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Liquid-Crystalline Dendrimers Designed by Click Chemistry

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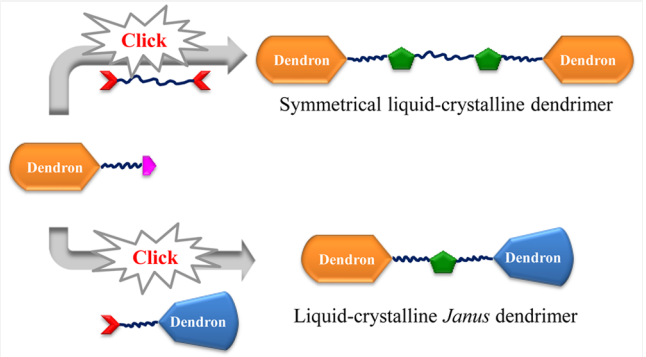
Supporting Information

ABSTRACT: Liquid-crystalline dendrimers have been prepared from second-generation Percec-type poly(benzyl ether) dendrons or second-generation poly(aryl ester) dendrons carrying cyanobiphenyl mesogens. The Janus dendrimer, which combines the two types of dendromesogens, has also been synthesized. Those compounds have been prepared under copper-catalyzed azide−alkyne cycloaddition conditions. The mesomorphic properties have been studied by thermal analysis (POM, DSC) and small-angle X-ray scattering. Smectic A, nematic, and columnar phases have been observed depending on the dendritic building blocks. The click reaction has proven to be a powerful and elegant synthetic tool for the design of complex dendritic liquid-crystalline architectures.



INTRODUCTION

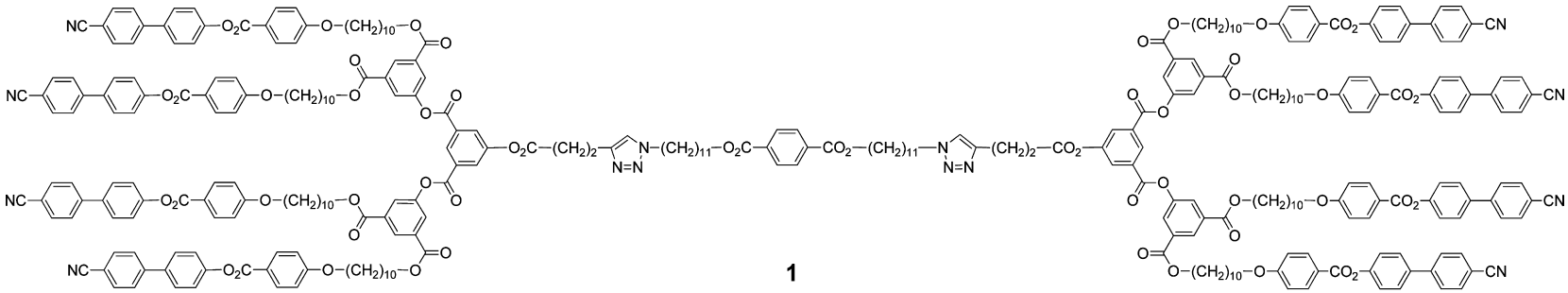
The development of nanoscale devices with specific properties (e.g., optical, magnetic, redox properties) obtained by the self-assembly of functional building blocks requires important efforts in the molecular design.[1,2] In this context, liquid crystals are a class of materials of particular interest due to their controllable self-organization behavior.[3] Structural engineering at the molecular level, by designing mesomorphic units with accurate shape, length, polarity, or chirality, is the key step to modulate the self-organization process and tune the physicochemical properties of the target supramolecular architectures.[4,5] Thus, the development of complex liquid-crystalline nanostructures with tailor-made and high performance properties requires effective and versatile synthetic tools.

The copper-catalyzed azide−alkyne "click" cycloaddition (CuAAC)[6−8] is of interest as it requires mild reaction conditions and simple work-up procedures, tolerates a wide range of functional groups, and leads to high yields. Thus, the CuAAC reaction was applied for the synthesis and modification of various supramolecular architectures such as gels,[9−11] polymers,[12−15] hyperbranched polymers,[16,17] fullerene derivatives,[18−20] micelles,[21−23] nanoparticles,[24−27] macrocycles,[28,29] dendrimers,[30−35] and metal−organic frameworks.[36−40] Furthermore, thermotropic liquid crystals, including small mesogenic molecules,[41−46] macrocycles,[47−52] polymers,[53,54] and dendrimers,[55] were also prepared by applying this chemical transformation.

In the field of liquid crystals, we successfully applied the CuAAC reaction for the synthesis of liquid-crystalline gold nanoparticles: first- and second-generation mesomorphic cyanobiphenyl-based dendrons were grafted onto the gold core, and the formation of smectic A phases was observed.[56,57] We also reported hexadducts of [60]fullerene (C_{60}) prepared by clicking 12 chiral or achiral first-generation poly(benzyl ether) dendrons onto a C_{60} derivative.[58] The materials gave rise to supramolecular helical columns.

The aim of this study is to exploit the click chemistry as an effective and elegant approach for the assembly of two dendrons leading to novel liquid-crystalline dendrimers. This strategy, which allows to connect dendrons with identical, similar, or different properties, is an interesting way to design liquid-crystalline dendrimers with tailor-made self-assembly properties based on the characteristics of each individual dendron.

We report, herein, the synthesis, characterization, and mesomorphic properties of three clicked dendrimers (**1**−**3**, Figures 1 and 2) as well as of their alkyne and azide precursors (**4**−**7**, Figure 3 and Scheme 1). The supramolecular organization of the investigated compounds is proposed based on small-angle X-ray diffraction analysis.



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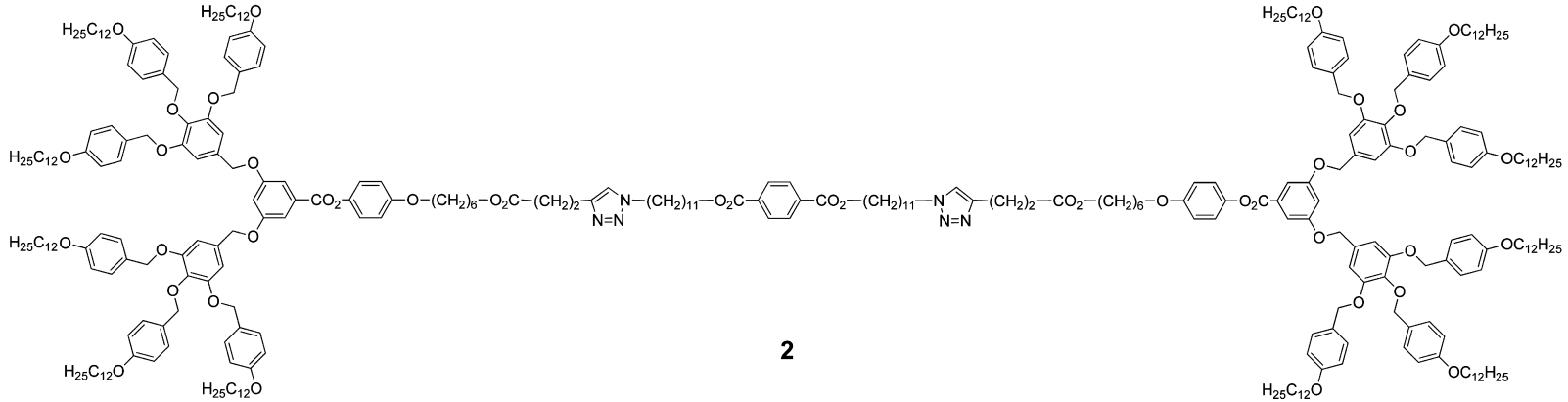

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Figure 1. Structures of symmetrical poly(aryl ester) **1** and poly(benzyl ether) **2** dendrimers.

