Topological Polymerization of *tert*-Butylcalix[4]arenes Containing Diynes

Chantana Lim,[†] Daniel J. Sandman,[‡] and Mongkol Sukwattanasinitt*,[†]

Organic Synthesis Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand, and Center for Advanced Materials, Department of Chemistry, University of Massachusetts, Lowell, Massachusetts 01854

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ABSTRACT: The new 25,26,27,28-tetra(8-hydroxylocta-2,4-diynyl)-*tert*-butylcalix[4]arene was synthesized in good yield from copper-catalyzed coupling reaction of 25,26,27,28-tetra(2-propynyl)-*tert*-butylcalix[4]arene with 5-iodo-4-pentynol in pyrrolidine. The hydroxyl end groups were converted to urethane groups through addition to alkyl or phenyl isocyanate. Di- and trisubstituted *tert*-butylcalix[4]arene analogs were also synthesized through the same approach. The solid-state photopolymerization study revealed that only the calix[4]arene derivatives containing four diyne units with alkyl urethane groups were substantially polymerized upon exposure to UV or gamma irradiation to give polydiacetylenes containing calix[4]arene. The visible absorption band at 350−600 nm and the Raman signals around 1500 and 2100 cm^{-1} characterized the ene−yne conjugation formed through the topological 1,4-addition polymerization of the diyne units.

Introduction

Topological polymerization of preorganized monomers can be used to control the structures of polymers at both the molecular and the supramolecular levels, which is vital for the preparation of unique materials with interesting properties that cannot be achieved by conventional polymerization.[1] Along this line, the favorable packing of diacetylene compounds has attracted much attention because their noncovalently organized structures can be topologically polymerized to form the corresponding polydiacetylenes. Closely-packed suprastructures of properly designed diacetylenes undergo 1,4-addition polymerization upon UV or gamma irradiation.[2] Tremendous interest in polydiacetylenes (PDAs) arises from the extensive ene−yne conjugation in the polymer backbone, leading to unique optical and electronic properties that are promising in a variety of applications such as chemical sensors,[3] biosensors,[4] nonlinear optical materials,[5] photoresists,[6] thermal,[7] and mechanical sensors.[8]

To make a polydiacetylene via topochemical polymerization, it is required that the monomer diyne units be arranged with a repeat distance (r) of ∼5 Å and an orientation angle (θ) of ∼45° relative to the translation axis, as shown in Figure 1.[9] These packing requirements limit the shape and size of the substituents (R) on diynes in that the sterically bulky substituents usually preclude the topopolymerization.[10] Due to this limitation, the design of molecules that can undergo intramolecular 1,4-addition reaction of diyne units is challenging and, to our knowledge, has not been reported.

Bisdiyne incorporated within an alkyl chain had been studied for topological polymerization in Langmuir−Blodgett films.[11] However, the mode of topological polymerization was purely intermolecular as the diyne units were not restricted to the parallel alignment. A molecule containing multiple diyne units aligned in an appropriate direction is required to demonstrate an intramolecular 1,4-addition reaction between the diyne groups.

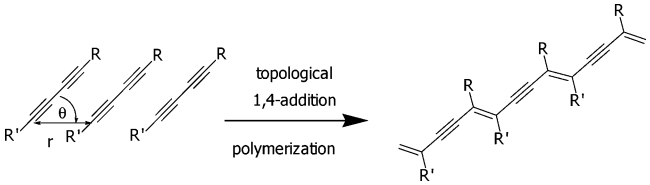

Figure 1. Packing parameters, r = ∼5 Å and θ = ∼45°, required for the topological polymerization of a diacetylene monomer.

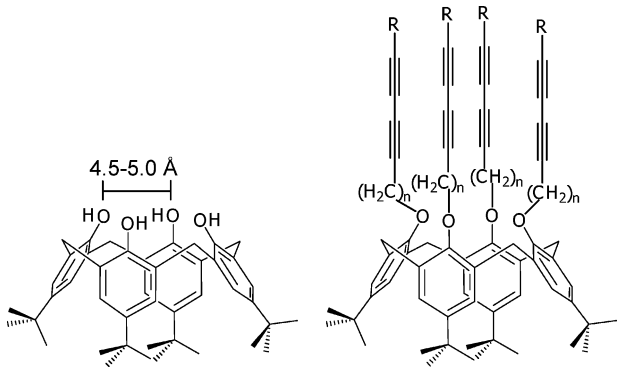

Figure 2. The structures of *tert*-butylcalix[4]arene and its tetradiyne derivative.

Calix[4]arene has a unique three-dimensional cavity-shaped architecture that its derivatives exhibit interesting supramolecular binding behaviors in solution[12] and in the solid state.[13] The self-assembled PDA/*tert*-butylcalix[4]arene bilayer on gold surface acts as a chemically sensitive interface for surface acoustic wave mass balances in vapor-phase sensing applications.[14] With the knowledge that *tert*-butylcalix[4]arene having four squarely arranged hydroxyl groups has a preorganized basket like structure and the distance between the neighboring hydroxyl groups is 4.5−5.0 Å (Figure 2),[15] we contemplated that its derivatives containing multiple diyne units may undergo topological polymerization to form PDA-containing *tert*-butylcalix[4]arene. Study of topological polymerization of *tert*-butylcalix[4]arene mounted with multiple diyne chains will not

* E-mail: smongkol@chula.ac.th.
[†] Chulalongkorn University.
[‡] University of Massachusetts.

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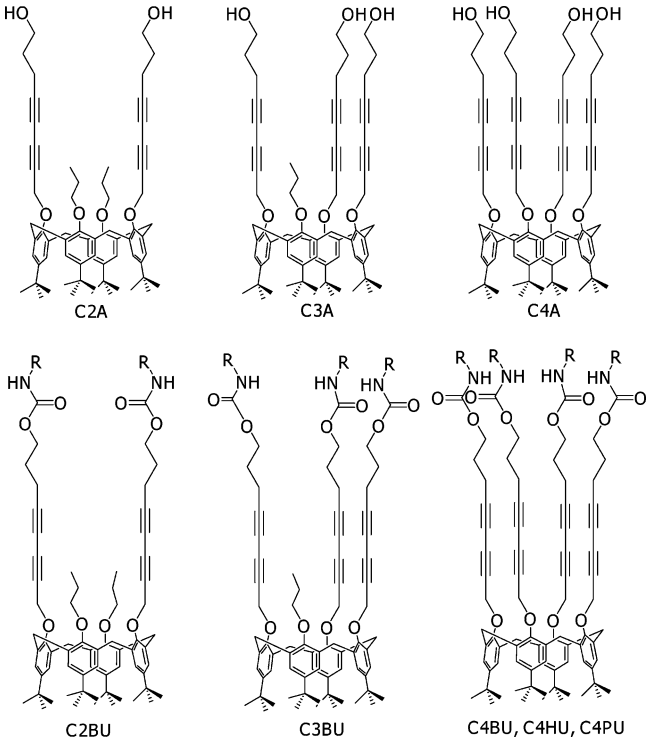


Figure 3. The structures of calix[4]arenes containing multiple diyne units synthesized in this work. The letters B, H, and P denote R = butyl, hexyl, and phenyl, respectively.

