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Synthesis, Structural Analysis, and Visualization of a Library of Dendronized Polyphenylacetylenes

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Abstract: A library of eleven high *cis*-content *cis*-transoidal polyphenylacetylenes (PPAs) dendronized with self-assembling dendrons was prepared from a library of fifteen convergently synthesized macromonomers. Using [Rh(C≡CPh)(nbd)(PPh$_3$)$_2$] (nbd = 2,5-norbornadiene) in the presence of 10 equiv of *N*,*N*-dimethylaminopyridine, predictive control over molecular weight and narrow molecular weight distribution are obtained. The PPA backbone serves as a helical scaffold for the self-assembling dendrons. The dendron primary structure dictates the diameter of the cylindrical PPAs in bulk, both in the self-organized hexagonal columnar (Φ_h) lattice determined by X-ray diffraction (XRD) and in monolayers on highly ordered pyrolytic graphite (HOPG) and mica visualized by atomic force microscopy (AFM). Thermal and bulk phase characteristics of the cylindrical PPAs reinforces the generality that flexible polymer backbones adopt a helical conformation within the cylindrical macromolecules generated by polymers jacketed with self-assembling dendrons.

Keywords: helical structures · polymers · retrostructural analysis · self-organization · visualization

Introduction

Dendronized polymers present an unparalleled level of architectural complexity in synthetic macromolecules by decorating each repeat unit of a linear polymer chain with a dendron.[1] Covalent connection of the dendron and backbone relies upon divergent,[2] attach-to,[3] or macromonomer synthetic strategies.[3b,4–8] The last provides the highest degree of structural perfection, particularly when combined with living polymerization techniques.[4a,5d,e,7b–d,8] The synthetic demands of the macromonomer strategy limit its utility. Consequently, supramolecular strategies have emerged.[9,10] Using electron donor–acceptor interactions, dendrons can bind to a linear polymer backbone.[9] Alternately, non-covalent association of apex functionalities in self-assembling dendrons generates dendronized supramolecular polymers.[10] The supramolecular strategies offer novel functionality, such as self-healing, ultra-high density arrays of helical wires, or arrays of helical porous protein mimics.[9,10]

While dendronized polymers exhibit a well-defined cylindrical shape in solution,[6c,11] it is difficult to utilize that structure as a building block for bottom-up self-assembly. We have demonstrated that polymers jacketed with self-assembling dendrons generate bulk order whose periodicity is dictated by the diameter of individual dendronized polymers.[5d,6,7d] The ability of these dendronized polymers to generate periodic order (i.e., self-organize) provides details about the internal order of dendronized polymers. Such internal order can be further harnessed to improve functional-

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ity. For example, X-ray diffraction (XRD) from oriented fiber samples and solid-state NMR spectroscopy demonstrated the helical internal order of electroactive dendronized polymers.[9a] Control over the helical handedness may enhance hole or electron mobility.

Polymers jacketed with covalently attached dendrons provide a model for understanding how to dictate the internal order of cylindrical dendronized polymers. Models constructed from XRD studies and AFM visualization for polystyrenes (PSs),[6] poly(methacrylate)s,[6,7a] poly(7-oxanorbornene)s[7b,c] and poly(maleimide)s[7b] dendronized with self-assembling dendrons suggest that the polymer backbone adopts short range helical order within the cylindrical structure. Polyarylacetylenes adopt a helical conformation[12,13] whose sense can be biased by incorporating chiral, non-racemic side chains.[14] Circular dichroism (CD) spectroscopy provides direct information about the helical bias of the conjugated polyarylacetylene backbone. Aoki and co-workers prepared dendronized PPAs that self-organized into a hexagonal lattice, but did not attempt to control helix sense.[5a,b] Meijer and co-workers prepared a dendronized PPA with a predominantly single-handed helix sense, but exhibits a smectic liquid crystalline phase.[5c] Sergeant-and-soldiers experiments using poly(N-substituted-2-ethynylcarbazole)s and poly(N-substituted-3-ethynylcarbazole)s demonstrated that the helical sense of the latter is more easily biased.[5d] The N_C phase displayed by these polymers precluded bulk observation of intracolumnar helical order by XRD.[5d]

The design and synthesis of dendronized PPAs that self-organize into a Φ_h phase and whose helix sense can be predictably controlled has been accomplished by surveying a library of such structures. We recently reported[5e] a particular dendron substitution pattern whose size matches the helical pitch of the backbone. A detailed model for the bulk structure was arrived at based on XRD studies of oriented fiber samples and molecular modeling studies. CD Spectroscopy of a dendronized PPA incorporating chiral, non-racemic tails in a solvent selective for the periphery confirmed selection of a particular helix sense. Herein we report the synthesis and structural analysis of the complete library of dendronized PPAs. Visualization of helical cylindrical PPAs confirmed that ordering on highly ordered pyrolytic graphite (HOPG) and mica surfaces is dictated by individual dendronized PPAs. Thermal and structural analysis of this library underscores the generality of the helical model arrived at for the aforementioned dendronized PPA to other flexible polymers jacketed with self-assembling dendrons.

Results and Discussion

Synthesis and structural analysis in solution: Following the convergent synthetic strategy outlined by our laboratory, we have prepared a library of self-assembling dendritic carboxylic acids.[6c,15] The polymerizable apex group, 4-ethynylbenzyl alcohol, was synthesized following a combination of literature reports.[16] Utilizing the esterification protocol of Moore and Stupp,[17] the dendritic carboxylic acids and 4-ethynylbenzyl alcohol were coupled using dicyclohexylcarbodiimide (DCC) and *N*,*N*-dimethylaminopyridinium tosylate (DPTS) in CH_2Cl_2. Typically, catalytic amounts of DPTS are needed to suppress formation of the undesired N-acyl urea byproduct. Nonetheless, trace amounts of the side product were observed during chromatography of reaction mixtures involving dendritic carboxylic acids in excess of 1 kDa. We found that substoichiometric or stoichiometric quantities of DPTS were necessary to eliminate this complication. A similar procedure has been employed for benzoyl ester dendron syntheses.[18]

The dendritic macromonomers were polymerized using $[Rh(C{\equiv}CPh)(nbd)(PPh_3)_2]$ (nbd = 2,5-norbornadiene) in the presence of 10 equiv of *N*,*N*-dimethylaminopyridine (DMAP) in THF.[19] The catalyst was chosen because it induces polymerization of arylacetylenes with living character: predictive control over molecular weight (M_n), narrow molecular weight distribution (M_w/M_n), and presence of active chain ends.[19] Rh^I-based catalysts effect the stereoselective polymerization of arylacetylenes containing a variety of functionalities.[19,20] Table 1 reports reaction conditions and structural characteristics of dendronized PPA obtained by polymerization of dendritic macromonomers. It is worth noting that **poly[(3,4)12G1-4EBn]** was also obtained using $[Rh(nbd)Cl]_2/NEt_3$ in THF, while polymerizations of benzyl ether-containing macromonomers proceeded to modest conversion providing intractable materials.

Gel permeation chromatography (GPC) typically underestimates M_n of dendronized polymers.[3b,6,8,11] Furthermore, light scattering on PSs and polymethacrylates jacketed with self-assembling dendrons confirmed this underestimation and showed that anomalous elution behavior occurs for extremely high molecular weight fractions.[6c] Comparison of the molecular weights reported therein to the results in Table 1 indicates that such behavior should not complicate the present results. In addition to M_n and M_w/M_n, Table 1 reports *cis*-content[12] determined by ^{1}H NMR spectroscopy of the polymers in $CDCl_3$. Figure 1 illustrates a representative spectrum and outlines the determination of *cis*-content according to the method outlined for PPA.[12] The estimate overlooks the presence of cyclohexadiene repeat units that result from electrocyclization of *cis*-1,3,5-hexatriene sequences in the polyene backbone (Scheme 1).[21–23] The vinylic proton resonances from the cyclohexadiene ring overlap the *cis*-polyene resonance. Due to the dendron structure, the cyclohexadiene content cannot be reliably determined, so this approximation is the best estimate of the backbone stereostructure.

Three different reaction protocols were employed. In most cases, solutions of monomer and catalyst (i.e., $[Rh(C{\equiv}CPh)(nbd)(PPh_3)_2]$/DMAP) were prepared independently and the monomer solution was added to the catalyst. Alternately, in some cases the catalyst solution was added to the monomer solution. Because the heat of reaction can alter the stereostructure of PPAs,[12] the monomer and catalyst solutions were maintained between 20 and 23 °C. Addition

Table 1. Polymerization of dendritic 4-ethynylbenzyl esters with $[Rh(C{\equiv}CPh)(nbd)(PPh_3)_2]$/DMAP 1:10 in THF.

Monomer	DP_{th}[a]	$[M]_0$ [M]	t [h]	Yield [%][b]	$M_n \times 10^{-3}$[c]	M_w/M_n[c]	*cis* Content [%][d]
(3,4)12G1-4EBn	57[e]	0.072	6	71	51.8	1.12	87
	65[e]	0.072	4	64	59.6	1.16	97
	66[e]	0.15	4	71	61.7	1.08	86
	63[f]	0.144	7.5	77	192.6	1.16	90
(3,4)12F8G1-4EBn	24[e]	0.060	120	62	–[g]	–[g]	–[g]
(3,4,5)12G1-4EBn	26[h]	0.034	7	57	33.9	1.16	79
	50[h]	0.046	8	74	50.9	1.22	89
	56[h]	0.048	12	76	65.8	1.20	72
	84[h]	0.063	7	92	82.4	1.38	88
(4-3,4)12G1-4EBn	44[e]	0.052	2.5	62	65.3	1.22	87
(4-3,4,5)AmylG1-4EBn	49[e]	0.050	6	68	61.0	1.14	82
(4-3,4,5)12G1-4EBn	50[h]	0.048	2.4	79	71.0	1.20	80
	113[h]	0.060	14	68	202.8	1.60	86
(3,4-3,4)12G2-4EBn	47[e]	0.051	5.5	72	64.4	1.10	85
(3,4-3,5)12G2-4EBn	27[h]	0.032	2.5	50	34.2	1.10	73
	44[e]	0.049	10	77	68.1	1.22	68
	51[h]	0.050	2.5	67	72.2	1.15	88
	51[e]	0.049	32	67	77.3	1.29	54
	103[h]	0.064	5	65	139.4	1.20	95
(3,4,5-3,4)12G2-4EBn	47[e]	0.050	21.5	75	54.2	1.21	80
(3,4,5-3,5)12G2-4EBn	23[h]	0.292	21	83	38.5	1.57	76
(4-3,4-3,5)12G2-4EBn	54[f]	0.106	8	56	109.3	1.10	100

[a] Theoretical degree of polymerization $= [4EBn]_0/[Rh]_0$. [b] Yields are corrected for conversion. [c] Determined by GPC (THF, 1 mL min^{-1}) calibrated with polystyrene standards. [d] Determined as prescribed in ref. [12]. [e] A solution of monomer was added to a solution of catalyst and the reaction vessel immersed in a water bath at 20–23 °C. [f] A solution of catalyst was added to a solution of monomer and the reaction vessel immersed in a water bath at 22–23 °C. [g] Insoluble in THF, benzene, $CHCl_3$, CH_2Cl_2, and α,α,α-trifluorotoluene. [h] Solvent was added to a solid mixture of monomer and catalyst and the reaction stirred without control over temperature.

of catalyst to the monomer introduced large variations in the molecular weight of the polymer obtained. For example, entries 3 and 4 in Table 1 for the polymerization of **(3,4)12G1-4EBn** and the anomalously high M_n obtained from polymerization of **(4-3,4-3,5)12G2-4EBn** (Table 1 entry 22). These discrepancies are, most likely, due to loss of some catalyst solution volume during transfer. Due to the small amount of solvent employed in these polymerizations, dissolution of a solid mixture of monomer and catalyst was found to be convenient, even without controlling for reaction temperature. Comparison of results in Table 1 show that this method provides results comparable to the method of adding the monomer solution to the catalyst.

Variation of $[M]_0/[Rh]_0$ allowed for predictive control of molecular weight. Figure 2 shows a plot of M_n determined by GPC versus $[M]_0/[Rh]_0$ for polymerizations of **(3,4)12G1-4EBn**, **(3,4,5)12G1-4EBn**, and **(3,4-3,5)12G2-4EBn**. The linear dependence of molecular weight on $[M]_0/[Rh]_0$ suggests that the polymerizations possess living character. All of the polymerizations reported in Table 1 proceed to 80 % conversion or higher. The low concentrations employed were chosen to ensure that the monomer is dissolved and that the reaction mixture remains fluid at high conversion. Unfortunately, the low concentrations lead to long reaction times for some monomers. Entries 16 and 18 of Table 1 for the polymerization of **(3,4-3,5)12G2-4EBn** show that longer reaction times lead to broadened polydispersity and lower *cis*-content. The latter likely results from cyclization or isomerization of the polyene backbone during polymerization. Comparison to polymerizations of **(3,4,5-3,4)12G2-4EBn** (entry 20) and **(3,4,5-3,5)12G2-4EBn** (entry 21), which are kinetically sluggish reactions, indicate that long reaction times are not inherently deleterious. In the absence of monomer, the Rh^I-based propagating species or byproduct formed during generation of the active catalyst[19b,20] may promote cyclization or isomerization. We have recently shown that cyclization in *cis*-transoidal PPA is accelerated in acidic media.[22]

Kinetic experiments for the polymerization of **(3,4-3,5)12G2-4EBn** were undertaken to elucidate the living character noted above. Figure 3 illustrates the results. The reaction proceeds to high conversion with time, but the semilogarithmic plot shows deviation from linearity at high conversion (Figure 3a). The reaction loses first-order character, which may be indicative of side reactions. The shape of the plot of $M_{n,GPC}$ versus the conversion corrected theoretical molecular weight ($M_{n,th}$, Figure 3b) is complicated by competing behavior. The $[Rh(C{\equiv}CPh)(nbd)(PPh_3)_2]$/DMAP system is noted for its low initiator efficiency,[19b] which leads to an upward deviation in the plot. Coincident with this behavior is the underestimation of M_n by GPC noted above. The plot of M_w/M_n versus the conversion corrected theoretical molecular weight (Figure 3b) clearly shows behavior uncharacteristic for a living polymerization. The molecular weight distribution increases with conversion, which is indicative of termination reactions. Close inspection of results for the polymerization of phenylacetylene using $[Rh(C{\equiv}CPh)(nbd)(PPh_3)_2]$/DMAP in Et_2O reveals similar behavior.[19b]

Termination of propagating species during arylacetylene polymerization appears to be most significant at high conversion. The side reactions become kinetically competent when the velocity of the propagation reaction becomes small due to low monomer concentration. As noted above, the steric demand and molecular weight of the dendritic macromonomers results in sluggish polymerization reactions. A decrease in rate constant of propagation with increasing dendron size is noted for polymerization of bisdendritic 7-oxanorbornene macromonomers appended with self-assembling dendrons.[7b,c] For large dendrons, the termination reac-

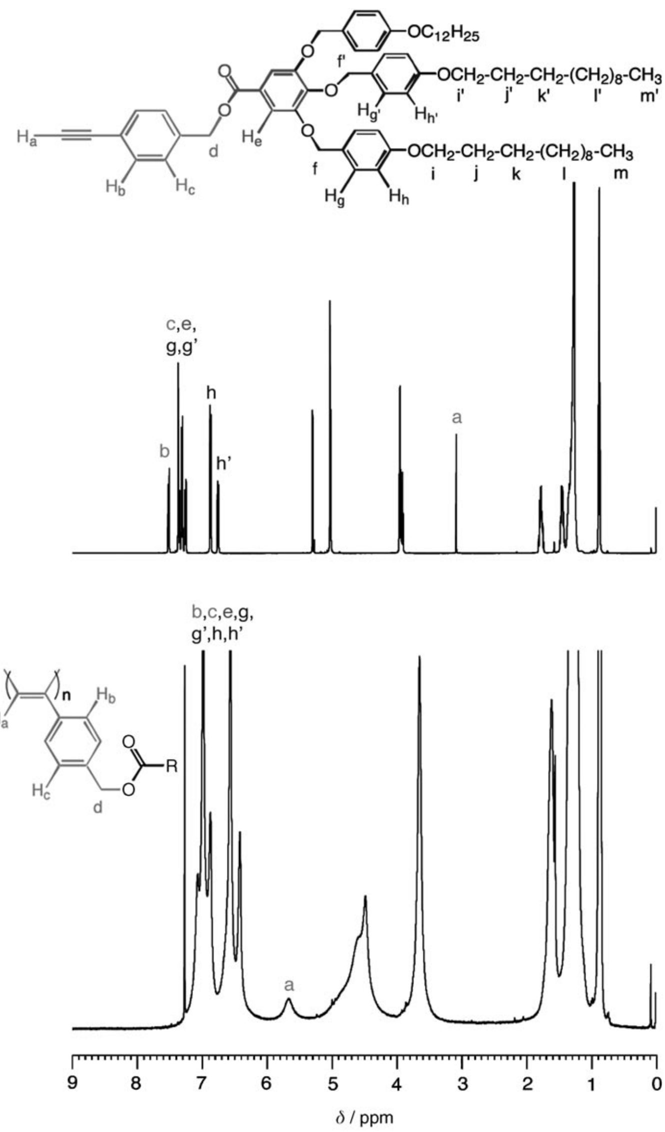


Figure 1. ^{1}H NMR spectra of **(4-3,4,5)12G1-4EBn** (top) and **poly[(4-3,4,5)12G1-4EBn]** (bottom).

tion(s) can be significant at modest conversions. We have observed that some macromonomers cannot be effectively polymerized using the [Rh(C≡CPh)(nbd)(PPh$_3$)$_2$]/DMAP catalyst. Despite this limitation, we have prepared the largest library of dendron structures appended to a single polymer backbone. Scheme 2 illustrates the complete library of dendronized PPAs.