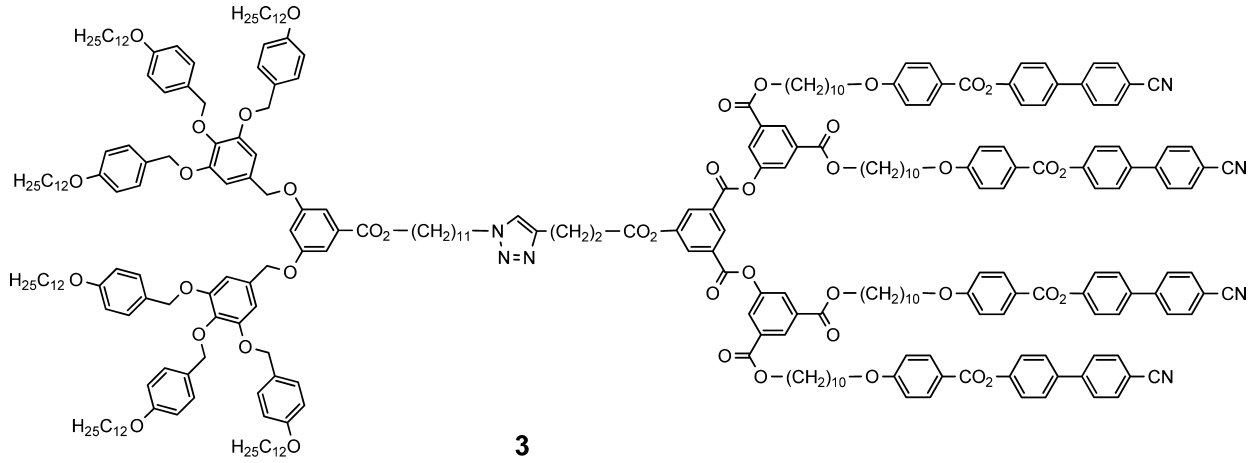


Figure 2. Structure of Janus dendrimer **3**.

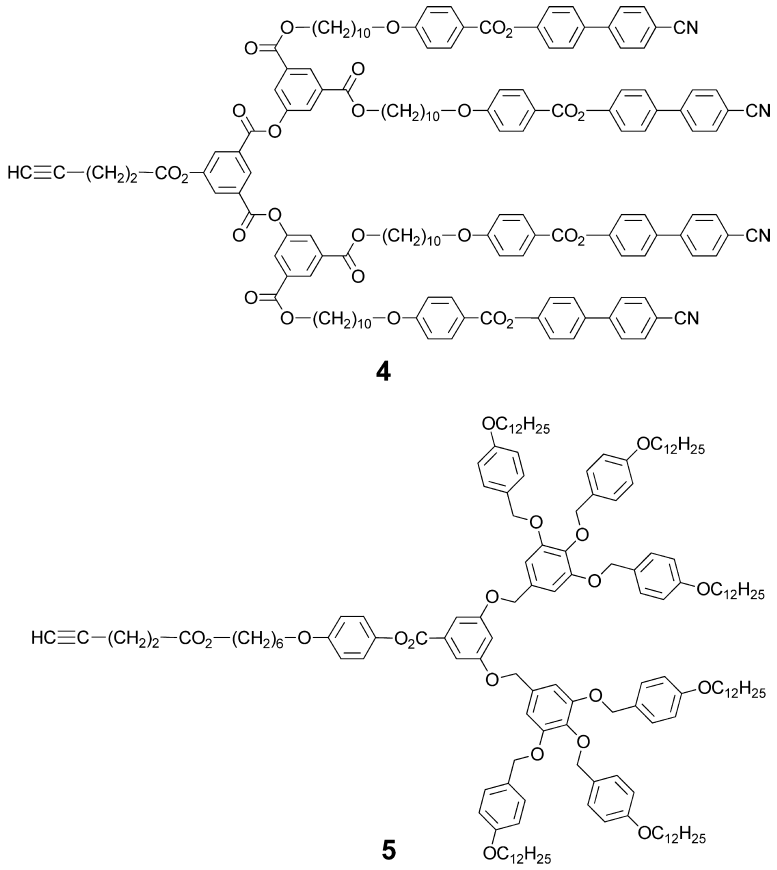


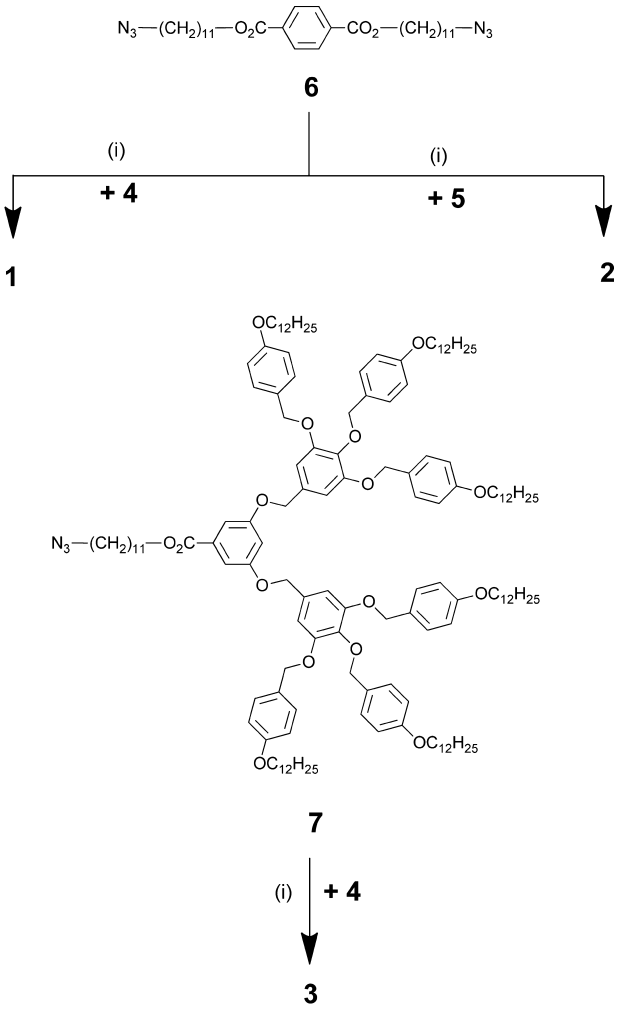
Figure 3. Structures of dendritic alkyne precursors **4** and **5**.

RESULTS AND DISCUSSION

Design. Inspired by the efficiency and versatility of the copper-mediated click transformation, we applied the CuAAC reaction for the construction of symmetrical (Figure 1) and nonsymmetrical (Figure 2) liquid-crystalline dendrimers. The target compounds were synthesized from mesomorphic dendritic building blocks functionalized with either an alkyne or an azide function. The building blocks were selected to generate either smectic phases [poly(aryl ester) dendrons carrying cyanobiphenyl units][59,60] or columnar ones [poly(benzyl ether) dendrons functionalized with dodecyloxy chains].[61−63]

Synthesis. Dendrimers **1**−**3** were prepared following the general click procedure shown in Scheme 1. In a typical reaction, a mixture of azide, alkyne, and $[Cu(CH_3CN)_4][PF_6]$ in THF/H_2O (1:1) was stirred at room temperature for 18 h. The crude product was recovered in CH_2Cl_2, washed with water, and purified by column chromatography (silica gel, CH_2Cl_2/Et_2O 100:0 → 95:5). A slight excess of the alkyne

Scheme 1. Synthesis of Dendrimers 1−3[a]



[a]Reagents and conditions: (i) $[Cu(CH_3CN)_4][PF_6]$, THF/H_2O (1:1), rt, 18 h. **1**: 78%; **2**: 56%; **3**: 37%.

derivative with respect to the azide derivative was used in order to increase the conversion in clicked products.

Alkynes **4** and **5** (Figure 3) were obtained by esterification of 4-pentynoic acid with the corresponding phenol or alcohol derivative. Esterification of 1-azidoundecan-11-ol with either terephthalic acid or the appropriate acid-based poly(benzyl ether) dendron gave azide derivatives **6** and **7**, respectively. The synthetic procedures and analytical data of **4**−**7** are reported in the Supporting Information. The structure and purity of all compounds were confirmed by NMR and IR spectroscopies, mass spectrometry, and elemental analysis.

