Click Chemistry Applied in the Synthesis of Symmetrical Triphenylene-Based Discotic Liquid-Crystalline Dimers

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Abstract: Symmetrical triphenylene dimers connected by a bis-triazole moiety have been synthesized and characterized. The bis-triazole part is formed as final step utilizing a straightforward double click reaction (CuAAC) allowing further structural variations of the linker. The 1,3-bis(triazol-1-yl)propyltriphenylene-based dimer display columnar mesophase over a wide range of temperatures starting at ambient temperature.

Key words: discotic, columnar mesophase, liquid-crystal dimer, triphenylene, click chemistry, azide–alkyne cycloaddition

Creating electronically useful micro- or nanostructures on flexible surfaces is the motivation for many research projects varying the structures of liquid-crystal-forming molecules. These studies try to reveal the design principles in view of a more rational approach to new useful materials. Most of these research projects are based on structure-property correlations. Discotic liquid crystals (DLCs), in particular, have received great attention in this context.¹ The self-organization of discotic molecules into columnar structures provides a one-dimensional pathway for charge migration, which make them promising candidates for application in flexible optoelectronic devices.² In DLCs the charge transport efficacy depends strongly on the degree of order within the columnar liquid-crystalline phase.³ Various non-covalent interactions play a crucial role in the formation of LC phases.⁴ The formation of columnar liquid-crystal phases is governed by the shape anisotropy of the molecules and by the anisotropy of the intermolecular interactions, mainly the π - π and steric interactions, between the highly anisometric disc-shaped molecules.

Amongst DLCs, triphenylene derivatives have been widely studied.⁵ The disc-shaped hexapentyloxytriphenylene (HAT5) consisting of the triphenylene core peripherically substituted with flexible alkoxy side chains that selfassemble into spatially ordered systems with hexagonal columnar symmetry in a liquid-crystalline mesophase.^{5a} A strategy improving the supramolecular organization of triphenylene-based DLCs within their columnar mesophases has been the formation of dimers⁶ in order to reduce the molecular degrees of freedom. The physical properties of LC dimers are significantly different from those of monomers.⁷ The dimers often display wider LC

SYNTHESIS 2011, No. 23, pp 3801–3806 Advanced online publication: 21.10.2011 DOI: 10.1055/s-0031-1289573; Art ID: Z72711SS © Georg Thieme Verlag Stuttgart · New York domain than their corresponding monomers. Since the work of Ringsdorf's group synthesizing, for the first time, triphenylene-based LC dimers, some HAT-dimers linked via flexible spacer have been described.⁸ Increasing the rigidity of the linker decreases the degree of rotational freedom. The 'crystalline character' of rigid dimers increases and influences the formation and the character of the mesophase. Kumar et al.⁹ have shown that short and rigid diacetylene-bridged triphenylene dimers lead to the formation of less-ordered discotic nematic mesophases, showing only orientational order, but no long-range translational order.



Figure 1 Structures of the symmetrical triphenylene dimers 1 and 2 connected by the bis-triazole moiety

Despite a large body of empirical data, the prediction of the mesomorphic behavior of a new material based on its molecular structure remains a challenge. The design of novel semi-rigid dimers may provide a good opportunity to develop structure–LC property relationships via careful structural characterization of the triphenylene dimers within the columnar mesophase.

Herein, we report an efficient synthesis and the properties of the triphenylene-based dimers 1 and 2 (Figure 1) containing a bis-triazole moiety, which were obtained via a double copper(I)-catalyzed azide–alkyne Huisgen cycloaddition.¹⁰ The advantage of using the 'click' methodology initially developed by Sharpless and his collaborators^{10a} is its ease of application, the broad scope of the reaction, and the modularity of the approach. Different central cores [1: propyl and 2: 1,4-bis(benzyl)] were used, not only to investigate the influence of the linker rigidity, but also to study the effect of an additional intermolecular π - π interaction between the central part of the spacer. We envisaged that incorporation of the phenyl moiety as a central core of the linker (compound 2) may enhance the columnar packing and might lead to a highly organized and more stable mesophase. Only dimer 1 exhibits mesogenic behavior over a wide temperature range (10 °C Col_h 153 °C I).