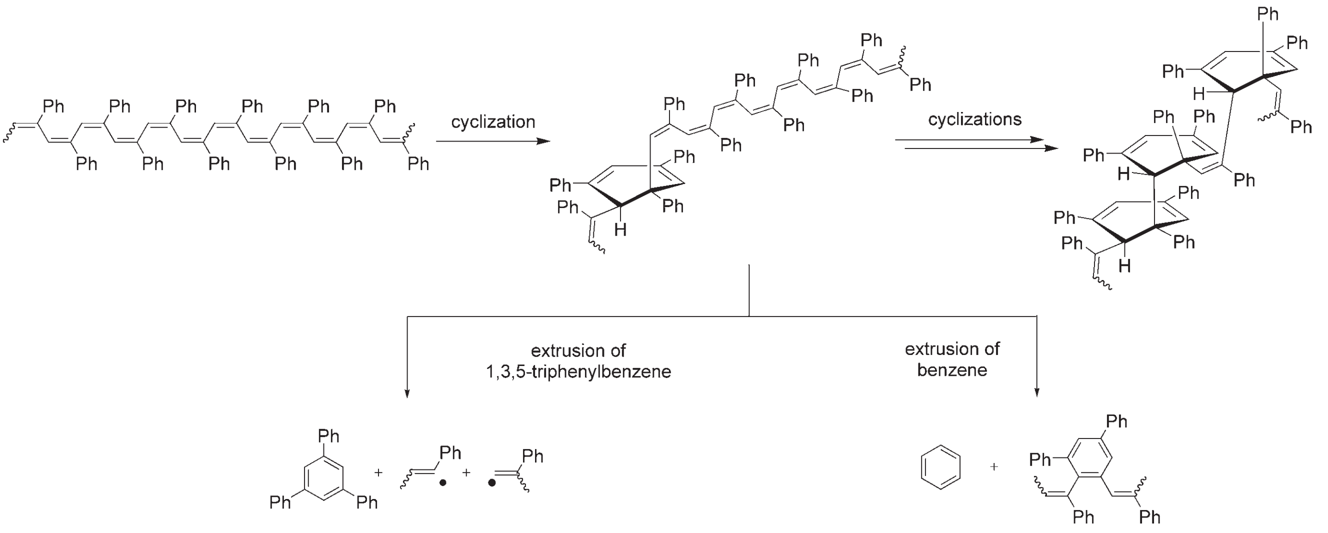
As a result of conjugation along the polyene backbone, the dendronized polymers are obtained as yellow powders after freeze drying from benzene. In a given solvent (e.g., THF or hexanes), comparison of UV/Vis spectra of several dendronized PPAs shows no observable difference (Figure 4). Therefore, the influence of dendron structure on the backbone conformation seems to be negligible in solution. By contrast, the choice of solvent does influence the long wavelength absorption associated with the polymer backbone. In hexanes, a solvent selective for the periphery of the dendron, the absorption maximum is red-shifted by 15–20 nm compared with THF. This suggests that solvophobic collapse of the benzyl ether region of the dendrons in hexanes results in stretching of the polymer backbone, which is manifested as the red shift of the UV/Vis spectra.

Structural analysis in bulk: Thermal phase behavior of the dendronized PPAs was determined by differential scanning calorimetry (DSC) and thermal optical polarized microscopy (TOPM). None of the textures observed by TOPM were distinctive. **Poly[(3,4)12G1-4EBn]** showed large homeotropically aligned domains. Also notable, this dendronized PPA is the only sample where isotropization occurs before decomposition. For the range of M_n reported in Table 1, the isotropization temperature during second heating only ranged between 76 and 78 °C. All other polymers decompose before isotropization. Nonetheless, reversible heating and cooling cycles can be obtained if the maximum temperature is kept 20 °C below the observed decomposition temperature. Table 2 summarizes the phase behavior determined by DSC. Representative second heating and cooling DSC cycles are shown in Figure 5.

The lattice symmetry of the self-organized phases was assigned based on XRD experiments. Two types of behavior were generally observed. Figure 6 illustrates representative diffraction patterns and plots of integrated diffraction intensity. Patterns characterized primarily by a broad, intense reflection indexed as d_{10} and a higher-order broad, diffuse reflection is indexed as overlapping d_{11} and d_{20} reflections of a hexagonal lattice (Figure 6a,b). In the case of **poly[(3,4)12G1-4EBn]**, which undergoes isotropization before decomposition, no improvement of ordering is observed on cooling and subsequent heating cycles. Similar behavior is observed in **poly[(4-3,4)12G1-4EBn]** and **poly[(3,4-3,4)12G2-4EBn]**. Except for **poly[(3,4,5-3,4)12G2-4EBn]**, the other dendronized PPAs exhibit diffraction patterns similar to that illustrated in Figure 6c,d. Three reflections that can be indexed as d_{10}, d_{11}, and d_{20} of a hexagonal lattice are observed.

Some higher order reflections were observed in oriented fiber samples of **poly[(3,4,5)12G1-4EBn]**, **poly[(4-3,4,5)12G1-4EBn]**, and **poly[(3,4-3,5)12G2-4EBn]**. Figure 7 shows representative wide angle XRD patterns and plots from **poly[(3,4,5)12G1-4EBn]** at 23 and 73 °C. We have recently discussed the structural significance of the observed Φ_h^{io}-to-Φ_h transition in **poly[(3,4-3,5)12G2-4EBn]**.[5e] A thermoreversible process of stretching along the column axis explains the structural changes observed by XRD: discontinuous column diameter contraction (expansion) and loss (appearance) of helical features on heating (on cooling). To accommodate these changes the polymer backbone undergoes conformational isomerization for *cis*-cisoidal to *cis*-transoidal upon heating in bulk. This inhibits the cyclization event typically associated with thermally-induced transformations of PPAs.[12,21–23]

Table 3 enumerates the lattice symmetry, observed d spacings, lattice parameter (a), experimental density measured



Scheme 1. 6π Electrocyclization of *cis*-1,3,5-hexatriene sequences in PPA and chain cleavage due to rearomatization of the resulting 1,3-cyclohexadiene repeat units.

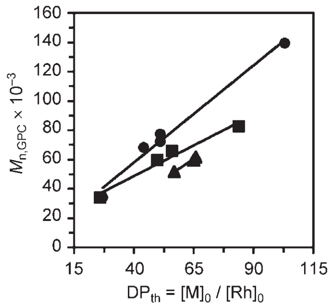


Figure 2. Plot of molecular weight determined by GPC ($M_{n,GPC}$) relative to polystyrene standards as a function of theoretical degree of polymerization ($DP_{th} = [M]_0/[Rh]_0$) for **poly[(3,4)12G1-4EBn]** (▲), **poly[(3,4,5)12G1-4EBn]** (■), and **poly[(3,4-3,5)12G2-4EBn]** (●).

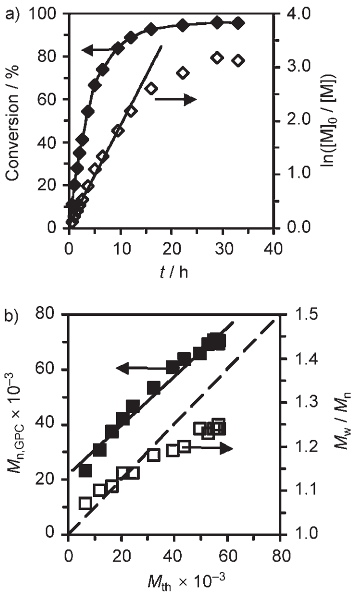
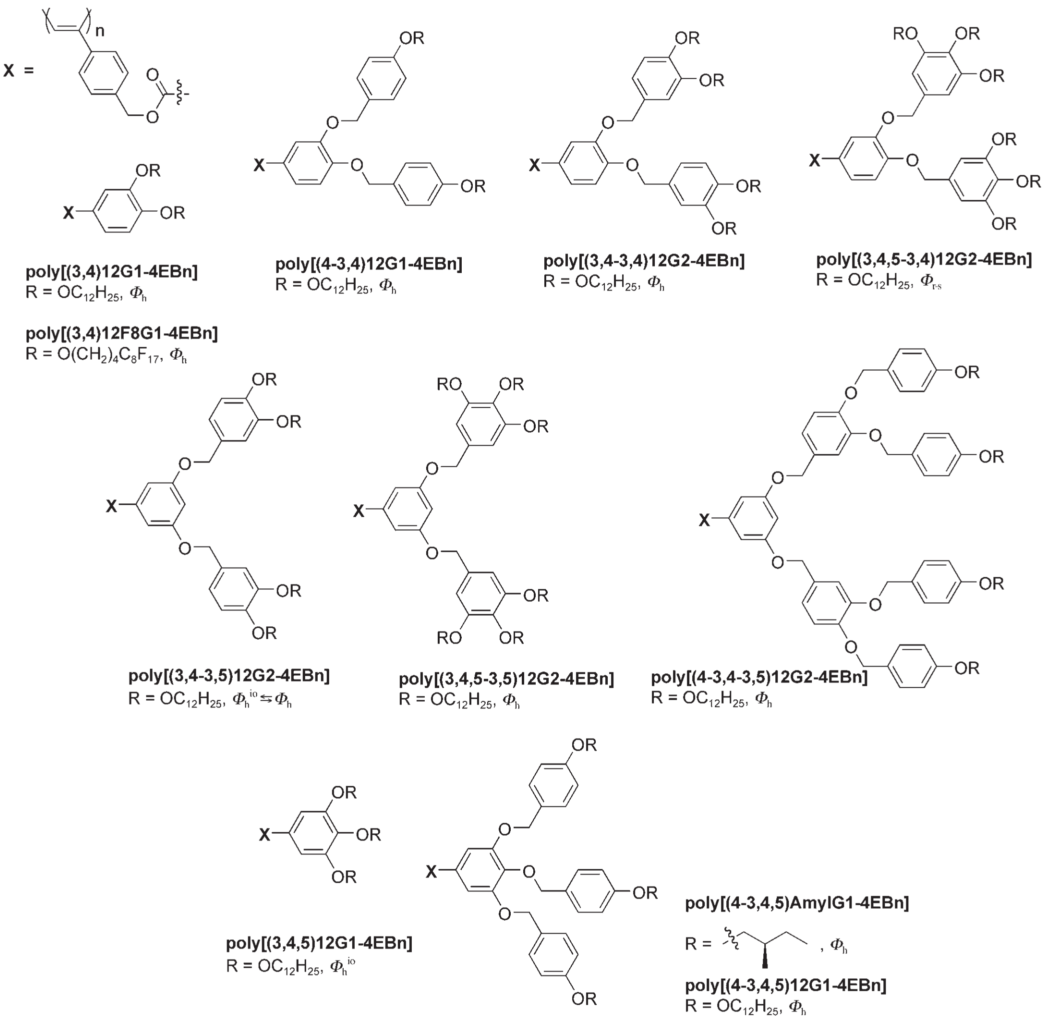


Figure 3. Polymerization of **(3,4-3,5)12G2-4EBn** with Rh(C≡CPh)(nbd)(PPh_3)$_2$/DMAP in THF at 23 °C; $[EBn]_0/[Rh]_0/[DMAP]_0$ = 50:1:10, $[M]_0 = 0.052$ M. a) Plot of conversion (◆) and first-order logarithm ($\ln([M]_0/[M])$, ◇) versus time for the same reaction. b) Plot of experimental $M_{n,GPC}$ (GPC vs PS standards) (■) and M_w/M_n (□) versus M_{th}.

at 20 °C (ρ_{20}), and number of dendrons per column stratum. Drawing on these assignments we identify dendrons with 3,4-branching elements adjacent to the polymer backbone as the source of poor hexagonal ordering. Additionally, **poly[(3,4,5-3,4)12G2-4EBn]** is self-organized in a simple rectangular columnar ($\Phi_{r\text{-}s}$) lattice. Unlike with flexible polymer backbones, the dendron is limited to how it can contort the PPA backbone. Semifluorination of the peripheral alkyl tails provides a strong driving force for microphase segregation within the cylindrical macromolecule. The semifluorinated alkyl tails fill a larger and more extended volume of space than their hydrocarbon analogues. For example, for **poly[(3,4)12G1-4EBn]** $a = 39.5$ Å while for **poly[(3,4)12F8G1-4EBn]** $a = 52.2$ Å. Space filling can also be compensated by 3,5- and 3,4,5-branching adjacent to the polymer backbone. The diameter of the cylindrical object is largely dictated by the length of the peripheral alkyl tail and the number of benzyl ether layers, regardless of substitution pattern. By this latter strategy we have prepared cylindrical PPAs with diameters of ~40 Å (e.g., **poly[(3,4,5)12G1-4EBn]**), ~50 Å (e.g., **poly[(4-3,4,5)12G1-4EBn]**), and ~60 Å (e.g., **poly[(4-3,4-3,5)12G2-4EBn]**).

Unique to polymers dendronized with self-assembling dendrons, bulk characterization provides direct measurement of the diameter of a single macromolecule in the self-organized lattice. We have previously shown that for polymers jacketed with self-assembling dendrons, the size of the cylindrical macromolecule defines the fundamental element for periodic order at interfaces.[5d,6,7d] Cylindrical PPAs can serve as structural building blocks for bottom-up self-assem-



Scheme 2. Library of dendronized polyphenylacetylenes.

bly. The helical conformation of the polymer backbone is of further interest to understand chirality at interfaces. Visualization of cylindrical PPAs using AFM confirms that periodic structures are formed on HOPG (Figure 8). Averaging over several cylindrical elements in the images we can estimate the length-scale of the periodic order. Table 4 reports the measured diameter by AFM visualization. We note good agreement between the results in Table 4 with *a* from Table 3, which underscores that individual cylindrical macromolecules define the observed self-organization on HOPG and mica.

Figure 8 illustrates monolayers of **poly[(3,4-3,5)12G2-4EBn]** on HOPG and mica. On both surfaces, domains of rod-like objects oriented parallel to each other can be identified. On HOPG, boundaries form between domains oriented ~120° to each other. This orientation reflects the underlying six-fold symmetry of the graphite surface and is driven by epitaxial adsorption of the peripheral alkyl chains.[6f] Mica is hydrophilic, so there is no preferential adsorption of the cylindrical PPA. The result of epitaxial adsorption is that the cylindrical PPA is deformed into a more oblate shape. This is reflected in the modest overestimation of macromolecular diameter determined by AFM on HOPG compared to XRD measurements in bulk (Figure 8c). In contrast, the cylindrical diameter measured by AFM on mica is remarkably close to that determined by XRD (Figure 8d).

Effect of stiffening the polymer backbone: Both PPA and PS offer relatively flexible scaffolds for dendronized polymers. Unmitigated by dendrons, PS adopts a random coil conformation, while PPA adopts a helical conformation due to fewer degrees of conformational freedom. The consequences of this restricted conformational flexibility are apparent in the observation of poorly ordered Φ_h lattices in specific samples. Since the dendron cannot force the backbone into a conformation that matches its preferred packing, nor can some dendrons appropriately fill space, the cylindrical macromolecules cannot pack well into a two-dimensional lattice.

Dendronized PPAs decompose at lower temperatures than the corresponding dendronized PSs.[6c] This can have origins in the mobility of the dendronized polymer due to

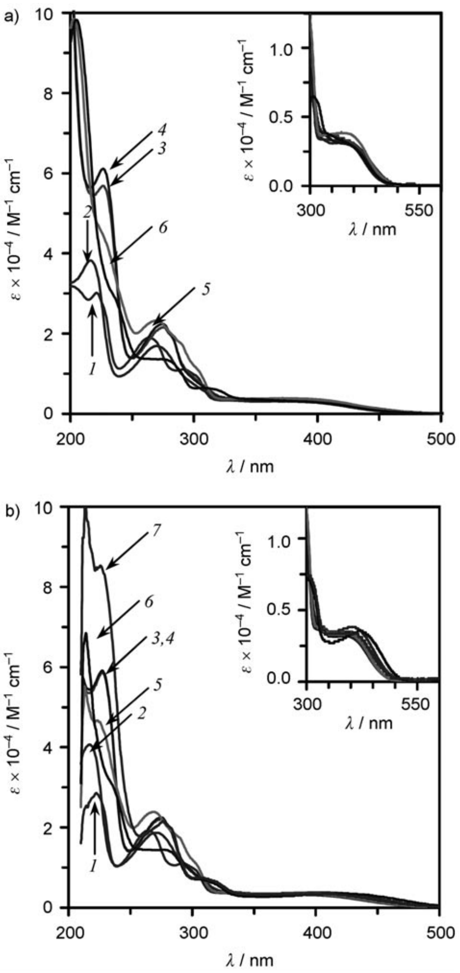


Figure 4. UV/Vis Spectra of **poly[(3,4)12G1-4EBn]** (1), **poly[(3,4,5)12G1-4EBn]** (2), **poly[(4-3,4,5)AmylG1-4EBn]** (3), **poly[(4-3,4,5)12G1-4EBn]** (4), **poly[(3,4-3,4)12G2-4EBn]** (5), **poly[(3,4-3,5)12G2-4EBn]** (6), and **poly[(4-3,4-3,5)12G2-4EBn]** (7) a) in hexanes ($0.6–1.8 \times 10^{-5}$ M) and b) in THF ($0.4–1.6 \times 10^{-5}$ M). The inset highlights the long wavelength absorption associated with main chain conjugation.

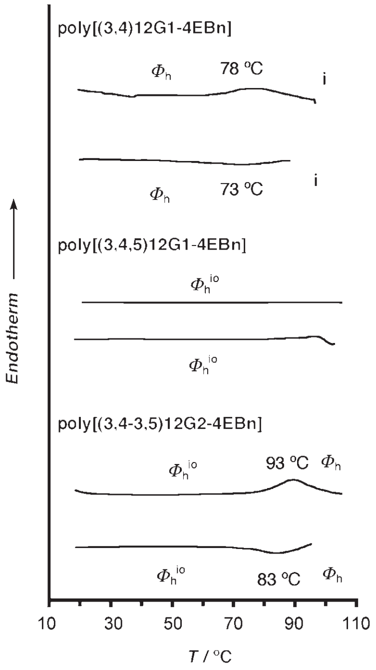


Figure 5. Representative second heating (top) and second cooling (bottom) DSC traces for **poly[(3,4)12G1-4EBn]**, **poly[(3,4,5)12G1-4EBn]**, and **poly[(3,4-3,5)12G2-4EBn]**.

molecular weight or macromolecular flexibility. With regard to the dendron architectures herein, PSs dendronized with self-assembling dendrons typically undergo isotropization at temperatures similar to the decomposition temperatures observed with dendronized PPAs. Dendronized polymers with M_n in excess of 100000 decompose (~290 °C) before isotropization. Given the relatively low M_n of the dendronized PPAs, the low decomposition temperatures need consideration.