Characterization. The formation of dendrimers **1**−**3** was confirmed by ^{1}H NMR and IR spectroscopies. The reaction of azide **6** with alkyne **4** to yield **1** is discussed as an illustrative example. First, the absence of azide and alkyne reagents in the clicked product was evidenced by the complete disappearance of both the azide asymmetric vibration at 2094 cm^{-1} in the IR spectrum of **1** (Figure 4) and the acetylenic proton signal at 2.08 ppm in the ^{1}H NMR spectrum (Figure 5c). Second, the formation of the 1,2,3-triazole ring in clicked dendrimer **1** was confirmed by its ^{1}H NMR spectrum, the diagnostic 1,2,3-triazole proton resonance being observed as a singlet at 7.39 ppm (Figure 5c). Finally, the formation of the 1,2,3-triazole aromatic heterocycle induced significant changes in chemical shifts for signals of the neighboring protons. For example, (i) the methylenic protons at α- and β-positions of the alkyne groups were shifted from 2.68 and 2.90 ppm to 3.08 and 3.15 ppm, respectively, and (ii) the methylenic protons at α-position of the azide group were shifted from 3.26 to 4.28 ppm (Figure 5). Similar data were obtained for dendrimers **2** and **3**.

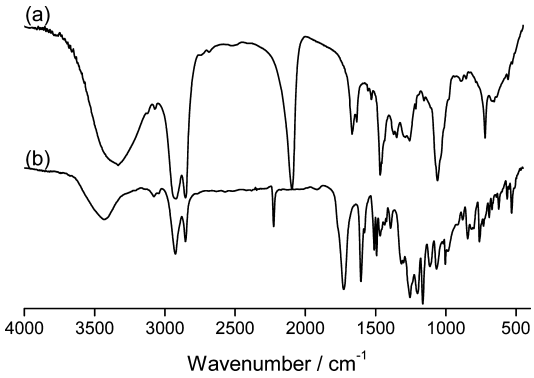


Figure 4. IR spectra of (a) azide **6** and (b) dendrimer **1**.

Liquid-Crystalline Behavior. The mesomorphic and thermal properties of dendrons **4**, **5**, and **7** and dendrimers **1**−**3** were investigated by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction. The phase-transition temperatures and enthalpies are reported in Table 1. The liquid-crystalline phases were identified by POM from the observation of typical textures: focal-conic fan texture and homeotropic area for the smectic A phase, pseudo-focal-conic fan texture for the columnar phase, and schlieren texture for the nematic phase. Typical examples of textures are shown in Figure 6.

All dendritic precursors as well as the final dendrimers displayed liquid-crystalline properties in agreement with their chemical nature and structure. Dendron **4** gave a smectic A phase with the cyanobiphenyl mesogens aligning parallel one to the others.[59,60] As for dendrons **5** and **7**, columnar phases were obtained resulting from the disc-like assembly of the Percec-type dendromesogens.[61−66] Dendrimers **1** and **2** developed similar mesophases as their precursors. Indeed, smectic A and columnar phases were observed for **1** and **2**, respectively. An additional nematic phase was also obtained for **1**. The contribution of each dendritic moiety, i.e., the poly(aryl ester)dendron and poly(benzyl ether)dendron, is observed in Janus dendrimer **3** for which both columnar and smectic A phases were obtained.

Supramolecular Organization. The molecular length (L) of all dendrons in their extended conformations was estimated using HyperChem software (modeling in the MM2 level) and was found to be 49, 53, and 48 Å for **4**, **5**, and **7**, respectively. Although compound **4** self-organized into a smectic A phase, only a very weak low-angle diffraction peak was detected. The layer spacing of **4** was estimated as d = 57 Å. The d/L ratio of 1.16 revealed that **4** organized into a bilayer structure with interdigitation of the mesogens between adjacent layers, which leads to a poorly defined electronic density. For compound **5**, a set of low-angle reflections at 39.2, 32.2, and 25.4 Å could be assigned respectively to the d_{11}, d_{20}, and d_{02} reflections of a 2D rectangular columnar lattice with a = 64.2 Å and b = 50.2 Å. Assuming a density of 1 g cm^{-3}, it can be estimated that two

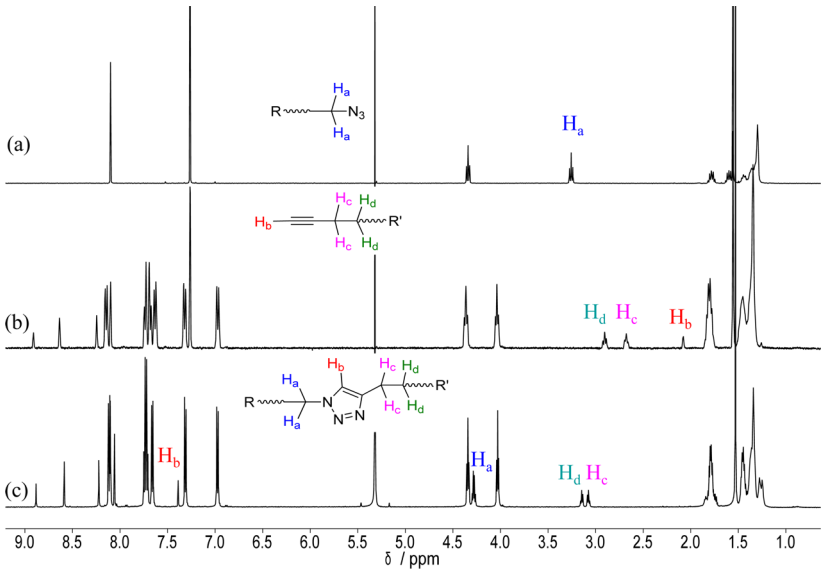


Figure 5. ^{1}H NMR spectra in CD_2Cl_2 of (a) azide **6**, (b) alkyne **4**, and (c) dendrimer **1**.

Table 1. Phase-Transition Temperatures and Enthalpy Changes of 1−5 and 7[a]

compd	T_g (°C)	transitions	T (°C)	ΔH (kJ/mol)
1	46	SmA → N	182	
		N → I	188	16.3[b]
2	23	Col_r → I	76	–[c]
3	42	Col_r → SmA	76	–[c]
		SmA → I	145	22.6
4	40	SmA → I	211	14.3
5	20	Col_r → I	78	8.5
7		Col_r → I	76[d]	21.5

[a] T_g = glass transition temperature, SmA = smectic A phase, N = nematic phase, I = isotropic liquid, Col_r = rectangular columnar phase. T_g is determined during the first cooling run; approximate value. Transition temperatures are given as the onset of the peaks obtained from the second heating run. [b] Combined enthalpies. [c] Too broad to be determined. [d] Temperature is given as peak value (broad peak).

molecules of **5** are required to fill a column stratum of 4.8 Å thickness. It is also deduced that in this mesophase, and in the rectangular phase of the other compounds in the series (**7**, **2**, and **3**), there are two columns per unit cell (see below). The fact that these molecules associate two by two in each column is consistent with the half-disc shape. A similar result was obtained for dendron **7**. Sharp peaks at 40.9 and 31.8 Å were identified as the d_{11} and d_{20} reflections, respectively. This result corresponds to a rectangular columnar phase with lattice constants a = 63.6 Å and b = 53.4 Å, each column stratum of 4.4 Å being filled by two molecules of **7**.