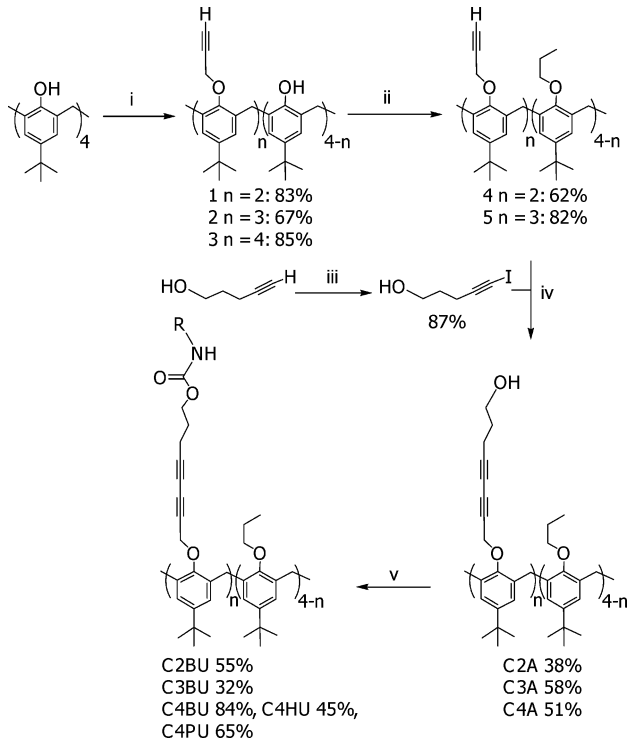
only be mechanistically interesting but may also give novel interesting sensing materials.

Results and Discussion

Synthesis of Calix[4]arenes Containing Multiple Diyne Units. Calix[4]arenes mounted with two, three, and four diyne units (Figure 3) were synthesized and studied for their possibility to undergo topological 1,4-addition polymerization. The synthesis was started from multiple *O*-alkylation of *tert*-butylcalix[4]arene with appropriate equivalents of propargyl bromide in the presence of a suitable inorganic base at reflux temperature.[16−18] Di-, tri-, and tetrapropargyl-*tert*-butylcalix[4]arenes were obtained in 65−85% yields (Scheme 1). The remaining phenolic hydroxyl groups of di- and tripropargyl-*tert*-butylcalix[4]arene were protected with propyl group prior to the subsequent coupling to form the diynes. The Cadiot−Chodkiewicz coupling[19] of the propargyl substituted *tert*-butylcalix[4]arenes with 5-iodo-4-pentynol afforded the desired calix[4]arenes containing multiple diyne units in good yields. The iodine-terminated alkyne used in the coupling step was generated from the iodination of 4-pentyn-1-ol with iodine in the presence of morpholine base.[20] Further modification of the hydroxyl end of the diyne chains to carbamate (urethane) was accomplished by the addition of hydroxyl group to an isocyanate. Unless commercially available, the isocyanates were generated in situ from the corresponding amine by reacting with triphosgene using triethylamine as a base in dry chloroform in the presence of dibutyltindilaurate as a catalyst.[21] All diacetylene products were purified by column chromatography until their ^{1}H NMR and ^{13}C NMR spectra were clean. The elemental analysis was used to confirm their purity prior to the study of their photopolymerization.

Solid-State Photopolymerization of *tert*-Butylcalix[4]arene Containing Four Diyne Units. UV irradiation (TUV 15W/G15 T18 lamp, Philips, Holland) at a distance of 30 cm of C4A, C4BU, C4HU, and C4PU powders showed that the white color

Scheme 1. Reagents and Conditions[a]



[a] Key: (i) Propargyl bromide, K_2CO_3, CH_3CN, reflux for $n = 2$ and 4; $Ba(OH)_2{\cdot}8H_2O$, BaO, THF, reflux for $n = 3$; (ii) NaH, propyl bromide, THF, Reflux; (iii) I_2, morpholine, toluene; (iv) CuI, pyrrolidine; (v) R−N═C═O, dibutyltindilaurate, THF.

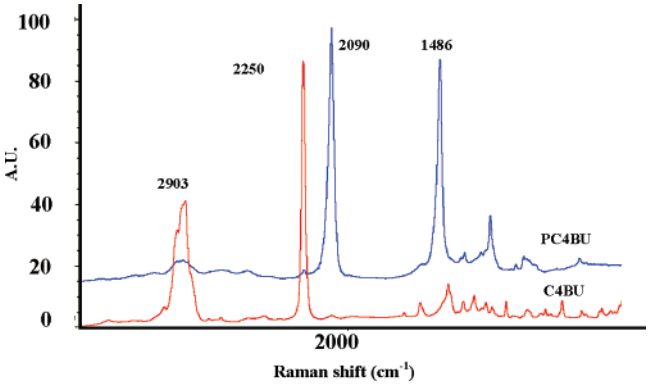


Figure 4. FT-Raman spectra of C4BU and PC4BU (in KBr).

of C4BU and C4HU rapidly turned into intense red color (within 5 min) while the white color of C4A and C4PU solids were virtually unchanged upon long exposure to UV irradiation (30 min) (Table 1). The intense color change of a diacetylene solid after UV irradiation typically signifies the formation of extensive ene−yne conjugation resulting from the topological 1,4-addition polymerization of the diyne units. Dissolution of the irradiated C4BU and C4HU in chloroform gave solutions of C4BU and C4HU (confirmed by TLC and NMR) and insoluble red powders. No significant insoluble solid was observed in the dissolution of irradiated C4A and C4PU in chloroform, and the soluble materials were identified as the starting C4A and C4PU. The red insoluble solids obtained from the irradiation of C4BU and C4HU are thus likely to be polydiacetylenes of the corresponding monomers which will be denoted as PC4BU and PC4HU, respectively, for later discussion.