Intramolecular 6π electrocyclization of *cis*-1,3,5-hexatriene sequences in the polyene backbone to form cyclohexadiene repeat units accounts for the thermal transformations of PPA in bulk and solution.[12,21–23] Rearomatization of cyclohexadiene repeat units results in extrusion of 1,3,5-triphenylbenzene and concomitant chain cleavage.[12,21–23] In bulk, these processes are detectable by DSC as endothermic events.[12] The decomposition of dendronized PPAs in bulk is exothermic, and not likely caused by cyclization and rearomatization. We further note, that the extruded 1,3,5-triarylbenzenes are expected to be discotic liquid crystalline dendrimers. Finally, we have observed that in bulk,

Table 2. Thermal characterization of cylindrical PPA macromolecules.

Polymer	$M_n \times 10^{-3}$[a]	Thermal transitions [°C] and corresponding enthalpy changes [kcal mol^{-1}][b] Heating	Cooling
poly[(3,4)12G1-4EBn]	61.7	k −4 (2.19) Φ_h[c] 78 (0.41) i	i 73 (0.44) Φ_h 6 (1.53) k
poly[(3,4)12F8G1-4EBn]	–	Φ_h 125 dec[d]	
poly[(3,4,5)12G1-4EBn]	50.9	Φ_h^{io}[e] 110 dec	
poly[(4-3,4)12G1-4EBn]	65.3	Φ_h 183 dec	
poly[(4-3,4,5)AmylG1-4EBn]	61.0	Φ_h 90 dec	
poly[(4-3,4,5)12G1-4EBn]	71.0	Φ_h^{io} 106 (0.29) Φ_h 115 dec	
poly[(3,4-3,4)12G2-4EBn]	64.4	Φ_h 130 dec	
poly[(3,4-3,5)12G2-4EBn]	68.1	$\Phi_{h,g}$[f] 0 (3.63) Φ_h^{io} 88 (1.11) Φ_h 140 dec	
poly[(3,4,5-3,4)12G2-4EBn]	54.2	$\Phi_{r\text{-}s}$[g] 130 dec	
poly[(3,4,5-3,5)12G2-4EBn]	38.5	Φ_h 160 dec	
poly[(4-3,4-3,5)12G2-4EBn]	109.3	Φ_h 120 dec	

[a] Determined by GPC (THF, 1 mL min^{-1}) calibrated with polystyrene standards. [b] Data from second heating and cooling DSC scans at 10 °C min^{-1}. [c] Φ_h, *p6mm* hexagonal columnar lattice. [d] dec, onset of decomposition as indicated by the lack of reversible heating/cooling cycles above this temperature. [e] Φ_h^{io}, *p6mm* hexagonal columnar lattice with intracolumnar order. [f] $\Phi_{h,g}$, glassy state of the *p6mm* hexagonal columnar lattice. [g] $\Phi_{r\text{-}s}$, *p2mm* simple rectangular columnar lattice.

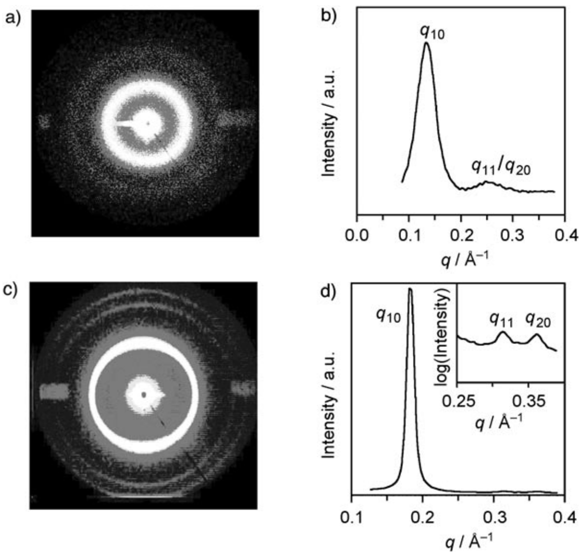


Figure 6. Representative XRD patterns (a and c) and plots of XRD intensity (b and d) from the hexagonal columnar (Φ_h) lattices exhibited by (a and b) **poly[(4-3,4)12G1-4EBn]** and c) and d) **poly[(3,4,5)12G1-4EBn]**.

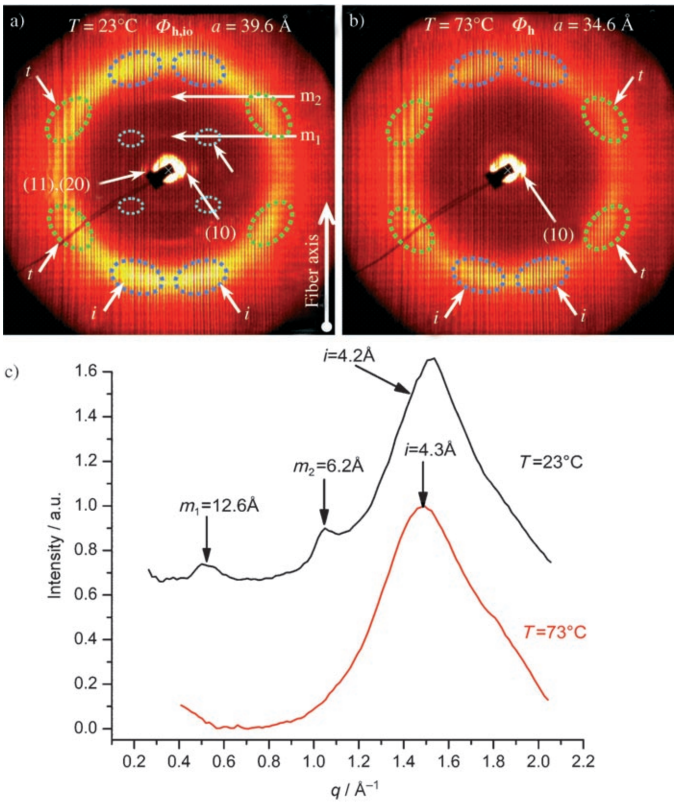


Figure 7. Wide angle X-ray diffraction patterns from **poly[(3,4,5)12G1-4EBn]** collected at a) 23 and b) 73 °C, and c) the corresponding stack meridional plots. Legend: i-short range helical feature; t–54 ± 9° dendron tilt angle; m_1 and m_2-meridional helical features; h_1-long range helical feature; (10), (11) and (20)-(hk0) reflections of the columnar hexagonal phase.

poly[(3,4-3,5)12G2-4EBn] is thermally stable due to cisoid-to-transoid conformational isomerization of the polyene backbone during the Φ_h-to-Φ_h^{io} phase transition.[5e]

Short-range helical order of the backbone has been proposed for flexible polymers dendronized with self-assembling dendrons.[6,7] This model is arrived at based on modeling of a backbone confined to the core of the cylindrical macromolecule, XRD experiments, and from conformational analysis of individual macromolecules visualized using AFM. Using XRD and CD spectroscopy, we have substantiated such a model for a series of **poly[(3,4-3,5)*m*G2-4EBn]s** with various peripheral alkyl chains (m).[5e] The structural characteristics of **poly[(4-3,4,5)12G1-4EBn]** and **poly[(3,4-3,5)12G2-4EBn]** (Table 3) in the Φ_h^{io} phase and their PS counterparts **poly[(4-3,4,5)12G1-4VBn]** ($a=49.3$ Å,[5c] $\mu=6.8$ assuming $t=4.75$ Å) and **poly[(3,4-3,5)12G2-4VBn]** ($a=48.8$ Å,[5c] $\mu=4.9$ assuming $t=4.75$ Å) are strikingly similar. Therefore, little difference is expected in the internal helical order of both structures. Given the predisposition of the PPA backbone to adopt a helical conformation and the quantitative correspondence between each of the dendronized PPAs and their PS analogue, it is consistent that polymers confined to the core of the cylinder exhibit short-range helical order that can be directed by chirality in the dendron.

Conclusion

High *cis*-content cylindrical *cis*-transoidal PPAs are prepared from self-assembling dendrons functionalized with polymerizable 4-ethynylbenzyl esters at their apex using [Rh(C≡CPh)(nbd)(PPh$_3$)$_2$]/DMAP (1:10) as catalyst. The catalyst system allows for predictive control over M_n and narrow M_w/M_n. Kinetic experiments reveal that the polymerization is limited by termination reactions, which become kinetically significant at low [M] or low k_p. The steric size of the dendron results in reduced k_p and, for some dendritic macromonomers, the catalyst is not competent. Nonetheless a library of dendronized PPAs comprised of eleven different dendron branching structures has been prepared.

Structural analysis in bulk and solution lead to a general picture of how the polymer backbone is accommodated in a helical arrangement in the core of the cylindrical object. Self-assembling dendrons are capable of forcing the polymer backbone into a conformation that matches the preferred packing of the dendrons. In solution, UV/Vis spectroscopy indicated that the dendron structure does not significantly alter the degree of conjugation along the polyene backbone. From XRD in the self-organized phase, we find that the less flexible PPA backbone impedes the ideal packing of the dendrons. Design principles related to how the dendron fills space are elucidated for distinguishing dendronized PPAs that self-organize into well-ordered Φ_h lattices. By correlation between a library of dendronized PSs and the present library of dendronized PPAs, we generalized the short-range

Table 3. Measured *d* spacings and structural analysis of the columnar lattices generated from cylindrical PPAs.

Polymer	T [°C]	Lattice	d Spacings [Å]				a (a,b)[a] [Å]	ρ_{20}[b] [g cm^{-3}]	μ[c]
			d_{100}[d] d_{100}[e]	d_{110}[d] d_{010}[e]	d_{200}[d] d_{120}[e]	d_{210}[e]			
poly[(3,4)12G1-4EBn]	25	*p6mm*	39.8		20.0		45.9		
poly[(3,4)12F8G1-4EBn]	25	*p6mm*	45.0	26.4	22.4		52.2		
poly[(3,4,5)12G1-4EBn]	25	*p6mm*	34.3	19.8	17.2		39.8	0.98	4.7
poly[(4-3,4)12G1-4EBn]	25	*p6mm*	46.8	26.0	23.4		53.4		
	85	*p6mm*	48.3	25.8	23.8		54.1		
poly[(4-3,4,5)AmylG1-4EBn]	120	*p6mm*	31.8	18.6			32.0		
poly[(4-3,4,5)12G1-4EBn]	25	*p6mm*	40.2	23.1	20.0		46.3	1.03	5.4
	85	*p6mm*	40.7	23.4	20.3		46.9		
	90	*p6mm*	41.0	23.1	20.8		47.2		
	115	*p6mm*	40.0	23.0	20.1		46.2		
poly[(3,4-3,4)12G2-4EBn]	30	*p6mm*	46.5	26.2	24.0		53.8		
	100	*p6mm*	45.5	25.3	22.8		51.9		
poly[(3,4-3,5)12G2-4EBn]	30	*p6mm*	43.7	25.2	22.0		50.6	1.01	5.25
	70	*p6mm*	43.2	24.9	21.7		49.6		
	105	*p6mm*	38.9	22.4	19.5		44.9		
poly[(3,4,5-3,4)12G2-4EBn]	70	*p2mm*	46.1	36.8	23.3	18.0	$a=46.5$[f] $b=36.1$[f]		
poly[(3,4,5-3,5)12G2-4EBn]	25	*p6mm*	39.8	23.0	20.0		46.0		
	60	*p6mm*	39.3	22.8	19.8		45.3		
poly[(4-3,4-3,5)12G2-4EBn]	30	*p6mm*	49.4	27.3	25.3		56.6		
	75	*p6mm*	53.2	31.1	27.6		62.5		

[a] Lattice parameter for the *p6mm* columnar hexagonal lattice $a=2\langle d_{100}\rangle 3^{-0.5}$, where $\langle d_{100}\rangle = 0.25(d_{100} + 3^{0.5}d_{110} + 2d_{200} + 7^{0.5}d_{210})$ and is equal to the diameter of a column (D_{col}). [b] ρ_{20}, Experimental density measured at 20 °C. [c] Number of dendrons in a column stratum $=(3^{0.5}N_A at\rho_{20})(2M)^{-1}$, where Avogadro's number $N_A = 6.0220455\times10^{23}$, layer thickness $t=4.75$ Å, and M is the molecular weight of the monomer. [d] *d* Spacings for the *p6mm* hexagonal columnar lattice. [e] *d* Spacings for the *p2mm* simple rectangular columnar lattice. [f] Lattice parameters $a=hd$ and $b=kd$ the *p2mm* simple rectangular columnar lattice.

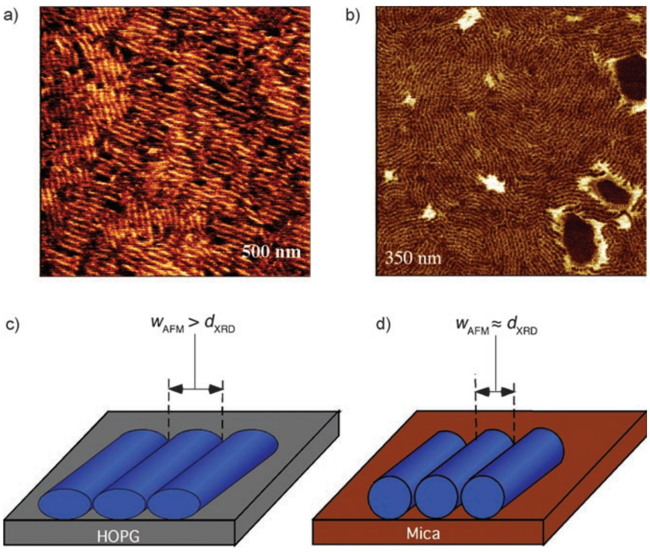


Figure 8. AFM Visualization of **poly[(3,4-3,5)12G2-4EBn]** on a) HOPG and b) mica. Illustration of cylindrical PPAs on c) HOPG and d) mica. The oblate shape on HOPG is due to epitaxial adsorption of the alkyl tails to the graphite underlayer.

helical order model for flexible polymers confined to the cylinder core.

Experimental Section

Materials: *N,N′*-Dicyclohexylcarbodiimide (DCC, 99%), and α,α,α-trifluorotoluene (99%) were used as received from Acros. 4-(*N,N*-Dimethylamino)pyridine (DMAP, Acros, 99%) was recrystallized from toluene before use. Dichloromethane (CH_2Cl_2, Fisher, A.C.S. reagent) was freshly distilled from CaH_2 (Sigma-Aldrich, coarse granules, ~20 mm, 95%) under argon. Tetrahydrofuran (THF, Fisher, A.C.S. reagent) was freshly distilled from sodium/benzophenone under argon. Benzene (Acros) dried by passing through a column of activated alumina under N_2 pressure. Hexanes, acetone, ethyl acetate (EtOAc, A.C.S. reagent), methanol (MeOH), NaOH, $MgSO_4$, anhydrous Na_2SO_4, and $NaHCO_3$ (all A.C.S. Certified or A.C.S. Certified PLUS) were used as received from Fisher. 4-(*N,N*-Dimethylamino)pyridinium tosylate (DPTS) was prepared according to a literature procedure.[17] $[Rh(C{\equiv}CPh)(nbd)(PPh_3)_2]$ was prepared according to a literature procedure and used *without* recrystallization.[19] The synthesis of 4-ethynylbenzyl alcohol[16] and **poly[(3,4-3,5)12G2-4EBn]** have been described previously.[5g] 3,4-Didodecyloxybenzoic acid (**(3,4)12G1-CO$_2$H**), 3,4-di(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluorododecan-1-yloxy)benzoic acid (**(3,4)12F8G1-CO$_2$H**), 3,4,5-tridodecyloxybenzoic acid (**(3,4,5)12G2-CO$_2$H**), 3,4-bis[(4′-dodecan-1-yloxy)benzyloxy]benzoic acid (**(4-3,4)12G1-4EBn**), 3,4,5-tris[4-((*S*)-3-methylbutan)-1-yloxy)benzyloxy]benzoic acid (**(4-3,4,5)AmylG1-CO$_2$H**), 3,4,5-tris[(4′-dodecan-1-yloxy)benzyloxy]benzoic acid (**(4-3,4,5)12G1-CO$_2$H**), 3,4-bis(3′,4′-bis(dodecan-1-yloxy)benzyloxy)benzoic acid (**(3,4-3,4)12G2-CO$_2$H**), 3,4,5-tris(3′,4′-bis(dodecan-1-yloxy)benzyloxy)benzoic acid (**(3,4-3,4,5)12G2-CO$_2$H**), 3,4-bis(3′,4′,5′-tris(dodecan-1-yloxy)benzyloxy)benzoic acid (**(3,4,5-3,4)12G2-CO$_2$H**), 3,5-bis(3′,4′,5′-tris(dodecan-1-yloxy)benzyloxy)benzoic acid (**(3,4,5-3,5)12G2-CO$_2$H**), 3,4,5-tris(3′,4′,5′-tris(dodecan-1-yloxy)benzyloxy)benzoic acid (**(3,4,5-3,4,5)12G2-CO$_2$H**), 3,5-bis{3′,4′-bis[(4″-dodecan-1-yloxy)benzyloxy]benzyloxy}benzoic acid (**(4-3,4-3,5)12G1-CO$_2$H**), 3,5-bis{3′,5′-bis[3″,4″-bis(dodecan-1-yloxy)benzyloxy]benzyloxy}benzoic acid (**(3,4-3,5-3,5)12G3-CO$_2$H**), and 3,5-bis(3′,5′-bis{3″,4″-bis[(4‴-dodecan-1-yloxy)benzyloxy]benzyloxy}benzyloxy)benzoic acid (**(4-3,4-3,5-3,5)12G3-CO$_2$H**) were prepared a described previously.[6c,15,24]

Table 4. Average column diameter measured from images visualized by AFM.