Since the 1960s, interest in the chemistry of triphenylenes has increased continuously. Pérez and Guitián¹¹ have recently reviewed the most useful strategies for the synthesis of triphenylenes. Oxidative trimerization of catechol derivatives¹² has been shown to be the method of choice for the synthesis of the symmetrically substituted 2,3,6,7,10,11-hexaalkoxytriphenylenes, such as **6**. We synthesized the discotic building block **7** in four steps in 10% overall yield from catechol (Scheme 1), an inexpensive and widely available starting material.



Scheme 1 Reaction conditions: (a) 1-bromohexane, K_2CO_3 , EtOH, reflux, 24 h, 90%; (b) MoCl₅, SiCl₄, CH₂Cl₂, -80 °C to -20 °C, 30 min, 88%; (c) 2-bromo-1,3,2-benzodioxaborole, CH₂Cl₂, 0 °C to r.t., 24 h; (d) propargyl bromide, K_2CO_3 , EtOH, reflux, 16 h, 12% (2 steps).

Catechol was alkylated to give 1,2-bis(hexyloxy)benzene (5). Oxidative trimerization of 5 was initially attempted by applying the procedure described by Kumar and Manickam^{12d} [MoCl₅ (1.0 equiv), CH₂Cl₂, r.t.], but this gave a poor yield in our hands compared to the reference.¹³ Lewis acids are known to enhance the power of oxidizing agents,^{14a} because they induce the removal of a ligand from the oxidatively active metal center; the resulting electrophilic species becomes a more efficient oxidant. The scope and efficiency of oxidative coupling reactions using molybdenum(V) chloride can be significantly improved by employing Lewis acidic additives such as TiCl₄, SnCl₄, or SiCl₄.^{14b} Compound **6** can be obtained in 88% yield under optimized conditions using an equimolar amount of silicon tetrachloride relative to mo-

lybdenum(V) chloride. The best result was obtained when **5** is added to a solution of molybdenum(V) chloride/silicon tetrachloride (1:1) in dichloromethane at -80 °C and the reaction mixture is stirred at -20 °C for 30 minutes. Recently, Cammidge et al.^{12j} have reported an optimized protocol for the synthesis of monohydroxy-pentaalkoxy-triphenylene. The reaction is performed carefully at 0 °C to provide a reasonable rate for the oxidative trimerization and minimize further hydrolysis of the product.

Selective ether cleavage¹⁵ was achieved with 2-bromo-1,3,2-benzodioxaborole in dichloromethane to give the pentakis(hexyloxy)triphenylene-monool in a complex mixture of the diol and the triol regioisomers that could not be separated efficiently. The crude mixture was filtered through a pad of silica gel to remove the catechol generated after quenching with cold water. The mixture of triphenylene-monool, -diol, and -triol was directly treated with propargyl bromide and potassium carbonate in ethanol at reflux to give the corresponding mono-, bis-, and tris-propargyl ether derivatives. In contrast to the partially deprotected triphenylen-ols, compound 7 could be isolated by chromatography on silica gel. The crude 7 was purified by recrystallization in ethanol to give a moderate yield of 12% after two steps.

The model dimers 3 and 4 were synthesized using a double copper(I)-catalyzed azide-alkyne Huisgen cycloaddition between the (prop-2-ynyloxy)benzene and the respective bis-azido derivative (Scheme 2). These reactions were carried out using copper sulfate pentahydrate (0.2 equiv) and sodium ascorbate (0.6 equiv) in tetrahydrofuran-water (1:1) mixture at room temperature. Dimers 3 and 4 could be obtained in 96% and 58% yields, respectively. The same conditions were applied to the synthesis of the triphenylene dimers 1 and 2, which were obtained in 40% and 11% yields, respectively. The crude dimers 1 and 2 were purified by column chromatography followed by preparative TLC and then recrystallized (EtOAc-EtOH, 1:1). The low yield obtained for 2 is due to the formation of a non-characterized side-product that was difficult to separate.

