W. Bruce and D. Wöhrle, *Adv. Mater.*, 1998, **10**, 419.

13 (*a*) S. Kumar, D. S. S. Rao and S. K. Prasad, *J. Mater. Chem.*, 1999, **9**, 2751; (*b*) I. Bury, B. Heinrich, C. Bourgogne, D. Guillon and B. Donnio, *Chem.–Eur. J.*, 2006, **12**, 8396; (*c*) M. Lehmann, M. Jahr and J. Gutmann, *J. Mater. Chem.*, 2008, **18**, 2995.

14 G. Ungar, V. Percec, M. N. Holerca, G. Johansson and J. A. Heck, *Chem.–Eur. J.*, 2000, **6**, 1258.

15 M. Yoshio, T. Kagata, K. Hoshino, T. Mukai, H. Ohno and T. Kato, *J. Am. Chem. Soc.*, 2006, **128**, 5570.