Polymer	w_{AFM} [Å]	
	HOPG	Mica
poly[(3,4)12G1-4EBn]	58	–
poly[(4-3,4,5)12G1-4EBn]	70	–
poly[(3,4-3,5)12G2-4EBn]	66	48
poly[(4-3,4-3,5)12G2-4EBn]	86	–

Techniques: NMR Spectra (^{1}H, 500 MHz, ^{13}C, 125 MHz, and ^{19}F, 470 MHz) were recorded on Bruker DRX 500 and Bruker AMX 500 spectrometers in $CDCl_3$ (with 5 v/v% tetramethylsilane (TMS) internal standard) at 27 °C unless otherwise noted. Chemical shifts are reported as δ, ppm. Circular dichroism (CD) and corresponding UV/Vis spectra were recorded on a Jacsco J-720 spectropolarimeter equipped with a Thermo NesLab RTE-111 variable temperature circulating bath. Specific optical rotations $[\alpha]_D$ were determined using a Jasco P-1010 polarimeter. UV/Vis Spectra were recorded using a Shimadzu UV-1601 spectrophotometer.

Thin layer chromatography (TLC) was performed on silica gel plates (Sigma-Aldrich) with UV indicator and the reported eluent. High-pressure liquid chromatography (HPLC) in THF ($1\,\mathrm{mL\,min^{-1}}$) using a Shimadzu LC-10 AT liquid chromatograph using equipped with a Perkin-Elmer LC-100 column oven at 40 °C, Shimadzu SPD-10 A UV/Vis (254 nm) and RID-10 A refractive index detectors, Nelson Analytical 900 Series integrator data station and two American Polymer Standards AM GPC gel columns of 500 Å (5 μm) and 10000 Å (5 μm). Gel permeation chromatography (GPC) in THF ($1\,\mathrm{mL\,min^{-1}}$) using a Shimadzu LC-10 AT liquid chromatograph equipped with a SIL-10 AD auto injector, CTO-10 A column oven at 40 °C, detection and data collection as for HPLC and two American Polymer Standards AM GPC gel columns of 500 Å (10 μm), 10000 Å (10 μm) and 100000 Å (10 μm). Relative molecular weights were determined according to a calibration with narrow polystyrene standards (American Polymer Standards). MALDI-TOF Mass spectrometry was performed on a PerSeptive Biosystems Voyager-DE in linear mode. Unless otherwise noted, all measurements were made using 2,5-dihydroxybenzoic acid as matrix. High-resolution electrospray ionization (HRMS-ESI) and chemical ionization (HRMS-CI) mass spectra measured at the Mass Spectrometry Facility of the Department of Chemistry at the University of Pennsylvania.

Melting point determinations using a uni-melt capillary melting point apparatus (Arthur H. Thomas Company, Philadelphia, PA, USA) are reported as uncorrected values. Thermal transitions were measured on a Thermal Analysis (TA) Instruments 2920 modulated differential scanning calorimeter or DSC Q100 differential scanning calorimeter (DSC) with refrigerated cooling system under nitrogen. In all cases, the heating and cooling rates were $10\,\mathrm{°C\,min^{-1}}$ unless otherwise noted. First-order transition temperatures are reported as the maximum and minimum of their endothermic and exothermic peak, respectively. Glass transition temperatures (T_g) are reported as the middle of the change in heat capacity. Indium was the calibration standard. An Olympus BX51 optical polarized microscope (10×/50× magnification) equipped with a Mettler Toledo FP82HT hot stage and Mettler Toledo FP90 central processor was used to verify thermal transitions and characterize anisotropic textures.

X-Ray diffraction measurements were performed with $\mathrm{Cu}_{K\alpha 1}$ radiation from a Bruker-Nonius FR-591 rotating anode X-ray source with a $0.2\times 2.0\,\mathrm{mm^2}$ filament operated at 3.4 kW. The beam was collimated and focused by a single bent mirror and sagitally focusing Ge(111) monochromator, resulting in a $0.2\times 0.2\,\mathrm{mm^2}$ spot on a Bruker-AXS Hi-Star multiwire area detector. To minimize attenuation and background scattering, an integral vacuum was maintained along the length of the flight tube and the sample chamber. Samples were kept inside a Linkham hot stage and controlled within ±0.1 °C. Oriented fibers were obtained fro the liquid crystalline phase. Both bulk and fiber samples were held in Lindeman-type capillaries during X-ray experiments. Electron density profiles were computed using programs developed by our laboratories with Silicon graphics (SGI) computers. Molecular models were constructed using Materials Studio (Accelrys Inc., San Diego, CA, USA) software suite.

Synthesis

4-Ethynylbenzyl 3,4-bis(dodecan-1-yloxy)benzoate [(3,4)12G1-4EBn]: A solution of **(3,4)12G1-$\mathbf{CO_2H}$** (1.48 g, 3.0 mmol), 4-ethynylbenzyl alcohol (492.4 mg, 3.2 mmol), DPTS (178.9 mg, 0.6 mmol) and DCC (751.2 mg, 3.6 mmol) in dry CH_2Cl_2 (30 mL) was stirred for 15 h. A colorless precipitate was removed by filtration of the crude reaction mixture. The filtrate was evaporated to dryness under reduced pressure. The crude monomer was subjected to chromatography on silica gel using CH_2Cl_2. Precipitated the monomer from CH_2Cl_2 into MeOH and collected it by filtration. Freeze drying from benzene provided **(3,4)12G1-4EBn** (1.52 g, 83 %). TLC (silica gel, hexanes/CH_2Cl_2 1:1): $R_f=0.47$; HPLC (THF): 99+ % pure; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta=7.67$ (dd, ^3J(H,H) = 8.4, ^4J(H,H) = 1.9 Hz, 1 H; aromatic C(6)*H*), 7.57 (d, J(H,H) = 1.9 Hz, 1 H; aromatic C(2)*H*), 7.50 (d, J(H,H) = 8.2 Hz, 2 H; 4EBn aromatic C(3)*H* and C(5)*H*), 7.39 (d, J(H,H) = 8.1 Hz, 2 H; 4EBn aromatic C(2)*H* and C(6)*H*), 7.31 (d, J(H,H) = 2.2 Hz, 2 H; aromatic C(2)H and C(6)H), 6.86 (d, J(H,H) = 8.1 Hz, 2 H; aromatic C(5)*H*), 5.33 (s, 2 H; 4EBn $\mathrm{ArC}H_2\mathrm{O}$), 4.04 (t, J(H,H) = 6.7 Hz, 2 H; $\mathrm{ArOC}H_2$), 4.03 (t, J(H,H) = 6.8 Hz, 2 H; $\mathrm{ArOC}H_2$), 3.08 (s, 1 H; alkyne C*H*), 1.83 (m, 4 H; $\mathrm{ArOCH_2C}H_2$), 1.48 (m, 4 H; $\mathrm{ArO(CH_2)_2C}H_2$), 1.36 (m, overlapped), 1.27 (overlapping s, 32 H; $\mathrm{ArO(CH_2)_3(C}H_2\mathrm{)_8}$), 0.89 (t, J(H,H) = 6.9 Hz, 6 H; $\mathrm{ArO(CH_2)_{11}C}H_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta=166.54$ ($C\mathrm{O_2CH_2}$), 153.87 (aromatic *C*(3)), 149.00 (aromatic *C*(4)), 137.48 (4EBn aromatic *C*(1)), 132.66 (4EBn aromatic *C*(3) and *C*(5)), 128.20 (4EBn aromatic *C*(2) and *C*(6)), 122.51 (aromatic *C*(1)), 122.28 (4EBn aromatic *C*(4)), 114.91 (aromatic *C*(2)), 112.38 (aromatic *C*(5)), 83.65 (alkyne Ar*C*), 77.86 (alkyne *C*H), 69.73 ($\mathrm{ArO}C\mathrm{H_2}$), 69.41 ($\mathrm{ArO}C\mathrm{H_2}$), 66.19 (4EBn $\mathrm{Ar}C\mathrm{H_2O}$), 32.27 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 30.04 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 30.03 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 30.00 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 29.70 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 29.95 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 29.76 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 29.72 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 29.70 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 29.55 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 29.43 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 26.36 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 26.32 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 23.03 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 14.44 ($\mathrm{ArO(CH_2)_{11}}C\mathrm{H_3}$); HRMS-ESI: m/z: calcd for $C_{40}H_{60}O_4Na$: 627.4389; found: 627.4398 $[M+\mathrm{Na}]^+$.

4-Ethynylbenzyl 3,4-bis(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluorododecan-1-yloxy)benzoate [(3,4)12F8G1-4EBn]: A solution of **(3,4)12F8G1-$\mathbf{CO_2H}$** (520 mg, 0.47 mmol), 4-ethynylbenzyl alcohol (74.8 mg, 0.56 mmol), DPTS (36.1 mg, 0.12 mmol) and DCC (125.4 mg, 0.61 mmol) in α,α,α-trifluorotoluene (5 mL) was stirred at 55 °C for 16 h. A colorless precipitate was removed by filtration of the crude reaction mixture. The filtrate was evaporated to dryness under reduced pressure. The crude monomer was subjected to chromatography on silica gel using CH_2Cl_2. Freeze drying from benzene provided **(3,4)12F8G1-4EBn** (450 mg, 78 %). TLC (silica gel, CH_2Cl_2): $R_f=0.20$; HPLC (THF): 99+ % pure; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta=7.70$ (dd, ^3J(H,H) = 8.5, ^4J(H,H) = 2.0 Hz, 1 H; aromatic C(6)*H*), 7.56 (d, J(H,H) = 2.0 Hz, 1 H; aromatic C(2)*H*), 7.51 (d, J(H,H) = 8.3 Hz, 2 H; 4EBn aromatic C(3)*H* and C(5)*H*), 7.39 (d, J(H,H) = 8.3 Hz, 2 H; 4EBn aromatic C(2)*H* and C(6)*H*), 6.87 (d, J(H,H) = 8.5 Hz, 1 H; aromatic C(5)*H*), 5.33 (s, 2 H; 4EBn $\mathrm{ArC}H_2\mathrm{O}$), 4.08 (t, J(H,H) = 5.7 Hz, 2 H; $\mathrm{ArOC}H_2$), 4.07 (t, J(H,H) = 5.7 Hz, 2 H; $\mathrm{ArOC}H_2$), 3.09 (s, 1 H; alkyne C*H*), 2.17 (m, 4 H; $\mathrm{ArOCH_2C}H_2$), 1.91 (m, 4 H; $\mathrm{ArO(CH_2)_2C}H_2$), 1.83 (m, 4 H; $\mathrm{ArO(CH_2)_3C}H_2$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta=166.41$ ($C\mathrm{O_2CH_2}$), 153.33 (aromatic *C*(3)), 148.61 (aromatic *C*(4)), 137.33 (4EBn aromatic *C*(1)), 132.69 (4EBn aromatic *C*(3) and *C*(5)), 128.28 (4EBn aromatic *C*(2) and *C*(6)), 124.33, 122.87 (aromatic *C*(1)), 122.34 (4EBn aromatic *C*(4)), 114.47 (aromatic *C*(2)), 111.13 (aromatic *C*(5)), 83.59 (alkyne Ar*C*), 77.94 (alkyne *C*H), 68.79 ($\mathrm{ArO}C\mathrm{H_2}$), 68.56 ($\mathrm{ArO}C\mathrm{H_2}$), 66.34 (4EBn $\mathrm{Ar}C\mathrm{H_2O}$), 30.96 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_3}$), 28.95 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_3}$), 17.68 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_3}$); ^{19}F NMR (470 MHz, $CDCl_3$, 25 °C, $CFCl_3$ external standard): $\delta=-81.44$ (t, J(F,F) = 9.4 Hz; $\mathrm{ArO(CH_2)_4(CF_2)_7C}F_3$), −115.17 (t, J(F,F) = 14.1 Hz; $\mathrm{ArO(CH_2)_4CF_2}$), −122.40 (s; $\mathrm{ArO(CH_2)_4CF_2(CF_2)_6}$), −122.60 (s; $\mathrm{ArO(CH_2)_4CF_2(CF_2)_6}$), −123.38 (s; $\mathrm{ArO(CH_2)_4CF_2(CF_2)_6}$), −124.04 (s; $\mathrm{ArO(CH_2)_4CF_2(CF_2)_6}$), −126.78 (s; $\mathrm{ArO(CH_2)_4CF_2(CF_2)_6}$).

4-Ethynylbenzyl 3,4,5-tris(dodecan-1-yloxy)benzoate [(3,4,5)12G1-4EBn]: A solution of **(3,4,5)12G1-$\mathbf{CO_2H}$** (1.52 g, 2.2 mmol), 4-ethynylbenzyl alcohol (355.4 mg, 2.7 mmol), DPTS (159.8 mg, 0.5 mmol) and DCC (605.0 mg, 2.9 mmol) in dry CH_2Cl_2 (10 mL) was stirred for 24 h. A colorless precipitate was removed by filtration of the crude reaction mixture. The filtrate was evaporated to dryness under reduced pressure. The crude monomer was subjected to chromatography on silica gel using hexanes/CH_2Cl_2 1:1. Precipitated the monomer from CH_2Cl_2 into MeOH and collected it by filtration. Freeze drying from benzene provided **(3,4,5)12G1-4EBn** (1.60 g, 90 %). TLC (silica gel, hexanes/CH_2Cl_2 1:2): $R_f=0.72$; HPLC (THF): 99+ % pure; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta=7.51$ (d, J(H,H) = 8.3 Hz, 2 H; 4EBn aromatic C(3)*H* and C(5)*H*), 7.38 (d, J(H,H) = 8.4 Hz, 2 H; 4EBn aromatic C(2)*H* and C(6)*H*), 7.28 (s, 2 H; aromatic C(2)*H* and C(6)*H*), 5.34 (s, 2 H; 4EBn $\mathrm{ArC}H_2\mathrm{O}$), 4.02 (t, J(H,H) = 6.6 Hz, 2 H; $\mathrm{ArOC}H_2$), 4.00 (t, J(H,H) = 6.5 Hz, 4 H; $\mathrm{ArOC}H_2$), 3.09 (s, 1 H; alkyne C*H*), 1.81 (m, 4 H; Ar-

OCH$_2$C*H*$_2$), 1.74 (m, 2H; ArOCH$_2$C*H*$_2$), 1.47 (m, 6H; ArO(CH$_2$)$_2$C*H*$_2$), 1.34 (m, overlapped), 1.27 (overlapping s, 48H; ArO(CH$_2$)$_3$(C*H*$_2$)$_8$), 0.89 (t, *J*(H,H) = 6.8 Hz, 9H; ArO(CH$_2$)$_{11}$C*H*$_3$); ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C, TMS): δ = 166.54 (*C*O$_2$CH$_2$), 153.01 (aromatic *C*(3) and *C*(5)), 143.16 (aromatic *C*(4)), 137.22 (4EBn aromatic *C*(1)), 132.69 (4EBn aromatic *C*(3) and *C*(5)), 128.23 (4EBn aromatic *C*(2) and *C*(6)), 125.03 (aromatic *C*(1)), 122.39 (4EBn aromatic *C*(4)), 109.86 (aromatic *C*(2) and *C*(6)), 83.62 (alkyne Ar*C*), 77.97 (alkyne *C*H), 73.31 (ArO*C*H$_2$), 73.26 (ArO*C*H$_2$), 66.45 (4EBn Ar*C*H$_2$O), 32.26 (ArOCH$_2$(*C*H$_2$)$_{10}$), 30.01 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.98 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.96 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.94 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.79 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.77 (ArOCH$_2$-(*C*H$_2$)$_{10}$), 29.69 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.65 (ArOCH$_2$(*C*H$_2$)$_{10}$), 26.41 (ArOCH$_2$(*C*H$_2$)$_{10}$), 23.02 (ArOCH$_2$(*C*H$_2$)$_{10}$), 14.44 (ArO(CH$_2$)$_{11}$*C*H$_3$); UV/VIS (hexanes): λ_{max} (ε) = 203 (68000), 220 (53000), 241 (32000), 251 (31000), 266 nm (19000 M^{-1}cm^{-1}); HRMS-ESI: *m*/*z*: calcd for C$_{52}$H$_{84}$O$_5$Na: 811.6216; found: 811.6221 [M+Na]$^+$.

