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Synthesis of Functionalized Triazatriangulenes for Application in Photo-Switchable Self-Assembled Monolayers

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Various triazatriangulenes are synthesized by nucleophilic attack at the central C atom of triazatriangulenium ions. The molecular functions, especially azobenzenes, are fixed via an ethynyl linker by in situ deprotection of trimethylsilyl-alkynes. The structure of two of these molecules is further investigated by X-ray crystallography. The photo-induced *trans*/*cis*-isomerization of the azobenzene substituted derivatives is analyzed in solution and shows great promise for the preparation of switchable functionalized monolayers, as the triazatriangulenes are known for their self-assembly on gold surfaces.[1]

Introduction

Rational approaches for the controlled functionalization of surfaces are the prerequisites to achieve more sophisticated applications such as data storage, molecular electronics, surface property switching, or directed motion on surfaces.[2–7] One of the most frequently used and simplest methods to attach organic molecules to a metal surface is the use of an alkane spacer and a terminal thiol group which has a high affinity in particular to gold. Self-assembled monolayers (SAMs) form spontaneously upon immersion of the gold target into a solution of the thiol substituted functional molecule.[2] A multitude of functionalities including azobenzenes have been immobilized as SAMs on Cu, Ag, and Au surfaces. The sulfur binds strongly to the metal and in a densely packed monolayer the alkane spacers with the functional molecules stand more or less upright like bristles in a brush. Azobenzenes are frequently used as functional molecules because they undergo a reversible *trans*/*cis*-isomerization upon irradiation. Upon exposure to UV light (usually 365 nm) the thermodynamically more stable *trans* configuration isomerizes to the *cis* form. The isomerization back to the *trans* form is achieved by irradiation with visible light or by heating.[8] Whereas switching in solution usually is quite effective, monolayers prepared by the alkanethiol method (with one exception[9]) exhibit no or moderate switching rates.[10] Sterical hindrance has been blamed to prevent isomerisation within the densely packed monolayers.[11] Only azobenzenes next to domain boundaries or defects in the monolayer have enough space to switch.[12] To overcome this problem the monolayers were "diluted" with short-chain alkane thiols to create the required free volume.[11,13–15] Disadvantage of this approach is the stochastical distribution of the azobenene units and thus the loss of an ordered surface. Moreover, phase segregation has been observed and the clustering of azobenzene-containing thiols gradually leads to the steric problem described above.[16] Another promising approach is the use of tripodal linker systems.[17–22] These linkers include three thiol groups for the fixation to the surface and cover a surface area that is sufficient to allow the conformational switching of the azobenzene function.

We recently presented a novel method to prepare ordered monolayers without using thiols. The "platform approach" is a modular, molecular system including a pedestal with a high affinity to gold and a reactive center in the middle which allows easy attachment of various functional groups perpendicular to the surface.[1,12,23] The triazatriangulenium (TATA) ion turned out to be an ideal molecular platform towards this end. It forms well ordered SAMs on Au(111). A number of carbanionic compounds can be attached to the carbocationic center of the TATA ion by simple polar C–C bond formation. Moreover, TATA platforms in different sizes can be easily prepared by variation of the alkane substituents at the three angular nitrogen atoms. Thus, by changing the size of the platforms the distance between the functional groups within the monolayer can be tuned.[1] Using propyl or larger substituents the free volume should be sufficient to allow the photo-induced isomerization of an attached azobenzene function.

Herein, we report preparative procedures that allow the covalent attachment of various groups to the cationic center of triazatriangulenium salts. The structures of two substituted triazatriangulenes, the phenylethynyl compound **4a**

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and the phenyl derivative **3a** were determined by single-crystal X-ray crystallography. The synthesis of 16 different azobenzene functionalized platforms is described and the photostationary equilibria upon irradiation with 365 and 440 nm light in solution is analysed for 8 representative examples. The half life of the *cis* isomers with respect to the thermal back isomerization was determined for these compounds.