A preliminary study of the liquid crystalline behavior of the dimers 1 and 2 was performed by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC) (Table 1). Compound 1 exhibits a liquid-crystal phase where conic fan-shaped texture (pseudofocal conic motif) is observed (Figure 2). The texture is characteristic of a hexagonal columnar mesophase (Col_b). The mesophase is stable over a wide temperature range (10 $^{\circ}$ C Col_b 153 °C I), as is apparent from the result obtained by DSC where no crystallization took place on cooling (Figure 3). In contrast, compound 2 did not show any mesomorphic behavior. Different reasons can be evoked, tracing back the behavior either to a destabilization of the mesophase or to a stabilization of the crystals. According to Kumar,¹⁶ who described analogous compounds, the incorporation of a rigid aromatic ring reduces the flexibility of the linker and renders the stacking of the triphenylene cores more difficult. The stiffened linker of compound 2 forces the



Scheme 2 Reaction conditions: (a) $CuSO_4.5$ H₂O, sodium ascorbate, THF, r.t., 16 h.

two triphenylene units into a stepped linearized arrangement. This will hinder the effective space filling in the zone occupied by the side chains lacking the flexibility to reconfigure optimally.¹⁷ The side chains tend to interdigitize optimizing the filling of the space between the triphenylene columns.¹⁸ The stiffened linker of compound 2 imposes an elongated intercolumnar spacing. Finally the presence of the three aligned aromatic rings in the central part of the linker generates the opportunity for further intermolecular interactions. The relatively large enthalpy value corresponding to the melting transition of 2 (Table 1, entry 2) $\Delta H_{(Cr \rightarrow I)} = 58.1 \text{ kJ} \cdot \text{mol}^{-1}$ may be tentatively attributed to additional interactions in the solid phase. In contrast to this observation the model compound 4 exhibits a lower enthalpy than 3, however at higher melting point (mp 146 °C) than 3 (mp 129 °C) (Table 1, entries 3 and 4).

In conclusion, we have reported a convenient and modular synthesis of triphenylene discotic dimers 1 and 2. Using a double copper(I)-catalyzed azide–alkyne Huisgen cyclo-addition to assemble the dimer in the last step offers easy

Table 1 'Click' Reaction Yields and LC Profile of Dimers 1-4

Compound	Yield (%)	Transition temperature ^a (°C)
1	40	$10 \text{ Col}_{h} 153 (\Delta H = 26.4 \text{ kJ} \cdot \text{mol}^{-1}) \text{ I}$
2	11	Cr 154 (Δ H = 58.1 kJ·mol ⁻¹) I
3	96	Cr 129 (ΔH = 45.0 kJ·mol ⁻¹) I
4	58	Cr 146 (ΔH = 39.4 kJ·mol ⁻¹) I



 Col_h = hexagonal columnar mesophase; I = isotropic liquid. For 1 the phase below 10 °C has not been identified.



Figure 2 Polarized optical microscopy image of dimer 1 obtained at 143.5 °C on cooling from the isotropic liquid



Figure 3 DSC trace of triphenylene discotic dimer 1 obtained on second heating run (rate $10 \text{ }^{\circ}\text{C/min}$)

access to further structural variation on the linker. The design of dimer 1 promotes the formation of hexagonal columnar mesophase (Col_h) over a wide temperature range (10 °C Col_h 153 °C I). Comparison of the different behaviors observed for 1 and 2 restricts the rigidity of the linkers acceptable for mesogenic triphenylene dimers.