4-Ethynylbenzyl 3,4-bis[(4′-dodecan-1-yloxy)benzyloxy]benzoate [(4-3,4)12G1-4EBn]: A 100 mL flask equipped with a magnetic stir bar was used to prepare a solution of **(4-3,4)12G1-CO$_2$H** (1.64 g, 2.3 mmol), 4-ethynylbenzyl alcohol (357.4 mg, 2.7 mmol), DPTS (155.0 mg, 0.5 mmol) and DCC (622.2 mg, 3.01 mmol) in dry CH$_2$Cl$_2$ (20 mL). The reaction was sealed with a rubber septum and left stirring for 16 h. The reaction mixture was filtered to remove the insoluble urea product, and the filtrate was evaporated to dryness under reduced pressure. The resulting solid was subjected to chromatography on silica gel using hexanes/CH$_2$Cl$_2$ 3:1. After removal of solvent form the collected product, the isolated solid was dissolved in CH$_2$Cl$_2$ (10 mL) and precipitated into cold methanol. Freeze drying from benzene provided the monomer as a white solid (1.82 g, 95%). TLC (silica gel, hexanes/CH$_2$Cl$_2$ 3:1): R_f = 0.12; HPLC (THF): 99+ % pure; ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.65 (overlapped d, *J*(H,H) = 1.8 Hz, 1H; aromatic C(2)*H*), 7.65 (overlapped dd, ^3J(H,H) = 8.8, ^4J(H,H) = 2.0 Hz, 1H; aromatic C(6)*H*), 7.50 (d, *J*(H,H) = 8.0 Hz, 2H; 4EBn aromatic C(3)*H* and C(5)*H*), 7.36 (d, *J*(H,H) = 8.0 Hz, 2H; 4EBn aromatic C(2)*H* and C(6)*H*), 7.33 (d, *J*(H,H) = 8.1 Hz, 2H; aromatic C(2′)*H* and C(6′)*H*), 7.32 (d, *J*(H,H) = 8.0 Hz, 2H; aromatic C(2′)*H* and C(6′)*H*), 6.93 (d, *J*(H,H) = 8.9 Hz, 1H; aromatic C(5)*H*), 6.88 (d, *J*(H,H) = 8.4 Hz, 2H; aromatic C(3′)*H* and C(5′)*H*), 6.86 (d, *J*(H,H) = 8.3 Hz, 2H; aromatic C(3′)*H* and C(5′)*H*), 5.30 (s, 2H; 4EBn ArC*H*$_2$O), 5.13 (s, 2H; ArC*H*$_2$O), 5.09 (s, 2H; ArC*H*$_2$O,), 3.95 (t, *J*(H,H) = 6.6 Hz, 4H; ArOC*H*$_2$), 3.08 (s, 1H; alkyne C*H*), 1.78 (m, 4H; ArOCH$_2$C*H*$_2$), 1.45 (m, 4H; ArO(CH$_2$)$_2$C*H*$_2$), 1.32 (overlapped m), 1.27 (overlapping s, 32H; ArO(CH$_2$)$_3$(C*H*$_2$)$_8$), 0.89 (t, *J*(H,H) = 6.4 Hz, 6H; ArO(CH$_2$)$_{11}$C*H*$_3$); ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C, TMS): δ = 166.33 (*C*O$_2$CH$_2$), 159.42 (aromatic *C*(4′)), 159.37 (aromatic *C*(4′)), 153.69 (aromatic *C*(3)), 148.83 (aromatic *C*(4)), 137.39 (4EBn aromatic *C*(1)), 132.66 (4EBn aromatic *C*(3) and *C*(5)), 129.46 (aromatic *C*(2′) and *C*(6′)), 129.22 (aromatic *C*(2′) and *C*(6′)), 129.03 (aromatic *C*(1′)), 128.68 (aromatic *C*(1′)), 128.17 (4EBn aromatic *C*(1)), 124.47 (aromatic *C*(6)), 123.03 (aromatic *C*(6)), 122.30 (4EBn aromatic *C*(4)), 116.42 (aromatic *C*(2)), 114.93 (aromatic *C*(3′) and *C*(5′)), 114.87 (aromatic *C*(3′) and *C*(5′)), 113.90 (aromatic *C*(5)), 83.66 (alkyne Ar*C*), 77.87 (alkyne *C*H), 71.58 (Ar*C*H$_2$O), 71.16 (Ar*C*H$_2$O), 68.44 (ArO*C*H$_2$), 68.42 (ArO*C*H$_2$), 66.22 (4EBn Ar*C*H$_2$O), 32.27 (ArOCH$_2$(*C*H$_2$)$_{10}$), 30.01 (ArOCH$_2$-(*C*H$_2$)$_{10}$), 29.98 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.95 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.94 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.77 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.69 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.66 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.64 (ArOCH$_2$(*C*H$_2$)$_{10}$), 26.42 (ArOCH$_2$-(*C*H$_2$)$_{10}$), 23.03 (ArOCH$_2$(*C*H$_2$)$_{10}$), 14.44 (ArO(CH$_2$)$_{11}$*C*H$_3$); UV/VIS (hexanes): λ_{max} (ε) = 203 (77000), 222 (47000), 241 (38000), 252 (40000), 292 nm (11000 M^{-1}cm^{-1}); HRMS-ESI: *m*/*z*: calcd for C$_{54}$H$_{72}$O$_6$Na: 839.5227; found: 839.5222 [*M*+Na]$^+$.

4-Ethynylbenzyl 3,4,5-tris[4-((*S*)-3-methylbutan)-1-yloxy)benzyloxy]benzoate [(4-3,4,5)AmylG1-4EBn]: A 50 mL flask equipped with a magnetic stir bar was used to prepare a solution of **(4-3,4,5)AmylG1-CO$_2$H** (1.97 g, 2.8 mmol), 4-ethynylbenzyl alcohol (477.7 mg, 3.3 mmol), DPTS (1.01 g, 3.4 mmol) and DCC (724.8 mg, 3.5 mmol) in dry CH$_2$Cl$_2$ (10 mL). The reaction was sealed with a rubber septum and left stirring for 19 h. The reaction mixture was filtered to remove the insoluble urea product, and the filtrate was evaporated to dryness under reduced pressure. The resulting solid was subjected to chromatography on silica gel using hexanes/CH$_2$Cl$_2$ 1:3→1:9. After removal of solvent from the collected product, the isolated solid was dissolved in CH$_2$Cl$_2$ (20 mL) and precipitated into cold methanol. Freeze drying from benzene provided the monomer as a white solid (2.08 g, 91%). $[\alpha]^{21}_{D}$ = +7.6° (*c* = 1.16 in THF); TLC (silica gel, hexanes/CH$_2$Cl$_2$ 1:6): R_f = 0.33; HPLC (THF): 99+ % pure; ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.52 (d, *J*(H,H) = 8.3 Hz, 2H; 4EBn aromatic C(3)*H* and C(5)*H*), 7.37 (s, 2H; aromatic C(2)*H* and C(6)*H*), 7.36 (d, *J*(H,H) = 8.4 Hz, 2H; 4EBn aromatic C(2)*H* and C(6)*H*), 7.31 (d, *J*(H,H) = 8.6 Hz, 4H; aromatic C(2′)*H* and C(6′)*H*), 7.26 (d, *J*(H,H) = 8.4 Hz, 2H; 4EBn aromatic C(2′)*H* and C(6′)*H*), 6.89 (d, *J*(H,H) = 8.7 Hz, 4H; aromatic C(3′)*H* and C(5′)*H*), 6.89 (d, *J*(H,H) = 8.6 Hz, 2H; aromatic C(3′)*H* and C(5′)*H*), 5.32 (s, 2H; 4EBn ArC*H*$_2$O), 5.04 (s, 4H; ArC*H*$_2$O), 5.03 (s, 2H; ArC*H*$_2$O,), 3.84 (dd, ^3J(H,H) = 6.0, ^2J(H,H) = 9.0 Hz, 2H; ArOC*H*$_2$), 3.80 (dd, ^3J(H,H) = 6.0, ^2J(H,H) = 9.0 Hz, 1H; ArOC*H*$_2$), 3.75 (dd, ^3J(H,H) = 6.6, ^2J(H,H) = 9.0 Hz, 2H; ArOC*H*$_2$), 3.71 (dd, ^3J(H,H) = 6.6, ^2J(H,H) = 9.0 Hz, 1H; ArOC*H*$_2$), 3.10 (s, 1H; alkyne C*H*), 1.88 (m, 3H; ArOCH$_2$C*H*), 1.59 (m, 2H; ArOCH$_2$CH(CH$_3$)C*H*$_2$), 1.58 (m, 1H; ArOCH$_2$C*H*(CH$_3$)CH$_2$), 1.29 (m, 2H; ArOCH$_2$CH-(CH$_3$)C*H*$_2$), 1.27 (m, 1H; ArOCH$_2$CH(CH$_3$)C*H*$_2$), 1.03 (d, *J*(H,H) = 6.8 Hz, 6H; ArOCH$_2$CH(C*H*$_3$)), 1.02 (d, *J*(H,H) = 7.0 Hz, 3H; ArOCH$_2$CH(C*H*$_3$)), 0.97 (t, *J*(H,H) = 7.5 Hz, 6H; ArOCH$_2$CH-(CH$_3$)CH$_2$C*H*$_3$), 0.97 (t, *J*(H,H) = 7.4 Hz, 3H; ArOCH$_2$CH-(CH$_3$)CH$_2$C*H*$_3$); ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C, TMS): δ = 166.27 (*C*O$_2$CH$_2$), 159.60 (4EBn aromatic *C*(4′)), 153.01 (aromatic *C*(3) and *C*(5)), 143.16 (aromatic *C*(4)), 137.22 (4EBn aromatic *C*(1)), 132.69 (4EBn aromatic *C*(3) and *C*(5)), 130.60 (aromatic *C*(2′) and *C*(6′)), 129.77 (aromatic *C*(1′)), 129.45 (aromatic *C*(2′) and *C*(6′)), 128.89 (aromatic *C*(1′)), 128.23 (4EBn aromatic *C*(2) and *C*(6)), 125.03 (aromatic *C*(1)), 122.39 (4EBn aromatic *C*(4)), 114.89 (aromatic *C*(3′) and *C*(5′)), 114.54 (aromatic *C*(3′) and *C*(5′)), 109.86 (aromatic *C*(2) and *C*(6)), 83.62 (alkyne Ar*C*), 77.97 (alkyne *C*H), 75.06 (Ar*C*H$_2$O), 73.31 (ArO*C*H$_2$), 73.26 (ArO*C*H$_2$), 71.52 (Ar*C*H$_2$O), 66.45 (4EBn Ar*C*H$_2$O), 35.10 (ArOCH$_2$*C*H), 26.52 (ArOCH$_2$CH(CH$_3$)*C*H$_2$), 16.89 ArOCH$_2$CH(*C*H$_3$)), 16.88 ArOCH$_2$CH(*C*H$_3$)), 11.66 (ArOCH$_2$CH(CH$_3$)CH$_2$*C*H$_3$); UV/VIS (hexanes): λ_{max} (ε) = 230 (68000), 251 (24000), 270 nm (18000 M^{-1}cm^{-1}); MALDI-TOF: *m*/*z*: calcd for C$_{52}$H$_{60}$O$_8$Na: 835.42; found: 836.44 [*M*+Na]$^+$.

4-Ethynylbenzyl 3,4,5-tris[(4′-dodecan-1-yloxy)benzyloxy]benzoate [(4-3,4,5)12G1-4EBn]: A 50 mL flask equipped with a magnetic stir bar was used to prepare a solution of **(4-3,4,5)12G1-CO$_2$H** (1.75 g, 1.8 mmol), 4-ethynylbenzyl alcohol (287.9 mg, 2.2 mmol), DPTS (519.7 mg 1.8 mmol) and DCC (441.7 mg, 2.1 mmol) in dry CH$_2$Cl$_2$ (10 mL). The reaction was sealed with a rubber septum and left stirring for 13 h. The reaction mixture was filtered to remove the insoluble urea product, and the filtrate was evaporated to dryness under reduced pressure. The resulting solid was subjected to chromatography on silica gel using hexanes/CH$_2$Cl$_2$ 1:2. After removal of solvent from the collected product, the isolated solid was dissolved in CH$_2$Cl$_2$ (10 mL) and precipitated into cold methanol. Freeze drying from benzene provided the monomer as a white solid (1.55 g, 79%). TLC (silica gel, hexanes/CH$_2$Cl$_2$ 1:2): R_f = 0.29; HPLC (THF): 99+ % pure; ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.51 (d, *J*(H,H) = 8.2 Hz, 2H; 4EBn aromatic C(3)*H* and C(5)*H*), 7.36 (s, 2H; aromatic C(2)*H* and C(6)*H*), 7.33 (d, *J*(H,H) = 8.2 Hz, 2H; 4EBn aromatic C(2)*H* and C(6)*H*,), 7.30 (d, *J*(H,H) = 8.6 Hz, 4H; aromatic C(2′)*H* and C(6′)*H*), 7.25 (d, *J*(H,H) = 9.0 Hz, 2H; aromatic C(2′)*H* and C(6′)*H*), 6.87 (d, *J*(H,H) = 8.6 Hz, 4H; aromatic C(3′)*H* and C(5′)*H*), 6.75 (d, *J*(H,H) = 8.6 Hz, 2H; aromatic C(3′)*H* and C(5′)*H*), 5.30 (s, 2H; 4EBn ArC*H*$_2$O), 5.03 (s, 4H; ArC*H*$_2$O), 5.02 (s, 2H; ArC*H*$_2$O), 3.95 (t, *J*(H,H) = 6.6 Hz, 4H; ArOC*H*$_2$), 3.91 (t, *J*(H,H) = 6.6 Hz, 2H; ArOC*H*$_2$), 3.08 (s, 1H; alkyne C*H*), 1.77 (m, 6H; ArOCH$_2$C*H*$_2$), 1.45 (m, 6H; ArO-(CH$_2$)$_2$C*H*$_2$), 1.31 (m overlapped), 1.27 (s overlapping, 48H; ArO(CH$_2$)$_2$-(C*H*$_2$)$_8$), 0.88 (t, *J*(H,H) = 6.7 Hz, 9H; ArO(CH$_2$)$_{11}$C*H*$_3$); ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C, TMS): δ = 166.23 (*C*O$_2$CH$_2$), 159.38 (4EBn aromatic *C*(4′)), 159.35 (4EBn aromatic *C*(4′)), 152.98 (aromatic *C*(3) and *C*(5)), 143.08 (aromatic *C*(4)), 137.17 (4EBn aromatic *C*(1)), 132.66 (4EBn aromatic *C*(3) and *C*(5)), 130.58 (aromatic *C*(2′) and *C*(6′)), 129.75 (aromatic *C*(1′)), 129.54 (aromatic *C*(2′) and *C*(6′)), 128.87 (aromatic *C*(1′)), 128.21 (4EBn aromatic *C*(2) and *C*(6)), 125.00 (aromatic *C*(1)), 122.36 (4EBn aromatic *C*(4)), 114.81 (aromatic *C*(3′) and *C*(5′)), 114.45 (aromatic *C*(3′) and *C*(5′)), 109.77 (aromatic *C*(2) and *C*(6)), 83.59 (alkyne Ar*C*), 77.96 (alkyne *C*H), 75.03 (Ar*C*H$_2$O), 71.47 (Ar*C*H$_2$O), 68.39 (ArO*C*H$_2$), 68.31 (ArO*C*H$_2$), 66.43 (4EBn Ar*C*H$_2$O), 32.26 (ArOCH$_2$(*C*H$_2$)$_{10}$), 30.01 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.98 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.96 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.94 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.79 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.77 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.69 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.65 (ArOCH$_2$(*C*H$_2$)$_{10}$), 26.41 (ArOCH$_2$(*C*H$_2$)$_{10}$), 23.02 (ArOCH$_2$(*C*H$_2$)$_{10}$), 14.44 (ArO(CH$_2$)$_{11}$*C*H$_3$); HRMS-ESI: *m*/*z*: calcd for $C_{73}H_{102}O_8Na$: 1129.7472; found: 1127.7371 [*M*+Na]$^+$.

4-Ethynylbenzyl 3,4-bis(3′,4′-bis(dodecan-1-yloxy)benzyloxy)benzoate [(3,4-3,4)12G2-4EBn]: A solution of **(3,4-3,4)12G2-CO$_2$H** (1.51 g, 1.4 mmol), 4-ethynylbenzyl alcohol (230.1 mg, 1.7 mmol), DPTS (419.8 mg, 1.4 mmol) and DCC (349.1 mg, 1.7 mmol) in CH_2Cl_2 (20 mL) was stirred for 21 h. A colorless precipitate was removed by filtration of the crude reaction mixture. The filtrate was evaporated to dryness under reduced pressure. The crude monomer was subjected to chromatography on silica gel using hexanes/CH_2Cl_2 1:4. Precipitated the monomer from CH_2Cl_2 into MeOH and collected it by filtration. Freeze drying from benzene provided **(3,4-3,4)12G2-4EBn** (1.53 g, 92 %). TLC (silica gel, hexanes/CH_2Cl_2 1:2): $R_f=0.16$; HPLC (THF): 99+ % pure; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta=7.65$ (d, *J*(H,H) = 1.9 Hz, 1 H; aromatic C(2)*H*), 7.65 (dd, ^3J(H,H) = 8.8, ^4J(H,H) = 1.9 Hz, 1 H; aromatic C(6)*H*), 7.50 (d, *J*(H,H) = 8.2 Hz, 2 H; 4EBn aromatic C(3)*H* and C(5)*H*), 7.36 (d, *J*(H,H) = 8.0 Hz, 2 H; 4EBn aromatic C(2)*H* and C(6)*H*), 6.98 (d, *J*(H,H) = 1.9 Hz, 1 H; aromatic C(2′)*H*), 6.96 (d, *J*(H,H) = 1.9 Hz, 1 H; aromatic C(2′)*H*), 6.93 (d, *J*(H,H) = 9.0 Hz, 1 H; aromatic C(5)*H*), 6.92 (dd, ^3J(H,H) = 6.0, ^4J(H,H) = 1.8 Hz, 1 H; aromatic C(6′)*H*), 6.91 (dd, ^3J(H,H) = 9.4, ^4J(H,H) = 1.9 Hz, 1 H; aromatic C(6′)*H*), 6.83 (d, *J*(H,H) = 8.0 Hz, 1 H; aromatic C(5′)*H*), 6.82 (d, *J*(H,H) = 8.1 Hz, 1 H; aromatic C(5′)*H*), 5.30 (s, 2 H; 4EBn ArC*H$_2$*O), 5.11 (s, 2 H; ArC*H$_2$*O), 5.08 (s, 2 H; ArC*H$_2$*O), 3.97 (t, *J*(H,H) = 6.6 Hz, 4 H; ArOC*H$_2$*), 3.93 (t, *J*(H,H) = 6.6 Hz, 2 H; ArOC*H$_2$*), 3.92 (t, *J*(H,H) = 6.6 Hz, 2 H; ArOC*H$_2$*), 3.08 (s, 1 H; alkyne C*H*), 1.78 (m, 8 H; ArOCH$_2$C*H$_2$*), 1.44 (m, 8 H; ArO(CH$_2$)$_2$C*H$_2$*), 1.30 (overlapped m), 1.26 (overlapping s, 64 H; ArO(CH$_2$)$_3$(C*H$_2$*)$_8$), 0.88 (t, *J*(H,H) = 6.8 Hz, 12 H; ArO(CH$_2$)$_{11}$C*H$_3$*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta=166.28$ (*C*O$_2$CH$_2$), 153.67 (aromatic *C*(3)), 149.76 (aromatic *C*(3′) or *C*(4′)), 149.71 (aromatic *C*(3′) or *C*(4′)), 149.48 (aromatic *C*(3′) or *C*(4′)), 149.40 (aromatic *C*(3′) or *C*(4′)), 148.83 (aromatic *C*(4)), 137.37 (4EBn aromatic *C*(1)), 132.66 (4EBn aromatic *C*(3) and *C*(5)), 129.80 (aromatic *C*(1′)), 129.46 (aromatic *C*(1′)), 128.14 (4EBn aromatic *C*(2) and *C*(6)), 124.50 (aromatic *C*(2)), 123.11 (aromatic *C*(1)), 122.32 (4EBn aromatic *C*(4)), 120.57 (aromatic *C*(6′)), 120.35 (aromatic *C*(6′)), 116.34 (aromatic *C*(6)), 114.20 (aromatic *C*(5′)), 114.17 (aromatic *C*(5′)), 113.86 (aromatic *C*(2′) and *C*(5)), 113.66 (aromatic *C*(2′)), 83.63 (alkyne Ar*C*), 77.87 (alkyne *C*H), 71.73 (Ar*C*H$_2$O), 71.35 (Ar*C*H$_2$O), 69.75 (ArO*C*H$_2$), 69.66 (ArO*C*H$_2$), 69.60 (ArO*C*H$_2$), 66.22 (4EBn Ar*C*H$_2$O), 32.27 (ArOCH$_2$(*C*H$_2$)$_{10}$), 30.07 (ArOCH$_2$(*C*H$_2$)$_{10}$), 30.01 (ArOCH$_2$(*C*H$_2$)$_{10}$), 30.00 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.82 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.71 (ArOCH$_2$(*C*H$_2$)$_{10}$), 26.44 (ArOCH$_2$(*C*H$_2$)$_{10}$), 26.42 (ArOCH$_2$(*C*H$_2$)$_{10}$), 23.02 (ArOCH$_2$(*C*H$_2$)$_{10}$), 14.42 (ArO(CH$_2$)$_{11}$*C*H$_3$); UV/VIS (hexanes): λ_{max} (ε) = 204 (129 000), 222 (52 000), 240 (44 000), 252 (34 000), 283 nm (14 000 $M^{-1}cm^{-1}$); MALDI-TOF: *m*/*z*: calcd for $C_{78}H_{120}O_8Na$: 1207.89; found: 1208.78 [*M*+Na]$^+$.