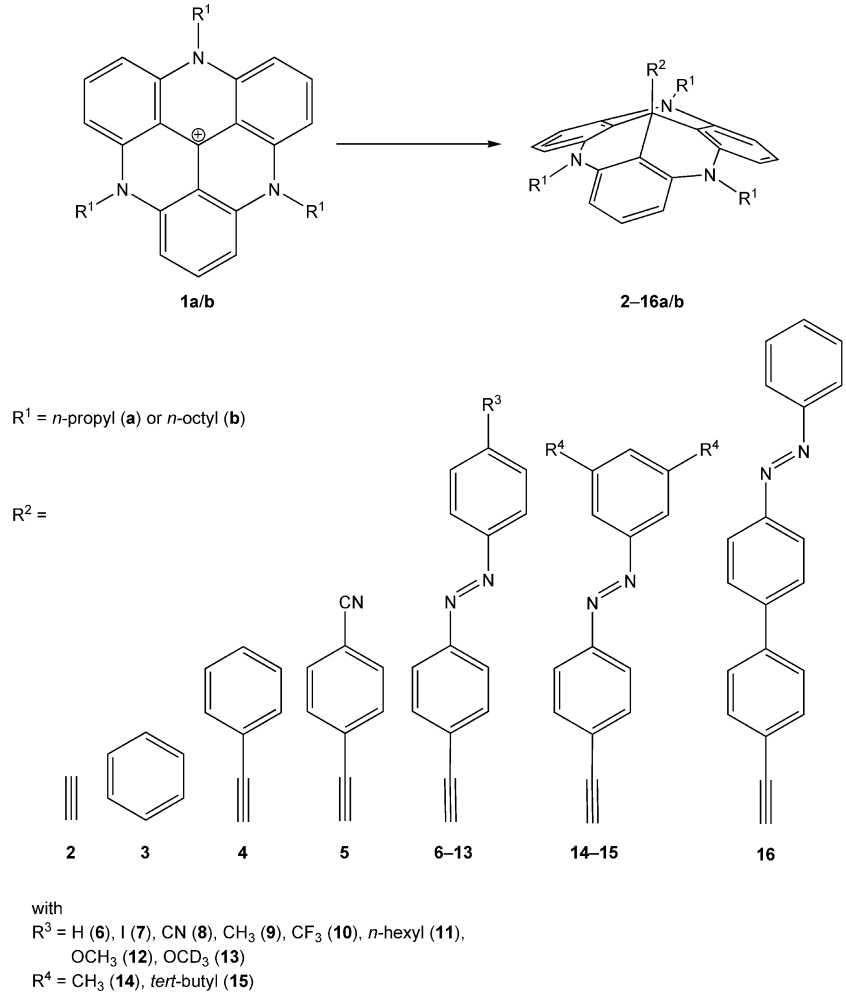
Results and Discussions

Syntheses of Functionalized Triazatriangulenes

The triazatriangulenium ions **1a/b** were synthesized according to a procedure of Laursen and Krebs.[24] According to previous STM experiments extended alkane chains at the three angular nitrogen atoms enhance the solubility and favour the formation of ordered monolayers.[1] Molecular functions are attached to the central C atom of the TATA ions by nucleophilic attack of sp (ethynyl) and sp^2 (phenyl) carbanions.

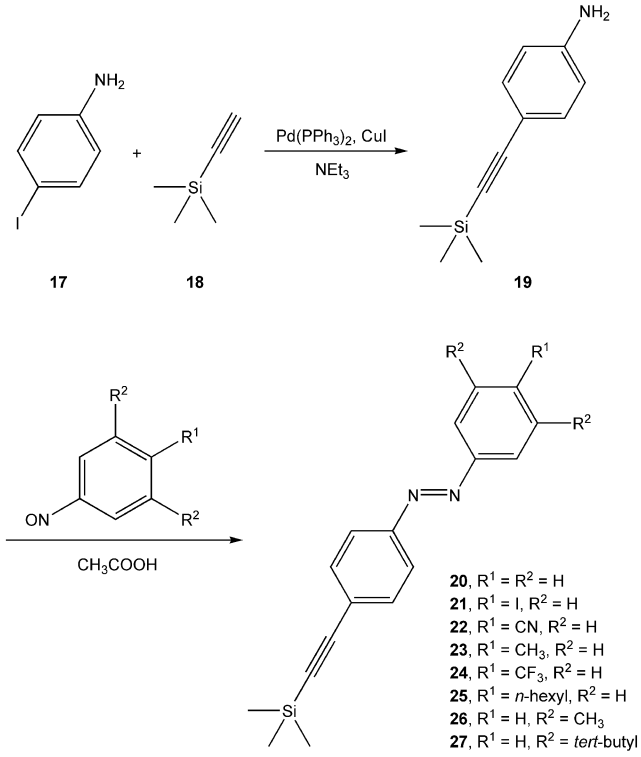
Acetylene is coupled to the platform by simply reacting sodium acetylide with the TATA ion at elevated temperatures. The terminal alkyne **2a/b** is a potential precursor for further derivatization by coupling reactions (e.g. Sonogashira, Glaser-Hay) or click-chemistry. The phenyl-substituted triazatriangulene **3a/b** is formed by reaction of phenyllithium with TATA in THF. Compound **3a** forms single crystals by recrystallization from diethyl ether, as well as compound **4a**, which is synthesized by deprotonation of phenylacetylene with a 2.5 M *n*-butyllithium solution and subsequent reaction with the TATA ion **1a**. A more general approach which is compatible to a multitude of functionalities, especially azobenzenes, is to use a TMS protected alkyne. In situ deprotection and coupling with the cationic center of the TATA ion **1a/b** is achieved with a base preferentially potassium hydroxide. Reactions times are drastically decreased if a strong ultra sound source (e.g., Branson Sonifier W-450) is used (Scheme 1).