All moisture-sensitive reactions were carried out under argon using oven-dried glassware. Purchased chemicals were used without further purification. CH₂Cl₂ was purchased from Sigma-Aldrich with the grade puriss., absolute, over molecular sieves (H₂O $\leq 0.005\%$), 99.5% (GC). Other solvents were freshly distilled prior to use. 2-Bromo-1,3,2-benzodioxaborole and MoCl₅ were purchased from Sigma-Aldrich in purum grade, 97.0% (AT) and 95% purity respectively. Compounds 1,3-bis(azido)propane,19 1,4-bis(azidomethyl)benzene20 were synthesized according to known procedures. TLC: Merck 60 F254 acid silica gel coated or neutral alumina-coated Al-plates; detection by UV light (254 nm) or with basic KMnO₄ soln. Chromatography columns were carried out on silica gel 60 A, 32-63 (Brunschwig). NMR spectra are referenced to the solvent. ¹H and ¹³C NMR spectra were recorded on Bruker Avance-400 (400 and 100 MHz) at 298 K. COSY, DEPT 135, HSQC, and HMBC were systematically measured for all compounds to allow the attribution of all signals. MS: electrospray (ESI) mass spectra were recorded with a Finnigan LCQ mass spectrometer HRMS: Bruker FTMS 4.7T BioAPEXII measured at University of Fribourg (Switzerland) by Mr. F. Nydegger. IR spectra: Perkin Elmer FT-IR Spectrum one version B; resolution 2 cm⁻¹. Solids were analyzed as KBr pellets. Melting points were measured on a Gallenkamp melting

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point apparatus and are uncorrected. LC properties: Transition temperatures (onset point) and enthalpies were determined with a differential scanning Mettler DSC 822 calorimeter, under N₂/He, at a rate of 10 °C/min. Optical studies were conducted using a Zeiss-Axioskop polarizing microscope equipped with a Linkam-THMS-600 variable-temperature stage, under N₂.

2,3,6,7,10,11-Hexakis(hexyloxy)triphenylene (6)²¹

MoCl₅ (490 mg, 1.78 mmol) and SiCl₄ (300 mg, 1.78 mmol) were dissolved in anhyd CH₂Cl₂ (1.0 mL). The mixture was cooled to -80 °C and a soln of **5** (250 mg, 0.89 mmol) dissolved in anhyd CH₂Cl₂ (1.0 mL) was added. The mixture was stirred at -80 °C to -20 °C for 30 min. It was then poured into cold MeOH (10 mL at -20 °C) and stirred for 20 min; a white precipitate formed. The mixture was stored at -24 °C overnight. The precipitate was filtered and washed (cold MeOH) and then recrystallized (MeOH) at 0 °C to give **6** (216 mg, 88%) as a white solid.

¹H NMR (400 MHz, CDCl₃): δ = 7.84 (s, 6 H, H_{Ar}), 4.27 (t, *J* = 6.6 Hz, 12 H, OCH₂), 1.98 (quint, *J* = 6.6 Hz, 12 H, CH₂), 1.62 (m, 12 H, CH₂), 1.45 (m, 24 H, CH₂), 0.98 (t, *J* = 6.8 Hz, 18 H, CH₃).

¹³C NMR (100 MHz, CDCl₃): δ = 149.2 (C_{Ar}O), 123.8 (C_{Ar}), 107.5 (C_{Ar}H), 69.9 (OCH₂), 31.9 [O(CH₂)₃CH₂], 29.6 (OCH₂CH₂), 26.0 [O(CH₂)₂CH₂], 22.8 [O(CH₂)₄CH₂], 14.2 (CH₃).

MS (EI, 70 eV): m/z (%) = 852.2 (100) [M + Na]⁺.