Due to its low penetration power, UV irradiation is known to lead to only surface reaction on the solid. To obtain higher

Table 1. Color Change of *tert*-Butylcalix[4]arene Derivatives Containing Four Diyne Units upon Exposure to UV Irradiation for 30 min

Compound	Color	
	Before irradiation	After irradiation
C4A	white	white
C4BU	white	red
C4HU	white	red
C4PU	light yellow	yellow

Table 2. Dispersion of PC4BU in Tetrahydrofuran and *N,N*-Dimethylformamide under Sonication and the Storage Stability of the Dispersion

Solvent	Appearance		
	Before sonication	After sonication	After 2 month in refrigerator
Tetrahydrofuran			
N,N-Dimethylformamide			

yields of PC4BU and PC4HU for a more definitive characterization, the polymerization was conducted by exposing C4BU and C4HU to 50 Mrad of γ radiation from ^{60}Co. The resulting deep red polymerized solid was dissolved in tetrahydrofuran with the assistance of ultrasonication. The red solution was filtered through a 0.45 μm cellulose acetate filter and concentrated under reduced pressure. The concentrated crude was dropped into methanol at room temperature to give a red insoluble precipitate. The precipitate was collected by filtration and dried under vacuum to afford pure red polydiacetylene (45% yield for PC4BU).

Raman scattering spectroscopy has been one of the most effective techniques to unambiguously characterize the ene−yne conjugation of polydiacetylenes especially for the insoluble polymers. The FT-Raman spectra of C4BU and PC4BU powders are shown in Figure 4. The spectrum of C4BU has a single C≡C stretching peak at 2250 cm^{-1} associated with the internal diyne groups. The C≡C stretching peak shifts to lower energy at 2090 cm^{-1} in the spectrum of PC4BU and a new C═C stretching peak appears at 1486 cm^{-1}, confirming the presence of ene−yne conjugation in the red PC4BU powder.

Initially, PC4BU appeared to be insoluble in all solvents tested. The polymer however formed clear red solution when sonicated in dimethylformamide or tetrahydrofuran for 5 min. The solution (5% w/w) was stable upon standing in refrigerator for months without noticeable precipitation as shown in Table 2. The electronic spectra of C4BU and PC4BU in tetrahydrofuran are shown in Figure 5 (For clarity sake, the similar spectra of C4HU and PC4HU are not included in the figure.) The spectrum of C4BU has no visible absorption, while that of PC4BU shows a broad absorption band in the range of 350−620 nm with maximum absorption peaks at 440 and 560 nm.

Due to the rigidity of the preorganized *tert*-butylcalix[4]arene platform, the topological 1,4-addition polymerization of the four diyne units of C4BU is most likely to proceed through a parallel intramolecular 1,4-addition (Scheme 2). The observation of polydiacetylene from C4BU thus provided us the first evidence of the intramolecular 1,4-addition of diynes. The resulting polydiacetylene also possesses intriguing molecular architecture containing a parallel conjugated ene−yne backbone with *tert*-butylcalix[4]arene as hollow side chains.

The good solubility of PC4BU and PC4HU in tetrahydrofuran indicated that the polymers were not crosslinked and allowed the molecular weight determination by gel permeation chromatography (GPC). The molecular weights of PC4BU and PC4HU were determined from the tetrahydrofuran eluted GPC chromatograms calculated against polystyrene standards using a universal calibration method. The GPC chromatograms of the purified PC4BU and the crude PC4HU have common bimodal features (Figure 6). The monomer peak appearing in the chromatogram of crude PC4HU but not in the chromatogram of purified PC4BU indicates that the purification of the polymers by precipitation is effective. The number average molecular weights of PC4BU are 3.62×10^5 Da ($M_w/M_n = 1.08$) and 5.31×10^4 Da ($M_w/M_n = 1.13$), and those of PC4HU are 7.39×10^5 Da ($M_w/M_n = 1.03$), 1.58×10^5 Da ($M_w/M_n = 1.03$), and 1.01×10^5 Da ($M_w/M_n = 1.15$).

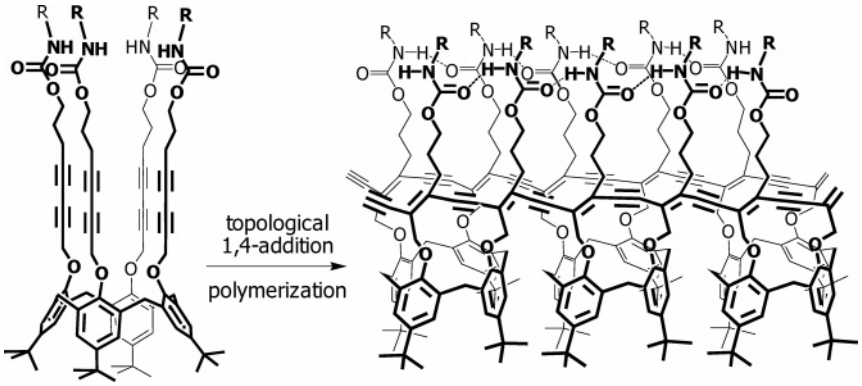
The inability to undergo topological polymerization of C4A indicated the importance of the carbamate group present at the movable end of the diyne chains. The strong hydrogen bonds among the carbamate groups in C4BU and C4HU are important for restraining the diyne units in an appropriate packing for topological polymerization. However, C4PU was also photoinactive despite having four carbamate groups probably due to the steric bulkiness of the phenyl end groups, preventing the intimate packing of the diyne chains.

Solid-State Polymerization of *tert*-Butylcalix[4]arene Containing Two and Three Diyne Units. The C2BU powder did not change its color while the color of C3BU powder changed to orange upon exposure to UV light. These results suggested that C2BU is photoinactive while C3BU can topologically polymerize somewhat but not as extensive as C4BU does. The difference in topological polymerizability of *tert*-butylcalix[4]-arene containing different number of diyne units maybe explained by the molecular packing in the solid state of the monomers. For C4BU to be effectively polymerized topologically, the calix[4]arene cones must arrange themselves in the same direction that will allow the diyne units to align side by side. This arrangement can be continued for at least in each row of C4BU molecules and can be attributed to inter- and intramolecular hydrogen bonding among the carbamate groups (Scheme 3). For C3BU, the same molecular arrangement is subjected to the possibility of some defects because of one missing diyne unit per each monomeric molecule. The topological polymerization of C3BU thus cannot proceed very far. With two diyne units missing, C2BU will not have any continuous alignment of the diyne units beyond two consecutive units, and thus its topological polymerization is totally forbidden. This packing analysis confirms that the topological polymerization of C4BU operates through parallel or antiparallel 1,4-addition involving both inter- and intramolecular reactions.