The TMS-ethynyl-substituted azobenzenes **20**–**27** (Scheme 2) are synthesized using the condensation reaction of anilines and nitroso compounds.[25] The nitrosoarenes are obtained by oxidation of aniline derivatives with



Scheme 1. Overview of synthesized triazatriangulenes **2**–**16a/b**.

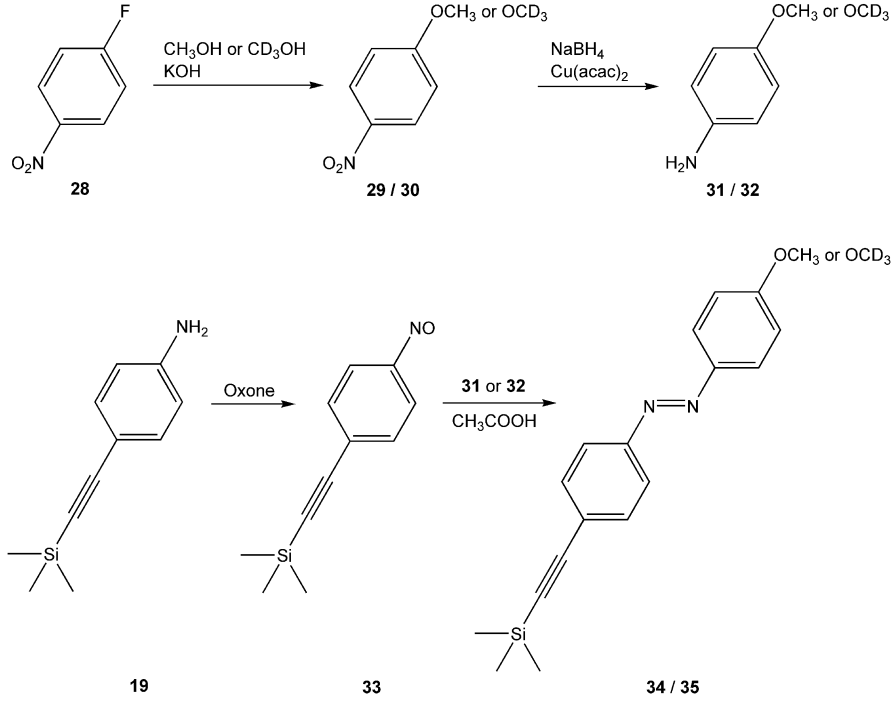
Oxone®[26] or by reduction of nitroarenes with tin.[27] As most of the nitrosoarenes are labile, purification was not attempted, and they are immediately converted into the corresponding azobenzenes by condensation with the respective aniline derivative in acetic acid.[26] In general, 4-[(trimethylsilyl)ethynyl]aniline (**19**), which is synthesized by Sonogashira reaction of 4-iodoaniline (**17**) and (trimethylsilyl)acetylene (**18**),[28] is used for the reaction with the corresponding nitrosoarene. However, oxidation of compound **19** to the nitroso derivative **33** is also appropriate, even though the yields are low.