4-Ethynylbenzyl 3,4,5-tris(3′,4′-bis(dodecan-1-yloxy)benzyloxy)benzoate [(3,4-3,4,5)12G2-4EBn]: A solution of **(3,4-3,4,5)12G2-CO$_2$H** (1.51 g, 0.98 mmol), 4-ethynylbenzyl alcohol (168.0 mg, 1.3 mmol), DPTS (276.8 mg, 0.94 mmol) and DCC (255.1 mg, 1.2 mmol) in CH_2Cl_2 (12 mL) was stirred for 13 h. A colorless precipitate was removed by filtration of the crude reaction mixture. The filtrate was evaporated to dryness under reduced pressure. The crude monomer was subjected to chromatography on silica gel using hexanes/CH_2Cl_2 2:3→1:4. Precipitated the monomer from CH_2Cl_2 into MeOH and collected it by filtration. Freeze drying from benzene provided **(3,4-3,4,5)12G2-4EBn** (1.03 g, 63 %). TLC (silica gel, hexanes/CH_2Cl_2 1:2): $R_f=0.28$; HPLC (THF): 99+ % pure; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta=7.52$ (d, *J*(H,H) = 8.1 Hz, 2 H; 4EBn aromatic C(3)*H* and C(5)*H*), 7.38 (s, 2 H; aromatic C(2)*H* and C(6)*H*), 7.36 (d, *J*(H,H) = 8.7 Hz, 2 H; 4EBn aromatic C(2)*H* and C(6)*H*), 6.98 (d, *J*(H,H) = 1.8 Hz, 2 H; aromatic C(2′)*H*), 6.95 (d, *J*(H,H) = 1.8 Hz, 1 H; aromatic C(2′)*H*), 6.90 (dd, ^3J(H,H) = 8.2, ^4J(H,H) = 1.6 Hz, 2 H; aromatic C(6′)*H*), 6.84 (dd, ^3J(H,H) = 8.0, ^4J(H,H) = 1.7 Hz, 1 H; aromatic C(6′)*H*), 6.82 (d, *J*(H,H) = 8.2 Hz, 2 H; aromatic C(5′)*H*), 6.72 (d, *J*(H,H); = 8.1 Hz, 1 H; aromatic C(5′)*H*), 5.31 (s, 2 H; 4EBn ArC*H$_2$*O), 5.03 (s, 2 H; ArC*H$_2$*O), 5.03 (s, 1 H; ArC*H$_2$*O), 3.98 (t, *J*(H,H) = 6.6 Hz, 4 H; ArOC*H$_2$*), 3.94 (t, *J*(H,H) = 6.7 Hz, 2 H; ArOC*H$_2$*), 3.91 (t, *J*(H,H) = 6.5 Hz, 4 H; ArOC*H$_2$*), 3.76 (t, *J*(H,H) = 6.5 Hz, 2H ArOC*H$_2$*), 1.80 (m, 10 H; ArOCH$_2$C*H$_2$*), 1.70 (m, 2 H; ArOCH$_2$C*H$_2$*), 1.43 (m, 10 H; ArO(CH$_2$)$_2$C*H$_2$*), 1.35 (m, overlapped), 1.26 (overlapping s, 98 H; ArO(CH$_2$)$_2$C*H$_2$* and ArO(CH$_2$)$_3$(C*H$_2$*)$_8$), 0.88 (t, *J*(H,H) = 6.7 Hz, 18 H; ArO(CH$_2$)$_{11}$C*H$_3$*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta=166.2$ (*C*O$_2$CH$_2$), 152.9 (aromatic *C*(4)), 149.6 (aromatic *C*(3′) or *C*(4′)), 149.4 (aromatic *C*(3′) or *C*(4′)), 149.3 (aromatic *C*(3′) or *C*(4′)), 149.29 (aromatic *C*(3′) or *C*(4′)), 143.0 (aromatic *C*(3) and*C*(5)), 137.7 (4EBn aromatic *C*(1)), 130.4 (4EBn aromatic *C*(2) and *C*(6)), 129.6 (aromatic *C*(1′)), 128.2 (4EBn aromatic *C*(3) and *C*(5)), 125.1 (aromatic *C*(1)), 122.4 (4EBn aromatic *C*(4)), 121.4 (aromatic *C*(6′)), 120.6 (aromatic *C*(6′)), 114.4 (aromatic *C*(5′)), 113.9 (aromatic *C*(5′)), 113.6 (aromatic *C*(2′)), 109.9 (aromatic *C*(2)), 83.6 (alkyne Ar*C*), 78.0 (alkyne *C*H), 75.3 (Ar*C*H$_2$O), 71.7 (Ar*C*H$_2$O), 69.6 (ArO*C*H$_2$), 69.5 (ArO*C*H$_2$), 69.2 (ArO*C*H$_2$), 66.4 (4EBn Ar*C*H$_2$O), 32.3 (ArOCH$_2$(*C*H$_2$)$_{10}$), 30.1 (ArOCH$_2$(*C*H$_2$)$_{10}$), 30.07 (ArOCH$_2$(*C*H$_2$)$_{10}$), 30.02 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.9 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.8 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.7 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.68 (ArOCH$_2$(*C*H$_2$)$_{10}$), 26.5 (ArOCH$_2$(*C*H$_2$)$_{10}$), 26.4 (ArOCH$_2$(*C*H$_2$)$_{10}$), 23.0 (ArOCH$_2$(*C*H$_2$)$_{10}$), 14.4 (ArO(CH$_2$)$_{11}$*C*H$_3$); UV/VIS (hexanes): λ_{max} (ε) = 204 (176 000), 276 nm (25 000 $M^{-1}cm^{-1}$); MALDI-TOF: *m*/*z*: calcd for $C_{109}H_{174}O_{11}Na$: 1682.30; found: 1683.55 [*M*+Na]$^+$.

4-Ethynylbenzyl 3,4-bis(3′,4′,5′-tris(dodecan-1-yloxy)benzyloxy)benzoate [(3,4,5-3,4)12G2-4EBn]: A solution of **(3,4,5-3,4)12G2-CO$_2$H** (1.06 g, 0.93 mmol), 4-ethynylbenzyl alcohol (122.7 mg, 0.93 mmol), DPTS (100.9 mg, 0.34 mmol) and DCC (192.9 mg, 0.93 mmol) in CH_2Cl_2 (10 mL) was stirred for 17 h. A colorless precipitate was removed by filtration of the crude reaction mixture. The filtrate was evaporated to dryness under reduced pressure. The crude monomer was subjected to chromatography on silica gel using hexanes/CH_2Cl_2 2:1→1:2. Precipitated the monomer from CH_2Cl_2 into MeOH and collected it by filtration. Freeze drying from benzene provided **(3,4,5-3,4)12G2-4EBn** (0.99 g, 86 %). TLC (silica gel, hexanes/ethyl acetate 1:1): $R_f=0.34$; HPLC (THF): 99+ % pure; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta=7.68$ (dd, ^3J(H,H) = 8.8, ^4J(H,H) = 2.0 Hz, 1 H; aromatic C(6)*H*), 7.68 (d, *J*(H,H) = 1.9 Hz, 1 H; aromatic C(2)*H*), 7.51 (d, *J*(H,H) = 8.2 Hz, 2 H; 4EBn aromatic C(3)*H* and C(5)*H*), 7.36 (d, *J*(H,H) = 8.2 Hz, 2 H; 4EBn aromatic C(2)*H* and C(6)*H*), 6.94 (d, *J*(H,H) = 9.0 Hz, 1 H; aromatic C(5)*H*), 6.65 (s, 2 H; aromatic C(2′)*H* and C(6′)*H*), 6.62 (s, 2 H; aromatic C(2′)*H* and C(6′)*H*), 5.32 (s, 2 H; 4EBn ArC*H$_2$*O), 5.10 (s, 2 H; ArC*H$_2$*O), 5.08 (s, 2 H; ArC*H$_2$*O), 3.94 (t, *J*(H,H) = 6.6 Hz, 4 H; ArOC*H$_2$*), 3.91 (t, *J*(H,H) = 6.4 Hz, 8 H; ArOC*H$_2$*), 3.08 (s, 1 H; alkyne C*H*), 1.76 (m, 12 H; ArOCH$_2$C*H$_2$*), 1.44 (m, 12 H; ArO(CH$_2$)$_2$C*H$_2$*), 1.27 (overlapped m and overlapping s, 96 H; ArO(CH$_2$)$_3$(C*H$_2$*)$_8$), 0.88 (t, *J*(H,H) = 6.9 Hz, 18 H; ArO(CH$_2$)$_{11}$C*H$_3$*); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta=166.24$ (*C*O$_2$CH$_2$), 153.70 (aromatic *C*(3)), 153.61 (aromatic *C*(3′) and *C*(5′)), 148.79 (aromatic *C*(4)), 138.43 (aromatic *C*(4′)), 138.37 (aromatic *C*(4′)), 137.30 (4EBn aromatic *C*(1), 132.67 (4EBn aromatic *C*(2) and *C*(6)), 132.05 (aromatic *C*(1′)), 131.78 (aromatic *C*(1′)), 128.12 (4EBn aromatic *C*(3) and *C*(5)), 124.62 (aromatic *C*(2)), 123.24 (aromatic *C*(1)), 122.34 (4EBn aromatic *C*(4)), 116.34 (aromatic *C*(6)), 113.88 (aromatic *C*(5)), 106.32 (aromatic *C*(2′) and *C*(6′)), 106.07 (aromatic *C*(2′) and *C*(6′)), 83.60 (alkyne Ar*C*), 77.89 (alkyne *C*H), 73.74 (ArO*C*H$_2$), 72.03 (Ar*C*H$_2$O), 71.65 (Ar*C*H$_2$O), 69.53 (ArO*C*H$_2$), 69.48 (ArO*C*H$_2$), 66.26 (4EBn Ar*C*H$_2$O), 32.82 (ArOCH$_2$(*C*H$_2$)$_{10}$), 30.74 (ArOCH$_2$(*C*H$_2$)$_{10}$), 30.11 (ArOCH$_2$(*C*H$_2$)$_{10}$), 30.08 (ArOCH$_2$(*C*H$_2$)$_{10}$), 30.02 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.82 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.80 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.72 (ArOCH$_2$(*C*H$_2$)$_{10}$), 26.51 (ArOCH$_2$(*C*H$_2$)$_{10}$), 26.50 (ArOCH$_2$(*C*H$_2$)$_{10}$), 23.03 (ArOCH$_2$(*C*H$_2$)$_{10}$), 14.43 (ArO(CH$_2$)$_{11}$*C*H$_3$). UV/VIS (hexanes): λ_{max} (ε) = 208 (126 000), 240 (43 000), 251 (36 000), 290 nm (8000 $M^{-1}cm^{-1}$); MALDI-TOF: *m*/*z*: calcd for $C_{102}H_{168}O_{10}Na$: 1576.25; found: 1576.67 [*M*+Na]$^+$.

4-Ethynylbenzyl 3,5-bis(3′,4′,5′-tris(dodecan-1-yloxy)benzyloxy)benzoate [(3,4,5-3,5)12G2-4EBn]: A solution of **(3,4,5-3,5)12G2-CO$_2$H** (1.38 g, 0.96 mmol), 4-ethynylbenzyl alcohol (160.3 mg, 1.2 mmol), DPTS (159.8 mg, 0.54 mmol) and DCC (263.1 mg, 1.3 mmol) in CH_2Cl_2 (10 mL) was stirred for 20 h. A colorless precipitate was removed by filtration of the crude reaction mixture. The filtrate was evaporated to dryness under reduced pressure. The crude monomer was subjected to chromatography on silica gel using hexanes/CH_2Cl_2 2:1→1:2. Precipitated the monomer from CH_2Cl_2 into MeOH and collected it by filtration. Freeze drying from benzene provided **(3,4,5-3,5)12G2-4EBn** (1.25 g, 84 %). TLC (silica gel, hexanes/CH_2Cl_2 1:2): $R_f = 0.48$; HPLC (THF): 99+ % pure; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.51$ (d, *J*(H,H) = 8.1 Hz, 2H; 4EBn aromatic C(3)*H* and C(5)*H*), 7.38 (d, *J*(H,H) = 8.0 Hz, 2H; 4EBn aromatic C(2)*H* and C(6)*H*), 7.32 (d, *J*(H,H) = 2.3 Hz, 2H; aromatic C(2,)*H* and C(6)*H*), 6.82 (t, *J*(H,H) = 2.2 Hz, 1H; aromatic C(5)*H*), 6.61 (s, 4H; aromatic C(2′)*H* and C(6′)*H*), 5.34 (s, 2H; 4EBn ArC*H*$_2$O), 4.95 (s, 4H; ArC*H*$_2$O), 3.97 (t, *J*(H,H) = 6.4 Hz, 8H; ArOC*H*$_2$), 3.95 (t, *J*(H,H) = 6.6 Hz, 4H; ArOC*H*$_2$), 3.08 (s, 1H; alkyne C*H*), 1.79 (m, 8H; ArOCH$_2$C*H*$_2$), 1.75 (m, 4H; ArOCH$_2$C*H*$_2$), 1.47 (m, 12H; ArO(CH$_2$)$_2$C*H*$_2$), 1.32 (overlapped m), 1.27 (overlapping s, 96H; ArO(CH$_2$)$_3$(C*H*$_2$)$_8$), 0.89 (t, *J*(H,H) = 7.2 Hz, 6H; ArO(CH$_2$)$_{11}$C*H*$_3$), 0.88 (t, *J*(H,H) = 6.8 Hz, 12H; ArO(CH$_2$)$_{11}$C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 166.34$ (*C*O$_2$CH$_2$), 160.22 (aromatic *C*(3) and *C*(5)), 153.73 (aromatic *C*(3′) and *C*(5′)), 138.60 (aromatic *C*(4′)), 137.00 (4EBn aromatic *C*(1)), 132.72 (4EBn aromatic *C*(3) and *C*(5)), 132.17 (aromatic *C*(1)), 131.56 (aromatic *C*(1′)), 128.22 (4EBn aromatic *C*(2) and *C*(6)), 122.42 (4EBn aromatic *C*(4)), 108.93 (aromatic *C*(2) and *C*(6)), 107.67 (aromatic *C*(5)), 106.74 (aromatic *C*(2′) and *C*(6′)), 83.57 (alkyne Ar*C*), 77.98 (alkyne *C*H), 73.80 (ArO*C*H$_2$), 71.15 (Ar*C*H$_2$O), 69.57 (ArO*C*H$_2$), 66.63 (4EBn Ar*C*H$_2$O), 32.30 (ArOCH$_2$(*C*H$_2$)$_{10}$), 32.28 (ArOCH$_2$(*C*H$_2$)$_{10}$), 30.72 (ArOCH$_2$(*C*H$_2$)$_{10}$), 30.11 (ArOCH$_2$(*C*H$_2$)$_{10}$), 30.10 (ArOCH$_2$(*C*H$_2$)$_{10}$), 30.06 (ArOCH$_2$(*C*H$_2$)$_{10}$), 30.00 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.79 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.74 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.71 (ArOCH$_2$(*C*H$_2$)$_{10}$), 26.50 (ArOCH$_2$(*C*H$_2$)$_{10}$), 26.48 (ArOCH$_2$(*C*H$_2$)$_{10}$), 23.04 (ArOCH$_2$(*C*H$_2$)$_{10}$), 14.44 (ArO(CH$_2$)$_{11}$*C*H$_3$); UV/VIS (hexanes): λ_{max} (ε) = 209 (127 000), 240 (41 000), 252 (31 000), 306 nm (4000 $\text{M}^{-1}\,\text{cm}^{-1}$); MALDI-TOF: *m*/*z*: calcd for $C_{102}H_{168}O_{10}Na$: 1576.25; found: 1576.50 $[M+Na]^+$.