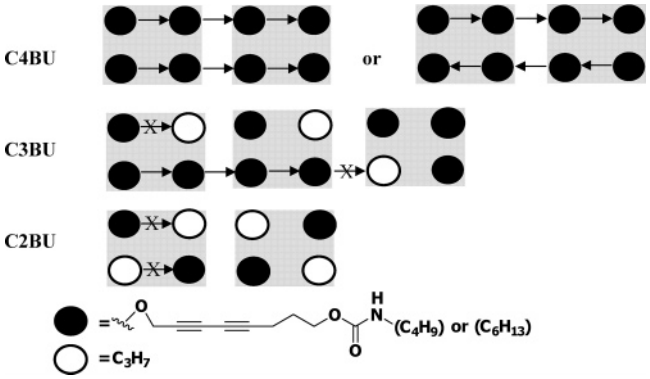
Conclusion

The derivatives of *tert*-butylcalix[4]arene containing two, three, and four diyne units were successfully synthesized. Only the derivatives that contain four diyne with *N*-alkyl carbamate moieties readily undergo solid-state topological photopolymerization to give ene−yne conjugated polydiacetylenes. The presence of carbamate groups is necessary for aligning the diynes through their continuous hydrogen bonding. The replacement one or two diyne units with a simple alkyl chain results

Scheme 2. Proposed Topological 1,4-Addition Polymerization of *tert*-Butylcalix[4]arene Containing Four Diyne Units



Scheme 3. Top View of the Proposed Molecular Packing Patterns in the Solid State of C4BU, C3BU, and C2BU[a]



[a] The arrow indicates the direction of the topological polymerization and X indicates the mismatched pair of the substituents to undergo the topological polymerization.

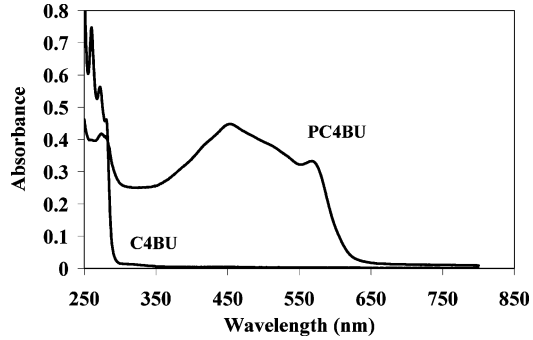


Figure 5. UV−vis spectra of 2.5 mM C4BU and 0.05 mM PC4BU in tetrahydrofuran.

in the reduction of the molecular symmetry and hence the topological polymerizability of the compound. The polymerizability of the tetradiyne derivatives provides not only the first evidence of the intramolecular 1,4-addition of diynes but also a route to synthesize some novel polydiacetylenes with interesting molecular architecture.

Experimental Section

Materials. Propargyl bromide, iodine, morpholine, copper(I) iodide, pyrrolidine, propyl bromide, sodium hydride, potassium carbonate, barium oxide, barium hydroxide octahydrate, triethylamine, and butylamine were purchased from Fluka (Switzerland). Dibutyltindilaurate, 4-pentyn-1-ol, butylamine, hexyl isocyanate, phenyl isocyanate, and triphosgene were purchased from Aldrich (USA). Butyl isocyanate was purchased from Merck (Germany) and used without further purification. *tert*-butylcalix[4]arene was prepared according to the literature.[22] Tetrahydrofuran was distilled over sodium and benzophenone, and acetonitrile was distilled over calcium hydride and stored over molecular sieves. Other analytical grade solvents were used as received without further distillation. Unless otherwise noted, all reactions were carried out under nitrogen atmosphere. Column chromatography was performed using Merck silica gel 60 (70−230 mesh).

Analytical Instruments. ^{1}H spectra were recorded on Varian Mercury 400 MHz NMR spectrometer (Varian, USA) and AC Bruker 200, 250, and 500 MHz NMR spectrometer (Bruker, USA) using the residual solvent proton resonance of $CDCl_3$ at 7.26 ppm as the reference. ^{13}C NMR spectra were recorded on the same instruments as ^{1}H NMR and the data are provided in Supporting Information. Elemental analysis was performed on PE 2400 Series II (Perkin-Elmer, USA). Infrared spectra (data provided in Supporting Information) were measured from KBr pellets on a Nicolet Impact 410 FT-IR spectrophotometer (Thermo Nicolet, USA). UV−vis spectra were recorded on Varian Cary 100 Bio UV−vis spectrophotometer (Varian, USA). The melting points were recorded on a Mettler Toledo DSC 823e (Mettler Toledo, USA) instrument with an aluminum standard cell (40 μL) as a holder at a heating rate of 10 °C/min. The FT-Raman experiments were performed by exciting neat solid samples with a cw Nd:YAG laser at 1.064 μm, and the Raman spectra were recorded on the same IR spectrometer with Raman accessories using 180° optical collection geometry. GPC analysis was measured on a Water system (Waters, USA) with a Water 600 pump, a Water 2414 refractive index detector, and a set of Styragel columns (HR1, HR3, and HR4) at 35 °C using tetrahydrofuran as an eluent at a flow rate of 1.00 mL/min.

Synthesis Procedures. *25,27-Dipropagyloxy-26,28-dihydroxy-tert-butylcalix[4]arene (**1**).* A mixture of potassium carbonate (1.71 g, 12.34 mmol) and *tert*-butylcalix[4]arene (4.01 g, 6.18 mmol) in acetonitrile (200 mL) was stirred at room temperature for 1 h. A solution of propargyl bromide (1.24 g, 12.98 mmol) in acetonitrile (50 mL) was added dropwise into the stirred mixture over 30 min. The reaction mixture was refluxed for 48 h and was then allowed to cool to room temperature. The reaction mixture was filtered to remove insoluble particles, and the filtrate was concentrated in a rotating evaporator. To the concentrated reaction mixture was added 2 M HCl (100 mL) and then extracted with dichloromethane (3 × 100 mL). The combined organic extracts were washed with brine (100 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness in vacuo. The crude mixture was crystallized from CH_2Cl_2/CH_3OH to afford **1** as a white solid (3.72 g, 83% yield). Mp: 232 °C (decomposed). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.13 (s, 4H, Ar-*H*), 6.78 (s, 4H, Ar-*H*), 6.55 (s, 2H, OH), 4.80 (d, J = 4.0 Hz, 4H, OCH_2), 4.42 (d, J = 14.0 Hz, 4H, ArCH_2Ar), 3.38 (d, J = 14.0 Hz, 4H, ArCH_2Ar), 2.58 (t, J = 4.0 Hz, 2H, C≡C*H*), 1.35 (s, 18H, (CH_3)$_3$), 0.94 (s, 18H, (CH_3)$_3$).