2,3,6,7,10-Pentakis(hexyloxy)-11-(prop-2-ynyloxy)triphenylene (7)^{8d,e}

Compound 6 (4.52 g, 5.5 mmol) was dissolved in anhyd CH₂Cl₂ (30 mL) and cooled to 0 °C. To this was added 0.2 M 2-bromo-1,3,2benzodioxaborole in CH2Cl2 (1.3 g, 6.5 mmol) at 0 °C and the mixture was stirred at r.t. for 24 h. The mixture was poured into icewater and extracted with CH₂Cl₂; the combined organic layers were dried (Na₂SO₄). The soln was concentrated under vacuum until 5 mL and the crude was filtered through a pad of silica gel with CH₂Cl₂ (to remove the catechol from the crude). The crude was concentrated until 5 mL and then diluted with EtOH (20 mL). K₂CO₃ (1.6 g, 11.6 mmol) was added and the mixture was stirred at reflux for 15 min. Then propargyl bromide (400 mg, 3.36 mmol) was added and the mixture was stirred at reflux overnight under an inert atmosphere. The mixture was concentrated in vacuo to remove EtOH and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with NH₄Cl (50 mL), then with sat. brine (50 mL), and dried (Na₂SO₄); the solvent was evaporated under vacuum. The product was purified by column chromatography (silica gel, cyclohexane-EtOAc, 95:5) and then recrystallized (EtOH) to give 7 (512 mg, 12%, 2 steps) as a brown solid; mp (DSC) 75 °C.

IR (KBr): 3249, 2924, 2854, 1617, 1519, 1438, 1387, 1259, 1175 $\rm cm^{-1}.$

¹H NMR (400 MHz, CDCl₃): $\delta = 8.09$ (s, 1 H, H1), 7.85–7.84 (m, 5 H, H4, H5, H8, H9, H12), 4.97 (d, J = 2.1 Hz, 2 H, H2¹), 4.23 (m, 10 H, OCH₂), 2.57 (t, J = 2.1 Hz, 1 H, H2³), 1.94 (m, 10 H, CH₂), 1.57 (m, 10 H, CH₂), 1.41 (m, 20 H, CH₂), 0.95 (m, 15 H, CH₃).

¹³C NMR (100 MHz, CDCl₃): δ = 149.4, 149.3, 149.2, 149.1, 149.0 (C3, C6, C7, C10, C11), 147.0 (C2), 124.2, 123.9, 123.8, 123.7, 123.4, 123.2 (C_{Ar}), 110.1 (C1), 107.7, 107.6, 107.5, 107.4, 106.9 (C4, C5, C8, C9, C12), 79.1 (C2²), 76.0 (C2³), 70.0, 69.9, 69.8, 69.6, 69.5 (OCH₂), 58.0 (C2¹), 32.0 [O(CH₂)₃CH₂], 29.7 (OCH₂CH₂), 26.1 [O(CH₂)₂CH₂], 22.8 [O(CH₂)₄CH₂], 14.3 (CH₃). HRMS: m/z [M + Na]⁺ calcd for C₅₁H₇₄NaO₆: 806.1194; found: 806.1190.

1,3-Bis[4-(phenoxymethyl)-1*H***-1,2,3-triazol-1-yl]propane (3)** (Prop-2-ynyloxy)benzene (275 μ L, 2.14 mmol) and 1,3-diazidopropane (90 mg, 0.71 mmol) were dissolved in THF (5 mL) at r.t. A

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IR (KBr): 3139, 3096, 2929, 2874, 1603, 1587, 1497, 1461, 1252, 1235, 1054, 746, 689 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.66 (s, 2 H, H_{trz}), 7.32–7.28 (m, 4 H, H_{Ar}), 7.01–6.93 (m, 6 H, H_{Ar}), 5.23 (s, 4 H, OCH₂), 4.38 (t, *J* = 6.5 Hz, 4 H, NCH₂), 2.58 (quint, *J* = 6.5 Hz, 2 H, CH₂).

¹³C NMR (100 MHz, CDCl₃): δ = 158.1 (C_{Ar}O), 144.5 (C_{trz}), 129.5 (C_{Ar}H), 123.4 (C_{trz}H), 121.3 (C_{Ar}H), 114.7 (C_{Ar}H), 61.8 (OCH₂), 46.7 (NCH₂), 30.4 (CH₂).

HRMS: m/z [M + H]⁺ calcd for C₂₁H₂₃N₆O₂: 391.18770; found: 391.18766.