4-Ethynylbenzyl 3,4,5-tris(3′,4′,5′-tris(dodecan-1-yloxy)benzyloxy)benzoate [(3,4,5-3,4,5)12G2-4EBn]: A solution of **(3,4,5-3,4,5)12G2-CO$_2$H** (1.99 g, 0.95 mmol), 4-ethynylbenzyl alcohol (147.2 mg, 1.1 mmol), DPTS (254.8 mg, 0.86 mmol) and DCC (243.1 mg, 1.2 mmol) in CH_2Cl_2 (20 mL) was stirred for 16 h. A colorless precipitate was removed by filtration of the crude reaction mixture. The filtrate was evaporated to dryness under reduced pressure. The crude monomer was subjected to chromatography on silica gel using hexanes/CH_2Cl_2 1:1→1:2. Precipitated the monomer from CH_2Cl_2 into MeOH and collected it by filtration. Freeze drying from benzene provided **(3,4,5-3,4,5)12G2-4EBn** (1.41 g, 67 %). TLC (silica gel, hexanes/CH_2Cl_2 1:2): $R_f = 0.38$; HPLC (THF): 99+ % pure; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.52$ (d, *J*(H,H) = 8.1 Hz, 2H; 4EBn aromatic C(3)*H* and C(5)*H*), 7.40 (s, 2H; aromatic C(2)*H* and C(6)*H*), 7.35 (d, *J*(H,H) = 8.0 Hz, 2H; 4EBn aromatic C(2)*H* and C(6)*H*), 6.62 (s, 4H; aromatic C(2′)*H* and C(6′)*H*), 6.61 (s, 2H; aromatic C(2′)*H* and C(6′)*H*), 5.32 (s, 2H; 4EBn ArC*H*$_2$O), 5.05 (s, 2H; ArC*H*$_2$O), 5.03 (s, 4H; ArC*H*$_2$O), 3.94 (t, *J*(H,H) = 6.6 Hz, 4H; ArOC*H*$_2$), 3.91 (t, *J*(H,H) = 6.4 Hz, 6H; ArOC*H*$_2$), 3.88 (t, *J*(H,H) = 6.4 Hz, 6H; ArOC*H*$_2$), 3.77 (t, *J*(H,H) = 6.4 Hz, 4H; ArOC*H*$_2$), 3.08 (s, 1H; alkyne C*H*), 1.75 (m, 18H; ArOCH$_2$C*H*$_2$), 1.42 (m, 18H; ArO(CH$_2$)$_2$C*H*$_2$), 1.32 (overlapped m), 1.27 (overlapping s, 144H; ArO(CH$_2$)$_3$(C*H*$_2$)$_8$), 0.89 (t, *J*(H,H) = 6.8 Hz, 27H; ArO(CH$_2$)$_{11}$C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 166.11$ (*C*O$_2$CH$_2$), 153.70 (aromatic *C*(4′)), 153.43 (aromatic *C*(4′)), 152.99 ((aromatic *C*(4)), 143.31 (aromatic *C*(3) and *C*(5)), 138.43 (aromatic *C*(1′)), 138.38 (aromatic *C*(1′)), 137.13 (4EBn aromatic *C*(1)), 132.74 (4EBn aromatic *C*(3) and *C*(5)), 132.70 (aromatic *C*(3′) and *C*(5′)), 131.99 (aromatic *C*(3′) and *C*(5′)), 128.11 (4EBn aromatic *C*(2) and *C*(6)), 125.34 (aromatic *C*(1)), 122.47 (4EBn aromatic *C*(4)), 110.32 (aromatic *C*(2) and *C*(6)), 106.82 (aromatic *C*(2′) and *C*(6′)), 106.21 (aromatic *C*(2′) and *C*(6′)), 83.57 (alkyne Ar*C*), 77.97 (alkyne *C*H), 75.57 (Ar*C*H$_2$O), 73.76 (ArO*C*H$_2$), 73.68 (ArO*C*H$_2$), 72.14 (Ar*C*H$_2$O), 69.53 (ArO*C*H$_2$), 69.35 (ArO*C*H$_2$), 66.51 (4EBn Ar*C*H$_2$O), 32.94 (ArOCH$_2$(*C*H$_2$)$_{10}$), 30.78 (ArOCH$_2$(*C*H$_2$)$_{10}$), 30.13 (ArOCH$_2$(*C*H$_2$)$_{10}$), 30.09 (ArOCH$_2$(*C*H$_2$)$_{10}$), 30.06 (ArOCH$_2$(*C*H$_2$)$_{10}$), 30.04 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.93 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.88 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.86 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.75 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.74 (ArOCH$_2$(*C*H$_2$)$_{10}$), 26.58 (ArOCH$_2$(*C*H$_2$)$_{10}$), 26.55 (ArOCH$_2$(*C*H$_2$)$_{10}$), 26.53 (ArOCH$_2$(*C*H$_2$)$_{10}$), 23.04 (ArOCH$_2$(*C*H$_2$)$_{10}$), 14.43 (ArO(CH$_2$)$_{11}$*C*H$_3$); UV/VIS (hexanes): λ_{max} (ε) = 210 (154 000), 266 nm (17 000 $\text{M}^{-1}\,\text{cm}^{-1}$); MALDI-TOF: *m*/*z*: calcd for $C_{145}H_{246}O_{14}Na$: 2234.84; found: 2235.05 $[M+Na]^+$.

4-Ethynylbenzyl 3,5-bis{3′,4′-bis[(4″-dodecan-1-yloxy)benzyloxy]benzyloxy}benzoate [(4-3,4-3,5)12G2-4EBn]: A solution of **(4-3,4-3,5)12G1-CO$_2$H** (1.03 g, 0.69 mmol), 4-ethynylbenzyl alcohol (106.8 mg, 0.80 mmol), DPTS (252.1 mg, 0.86 mmol) and DCC (190.9 mg, 0.92 mmol) in CH_2Cl_2 (10 mL) was stirred for 43 h. A colorless precipitate was removed by filtration of the crude reaction mixture. The filtrate was evaporated to dryness under reduced pressure. The crude monomer was subjected to chromatography on silica gel using hexanes/CH_2Cl_2 1:1→0:1. Precipitated the monomer from CH_2Cl_2 into MeOH and collected it by filtration. Freeze drying from benzene provided **(4-3,4-3,5)12G2-4EBn** (0.99 g, 86 %). TLC (silica gel, hexanes/CH_2Cl_2 4:1): $R_f = 0.38$; HPLC (THF): 99+ % pure; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.51$ (d, *J*(H,H) = 8.3 Hz, 2H; 4EBn aromatic C(3)*H* and C(5)*H*), 7.37 (d, *J*(H,H) = 8.1 Hz, 2H; 4EBn aromatic C(2)*H* and C(6)*H*), 7.32 (d, *J*(H,H) = 8.5 Hz, 8H; aromatic C(2″)*H* and C(6″)*H*), 7.29 (d, *J*(H,H) = 2.3 Hz, 2H; aromatic C(2)*H* and C(6)*H*), 7.03 (d, *J*(H,H) = 1.2 Hz, 2H; aromatic C(5′)*H*), 6.94 (s, 2H; aromatic C(2′)*H*), 6.93 (d, *J*(H,H) = 2.1 Hz, 2H; aromatic C(6′)*H*), 6.87 (d, *J*(H,H) = 8.7 Hz, 4H; aromatic C(3″)*H* and C(5″)*H*), 6.86 (d, *J*(H,H) = 8.7 Hz, 4H; aromatic C(3″)*H* and C(5″)*H*), 6.76 (t, *J* = 2.3 Hz, 1H; aromatic C(4)*H*), 5.34 (s, 2H; 4EBn ArC*H*$_2$O), 5.06 (s, 4H; ArC*H*$_2$O), 5.05 (s, 4H; ArC*H*$_2$O), 4.94 (s, 4H; ArC*H*$_2$O), 3.95 (t, *J*(H,H) = 6.6 Hz, 4H; ArOC*H*$_2$), 3.94 (t, *J*(H,H) = 6.6 Hz, 4H; ArOC*H*$_2$), 1.78 (m, 8H; ArOCH$_2$C*H*$_2$), 1.45 (m, 8H; ArO(CH$_2$)$_2$C*H*$_2$), 1.31 (overlapped m), 1.27 (overlapping s, 64H; ArO(CH$_2$)$_3$(C*H*$_2$)$_8$), 0.89 (t, *J*(H,H) = 6.9 Hz, 12H; ArO(CH$_2$)$_3$(CH$_2$)$_8$C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 166.35$ (*C*O$_2$CH$_2$), 160.18 (aromatic *C*(3) and *C*(5)), 159.30 (aromatic *C*(4″)), 159.28 (aromatic *C*(4″)), 149.74 (aromatic *C*(4′)), 149.50 (aromatic *C*(3′)), 137.04 (4EBn aromatic *C*(1)), 132.71 (4EBn aromatic *C*(3) and *C*(5)), 132.11 (aromatic *C*(1)), 129.97 (aromatic *C*(2″) and *C*(6″)), 129.46 (aromatic *C*(1″)), 129.34 (aromatic *C*(2″) and *C*(6″)), 128.26 (4EBn aromatic *C*(2) and *C*(6)), 122.44 (4EBn aromatic *C*(4)), 121.35 (aromatic *C*(6′)), 115.80 (aromatic *C*(2′)), 115.39 (aromatic *C*(5′)), 114.83 (aromatic *C*(3″) and *C*(5″)), 108.95 (aromatic *C*(2) and *C*(6)), 107.70 (aromatic *C*(4)), 83.62 (alkyne Ar*C*), 77.98 (alkyne *C*H), 71.68 (Ar*C*H$_2$O), 70.63 (Ar*C*H$_2$O), 68.42 (ArO*C*H$_2$), 66.61 (4EBn Ar*C*H$_2$O), 32.27 (ArOCH$_2$(*C*H$_2$)$_{10}$), 30.02 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.99 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.96 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.94 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.79 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.70 (ArOCH$_2$(*C*H$_2$)$_{10}$), 29.67 (ArOCH$_2$(*C*H$_2$)$_{10}$), 26.43 (ArOCH$_2$(*C*H$_2$)$_{10}$), 23.03 (ArOCH$_2$(*C*H$_2$)$_{10}$), 14.45 (ArO(CH$_2$)$_{11}$*C*H$_3$); UV/VIS (hexanes): λ_{max} (ε) = 229 (92 000), 276 (18 000), 304 nm (8000 $\text{M}^{-1}\,\text{cm}^{-1}$).

4-Ethynylbenzyl 3,5-bis{3′,5′-bis[3″,4″-bis(dodecan-1-yloxy)benzyloxy]benzyloxy}benzoate [(3,4-3,5-3,5)12G3-4EBn]: A solution of **(3,4-3,5-3,5)12G3-CO$_2$H** (665.4 mg, 0.30 mmol), 4-ethynylbenzyl alcohol (57.8 mg, 0.45 mmol), DPTS (127.5 mg, 0.43 mmol) and DCC (85.6 mg, 0.41 mmol) in CH_2Cl_2 (5 mL) was stirred for 24 h. A colorless precipitate was removed by filtration of the crude reaction mixture. The filtrate was evaporated to dryness under reduced pressure. The crude monomer was subjected to chromatography on silica gel using hexanes/CH_2Cl_2 6:4→0:1. Precipitated the monomer from CH_2Cl_2 into MeOH and collected it by filtration. Freeze drying from benzene provided **(3,4-3,5-3,5)12G3-4EBn** (130.8 mg, 19 %). TLC (silica gel, hexanes/CH_2Cl_2 1:2): $R_f = 0.56$; HPLC (THF): 99+ % pure; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.49$ (d, *J*(H,H) = 8.2 Hz, 2H; 4EBn aromatic C(3)*H* and C(5)*H*), 7.36 (d, *J*(H,H) = 8.2 Hz, 2H; 4EBn C(2)*H* and C(6)*H*), 7.30 (d, *J*(H,H) = 2.3 Hz, 2H; aromatic C(2)*H* and C(6)*H*), 6.95 (d, *J*(H,H) = 1.8 Hz, 4H; aromatic C(2″)*H*), 6.91 (dd, ^{3}*J*(H,H) = 8.2, ^{4}*J*(H,H) = 1.8 Hz, 2H; aromatic C(6″)*H*), 6.86 (d, *J*(H,H) = 8.2 Hz, 4H; aromatic C(5″)*H*), 6.80 (t, *J*(H,H) = 2.3 Hz, 1H; aromatic C(4)*H*), 6.67 (d, *J*(H,H) = 2.2 Hz, 4H; aromatic C(2′)*H* and C(6′)*H*), 6.57 (t, *J*(H,H) = 2.1 Hz, 4H; aromatic C(4′)*H*), 5.33 (s, 2H; 4EBn ArC*H*$_2$O), 5.00 (s, 4H; ArC*H*$_2$O), 4.92 (s, 8H; ArC*H*$_2$O), 3.99 (t, *J*(H,H) = 6.6 Hz, 8H; ArOC*H*$_2$), 3.98 (t, *J*(H,H) =

6.6 Hz, 8H; $\mathrm{ArOC}H_2$), 3.07 (s, 1H; alkyne CH), 1.80 (m, 16H; $\mathrm{ArOCH_2C}H_2$), 1.46 (m, 16H; $\mathrm{ArO(CH_2)_2C}H_2$), 1.33 (overlapped m), 1.26 (overlapping s, 128H; $\mathrm{ArO(CH_2)_3(C}H_2)_8$), 0.88 (t, J(H,H) = 6.9 Hz, 12H; $\mathrm{ArO(CH_2)_3(CH_2)_8C}H_3$), 0.87 (t, J(H,H) = 6.9 Hz, 12H; $\mathrm{ArO(CH_2)_3(CH_2)_8C}H_3$); ^{13}C NMR (125 MHz, $\mathrm{CDCl_3}$, 25 °C, TMS): $\delta = 166.31$ ($C\mathrm{O_2CH_2}$), 160.64 (aromatic $C(3')$ and $C(5')$), 160.14 (aromatic $C(3)$ and $C(5)$), 149.72 (aromatic $C(3'')$ or $C(4'')$), 149.51 (aromatic $C(3'')$ or $C(4'')$), 139.04 (aromatic $C(1')$), 136.99 (4EBn aromatic $C(1)$), 132.72 (4EBn aromatic $C(3)$ and $C(5)$), 132.19 (aromatic $C(1)$), 129.58 (aromatic $C(1'')$), 128.22 (4EBn aromatic $C(2)$ and $C(6)$), 122.42 (4EBn aromatic $C(4)$), 120.93 (aromatic $C(6'')$), 114.20 (aromatic $C(5'')$), 114.08 (aromatic $C(2'')$), 108.95 (aromatic $C(2)$ and $C(6)$), 107.59 (aromatic $C(4)$), 106.72 (aromatic $C(2')$ and $C(6')$), 102.03 (aromatic $C(4')$), 83.60 (alkyne ArC), 77.96 (alkyne CH), 70.64 ($\mathrm{Ar}C\mathrm{H_2O}$), 69.75 ($\mathrm{ArO}C\mathrm{H_2}$), 69.67 ($\mathrm{ArO}C\mathrm{H_2}$), 66.63 (4EBn $\mathrm{Ar}C\mathrm{H_2O}$), 32.28 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 30.06 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 30.00 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 29.82 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 29.81 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 29.72 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 29.70 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 29.68 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 26.43 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 26.41 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 23.04 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 14.46 ($\mathrm{ArO(CH_2)_{11}}C\mathrm{H_3}$); MALDI-TOF: m/z: calcd for $\mathrm{C_{154}H_{240}O_{16}Na}$: 2368.79; found: 2369.85 $[M+\mathrm{Na}]^+$.