*25,26,27-Tripropargyloxy-28-hydroxy-tert-butylcalix[4]arene (**2**).* A mixture of $Ba(OH)_2{\cdot}8H_2O$ (3.66 g, 11.60 mmol), BaO (1.02 g, 6.63 mmol), and *tert*-butylcalix[4]arene (2.15 g, 3.31 mmol) were dissolved in tetrahydrofuran (50.0 mL), and the solution was stirred at room temperature for 1 h. A solution of propargyl bromide (4.93 g, 33.0 mmol) in tetrahydrofuran (30 mL) was added dropwise into

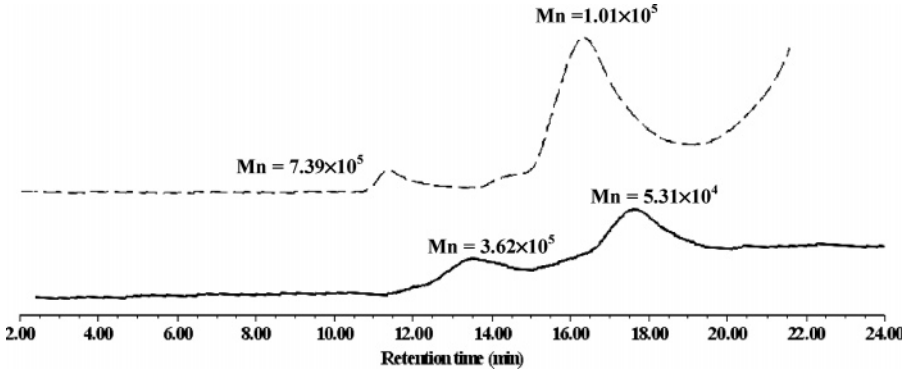


Figure 6. GPC traces of purified PC4BU (solid line) and crude PC4HU (dash line) using tetrahydrofuran as an eluent.

the stirred mixture over 30 min. The reaction mixture was refluxed for 48 h and was then allowed to cool to room temperature. The reaction mixture was filtered to remove insoluble particles, and the filtrate was concentrated in a rotating evaporator. To the concentrated reaction mixture was added 2 M HCl (50 mL) and then extracted with dichloromethane (3 × 60 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and filtered, and the solvent was removed to give a brown oily residue. The residue was purified by column chromatography with dichloromethane/hexane (15/85) to give **2** as a white solid (67% yield, 1.69 g). Mp: 157 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.18 (s, 2H, Ar-*H*), 7.13 (s, 2H, Ar-*H*), 6.63 (s, 2H, Ar-*H*), 6.59 (s, 2H, Ar-*H*), 5.83 (s, 1H, OH), 5.08 (d, J = 2.5 Hz, 2H, OCH_2), 4.70 (d, J = 3.0 Hz, 4H, OCH_2), 4.66 (d, J = 14.0 Hz, 2H, ArCH_2Ar), 4.43 (d, J = 14.0 Hz, 2H, ArCH_2Ar), 3.36 (d, J = 14.0 Hz, 2H, ArCH_2Ar), 3.27 (d, J = 14.0 Hz, 2H, ArCH_2Ar), 2.56 (t, J = 3.0 Hz, 2H, C≡C*H*), 2.50 (t, J = 2.5 Hz, 1H, C≡C*H*), 1.37 (s, 18H, (CH_3)$_3$), 0.90 (s, 9H, (CH_3)$_3$), 0.89 (s, 9H, (CH_3)$_3$).

*25,26,27,28-Tetra(propargyloxy)-tert-butylcalix[4]arene (**3**).* A mixture of potassium carbonate (43.37 g, 313.76 mmol) and *tert*-butylcalix[4]arene(10.18 g, 15.68 mmol) in acetonitrile (200 mL) was stirred at room temperature for 1 h. A solution of propargyl bromide (23.33 g, 156.88 mmol) in acetonitrile (50 mL) was added dropwise into the stirred mixture over 30 min. The reaction mixture was allowed to reflux for 48 h and then allowed to cool to room temperature. The reaction mixture was filtered to remove insoluble particles, and the filtrate was concentrated in a rotating evaporator. To the concentrated reaction mixture was added 2 M HCl (100 mL) and then extracted with dichloromethane (3 × 100 mL). The combined organic extracts were washed with brine (100 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness in vacuo. The crude mixture was crystallized from CH_2Cl_2/CH_3OH to afford **3** as a white solid (10.68 g, 85% yield). Mp: 107 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78 (s, 8H, Ar-*H*), 4.80 (d, J = 2.4 Hz, 8H, OCH_2), 4.60 (d, J = 13.2 Hz, 4H, ArCH_2Ar), 3.16 (d, J = 13.2 Hz, 4H, ArCH_2Ar), 2.48 (t, J = 2.4 Hz, 3H, C≡C*H*), 1.07 (s, 36H, (CH_3)$_3$).

*25,27-Dipropargyloxy-26,28-dipropyl-tert-butylcalix[4]arene (**4**).* **1** (1.03 g, 1.42 mmol) and NaH (0.40 g, 14.16 mmol), which was washed with hexane (3 × 10 mL), were dissolved in tetrahydrofuran (20 mL), and the solution was stirred at room temperature for 1 h. Then a solution of propyl bromide (1.74 g, 14.16 mmol) in tetrahydrofuran (20 mL) was added dropwise to the above mixture. After the addition was complete, the reaction mixture was allowed to reflux for 24 h. The reaction mixture was then allowed to cool to room temperature and quenched with ethanol (20 mL). The solvent was removed in vacuo to obtain a yellow residue, and then the residue was extracted with dichloromethane (3 × 30 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous Na_2SO_4, and filtered, and the solvent was removed in vacuo to give a brown oily residue. The residue was isolated by column chromatography with dichloromethane as an eluent to afford **4** as a white solid (0.35 g, 31% yield). Mp: 190 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (s, 4H, Ar-*H*), 6.45 (s, 4H, Ar-*H*), 5.02 (s, J = 2.4 Hz, 4H, OCH_2Ar), 4.52 (d, J = 12.0 Hz, 4H, ArCH_2Ar), 3.71 (t, J = 6.0 Hz, 4H, CH_2CH$_2$CH$_3$), 3.14 (d, J = 12.0 Hz, 4H, ArCH_2Ar), 2.39 (t, J = 2.4 Hz, 3H, C≡C*H*), 2.00 (m, 4H, CH$_2$CH_2-CH$_3$), 1.33 (s, 18H, (CH_3)$_3$), 1.05 (t, J = 6.0 Hz, 6H, CH$_2$CH$_2$CH_3), 0.83 (s, 18H, (CH_3)$_3$).