1,4-Bis{[4-(phenoxymethyl)-1*H*-1,2,3-triazol-1-yl]methyl}benzene (4)

(Prop-2-ynyloxy)benzene (15 μ L, 0.116 mmol) and 1,4-bis(azidomethyl)benzene (10 mg, 0.053 mmol) were dissolved in THF (1 mL) at r.t. A soln of sodium ascorbate (6.3 mg, 0.032 mmol) in H₂O (0.5 mL) was added followed by addition of a soln of CuSO₄·5 H₂O (2.6 mg, 0.011 mmol) in H₂O (0.5 mL). The mixture was stirred at r.t. for 16 h under an argon atmosphere. CHCl₃ (10 mL) was added and the soln was washed with 1 M aq NH₃ soln (2 × 10 mL) and brine (2 × 10 mL), and dried (MgSO₄). The solvent was evaporated off and the crude product was purified by column chromatography (silica gel, CH₂Cl₂–MeOH, 99.5:0.5 and 98:2) to afford **4** (14 mg, 58%) as a white solid; mp (DSC) 146 °C.

IR (KBr): 3076, 2929, 1602, 1588, 1498, 1466, 1252, 1213, 1055, 757, 750, 691 cm⁻¹.

¹H NMR (400 MHz, DMSO- d_6): $\delta = 8.26$ (s, 2 H, H_{trz}), 7.32 (s, 4 H, H_{Ar}), 7.28 (dd, J = 7.4, 7.9 Hz, 4 H, H_{Ar}), 7.00 (d, J = 7.9 Hz, 4 H, H_{Ar}), 6.94 (t, J = 7.4 Hz, 2 H, H_{Ar}), 5.60 (s, 4 H, NCH₂), 5.11 (s, 4 H, OCH₂).

¹³C NMR (100 MHz, DMSO-*d*₆): δ = 158.0 (C_{Ar}O), 143.1 (C_{trz}), 136.0 (C_{Ar}), 129.5 (C_{Ar}H), 128.4 (C_{Ar}H), 124.7 (C_{trz}H), 120.9 (C_{Ar}H), 114.7 (C_{Ar}H), 61.0 (OCH₂), 52.5 (NCH₂).

HRMS: m/z [M + H]⁺ calcd for C₂₆H₂₅N₆O₂: 453.20335; found: 453.20386.

1,3-Bis(4-{[3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yloxy]methyl}-1H-1,2,3-triazol-1-yl)propane (1)

Compound 7 (140 mg, 0.18 mmol) and 1,3-diazidopropane (10 mg, 0.08 mmol) were dissolved in THF (4 mL) at r.t. A soln of sodium ascorbate (10 mg, 0.05 mmol) in H_2O (2 mL) was added followed by addition of a soln of $CuSO_4 \cdot 5 H_2O$ (5 mg, 0.02 mmol) in H_2O (2 mL). The mixture was stirred at r.t. for 24 h under an argon atmosphere. CHCl₃ (10 mL) was added and the soln was washed with 1 M aq NH₃ soln (2 × 10 mL) and brine (2 × 10 mL), and dried (MgSO₄). The solvent was evaporated off and the crude product was purified by column chromatography (silica gel, CH₂Cl₂ and CH₂Cl₂–MeOH, 99.5:0.5) and preparative TLC (silica gel, CH₂Cl₂–MeOH, 98:2) followed by recrystallization (EtOAc–EtOH, 1:1) to afford **1** (54 mg, 40%) as a yellowish solid.

IR (KBr): 2956, 2930, 2858, 1618, 1518, 1468, 1437, 1391, 1262, 1168, 1042, 831 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 8.07 (s, 2 H, H1), 7.82–7.84 (m, 10 H, H4, H5, H8, H9, H12), 7.64 (s, 2 H, H_{uz}), 5.48 (s, 4 H, OCH₂),

4.28–4.20 (m, 24 H, NCH₂, OCH₂), 2.48 (quint, *J* = 6.5 Hz, 2 H, CH₂), 1.95 (m, 20 H, CH₂), 1.57 (m, 20 H, CH₂), 1.39 (m, 40 H, CH₂), 0.93 (m, 30 H, CH₃).