For dendrimers **1**−**3**, the molecular length (L) was estimated in the extended conformation by HyperChem and found to be 133, 144, and 96 Å for **1**, **2**, and **3**, respectively. For dendrimer **1**, XRD measurements did not give any sharp reflections and consequently did not allow an estimation of the lamellar spacing. This result, as well as for compound **4**, could be attributed to the not-well-defined layers within the smectic phase, a phenomenon already described in several of our publications for related dendrimers.[67,68] On the contrary, the sharp and intense reflections of dendrimer **2** suggested a rectangular columnar phase with lattice parameters a = 77.8 Å and b = 34.8 Å and a disc thickness of 6.4 Å. Taking into account these parameters, one single molecule is needed to generate the disc-like unit. To preserve a reasonable packing density, the molecule is forced to adopt a curled conformation (compare the lattice constants with the estimated molecular length), and this accounts for the large value of the stratum thickness. For the Janus dendrimer **3**, two different self-organizations were detected through the range of temperatures. At low temperature (55 °C), the self-organization of two molecules per disc led to a rectangular columnar phase with lattice parameters a = 88.4 Å and b = 55 Å and a column thickness of 6.4 Å. The association of two molecules in this case is reasonable and consistent with the mutual interdigitation of their CN groups. At higher temperature (90 °C), a set of five equally spaced sharp reflections observed in the low-angle region indicated that **3** reorganized into a smectic A phase with a large lamellar spacing of 111 Å. Considering the d/L ratio of 1.16, it is deduced that a bilayer interdigitated structure similar to that of **4** was promoted, most likely, due to dipolar and $\pi-\pi$ interactions between the cyanobiphenyl groups. Each layer, therefore, must contain two sublayers in which molecules have their CN groups pointing to the middle of the layer and the dodecyloxy chains pointing to the exterior. The CN groups of a sublayer join the CN groups of the other sublayers and interact with each other by dipolar forces. The presence of five layer reflection orders in the X-ray patterns of **3** is noticeable, in contrast to the patterns of the smectic phases of **1** and **4**. This is related to the different molecular structures. The presence in **3** of the poly(benzyl ether) dendron at one end of the molecules reduces interdigitation compared to **1** and **4** and, instead, allows a well-defined layer organization and hence a reinforced modulation of the electron density. Finally, the observation of both Col_r and SmA phases in **3** is in agreement with our previous reports for analogous compounds[66] and further confirms our hypothesis that the driving force to generate columnar and/or smectic phases depends on the nature and competitive size of the two dendritic parts. The postulated supramolecular organization of **3** within the rectangular columnar and smectic A phases is presented in Figure 7. Such a columnar−lamellar transition should occur via an undulated lamellar state (Figure 7).[44,69]

Table 2. Structural Characterization of the Mesophases Displayed by the Dendrons (4, 5, and 7) and Dendrimers (2 and 3)[a]

compd	L (Å)	mesophase	T (°C)	d (Å)	parameters	d_{SmA}	d_{SmA}/L	μ
4	49	SmA	25	d_{001} = 57		57	1.16	
5	53	Col_r	60	d_{11} = 39.2	a_r = 64.2			2
				d_{20} = 32.2	b_r = 50.2			
				d_{02} = 25.4	l = 4.8			
7	48	Col_r	70	d_{11} = 40.9	a_r = 63.6			2
				d_{20} = 31.8	b_r = 53.4			
					l = 4.4			
2	144	Col_r	70	d_{10} = 77.6	a_r = 77.8			1
				d_{20} = 39.1	b_r = 34.8			
				d_{11} = 31.7	l = 6.4			
				d_{21} = 26.0				
3	96	Col_r	55	d_{10} = 88.0	a_r = 88.4			2
				d_{20} = 44.4	b_r = 55.0			
				d_{21} = 34.4	l = 6.4			
				d_{31} = 26.1				
		SmA	90	d_{001} = 110.0		111	1.16	
				d_{002} = 55.3				
				d_{003} = 37.5				
				d_{004} = 27.7				
				d_{005} = 22.4				

[a] L = molecular length (estimated by Hyperchem), T = temperature of the XRD measurements, d = periodicities, d_{SmA} = layer separation of the smectic A phase, a_r and b_r = rectangular columnar lattice parameters, l = thickness of the disc, μ = number of dendrons/dendrimers per disc. For calculation details, see refs 21 and 22.

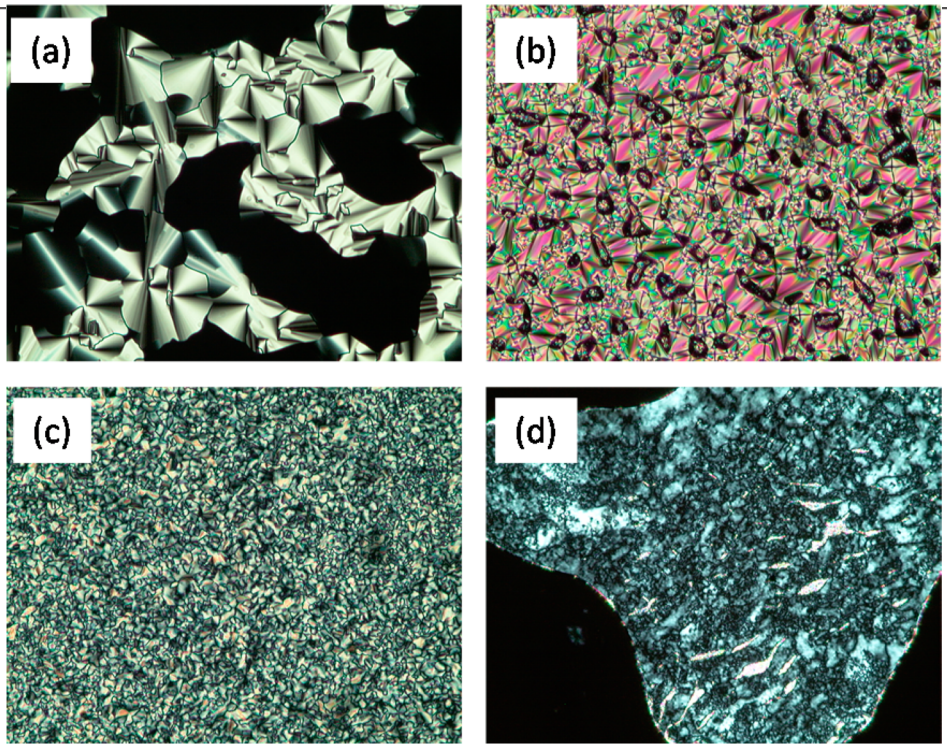


Figure 6. Thermal-polarized optical micrographs of (a) the pseudo-focal-conic fan texture displayed by **5** in the rectangular columnar phase at 78 °C, (b) the focal-conic fan texture displayed by **1** in smectic A phase at 177 °C, (c) the texture displayed by **2** in the rectangular columnar phase at 60 °C, and (d) the texture displayed by **3** in the rectangular columnar phase at 65 °C.

The X-ray patterns of the rectangular columnar phases could be consistent, in principle, not only with a columnar structure but also with a ribbon phase. However, this possibility must be ruled out considering that all the compounds that show rectangular columnar mesomorphism contain a poly(benzyl ether) dendron.[61,63] This dendron is known to promote columnar mesomorphism.[61,63]

From the observed reflections, the 2D space groups for the rectangular columnar phases of compounds **2**, **3**, **5**, and **7** can be deduced on the basis of the extinction rules that govern the space-groups attribution.[70] For **5** and **7** this attribution can only

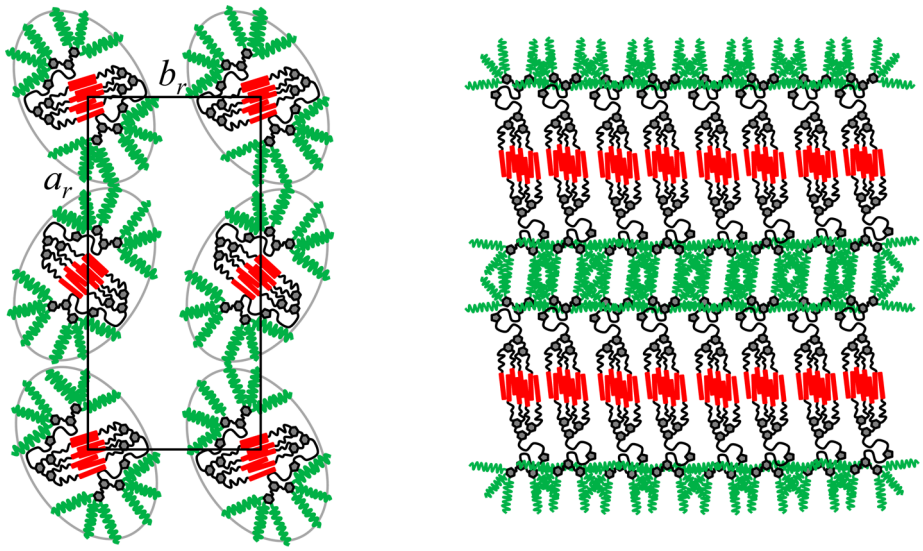


Figure 7. Postulated models of the supramolecular organization of **3** within the rectangular columnar (left) and smectic A (right) phases (red: cyanobiphenyl groups; green: alkoxy chains). The rectangular columnar phase is displayed with the *p2mg* symmetry which seems to be the most probable one regarding the X-ray results.

be tentative because of the low number of observed reflections. For these two compounds, the most probable symmetry group of their columnar phase is *c2mm* (Figure S17), for which the expected presence of reflection peaks are (1) *hk*: $h + k = 2n$; (2) *h*0: $h = 2n$; (3) 0*k*: $k = 2n$. For **2** and **3** the data are consistent with a *p2mg* plane group. This symmetry is in agreement with the presence of two columns per unit cell and with the expected conditions for the presence of reflection peaks: (1) *hk*: no conditions; (2) *h*0: no conditions; (3) 0*k*: $k = 2n$.