*25,26,27-Tripropargyloxy-28-propyl-tert-butylcalix[4]arene (**5**).* **2** (0.93 g, 1.22 mmol) and NaH (0.15 g, 6.08 mmol), which was washed with hexane (3 × 10 mL), were dissolved in tetrahydrofuran (20 mL), and the solution was stirred at room temperature for 1 h. Then a solution of propyl bromide (0.75 g, 6.08 mmol) in tetrahydrofuran (20 mL) was added by dropwise to the above mixture. After the addition was complete, the reaction mixture was allowed to reflux for 24 h. The reaction mixture was then allowed to cool to room temperature and quenched with ethanol (20 mL). The solvent was removed in vacuo to obtain a yellow residue, and then the residue was extracted with dichloromethane (3 × 30 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous Na_2SO_4, and filtered, and the solvent was removed in vacuo to give a brown oily residue. The residue was isolated by column chromatography with dichloromethane as an eluent to afford **5** as a white solid (0.80 g, 82% yield). Mp: 140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00 (s, 2H, Ar-*H*), 6.98 (s, 2H, Ar-*H*), 6.60 (s, 2H, Ar-*H*), 6.54 (s, 2H, Ar-*H*), 4.98 (d, J = 2.4 Hz, 2H, CH_2C≡C), 4.89 (d, J = 2.4 Hz, 2H, CH_2C≡C), 4.63 (d, J = 2.0 Hz, 2H, CH_2C≡C), 4.59 (d, J = 12.5 Hz, 2H, ArCH_2Ar), 4.51 (d, J = 12.5 Hz, 2H, ArCH_2Ar), 3.76 (t, J = 7.4 Hz, 2H, CH_2CH$_2$CH$_3$), 3.17 (d, J = 5.6 Hz, 2H, ArCH_2Ar), 3.13 (d, J = 5.6 Hz, 2H, ArCH_2Ar), 2.4 (t, J = 2.0 Hz, 1H, C≡C*H*), 2.44 (t, J = 2.4 Hz, 2H, C≡C*H*), 2.00 (m, 2H, CH$_2$CH_2CH$_3$), 1.28 (s, 18H, (CH_3)$_3$), 1.07 (t, J = 7.4 Hz, 3H, CH$_2$CH$_2$CH_3), 0.96 (s, 9H, (CH_3)$_3$), 0.94 (s, 9H, (CH_3)$_3$).

5-Iodo-4-pentynol. A solution of morpholine (33.25 mL, 381.60 mmol) in toluene (350 mL) at 45 °C was treated with iodine (13.56 g, 53.42 mmol) shielded from light and stirred for 1 h. A solution of 4-pentyn-1-ol (3.21 g, 38.16 mmol) in toluene (30 mL) was added and the reaction mixture was stirred at 45 °C for 1 h. The reaction mixture was cooled to room temperature and filtered to remove the salt. The filtrate was poured over a mixture of diethylether (200 mL) and a saturated aqueous solution of $Na_2S_2O_3$ (100 mL) and shaken vigorously until the organic layer was colorless. The organic layer was separated, washed with $Na_2S_2O_3$ (100 mL), dried over anhydrous Na_2SO_4, filtered, concentrated, and purified by column chromatography (ethyl acetate/hexane = 7/93) to afford 5-iodo-4-pentynol as a light yellow oil (6.97 g, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.78 (t, J = 6.0 Hz, 2H, CH_2OH), 2.53 (t, J = 6.0 Hz, 2H, C≡CCH_2), 1.80 (quintet, J = 6.0 Hz, 2H, CH$_2$CH_2-CH$_2$OH), 1.61 (br s, 1H, OH).

25,27-Di(octa-4,6-diyn-1-ol)oxy-26,28-dipropyl-tert-butylcalix-[4]arene (C2A). To a stirred solution of **4** (0.22 g, 0.27 mmol) and 5-iodo-4-pentynol (0.28 g, 1.34 mmol) in pyrrolidine (1.0 mL) was added copper(I) iodide (0.01 g, 0.05 mmol). After the reaction mixture was stirred at room temperature for 2 h, it was hydrolyzed with a saturated aqueous solution of ammonium chloride (30 mL) and extracted with diethyl ether (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the solvent was removed in vacuo. The crude product was purified by

column chromatography (dichloromethane/ethyl acetate = 10/90) to obtain C2A as a light yellow solid (0.10 g, 38% yield). Mp: 168 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (s, 4H, Ar-*H*), 6.43 (s, 4H, Ar-*H*), 5.01 (s, 4H, OCH_2C≡C), 4.48 (d, J = 13.6 Hz, 4H, ArCH_2Ar), 3.76 (t, J = 6.0 Hz, 4H, CH_2CH$_2$CH$_3$), 3.71 (t, J = 7.5 Hz, 4H, CH_2OH), 3.14 (d, J = 13.6 Hz, 4H, ArCH_2Ar), 2.43 (t, J = 7.5 Hz, 4H, CH_2CH$_2$CH$_2$OH), 2.00 (m, 4H, CH$_2$CH_2CH$_3$), 1.81 (quintet, J = 7.5 Hz, 4H, CH_2CH$_2$OH), 1.33 (s, 18H, (CH_3)$_3$), 1.05 (t, J = 6.0 Hz, 6H, CH$_2$CH$_2$CH_3), 0.82 (s, 18H, (CH_3)$_3$).

25,26,27-Tri(octa-4,6-diyn-1-ol)oxy-28-propyl-tert-butylcalix[4]-arene (C3A). To a stirred solution of **5** (0.24 g, 0.30 mmol) and 5-iodo-4-pentynol (0.36 g, 1.79 mmol) in pyrrolidine (2.00 mL) was added copper(I) iodide (0.02 g, 0.08 mmol). After the reaction mixture was stirred at room temperature for 2 h, it was hydrolyzed with a saturated aqueous solution of ammonium chloride (30 mL) and extracted with diethyl ether (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the solvent was removed in vacuo. The crude product was purified by column chromatography (dichloromethane/ethyl acetate = 50/50) to give C3A as a light yellow solid (0.18 g, 58% yield). Mp: 145 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00 (s, 4H, Ar-*H*), 6.58 (s, 2H, Ar-*H*), 6.51 (s, 2H, Ar-*H*), 5.01 (s, 2H, CH_2C≡C), 4.87 (s, 2H, CH_2C≡C), 4.71 (s, 2H, CH_2C≡C), 4.55 (d, J = 12.5 Hz, 2H, ArCH_2Ar), 4.46 (d, J = 12.5 Hz, 2H, ArCH_2Ar), 3.76 (m, 8H, CH_2CH$_2$CH$_3$ and CH_2OH), 3.17 (d, J = 6.4 Hz, 2H, ArCH_2Ar), 3.14 (d, J = 6.4 Hz, 2H, ArCH_2Ar), 2.44 (t, J = 6.6 Hz, 6H, CH_2-CH$_2$CH$_2$OH), 2.00 (m, 4H, CH$_2$CH_2CH$_3$), 1.81 (m, 6H, CH_2CH$_2$-OH), 1.25 (s, 18H, (CH_3)$_3$), 1.08 (t, J = 7.4 Hz, 3H, CH$_2$CH$_2$CH_3), 0.92 (s, 9H, (CH_3)$_3$), 0.87 (s, 9H, (CH_3)$_3$).