¹³C NMR (100 MHz, CDCl₃): δ = 149.3, 149.2, 148.9, 148.83, 148.79 (C3, C6, C7, C10, C11), 147.5 (C2), 144.7 (C_{trz}), 124.3, 123.9 (C_{Ar}), 123.6 (C_{trz}H), 123.56, 123.38, 123.17, 123.15 (C_{Ar}), 109.4 (C1), 107.5, 107.4, 107.1, 106.7, 106.5 (C4, C5, C8, C9, C12), 69.83, 69.77, 69.57, 69.36, 69.28 (OCH₂), 63.8 (OCH₂), 46.6 (NCH₂), 31.6 [O(CH₂)₃CH₂], 30.5 (CH₂), 29.4, 29.3 (OCH₂CH₂), 25.8 [O(CH₂)₂CH₂], 22.6 [O(CH₂)₄CH₂], 14.0 (CH₃).

HRMS: $m/z [M + H]^+$ calcd for $C_{105}H_{155}N_6O_{12}$: 1692.17030; found: 1692.17066.

1,4-Bis[(4-{[3,6,7,10,11-pentakis(hexyloxy)triphenylen-2yloxy]methyl}-1H-1,2,3-triazol-1-yl)methyl}benzene (2)

Compound **2** (213 mg, 0.27 mmol) and 1,4-bis(azidomethyl)benzene (23 mg, 0.12 mmol) were dissolved in CH₂Cl₂ (3 mL) at r.t. A soln of sodium ascorbate (14.7 mg, 0.07 mmol) in H₂O (1.5 mL) was added followed by addition of a soln of CuSO₄·5 H₂O (6.2 mg, 0.02 mmol) in H₂O (1.5 mL). The mixture was stirred at r.t. for 15 h under an argon atmosphere. CHCl₃ (10 mL) was added and the soln was washed with 1 M aq NH₃ soln (2 × 10 mL) and brine (2 × 10 mL), and dried (MgSO₄). The solvent was evaporated off and the crude product was purified by column chromatography (silica gel, CH₂Cl₂ and CH₂Cl₂–MeOH, 99.5:0.5) and preparative TLC (silica gel, CH₂Cl₂–MeOH, 99.5:0.5) followed by recrystallization (EtOAc–EtOH, 1:1) to afford **2** (24 mg, 11%) as a white solid.

IR (KBr): 2955, 2930, 2858, 1618, 1518, 1467, 1438, 1389, 1262, 1174, 1048, 837 $\rm cm^{-1}.$

¹H NMR (400 MHz, CDCl₃): δ = 8.04 (s, 2 H, H1), 7.84–7.80 (5 s, 10 H, H4, H5, H8, H9, H12), 7.52 (s, 2 H, H_{trz}), 7.03 (s, 4 H, H_{Ar}), 5.48 (s, 4 H, OCH₂), 5.41 (s, 4 H, NCH₂), 4.23 (m, 20 H, OCH₂), 1.93 (m, 20 H, CH₂), 1.58 (m, 20 H, CH₂), 1.39 (m, 40 H, CH₂), 0.92 (m, 30 H, CH₃).

¹³C NMR (100 MHz, CDCl₃): δ = 149.5, 149.4, 149.0, 148.9 (C3, C6, C7, C10, C11), 147.6 (C2), 145.3 (C_{trz}), 135.3 (C_{ph}), 128.6 (C_{ph}H), 124.4, 124.1, 123.8, 123.6, 123.4, 123.3 (C_{Ar}), 123.1 (C_{trz}H), 109.6 (C1), 107.7, 107.6, 107.3, 106.9, 106.6 (C4, C5, C8, C9, C12), 70.1, 70.0, 69.8, 69.6, 69.4 (OCH₂), 64.1 (OCH₂), 53.7 (NCH₂), 31.8, 31.7 [O(CH₂)₃CH₂], 29.6, 29.5, 29.4 (OCH₂CH₂), 26.0, 25.9 [O(CH₂)₂CH₂], 22.8, 22.7 [O(CH₂)₄CH₂], 14.2 (CH₃).

HRMS: $m/z [M + H]^+$ calcd for $C_{110}H_{157}N_6O_{12}$: 1754.18595; found: 1754.18534.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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