CONCLUSIONS

This study demonstrates that click chemistry is an interesting and powerful reaction for the coupling of liquid-crystalline macromolecular building blocks. Symmetrical and Janus-type mesomorphic dendrimers were prepared from cyanobiphenyl-based poly(aryl ester) dendrons and Percec-type dendrons. Smectic and columnar phases were obtained in agreement with the structure and nature of the liquid-crystalline promoters. Interestingly, our concept is not limited to the materials described herein but can be applied to many other compounds. Our strategy opens the door toward the design of liquid-crystalline macromolecules with tailor-made properties.

EXPERIMENTAL SECTION

General Procedure for Click Reaction. To a mixture of azide **6** or **7** and the appropriate alkyne **4** or **5** in THF/H_2O (1:1), was added $[Cu(CH_3CN)_4][PF_6]$. The mixture was stirred at room temperature for 18 h under Ar. THF was evaporated. H_2O was added, and the product extracted with CH_2Cl_2. The organic phase was washed (H_2O), dried ($MgSO_4$), filtered, and concentrated to dryness. Purification by CC (SiO_2, CH_2Cl_2/Et_2O 100:0 → 95:5) gave pure **1**–**3**.

Compound ***1***. From **6** (20 mg, 3.59×10^{-2} mmol), **4** (181 mg, 7.54×10^{-2} mmol), and $[Cu(CH_3CN)_4][PF_6]$ (13 mg, 3.59×10^{-2} mmol) in THF/H_2O (4 mL); yield: 150 mg (78%). ^{1}H NMR (δ in ppm, 600 MHz, CD_2Cl_2): 8.88 (t, 2H, arom H), 8.59 (t, 4H, arom H), 8.22 (d, 4H, arom H), 8.11 (d, 16H, arom H), 8.10 (d, 8H, arom H), 8.06 (s, 4H, arom H), 7.75 and 7.69 (2d, AB system, 32H, arom H), 7.66 (d, 16H, arom H), 7.39 (s, 2H, C═CHN), 7.31 (d, 16H, arom H), 6.97 (d, 16H, arom H), 4.34 (t, 16H, CO_2CH_2), 4.29 and 4.28 [2 superimposed t, 8H, $Ar_{central}(CO_2CH_2)_2$ and 2 × CH_2N], 4.03 (t, 16H, CH_2OAr), 3.15 (t, 4H, CH_2C═CHN), 3.08 (t, 4H, CH_2CO_2), 1.85–1.82 [m, 4H, $Ar_{central}(CO_2CH_2CH_2)_2$], 1.82–1.76 (m, 32H, 8 × CH_2CH_2OAr and 8 × $ArCO_2CH_2CH_2$), 1.76–1.72 (m, 4H, NCH_2CH_2), 1.48–1.21 (m, 124H, aliph H). ^{13}C NMR (δ in ppm, 150 MHz, CD_2Cl_2): 171.11, 165.73, 164.82, 164.77, 163.82, 163.14, 151.74, 150.72, 145.45, 144.73, 136.76, 134.36, 132.80, 132.74, 132.25, 131.27, 129.41, 128.96, 128.78, 128.35, 128.14, 127.72, 127.50, 126.89, 122.63, 121.32, 121.11, 118.88, 114.40, 111.10, 68.51, 65.93, 65.57, 50.27, 33.69, 30.39, 29.51, 29.46, 29.39, 29.31, 29.16, 29.07, 28.69, 26.56, 26.03, 26.01, 20.93. IR (KBr, ν in cm^{-1}): 2226 (CN). MS (MALDI): 5388.38 ([M + Na]$^+$, calcd for $C_{328}H_{332}N_{14}O_{56}Na$: 5385.3459). Anal. Calcd for $C_{328}H_{332}N_{14}O_{56}$ (5366.21): C 73.41, H 6.24, N 3.65%. Found: C 73.18, H 6.29, N 3.52%.

Compound ***2***. From **6** (11 mg, 2.03×10^{-2} mmol), **5** (100 mg, 4.26×10^{-2} mmol) and $[Cu(CH_3CN)_4][PF_6]$ (8 mg, 2.03×10^{-2} mmol) in THF/H_2O (4 mL); yield: 60 mg (56%). ^{1}H NMR (δ in ppm, 600 MHz, CD_2Cl_2): 8.10 (s, 4H, arom H), 7.45 (d, 4H, arom H), 7.34 [d, 18H, 16 arom H and 2 × (C═CHN)], 7.26 (d, 8H, arom H), 7.14 (d, 4H, arom H), 6.94 (d, 4H, arom H), 6.89 (d, 18H, arom H), 6.79 (s, 8H, arom H), 6.76 (d, 8H, arom H), 5.05 (s, 8H, 4 × OCH_2Ar), 5.02 (s, 16H, 8 × OCH_2Ar), 4.91 (s, 8H, 4 × OCH_2Ar), 4.33 [t, 4H, $Ar_{central}(CO_2CH_2)_2$], 4.28 (t, 4H, CH_2N), 4.10 (t, 4H, CO_2CH_2), 4.00–3.92 (m, 28H, $ArOCH_2CH_2$), 3.01 (t, 4H, CH_2C═CHN), 2.71 (t, 4H, CH_2CO_2), 1.90–1.82 [m, 4H, $Ar_{central}(CO_2CH_2CH_2)_2$], 1.82–1.74 (m, 32H, OCH_2CH_2), 1.71–1.64 (m, 4H, NCH_2CH_2), 1.50–1.29 (m, 252H, aliph H), 0.90 (t, 36H, CH_3). ^{13}C NMR (δ in ppm, 150 MHz, CD_2Cl_2): 172.72, 165.76, 165.19, 159.98, 159.21, 159.07, 157.08, 153.16, 146.28, 144.39, 137.98, 134.39, 132.00, 131.75, 130.22, 130.11, 129.97, 129.42, 128.90, 122.48, 120.95, 115.05, 144.44, 114.03, 108.87, 107.59, 106.87, 74.74, 70.99, 70.59, 68.38, 68.16, 68.07, 65.59, 64.50, 50.20, 33.76, 32.02, 30.40, 29.77, 29.74, 29.72, 29.55, 29.54, 29.45, 29.42, 29.39, 29.33, 29.28, 29.10, 28.72, 28.67, 26.57, 26.14, 26.07, 25.82, 25.46, 22.78, 21.12, 13.97. MS (MALDI): 5277.35 ([M + Na]$^+$, calcd for $C_{334}H_{484}N_6O_{42}Na$: 5274.5819). Anal. Calcd for $C_{334}H_{484}N_6O_{42}$ (5255.5): C 76.33, H 9.28, N 1.60%. Found: C 76.27, H 9.47, N 1.57%.