25,26,27,28-Tetra(octa-4,6-diyn-1-ol)oxy-tert-butylcalix[4]-arene (C4A). To a stirred solution of **3** (4.18 g, 5.22 mmol), and 5-iodo-4-pentynol (10.96 g, 52.18 mmol) in pyrrolidine (40.00 mL) was added copper(I) iodide (0.40 g, 2.09 mmol). After the reaction mixture was stirred at room temperature for 2 h, it was hydrolyzed with a saturated aqueous solution of ammonium chloride (200 mL) and extracted with diethyl ether (3 × 150 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the solvent was removed in vacuo. The crude product was purified by column chromatography (ethyl acetate) to afford C4A as a light yellow solid (2.73 g, 51% yield). Mp: 212 °C (decomposed). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.77 (s, 8H, Ar-*H*), 4.82 (s, 8H, OCH_2), 4.53 (d, J = 13.2 Hz, 4H, ArCH_2Ar), 3.77 (t, J = 7.0 Hz, 8H, CH_2OH), 3.17 (d, J = 13.2 Hz, 4H, ArCH_2Ar), 2.45 (t, J = 7.0 Hz, 8H, C≡CCH_2), 1.90 (bs, 1H, OH), 1.81 (quintet, J = 7.0 Hz, 8H, CH$_2$CH_2CH$_2$), 1.07 (s, 36H, (CH_3)$_3$).

Urethane Formation of C2BU and C3BU. *General Procedure for Synthesis.*

Butylamine was dissolved in chloroform. Triphosgene was gradually added to this solution with stirring. Triethylamine was added dropwise to this stirred mixture (a water bath may be needed to keep the temperature below 30 °C). The reaction mixture was refluxed for 2 h before diacetylenic alcohol-*tert*-butylcalix[4]arene derivatives [C2A or C3A] and dibutyltindilaurate were added. The stirring was continued for 10 h at room temperature. The solvent was evaporated, and the residue was redissolved in hexane. The resulting solution was filtered, and the solid was washed several times with hexane. The filtrate was collected, and the solvent was evaporated. The residue was eluted through a silica gel column.

25,27-Di[octa-4,6-diyn-1-ol-(carboxy-butyl-urethane)]oxy-26,28-dipropyl-tert-butylcalix-[4]arene (C2BU). C2BU was synthesized according to the above urethane formation procedure from C2A (0.07 g, 0.07 mmol), butylamine (0.32 g, 4.32 mmol), triphosgene (0.43 g, 1.44 mmol), triethylamine (1.20 mL, 8.63 mmol), and dibutyltindilaurate (0.18 g, 0.29 mmol) in chloroform (10 mL) and purified by column chromatography (ethyl acetate/dichloromethane = 1/99). A light yellow solid (0.05 g, 55% yield) was obtained. Mp: 100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (s, 4H, Ar-*H*), 6.42 (s, 4H, Ar-*H*), 5.01 (s, 4H, OCH_2C≡C), 4.69 (br s, 2H, NH), 4.48 (d, J = 13.6 Hz, 4H, ArCH_2Ar), 4.12 (t, J = 5.8 Hz, 4H, OCOCH_2), 3.70 (t, J = 6.0 Hz, 4H, CH_2CH$_2$CH$_3$), 3.14 (m, J = 13.6 Hz, 8H, ArCH_2Ar and NCH_2), 2.38 (t, J = 6.6 Hz, 4H, C≡CCH_2), 2.00 (m, 4H, CH$_2$CH_2CH$_3$), 1.84 (quintet, J = 5.8 Hz, 4H, C≡CCH$_2$CH_2), 1.47 (m, 4H, CH$_2$CH_2CH$_2$CH$_3$), 1.32 (s, 18H, (CH_3)$_3$), 1.05 (t, J = 6.0 Hz, 6H, CH$_2$CH$_2$CH_3), 0.92 (m, 6H, CH$_2$-CH$_2$CH$_2$CH_3), 0.81 (s, 18H, (CH_3)$_3$). Anal. Calcd for $C_{76}H_{102}N_2O_8$: C, 77.91; H, 8.77; N, 2.89. Found: C, 76.28; H, 8.43; N, 3.19.

25,26,27-Tri[octa-4,6-diyn-1-ol-(carboxy-butyl-urethane)]oxy-28-propyl-tert-butylcalix[4]arene (C3BU). C3BU was synthesized according to the above urethane formation procedure from C3A (0.07 g, 0.07 mmol), butylamine (0.07 g, 1.00 mmol), triphosgene (0.10 g, 0.30 mmol), triethylamine (0.28 mL, 2.00 mmol), and dibutyltindilaurate (0.13 g, 0.21 mmol) in chloroform (10 mL) and purified by column chromatography (ethyl acetate/hexane = 15/85). A light yellow solid (0.03 g, 32% yield) was obtained. Mp: 117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00 (s, 4H, Ar-*H*), 6.56 (s, 2H, Ar-*H*), 6.50 (s, 2H, Ar-*H*), 4.99 (s, 2H, OCH_2C≡C), 4.88 (s, 2H, OCH_2C≡C), 4.80 (br s, 3H, NH), 4.70 (s, 2H, OCH_2C≡C), 4.54 (d, J = 13.0 Hz, 2H, ArCH_2Ar), 4.47 (d, J = 13.0 Hz, 2H, ArCH_2Ar), 4.12 (t, J = 5.6 Hz, 6H, CH_2OCO), 3.74 (t, 2H, CH_2CH$_2$CH$_3$), 3.15 (m, 10H, ArCH_2Ar and NHCH_2), 2.39 (t, J = 6.4 Hz, 6H, CH_2CH$_2$CH$_2$OCO), 2.03 (m, 4H, CH$_2$CH_2CH$_3$), 1.86 (m, 6H, CH_2CH$_2$OCO), 1.47 (m, 6H, CH$_2$CH_2CH$_2$CH$_3$), 1.34 (m, 6H, CH$_2$CH$_2$CH_2CH$_3$), 1.25 (s, 18H, (CH_3)$_3$), 1.07 (m, 9H, CH$_2$-CH$_2$CH$_2$CH_3), 0.91 (s, 9H, (CH_3)$_3$), 0.86 (s, 9H, (CH_3)$_3$). Anal. Calcd for $C_{86}H_{113}N_3O_{10}$: C, 76.58; H, 8.44; N, 3.12. Found: C, 74.40; H, 7.71; N 3.21.