4-Ethynylbenzyl 3,5-bis(3′,5′-bis{3″,4″-bis[(4‴-dodecan-1-yloxy)benzyloxy]benzyloxy}benzyloxy)benzoate [(4-3,4-3,5-3,5)12G2-4EBn]: A solution of **(4-3,4-3,5-3,5)12G3-CO$_2$H** (435.0 mg; 0.14 mmol), 4-ethynylbenzyl alcohol (23.1 mg, 0.17 mmol), DPTS (69.2 mg, 0.23 mmol) and DCC (43.3 mg, 0.21 mmol) in $\mathrm{CH_2Cl_2}$ (5 mL) was stirred for 26 h. A colorless precipitate was removed by filtration of the crude reaction mixture. The filtrate was evaporated to dryness under reduced pressure. The crude monomer was subjected to chromatography on silica gel using hexanes/$\mathrm{CH_2Cl_2}$ 3:7→0:1. Precipitated the monomer from $\mathrm{CH_2Cl_2}$ into MeOH and collected it by filtration. Freeze drying from benzene provided **(4-3,4-3,5-3,5)12G3-4EBn** (194.0 mg, 43 %). TLC (silica gel, hexanes/$\mathrm{CH_2Cl_2}$ 1:9): $R_f = 0.63$; HPLC (THF): 99+ % pure; ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, 25 °C, TMS): $\delta = 7.47$ (d, J(H,H) = 8.3 Hz, 2H; 4EBn aromatic C(3)H and C(5)H), 7.34 (d, J(H,H) = 8.1 Hz, 2H; 4EBn aromatic C(2)H and C(6)H), 7.31 (d, J(H,H) = 8.6 Hz, 8H; aromatic C(2‴)H and C(6‴)H), 7.30 (d, J(H,H) = 8.3 Hz, 8H; aromatic C(2‴)H and C(6‴)H), 7.30 (overlapped d, 2H; aromatic C(2)H and C(6)H), 7.03 (s, 4H; aromatic C(2″)H), 6.90 (s, 8H; aromatic C(5″)H and C(6″)H), 6.85 (d, J(H,H) = 8.7 Hz, 8H; aromatic C(3‴)H and C(5‴)H), 6.84 (d, J(H,H) = 8.7 Hz, 8H; aromatic C(3‴)H and C(5‴)H), 6.70 (t, J(H,H) = 2.3 Hz, 1H; aromatic C(4)H), 6.64 (d, J(H,H) = 2.0 Hz, 4H; aromatic C(2′)H and C(6′)H), 6.53 (t, J(H,H) = 2.0 Hz, 2H; aromatic C(4′)H), 5.31 (s, 2H; 4EBn $\mathrm{ArC}H_2\mathrm{O}$), 5.03 (s, 16H; $\mathrm{ArC}H_2\mathrm{O}$), 4.99 (s, 4H; $\mathrm{ArC}H_2\mathrm{O}$), 4.89 (s, 8H; $\mathrm{ArC}H_2\mathrm{O}$), 3.93 (t, J(H,H) = 6.7 Hz, 8H; $\mathrm{ArOC}H_2$), 3.92 (t, J(H,H) = 6.8 Hz, 8H; $\mathrm{ArOC}H_2$), 3.05 (s, 1H; alkyne CH), 1.76 (m, 16H; $\mathrm{ArOCH_2C}H_2$), 1.43 (m, 16H; $\mathrm{ArO(CH_2)_2C}H_2$), 1.31 (overlapped m), 1.26 (overlapping s, 128H; $\mathrm{ArO(CH_2)_3(C}H_2)_8$), 0.88 (t, J(H,H) = 7.2 Hz, 12H; $\mathrm{ArO(CH_2)_3(CH_2)_8C}H_3$), 0.87 (t, J(H,H) = 7.0 Hz, 12H; $\mathrm{ArO(CH_2)_3(CH_2)_8C}H_3$); ^{13}C NMR (125 MHz, $\mathrm{CDCl_3}$, 25 °C, TMS): $\delta = 166.33$ ($C\mathrm{O_2CH_2}$), 160.56 (aromatic $C(3')$ and $C(5')$), 160.16 (aromatic $C(3)$ and $C(5)$), 160.10 (aromatic $C(4''')$), 159.24 (aromatic $C(4''')$), 149.72 (aromatic $C(3'')$ or $C(4'')$), 149.51 (aromatic $C(3'')$ or $C(4'')$), 139.04 (aromatic $C(1')$), 137.02 (4EBn aromatic $C(1)$), 132.72 (4EBn aromatic $C(3)$ and $C(5)$), 132.15 (aromatic $C(1)$), 129.58 (aromatic $C(1'')$), 129.48 (aromatic $C(2''')$ and $C(6''')$), 129.38 (aromatic $C(1''')$), 129.35 (aromatic $C(2''')$ and $C(6''')$), 128.20 (4EBn aromatic $C(2)$ and $C(6)$), 122.43 (4EBn aromatic $C(4)$), 121.34 (aromatic $C(6'')$), 114.78 (aromatic $C(3''')$ and $C(5''')$), 115.72 (aromatic $C(5'')$), 115.28 (aromatic $C(2'')$), 108.95 (aromatic $C(2)$ and $C(6)$), 107.65 (aromatic $C(4)$), 106.72 (aromatic $C(2')$ and $C(6')$), 102.03 (aromatic $C(4')$), 83.61 (alkyne ArC), 77.97 (alkyne CH), 71.66 ($\mathrm{Ar}C\mathrm{H_2O}$), 71.60 ($\mathrm{Ar}C\mathrm{H_2O}$), 70.47 ($\mathrm{Ar}C\mathrm{H_2O}$), 70.43 ($\mathrm{Ar}C\mathrm{H_2O}$), 68.40 ($\mathrm{ArO}C\mathrm{H_2}$), 66.62 (4EBn $\mathrm{Ar}C\mathrm{H_2O}$), 32.28 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 30.03 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 30.00 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 29.97 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 29.95 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 29.79 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 29.70 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 29.66 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 26.43 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 23.04 ($\mathrm{ArOCH_2(}C\mathrm{H_2)_{10}}$), 14.47 ($\mathrm{ArO(CH_2)_{11}}C\mathrm{H_3}$).

General procedure for the polymerization of dendritic phenylacetylene macromonomers by addition of a monomer solution to a solution of catalyst.

Poly{4-[3,4-bis(dodecan-1-yloxy)benzoyloxymethyl]phenylacetylene} {poly[(3,4)12G1-4EBn]}: A flame dried, argon filled Schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with $[\mathrm{Rh(C{\equiv}CPh)(nbd)(PPh_3)_2}]$ (6.21 mg, 0.008 mmol) and DMAP (11.17 mg, 0.091 mmol). Another flame dried, argon filled Schlenk tube was charged with **(3,4)12G1-4EBn** (298.4 mg, 0.493 mmol). The solids were degassed by three cycles of evacuation followed by backfilling with argon. Via glass syringe, dry THF (1.5 mL) was added to the monomer and was added to the catalyst (1.6 mL). The monomer solution was transferred to the catalyst solution at 22 °C under argon using a glass syringe. The reaction was stirred under argon for 4 h. The reaction mixture was precipitated into cold MeOH (90 mL) and the polymer was collected by filtration. Excess monomer was removed by filtration through a plug of basic $\mathrm{Al_2O_3}$ using hexanes/$\mathrm{CH_2Cl_2}$ 10:1. Freeze-drying from benzene provided the polymer (191.7 mg 71 % based on conversion). ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, 25 °C, TMS): $\delta = 7.40$ (brs, 1H; aromatic C(5)H), 7.38 (brs, 1H; aromatic C(2)H), 6.90 (brs, 2H; PPA C(2)H and C(6)H), 6.59 (brs, 3H; PPA aromatic C(3)H and C(5)H and aromatic C(6)H), 5.75 (brs, 1H; PPA *cis*-alkene), 4.94 (brs, 2H; PPA $\mathrm{ArC}H_2\mathrm{O}$), 3.81 (brs, 4H; $\mathrm{ArOC}H_2$), 1.68 (brs, 4H; $\mathrm{ArOCH_2C}H_2$), 1.36 (brs, 4H; $\mathrm{ArO(CH_2)C}H_2$), 1.23 (brs, 32H; $\mathrm{ArO(CH_2)_3(C}H_2)_8$), 0.86 (t, J(H,H) = 6.6 Hz, 3H; $\mathrm{ArO(CH_2)_{11}C}H_3$), 0.85 (t, J(H,H) = 6.6 Hz, 6H; $\mathrm{ArO(CH_2)_{11}C}H_3$); $M_n = 61\,700$, $M_w/M_n = 1.08$.

General procedure for the polymerization of dendritic phenylacetylene macromonomers by addition of a catalyst solution to a solution of monomer

{poly[(3,4)12G1-4EBn]}: A flame dried, argon filled Schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with $[\mathrm{Rh(C{\equiv}CPh)(nbd)(PPh_3)_2}]$ (6.82 mg, 0.008 mmol) and DMAP (14.51 mg, 0.119 mmol). Another flame dried, argon filled Schlenk tube was charged with **(3,4)12G1-4EBn** (315.2 mg, 0.521 mmol). The solids were degassed by three cycles of evacuation followed by backfilling with argon. Via glass syringe, dry THF (2.8 mL) was added to the monomer and to the catalyst (0.5 mL). The catalyst solution was transferred to the monomer solution at 22 °C under argon using a glass syringe. The reaction was stirred under argon for 7.5 h. The reaction mixture was precipitated into cold MeOH (90 mL). The polymer was collected by filtration and freeze-dried from benzene to yield the polymer (216.7 mg, 77 % based on conversion). $M_n = 192\,600$, $M_w/M_n = 1.16$.

General procedure for the polymerization of dendritic phenylacetylene macromonomers by addition solvent to a solid mixture of monomer and catalyst

Poly{4-[3,4,5-tris(dodecan-1-yloxy)benzoyloxymethyl]phenylacetylene} {poly[(3,4,5)12G1-4EBn]}: A flame dried, argon filled Schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **(3,4,5)12G1-4EBn** (287.9 mg, 0.365 mmol), $[\mathrm{Rh(C{\equiv}CPh)(nbd)(PPh_3)_2}]$ (5.94 mg, 0.007 mmol), and DMAP (10.23 mg, 0.084 mmol). The solids were degassed by three cycles of evacuation followed by backfilling with argon. Via glass syringe, dry THF (7.6 mL) was added to the solid mixture. The reaction was stirred at ambient temperature (i.e., ~23 °C) under argon for 8 h. The reaction mixture was precipitated into cold MeOH (125 mL) and collected by filtration. Excess monomer was removed by filtering the polymer through a plug of silica gel using hexanes. Freeze-drying from benzene provided the polymer (216.7 mg, 74 % based on conversion). ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, 25 °C, TMS): $\delta = 7.10$ (s, 2H; aromatic C(2)H and C(6)H), 6.93 (brs, 2H; PPA C(2)H and C(6)H), 6.59 (brs, 2H; PPA aromatic C(3)H and C(5)H), 5.64 (brs, 1H; PPA *cis*-alkene), 4.93 (brs, 2H; PPA $\mathrm{ArC}H_2\mathrm{O}$), 3.87 (brs, 2H; $\mathrm{ArOC}H_2$), 3.82 (brs, 2H; $\mathrm{ArOC}H_2$), 1.66 (brs, 6H; $\mathrm{ArOCH_2C}H_2$), 1.38 (brs, 6H; $\mathrm{ArO(CH_2)C}H_2$), 1.22 (brs 48H;, $\mathrm{ArO(CH_2)_3(C}H_2)_8$), 0.86 (t, J(H,H) = 6.5 Hz, 9H; $\mathrm{ArO(CH_2)_{11}C}H_3$); $M_n = 50\,900$, $M_w/M_n = 1.22$.

Poly(4-{3,4-bis[(4′-dodecan-1-yloxy)benzyloxy]benzoyloxymethyl}phenylacetylene) {poly[(4-3,4)12G1-4EBn]}: ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, 25 °C, TMS): $\delta = 7.47$ (brs, 1H; aromatic C(5)H), 7.40 (brs, 1H; aromatic C(2)H), 7.04 (d, J = 5.0 Hz, 4H; aromatic C(2′)H and C(6′)H), 6.93 (brs, 2H; PPA C(2)H and C(6)H), 6.65 (brs, 3H; PPA aromatic C(3)H and C(5)H and aromatic C(6)H), 6.60 (d, J(H,H) = 5.0 Hz, 4H; aromatic C(3′)H and C(5′)H), 5.84 (brs, 1H; PPA *cis*-alkene), 4.96 (brs, 2H; PPA

ArCH_2O), 4.63 (brs, 4H; ArCH_2O), 3.68 (brs, 4H; ArOCH_2), 1.63 (brs, 4H; ArOCH$_2$CH_2), 1.33 (brs, 4H; ArO(CH$_2$)CH_2), 1.24 (brs, 32H; ArO(CH$_2$)$_3$(CH_2)$_8$), 0.86 (t, *J*(H,H) = 6.7 Hz, 6H; ArO(CH$_2$)$_{11}$CH_3).

Poly(4-{3,4,5-tris[4-((*S*)-3-methylbutan)-1-yloxy)benzyloxy]benzoyloxymethyl}phenylacetylene} {poly[(4-3,4,5)AmylG1-4EBn]}: ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): $\delta=7.11$ (s, 2H; aromatic C(2)*H* and C(6)*H*), 7.01 (d, *J*(H,H) = 7.7 Hz, 6H; aromatic C(2′)*H* and C(6′)*H*), 6.92 (d, *J*(H,H) = 7.6 Hz, 2H; PPA C(2)*H* and C(6)*H*), 6.61 (d, *J*(H,H) = 7.7 Hz, 6H; aromatic C(3′)*H* and C(5′)*H*), 6.48 (d, *J*(H,H) = 7.6 Hz, 2H; PPA C(3)*H* and C(5)*H*), 5.62 (brs, 1H; PPA *cis*-alkene), 4.97 (brs, 2H; PPA ArCH_2O), 4.62 (brs, 3H; ArCH_2O), 4.56 (brs, 3H; ArCH_2O), 3.57 (brs, 3H; ArOCH_2), 3.49 (brs, 3H; ArOCH_2), 1.69 (m, 3H; ArOCH$_2$C*H*), 1.43 (m, 3H; ArOCH$_2$CH(CH$_3$)CH_2), 1.13 (m, 3H; ArOCH$_2$CH(CH$_3$)CH_2), 0.89 (overlapping d and t, 18H; ArOCH$_2$CH(CH_3) and ArOCH$_2$CH(CH_3)CH$_2$CH_3).

Poly(4-{3,4,5-tris[4′-(dodecan-1-yloxy)benzyloxy]benzoyloxymethyl}phenylacetylene {poly[(4-3,4,5)12G1-4EBn]}: ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): $\delta=7.08$ (brs, 2H; aromatic C(2)*H* and C(6)*H*,), 6.99 (brs, 6H; aromatic C(2′)*H* and C(6′)*H*), 6.88 (brs, 2H; PPA C(2)*H* and C(6)*H*), 6.57 (brs, 6H; aromatic C(3′)*H* and C(5′)*H*), 6.43 (brs, 2H; PPA C(3)*H* and C(5)*H*), 5.66 (brs, 1H; PPA *cis*-alkene), 4.97 (brs, 2H; PPA ArCH_2O), 4.60 (brs, 6H; ArCH_2O), 3.65 (brs, 6H; ArOCH_2), 1.60 (brs, 6H; ArOCH$_2$CH_2), 1.23 (brs, 60H; ArO(CH$_2$)$_2$(CH_2)$_{10}$), 0.87 (t, *J*(H,H) = 9.2 Hz, 3H; ArO(CH$_2$)$_{11}$CH_3), 0.86 (t, *J*(H,H) = 9.1 Hz, 6H; ArO(CH$_2$)$_{11}$CH_3).

Poly(4-{3,4-bis[3′,4′-bis(dodecan-1-yloxy)benzyloxy]benzoyloxymethyl}-phenylacetylene) {poly[(3,4-3,4)12G2-4EBn]}: ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): $\delta=7.10$ (brs, 2H; aromatic C(2)*H* and C(6)*H*), 7.05 (brs, 1H; aromatic C(5)*H*), 6.91 (brs, 2H; PPA C(2)*H* and C(6)*H*), 6.72 (s, 4H; aromatic C(2′)*H* and C(5′)*H*), 6.67 (brs, 2H; aromatic C(6′)*H*), 6.62 (brs, 2H; PPA C(3)*H* and C(5)*H*), 5.61 (brs, 1H; PPA *cis*-alkene), 5.01 (brs, 2H; PPA ArCH_2O), 4.61 (brs, 4H; ArCH_2O), 3.73 (brs, 8H; ArOCH_2), 1.64 (brs, 8H; ArOCH$_2$CH_2), 1.30 (brs, 8H; ArO(CH$_2$)$_2$CH_2), 1.23 (brs, 64H; ArO(CH$_2$)$_3$(CH_2)$_8$), 0.83 (t, *J*(H,H) = 6.9 Hz, 6H; ArO(CH$_2$)$_{11}$CH_3), 0.80 (t, *J*(H,H) = 6.6 Hz, 6H; ArO(CH$_2$)$_{11}$CH_3).

Poly(4-{3,4-bis[3′,4′,5′-tris(dodecan-1-yloxy)benzyloxy]benzoyloxymethyl}phenylacetylene) {poly[(3,4,5-3,4)12G2-4EBn]}: ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): $\delta=7.12$ (brs, 2H; aromatic C(2)*H* and C(6)*H*), 7.09 (brs, 1H; aromatic C(5)*H*), 6.96 (brs, 2H; PPA C(2)*H* and C(6)*H*), 6.72 (s, 4H; aromatic C(2′)*H* and C(6′)*H*), 6.62 (brs, 2H; PPA C(3)*H* and C(5)*H*), 5.75 (brs, 1H; PPA *cis*-alkene), 4.98 (brs, 2H; PPA ArCH_2O), 4.59 (brs, 4H; ArCH_2O), 3.75 (brs, 12H; ArOCH_2), 1.59 (brs, 12H; ArOCH$_2$CH_2), 1.28 (brs, 12H; ArO(CH$_2$)$_2$CH_2), 1.20 (brs, 108H; ArO(CH$_2$)$_2$(CH_2)$_9$), 0.83 (brs, 18H; ArO(CH$_2$)$_{11}$CH_3).

Poly(4-{3,5-bis[3′,4′,5′-tris(dodecan-1-yloxy)benzyloxy]benzoyloxymethyl}phenylacetylene {poly[(3,4,5-3,5)12G2-4EBn]}: ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): $\delta=7.04$ (brs, 2H; aromatic C(2)*H* and C(6)*H*), 6.97 (brs, 2H; PPA C(2)*H* and C(6)*H*), 6.81 (s, 4H; aromatic C(2′)*H* and C(6′)*H*), 6.64 (brs, 2H; PPA C(3)*H* and C(5)*H*), 6.40 (brs, 1H; aromatic C(4)*H*), 5.67 (brs, 1H; PPA *cis*-alkene), 4.99 (brs, 2H; PPA ArCH_2O), 4.57 (brs, 4H; ArCH_2O), 3.72 (brs, 12H; ArOCH_2), 1.62 (brs, 12H; ArOCH$_2$CH_2), 1.25 (brs, 108H; ArO(CH$_2$)$_2$(CH_2)$_9$), 0.86 (brs, 18H; ArO(CH$_2$)$_9$CH_3).

Poly[4-(3,5-bis{3′,4′-bis[(4″-dodecan-1-yloxy)benzyloxy]benzyloxy}benzoyloxymethyl)phenylacetylene] {poly[(4-3,4-3,5)12G2-4EBn]}: ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): $\delta=7.21$ (brs, 2H; aromatic C(2)*H* and C(6)*H*), 6.94 (brs, 8H; aromatic C(2″)*H* and C(6″)*H*), 6.75 (brs, 4H; aromatic C(2′)*H* or C(5′)*H*), 6.67 (brs, 4H; aromatic C(2′)*H* or C(5′)*H*), 6.52 (brs, 11H; aromatic C(3″)*H*, C(5″)*H*, C(6′)*H*, and C(5)*H*), 5.72 (brs, 1H; PPA *cis*-alkene), 4.53 (brs, 14H; ArCH_2O), 3.61 (brs, 8H; ArOCH_2), 1.58 (brs, 8H; ArOCH$_2$CH_2), 1.24 (brs, 72H; ArO(CH$_2$)$_2$(CH_2)$_9$), 0.86 (brs, 12H; ArO(CH$_2$)$_{11}$CH_3).

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