Compound ***3***. From **4** (116 mg, 4.82×10^{-2} mmol), **7** (100 mg, 4.40×10^{-2} mmol) and $[Cu(CH_3CN)_4][PF_6]$ (16 mg, 4.40×10^{-2} mmol) in THF/H_2O (4 mL); yield: 76 mg (37%). ^{1}H NMR (δ in ppm, 600 MHz, CD_2Cl_2): 8.88 (t, 1H, arom H), 8.59 (t, 2H, arom H), 8.22 (d, 2H, arom H), 8.12 (d, 8H, arom H), 8.10 (d, 4H, arom H), 7.74 and 7.71 (2d, AB system, 16H, arom H), 7.66 (d, 8H, arom H), 7.36 (s, 1H, C═CHN), 7.32 (d, 8H, arom H), 7.31 (d, 8H, arom H), 7.29 (d, 2H, arom H), 7.24 (d, 4H, arom H), 6.98 (d, 8H, arom H),

6.88 (d, 8H, arom H), 6.78 (t, 1H, arom H), 6.77 (s, 4H, arom. H), 6.74 (d, 4H, arom H), 4.99 (s, 8H, 4 × OCH_2Ar), 4.95 (s, 4H, 2 × OCH_2Ar), 4.89 (s, 4H, 2 × OCH_2Ar), 4.34 (t, 8H, CO_2CH_2), 4.30 (t, 2H, CO_2CH_2), 4.25 (t, 2H, CH_2N), 4.03 (t, 8H, CH_2OAr), 3.95 (t, 8H, 4 × $ArOCH_2CH_2$), 3.92 (t, 4H, 2 × $ArOCH_2CH_2$), 3.15 (t, 2H, $CH_2C{=}CHN$), 3.05 (t, 2H, CH_2CO_2), 1.85−1.70 (m, 32H, 10 × CH_2CH_2OAr and 5 × $ArCO_2CH_2CH_2$ and NCH_2CH_2), 1.50−1.26 (m, 170H, aliph H), 0.87 (t, 18H, CH_3). ^{13}C NMR (δ in ppm, 150 MHz, CD_2Cl_2): 171.24, 166.00, 164.94, 164.83, 163.82, 163.15, 159.93, 159.41, 159.03, 151.72, 151.40, 150.43, 145.60, 144.74, 138.00, 136.76, 135.20, 132.90, 132.74, 132.25, 132.10, 131.25, 130.21, 130.20, 129.70, 129.42, 129.30, 129.00, 128.76, 128.14, 127.72, 126.89, 122.63, 121.60, 121.51, 118.89, 114.43, 114.41, 114.02, 111.11, 108.78, 107.00, 106.88, 74.74, 70.97, 70.52, 68.51, 68.16, 68.06, 65.94, 65.41, 50.27, 33.68, 30.40, 29.77, 29.73, 29.72, 29.55, 29.52, 29.45, 29.41, 29.32, 29.16, 28.78, 28.70, 26.57, 26.13, 26.04, 26.02, 22.78, 20.93, 13.97. IR (KBr, ν in cm^{-1}): 2226 (CN). MS (MALDI): 4699.63 ($[M + Na]^+$, calcd for $C_{295}H_{361}N_7O_{42}Na$: 4696.6225). Anal. Calcd for $C_{295}H_{361}N_7O_{42}$ (4677.1): C 75.76, H 7.78, N 2.10%. Found: C 75.60, H 7.76, N 2.00%.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.6b00432.

Synthesis and analytical data of the intermediates, NMR spectra, DSC thermograms, thermal-polarized optical micrographs, and XRD patterns (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. Artificial Molecular Machines. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348−3391.

(2) Mulder, A.; Huskens, J.; Reinhoudt, D. N. Multivalency in Supramolecular Chemistry and Nanofabrication. *Org. Biomol. Chem.* **2004**, *2*, 3409−3424.

(3) Saez, I. M.; Goodby, J. W. Supermolecular Liquid Crystals. *Struct. Bonding (Berlin)* **2008**, *128*, 1−62.

(4) Saez, I. M.; Goodby, J. W. Supramolecular Liquid Crystals. *J. Mater. Chem.* **2005**, *15*, 26−40.

(5) Tschierske, C. Development of Structural Complexity by Liquid-Crystal Self-Assembly. *Angew. Chem., Int. Ed.* **2013**, *52*, 8828−8878.

(6) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. Click Chemistry: Diverse Chemical Function from a Few Good Reactions. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004−2021.

(7) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. A Stepwise Huisgen Cycloaddition Process: Copper(I)-Catalyzed Regioselective "Ligation" of Azides and Terminal Alkynes. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596−2599.

(8) Tornøe, C. W.; Christensen, C.; Meldal, M. Peptidotriazoles on Solid Phase: [1,2,3]-Triazoles by Regiospecific Copper(I)-Catalyzed 1,3-Dipolar Cycloadditions of Terminal Alkynes to Azides. *J. Org. Chem.* **2002**, *67*, 3057−3064.

(9) Díaz, D. D.; Rajagopal, K.; Strable, E.; Schneider, J.; Finn, M. G. "Click" Chemistry in a Supramolecular Enviroment: Stabilization of Organogels by Copper(I)-Catalyzed Azide-Alkyne [3 + 2] Cycloaddition. *J. Am. Chem. Soc.* **2006**, *128*, 6056−6057.

(10) Malkoch, M.; Vestberg, R.; Gupta, N.; Mespouille, L.; Dubois, P.; Mason, A. F.; Hedrick, J. L.; Liao, Q.; Frank, C. W.; Kingsbury, K.; Hawker, C. J. Synthesis of Well-Defined Hydrogel Networks using Click Chemistry. *Chem. Commun.* **2006**, 2774−2776.

(11) Li, Y.; Zhou, C.; Xu, L.; Yao, F.; Cen, L.; Fu, G. D. Stimuli-Responsive Hydrogels Prepared by Simultaneous "Click Chemistry" and Metal-Ligand Coordination. *RSC Adv.* **2015**, *5*, 18242−18251.

(12) Englert, B. C.; Bakbak, S.; Bunz, U. H. F. Click Chemistry as a Powerful Tool for the Construction of Functional Poly(*p*-phenyleneethynylene)s: Comparison of Pre- and Postfunctionalization Schemes. *Macromolecules* **2005**, *38*, 5868−5877.

(13) Qin, A.; Lam, J. W. Y.; Tang, B. Z. Click Polymerization. *Chem. Soc. Rev.* **2010**, *39*, 2522−2544.

(14) Zhang, M.; Rupar, P. A.; Feng, C.; Lin, K.; Lunn, D. J.; Olivier, A.; Nunns, A.; Whittell, G. R.; Manners, I.; Winnik, M. A. Modular Synthesis of Polyferrocenylsilane Block Copolymers by Cu-Catalyzed Alkyne/Azide "Click" Reactions. *Macromolecules* **2013**, *46*, 1296−1304.

(15) Rapakousiou, A.; Deraedt, C.; Gu, H.; Salmon, L.; Belin, C.; Ruiz, J.; Astruc, D. Mixed-Valent Click Intertwined Polymer Units Containing Biferrocenium Chloride Side Chains Form Nanosnakes that Encapsulate Gold Nanoparticles. *J. Am. Chem. Soc.* **2014**, *136*, 13995−13998.

(16) Qin, A.; Lam, J. W. Y.; Jim, C. K. W.; Zhang, L.; Yan, J.; Häussler, M.; Liu, J.; Dong, Y.; Liang, D.; Chen, E.; Jia, G.; Tang, B. Z. Hyperbranched Polytriazoles: Click Polymerization, Regioisomeric Structure, Light Emission, and Fluorescent Patterning. *Macromolecules* **2008**, *41*, 3808−3822.

(17) Shi, Y.; Graff, R. W.; Cao, X.; Wang, X.; Gao, H. Chain-Growth Click Polymerization of AB_2 Monomers for the Formation of Hyperbranched Polymers with Low Polydispersities in a One-Pot Process. *Angew. Chem., Int. Ed.* **2015**, *54*, 7631−7635.

(18) Iehl, J.; de Freitas, R. P.; Delavaux-Nicot, B.; Nierengarten, J.-F. Click Chemistry for the Efficient Preparation of Functionalized [60]Fullerene Hexakis-adducts. *Chem. Commun.* **2008**, 2450−2452.

(19) Iehl, J.; de Freitas, R. P.; Nierengarten, J.-F. Click Chemistry with Fullerene Derivatives. *Tetrahedron Lett.* **2008**, *49*, 4063−4066.