Urethane Formation of C4BU, C4HU, and C4PU. *General Procedure for Synthesis.* Diacetylenic alcohol-*tert*-butylcalix[4]arene derivatives and dibutyltindilaurate were dissolved in tetrahydrofuran, and R— N=C=O (commercially available) was added dropwise to this solution with stirring at 0 °C. The mixture was allowed to warm up to room temperature and the stirring was continued for another 2 h before ice/water was added. Tetrahydrofuran was evaporated, and the aqueous residue was extracted several times with CH_2Cl_2 and brine. The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the solvent was removed in vacuo. The crude product was eluted through a silica gel column.

25,26,27,28-Tetra[octa-4,6-diyn-1-ol-(carboxy-butyl-urethane)]-oxy-tert-butylcalix[4]arene (C4BU). C4BU was synthesized according to the above urethane formation procedure from C4A (0.85 g, 0.75 mmol), butyl isocyanate (0.75 g, 7.53 mmol), and dibutyltindilaurate (1.90 g, 3.01 mmol) in tetrahydrofuran (20 mL) and purified by column chromatography (ethyl acetate/hexane = 45/55). A white solid (0.96 g, 84% yield) was obtained. Mp: 119 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.77 (s, 8H, Ar-*H*), 4.82 (s, 8H, OCH_2 and NH), 4.53 (d, J = 13.2 Hz, 4H, ArCH_2Ar), 4.13 (t, J = 5.8 Hz, 8H, OCOCH_2), 3.17 (m, 12H, ArCH_2Ar and NCH_2), 2.39 (t, J = 6.8 Hz, 8H, C≡CCH_2CH$_2$), 1.87 (quintet, J = 6.0 Hz, 8H, C≡CCH$_2$CH_2), 1.47 (quintet, J = 6.6 Hz, 8H, CH$_2$CH_2CH$_2$CH$_3$), 1.33 (m, 8H, CH_2CH$_3$), 1.06 (s, 36H (CH_3)$_3$), 0.95 (t, J = 7.4 Hz, 12H, CH_3). Anal. Calcd for $C_{96}H_{124}N_4O_{12}$: C, 75.56; H, 8.19; N, 3.67. Found: C, 75.58; H, 8.39; N 3.65. Raman: 2250 cm^{-1} (—C≡C—C≡C—).

25,26,27,28-Tetra[octa-4,6-diyn-1-ol-(carboxy-hexyl-urethane)]-oxy-tert-butylcalix[4]arene (C4HU). C4HU was prepared as described above from C4A (0.54 g, 0.48 mmol), butyl isocyanate (0.61 g, 4.78 mmol), and dibutyltindilaurate (1.21 g, 1.91 mmol) in tetrahydrofuran (15 mL) and purified by column chromatography (ethyl acetate/hexane = 27/73). A white solid (0.35 g, 45% yield) was obtained. Mp: 103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.76 (s, 8H, Ar-*H*), 4.91 (br s, NH), 4.80 (s, 8H, OCH_2), 4.53 (d, J = 12.8 Hz, 4H, ArCH_2Ar), 4.12 (t, J = 6.0 Hz, 8H, CH_2OCO), 3.16 (d, J = 12.8 Hz, 4H, ArCH_2Ar), 3.12 (t, J = 6.0 Hz, 8H, NHCH_2), 2.38 (t, J = 6.4 Hz, 8H, C≡CCH_2), 1.85 (quintet, J = 6.4 Hz, 8H, C≡CCH$_2$CH_2), 1.47 (m, 8H, NHCH$_2$CH_2), 1.27 (m, 24H, CH_2CH$_2$CH$_2$-CH$_3$), 1.05 (s, 36H, (CH_3)$_3$), 0.87 (t, J = 6.2 Hz, 12H, CH_3). Anal. Calcd for $C_{104}H_{140}N_4O_{12}$: C, 76.25; H, 8.61; N, 3.42. Found: C, 76.24; H, 8.64; N 3.76.

25,26,27,28-Tetra[octa-4,6-diyn-1-ol-(carboxy-phenyl-urethane)]-oxy-tert-butylcalix[4]arene (C4PU). C4PU was prepared as described above from C4A (0.36 g, 0.32 mmol), phenyl isocyanate

(0.38 g, 3.19 mmol), and dibutyltindilaurate (0.81 g, 1.27 mmol) in tetrahydrofuran (15 mL) and purified by column chromatography (ethyl acetate/hexane = 22/78). A light yellow solid (0.33 g, 65% yield) was obtained. Mp: 107 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 8.0 Hz, 8H, H_{ortho}-Ar), 7.28 (t, J = 8.0 Hz, 8H, H_{meta}-Ar), 7.04 (t, J = 8.0 Hz, 4H, H_{para}-Ar), 6.90 (br s, NH), 6.78 (s, 8H, H-Ar_{calix}), 4.82 (s, 8H, OCH_2), 4.54 (d, J = 12.8 Hz, 4H, $ArCH_2Ar$), 4.27 (t, J = 6.0 Hz, 8H, $OCOCH_2$), 3.18 (d, J = 12.8 Hz, 4H, $ArCH_2Ar$), 2.44 (t, J = 7.0 Hz, 8H, $C{\equiv}CCH_2$), 1.96 (m, 8H, $CH_2CH_2CH_2$), 1.06 (s, 36H, $(CH_3)_3$). Anal. Calcd for $C_{104}H_{108}N_4O_{12}$: C, 77.78; H, 6.78; N, 3.49. Found: C, 77.39; H, 6.78; N 3.24.

Poly(25,26,27,28-Tetra[octa-4,6-diyn-1-ol-(carboxy-butyl-urethane)]oxy-*tert*-butylcalix[4]arene) (PC4BU). The monomer C4BU (50 mg) was exposed to 50 Mrad of γ radiation from ^{60}Co. The resulting deep red polymerized solid was dissolved in 20 mL tetrahydrofuran with the assistance of ultrasonication. The red solution was filtered through a 0.45 μm cellulose acetate filter and concentrated to 2 mL under reduced pressure. The concentrated crude was dropped into methanol (100 mL) and stirred for 2 h at room temperature to give a red precipitate. The precipitate was collected by filtration and dried under vacuum to afford pure red polydiacetylene (23 mg, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (br, 8H), 6.77 (br, 8H), 4.97 (br, 8H), 4.82 (br, 8H), 4.54 (br, 8H), 4.15 (br), 4.00 (br), 3.12 (br), 2.39 (br, 8H), 1.66−0.90 (br). Raman: 2090 cm^{-1} (−C≡C−), 1486 cm^{-1} (−C═C−).

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Supporting Information Available: Preparation procedures and full spectroscopic data of all compounds synthesized. This material is available free of charge via the Internet at http://pubs.acs.org.

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