(20) Nierengarten, I.; Nierengarten, J.-F. The Impact of Copper-Catalyzed Alkyne-Azide 1,3-Dipolar Cycloaddition in Fullerene Chemistry. *Chem. Rec.* **2015**, *15*, 31−51.

(21) O'Reilly, R. K.; Joralemon, M. J.; Wooley, K. L.; Hawker, C. J. Functionalization of Micelles and Shell Cross-Linked Nanoparticles Using Click Chemistry. *Chem. Mater.* **2005**, *17*, 5976−5988.

(22) Sousa-Herves, A.; Fernandez-Megia, E.; Riguera, R. Synthesis and Supramolecular Assembly of Clicked Anionic Dendritic Polymers into Polyion Complex Micelles. *Chem. Commun.* **2008**, 3136−3138.

(23) Rodionov, V.; Gao, H.; Scroggins, S.; Unruh, D. A.; Avestro, A.-J.; Fréchet, J. M. J. Easy Access to a Family of Polymer Catalysts from Modular Star Polymers. *J. Am. Chem. Soc.* **2010**, *132*, 2570−2572.

(24) Tchoul, M. N.; Fillery, S. P.; Koerner, H.; Drummy, L. F.; Oyerokun, F. T.; Mirau, P. A.; Durstock, M. F.; Vaia, R. A. Assemblies of Titanium Dioxide-Polystyrene Hybrid Nanoparticles for Dielectric Applications. *Chem. Mater.* **2010**, *22*, 1749−1759.

(25) Tao, P.; Li, Y.; Rungta, A.; Viswanath, A.; Gao, J.; Benicewicz, B. C.; Siegel, R. W.; Schadler, L. S. TiO_2 Nanocomposites with High Refractive Index and Transparency. *J. Mater. Chem.* **2011**, *21*, 18623−18629.

(26) Rapakousiou, A.; Djeda, R.; Grillaud, M.; Li, N.; Ruiz, J.; Astruc, D. "Click" Assemblies and Redox Properties of Arene- and Gold-Nanoparticle-Cored Triazolylbiferrocene-Terminated Dendrimers. *Organometallics* **2014**, *33*, 6953−6962.

(27) He, Y.; Liang, Y.; Wang, D. The Highly Sensitive and Facile Colorimetric Detection of the Glycidyl Azide Polymer Based on

Propargylamine Functionalized Gold Nanoparticles Using Click Chemistry. *Chem. Commun.* **2015**, *51*, 12092−12094.
(28) Aucagne, V.; Hänni, K. D.; Leigh, D. A.; Lusby, P. J.; Walker, D. B. Catalytic "Click" Rotaxanes: A Substoichiometric Metal-Template Pathway to Mechanically Interlocked Architectures. *J. Am. Chem. Soc.* **2006**, *128*, 2186−2187.
(29) Noor, A.; Lewis, J. E. M.; Cameron, S. A.; Moratti, S. C.; Crowley, J. D. A Multi-Component CuAAC "Click" Approach to an *exo* Functionalised Pyridyl-1,2,3-triazole Macrocycle: Synthesis, Characterisation, Cu(I) and Ag(I) Complexes. *Supramol. Chem.* **2012**, *24*, 492−498.
(30) Wu, P.; Feldman, A. K.; Nugent, A. K.; Hawker, C. J.; Scheel, A.; Voit, B.; Pyun, J.; Fréchet, J. M. J.; Sharpless, K. B.; Fokin, V. V. Efficiency and Fidelity in a Click-Chemistry Route to Triazole Dendrimers by the Copper(I)-Catalyzed Ligation of Azides and Alkynes. *Angew. Chem., Int. Ed.* **2004**, *43*, 3928−3932.
(31) Boisselier, E.; Diallo, A. K.; Salmon, L.; Ornelas, C.; Ruiz, J.; Astruc, D. Encapsulation and Stabilization of Gold Nanoparticles with "Click" Polyethyleneglycol Dendrimers. *J. Am. Chem. Soc.* **2010**, *132*, 2729−2742.
(32) Ornelas, C.; Broichhagen, J.; Weck, M. Strain-Promoted Alkyne Azide Cycloaddition for the Functionalization of Poly(amide)-Based Dendrons and Dendrimers. *J. Am. Chem. Soc.* **2010**, *132*, 3923−3931.
(33) Franc, G.; Kakkar, A. K. "Click" Methodologies: Efficient, Simple and Greener Routes to Design Dendrimers. *Chem. Soc. Rev.* **2010**, *39*, 1536−1544.
(34) Astruc, D.; Liang, L.; Rapakousiou, A.; Ruiz, J. Click Dendrimers and Triazole-Related Aspects: Catalysts, Mechanism, Synthesis, and Functions. A Bridge between Dendritic Architectures and Nanomaterials. *Acc. Chem. Res.* **2012**, *45*, 630−640.
(35) Li, N.; Echeverria, M.; Moya, S.; Ruiz, J.; Astruc, D. "Click" Synthesis of Nona-PEG-Branched Triazole Dendrimers and Stabilization of Gold Nanoparticles That Efficiently Catalyze *p*-Nitrophenol Reduction. *Inorg. Chem.* **2014**, *53*, 6954−6961.
(36) Devic, T.; David, O.; Valls, M.; Marrot, J.; Couty, F.; Férey, G. An Illustration of the Limit of the Metal-Organic Framework's Isoreticular Principle Using a Semirigid Tritopic Linker Obtained by "Click" Chemistry. *J. Am. Chem. Soc.* **2007**, *129*, 12614−12615.
(37) Liu, C.; Li, T.; Rosi, N. L. Strain-Promoted "Click" Modification of a Mesoporous Metal-Organic Framework. *J. Am. Chem. Soc.* **2012**, *134*, 18886−18888.
(38) Tuci, G.; Rossin, A.; Xu, X.; Ranocchiari, M.; van Bokhoven, J. A.; Luconi, L.; Manet, I.; Melucci, M.; Giambastiani, G. "Click" on MOFs: A Versatile Tool for the Multimodal Derivatization of N_3-Decorated Metal Organic Frameworks. *Chem. Mater.* **2013**, *25*, 2297−2308.
(39) Morris, W.; Briley, W. E.; Auyeung, E.; Cabezas, M. D.; Mirkin, C. A. Nucleic Acid-Metal Organic Framework (MOF) Nanoparticle Conjugates. *J. Am. Chem. Soc.* **2014**, *136*, 7261−7264.
(40) Wu, S.; Chen, L.; Yin, B.; Li, Y. "Click" Post-Functionalization of a Metal-Organic Framework for Engineering Active Single-Site Heterogeneous Ru(III) Catalysts. *Chem. Commun.* **2015**, *51*, 9884−9887.
(41) Gallardo, H.; Bortoluzzi, A. J.; De Oliveira Santos, D. M. P. Synthesis, Liquid Crystalline Structure and Mesomorphic Properties of New Liquid Crystalline 1,2,3-Triazole Derivatives. *Liq. Cryst.* **2008**, *35*, 719−725.
(42) Ryu, M.-H.; Choi, J.-W.; Cho, B.-K. Design, Synthesis, and Self-Assembly Behavior of C_3-Symmetry Discotic Molecules *via* Click Chemistry. *J. Mater. Chem.* **2010**, *20*, 1806−1810.
(43) Beltrán, E.; Serrano, J. L.; Sierra, T.; Giménez, R. Functional Star-Shaped Tris(triazolyl)triazines: Columnar Liquid Crystal, Fluorescent, Solvatofluorochromic and Electrochemical Properties. *J. Mater. Chem.* **2012**, *22*, 7797−7805.
(44) Gimeno, N.; Martín-Rapún, R.; Rodríguez-Conde, S.; Serrano, J. L.; Folcia, C. L.; Pericás, M. A.; Ros, M. B. "Click Chemistry" as a Versatile Route to Synthesize and Modulate Bent-Core Liquid Crystalline Materials. *J. Mater. Chem.* **2012**, *22*, 16791−16800.
(45) Kayal, H.; Ahmida, M. M.; Dufour, S.; Taing, H.; Eichhorn, S. H. Cross-Linking of Discotic Tetraazaporphyrin Dyes in 2 and 3 Dimensions by "Click" Chemistry. *J. Mater. Chem. C* **2013**, *1*, 7064−7072.
(46) Yeap, G.-Y.; Balamurugan, S.; Srinivasan, M. V.; Kannan, P. Synthesis and Comparative Study on Phase Transition Behavior of Triazole-Cored Liquid Crystals Armed with Cholesterol and Double or Triple Aromatic Rings Systems. *New J. Chem.* **2013**, *37*, 1906−1911.
(47) Nierengarten, I.; Guerra, S.; Holler, M.; Nierengarten, J.-F.; Deschenaux, R. Building Liquid Crystals from the 5-Fold Symmetrical Pillar[5]arene Core. *Chem. Commun.* **2012**, *48*, 8072−8074.
(48) Nierengarten, I.; Guerra, S.; Holler, M.; Karmazin-Brelot, L.; Barberá, J.; Deschenaux, R.; Nierengarten, J.-F. Macrocyclic Effects in the Mesomorphic Properties of Liquid-Crystalline Pillar[5]- and Pillar[6]arenes. *Eur. J. Org. Chem.* **2013**, *2013*, 3675−3684.
(49) Yang, F.; Zhang, Y.; Guo, H. Novel Supramolecular Liquid Crystals: Cyclodextrin-Triphenylene Column Liquid Crystals Based on Click Chemistry. *New J. Chem.* **2013**, *37*, 2275−2279.
(50) Milev, R.; Lopez-Pacheco, A.; Nierengarten, I.; Trinh, T. M. N.; Holler, M.; Deschenaux, R.; Nierengarten, J.-F. Preparation of Pillar[5]arene-Based [2]Rotaxanes from Acyl Chlorides and Amines. *Eur. J. Org. Chem.* **2015**, *2015*, 479−485.
(51) Pan, S.; Ni, M.; Mu, B.; Li, Q.; Hu, X.-Y.; Lin, C.; Chen, D.; Wang, L. Well-Defined Pillararene-Based Azobenzene Liquid Crystalline Photoresponsive Materials and Their Thin Film with Photomodulated Surfaces. *Adv. Funct. Mater.* **2015**, *25*, 3571−3580.
(52) Nierengarten, I.; Guerra, S.; Aziza, H. B.; Holler, M.; Abidi, R.; Barberá, J.; Deschenaux, R.; Nierengarten, J.-F. Pilling Up Pillar[5]-arenes To Self-Assemble Nanotubes. *Chem.—Eur. J.* **2016**, DOI: 10.1002/chem.201600688.
(53) Li, Z.; Zhang, Y.; Zhu, L.; Shen, T.; Zhang, H. Efficient Synthesis of Photoresponsive Azobenzene-Containing Side-Chain Liquid Crystalline Polymers with High Molecular Weights by Click Chemistry. *Polym. Chem.* **2010**, *1*, 1501−1511.
(54) Royes, J.; Rebolé, J.; Custardoy, L.; Gimeno, N.; Oriol, L.; Tejedor, R. M.; Piñol, M. Preparation of Side-Chain Liquid Crystalline Azopolymers by CuAAC Postfunctionalization using Bifunctional Azides: Induction of Chirality Using Circularly Polarized Light. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 1579−1590.
(55) Gimeno, N.; Vergara, J.; Cano, M.; Serrano, J. L.; Ros, M. B.; Ortega, J.; Folcia, C. L.; Rodríguez-Conde, S.; Sanz-Enguita, G.; Etxebarria, J. Janus-Type Dendromesogens: A Tool to Control the Nanosegregation and Polar Organization of Bent-Core Structures. *Chem. Mater.* **2013**, *25*, 286−296.
(56) Mischler, S.; Guerra, S.; Deschenaux, R. Design of Liquid-Crystalline Gold Nanoparticles by Click Chemistry. *Chem. Commun.* **2012**, *48*, 2183−2185.
(57) Nguyen, T. T.; Albert, S.; Nguyen, T. L. A.; Deschenaux, R. Liquid-Crystalline Fullerene-Gold Nanoparticles. *RSC Adv.* **2015**, *5*, 27224−27228.
(58) Guerra, S.; Iehl, J.; Holler, M.; Peterca, M.; Wilson, D. A.; Partridge, B. E.; Zhang, S.; Deschenaux, R.; Nierengarten, J.-F.; Percec, V. Self-Organisation of Dodeca-Dendronized Fullerene into Supramolecular Discs and Helical Columns Containing a Nanowires-Like Core. *Chem. Sci.* **2015**, *6*, 3393−3401.
(59) Dardel, B.; Guillon, D.; Heinrich, B.; Deschenaux, R. Fullerene-Containing Liquid-Crystalline Dendrimers. *J. Mater. Chem.* **2001**, *11*, 2814−2831.
(60) Donnio, B.; Guillon, D. Liquid Crystalline Dendrimers and Polypedes. *Adv. Polym. Sci.* **2006**, *201*, 45−155.
(61) Percec, V.; Cho, W.-D.; Ungar, G.; Yeardley, D. J. P. Synthesis and Structural Analysis of Two Constitutional Isomeric Libraries of AB_2-Based Monodendrons and Supramolecular Dendrimers. *J. Am. Chem. Soc.* **2001**, *123*, 1302−1315.
(62) Percec, V.; Won, B. C.; Peterca, M.; Heiney, P. A. Expanding the Structural Diversity of Self-Assembling Dendrons and Supramolecular Dendrimers via Complex Building Blocks. *J. Am. Chem. Soc.* **2007**, *129*, 11265−11278.

(63) Donnio, B.; Buathong, S.; Bury, I.; Guillon, D. Liquid Crystalline Dendrimers. *Chem. Soc. Rev.* **2007**, *36*, 1495−1513.
(64) Percec, V.; Mitchell, C. M.; Cho, W.-D.; Uchida, S.; Glodde, M.; Ungar, U.; Zeng, X.; Liu, Y.; Balagurusamy, V. S. K.; Heiney, P. A. Designing Libraries of First Generation AB_3 and AB_2 Self-Assembling Dendrons via the Primary Structure Generated from Combination of $(AB)_y$-AB_3 and $(AB)_y$-AB_2 Building Blocks. *J. Am. Chem. Soc.* **2004**, *126*, 6078−6094.
(65) Lenoble, J.; Maringa, N.; Campidelli, S.; Donnio, B.; Guillon, D.; Deschenaux, R. Liquid-Crystalline Fullerodendrimers which Display Columnar Phases. *Org. Lett.* **2006**, *8*, 1851−1854.
(66) Lenoble, J.; Campidelli, S.; Maringa, N.; Donnio, B.; Guillon, D.; Yevlampieva, N.; Deschenaux, R. Liquid-Crystalline Janus-Type Fullerodendrimers Displaying Tunable Smectic-Columnar Mesomorphism. *J. Am. Chem. Soc.* **2007**, *129*, 9941−9952.
(67) Frein, S.; Camerel, F.; Ziessel, R.; Barberá, J.; Deschenaux, R. Highly Fluorescent Liquid-Crystalline Dendrimers Based on Borondipyrromethene Dyes. *Chem. Mater.* **2009**, *21*, 3950−3959.
(68) Mula, S.; Frein, S.; Russo, V.; Ulrich, G.; Ziessel, R.; Barberá, J.; Deschenaux, R. Red and Blue Liquid-Crystalline Borondipyrromethene Dendrimers. *Chem. Mater.* **2015**, *27*, 2332−2342.
(69) Rueff, J.-M.; Barberá, J.; Donnio, B.; Guillon, D.; Marcos, M.; Serrano, J.-L. Lamellar to Columnar Mesophase Evolution in a Series of PAMAM Liquid-Crystalline Codendrimers. *Macromolecules* **2003**, *36*, 8368−8375.
(70) Godbert, N.; Crispini, A.; Ghedini, M.; Carini, M.; Chiaravalloti, F.; Ferrise, A. LCDiXRay: a User-Friendly Program for Powder Diffraction Indexing of Columnar Liquid Crystals. *J. Appl. Crystallogr.* **2014**, *47*, 668−679.