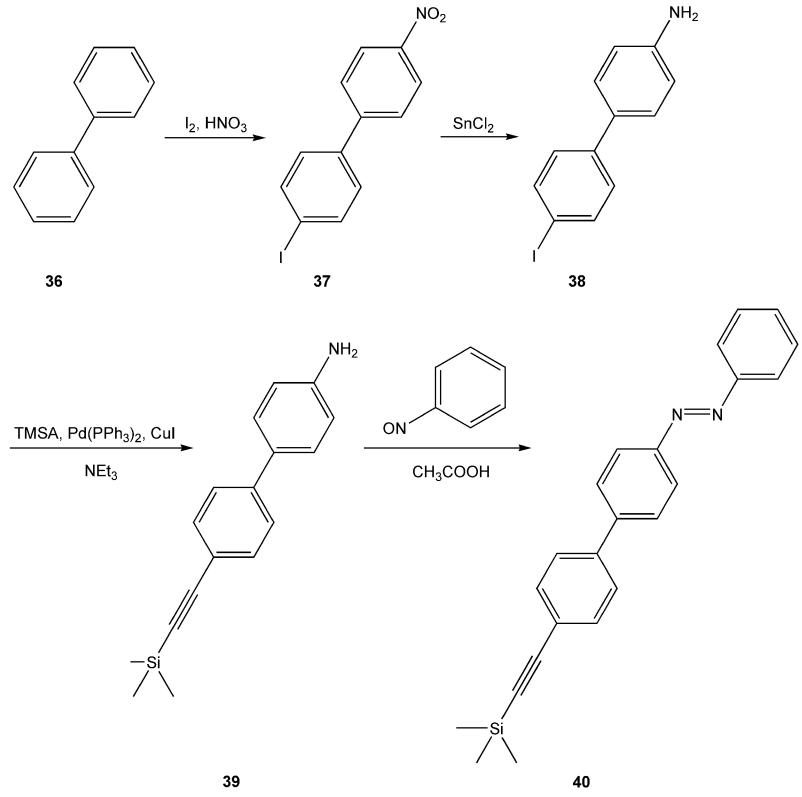
Scheme 2. Synthesis of TMS-ethynyl-substituted azobenzenes **20**–**27**.

Particularly in cases where the nitroso derivatives cannot be easily synthesized from commercially available compounds, oxidation of **19** to the nitroso derivative **33** is preferred. For example, 4-methoxyaniline **31** as well as the deuterated derivative **32** are converted into the corresponding azobenzenes **34** and **35** (Scheme 3) by condensation with 4-[(trimethylsilyl)ethynyl]nitrosobenzene (**33**). The deuterated 4-methoxyaniline **32** is synthesized from 4-nitrofluorobenzene **28** by nucleophilic aromatic substitution with an alkaline solution of deuterated methanol.[29] The reduction of the obtained nitro compound to the corresponding amine is carried out using sodium borohydride and copper(II) acetylacetonate as a catalyst.[30]

To increase the distance between the molecular functions and the TATA platform (and accordingly the surface) a phenyl ring was introduced as an additional spacer. Biphenyl (**36**) can be substituted in 4,4′ position by an iodo as well as a nitro group in one step.[31] Less than equimolar amounts of iodine must be used because otherwise an inseparable mixture of 4,4′-diiodo-1,1′-biphenyl and **37** is formed.[32] The unsymmetrically substituted biphenyl **37** is reduced to the amine using tin(II) chloride.[33] The TMS protected acetylene is attached by Sonogashira coupling[28]



Scheme 3. Synthesis of (*E*)-1-(4-methoxyphenyl)-2-{4-[(trimethylsilyl)ethynyl]phenyl}diazene (**34**) and the deuterated derivative **35**.



Scheme 4. Synthesis of (*E*)-1-phenyl-2-(4-{4-[(trimethylsilyl)ethynyl]phenyl}phenyl)diazene (**40**).

yielding compound **39**. The corresponding azobenzene **40** is finally obtained by condensation with nitrosobenzene. The attachment of **40** to the TATA platform **1b** proceeds as described above (Scheme 4).

Crystal Structures of 3a and 4a

Upon recrystallization from diethyl ether, compounds **3a** and **4a** formed single crystals suitable for X-ray single crystal structure analysis. The phenyl-substituted triazatriangulene **3a** crystallizes orthorhombic in space group *Pnma* with the molecule located on a crystallographic mirror plane. This compound contains additional diethyl ether as solvent also located on a mirror plane. In contrast to the unsubstituted cation **1a**,[24] the central C-atom C1 is sp^3-hybridized and thus the platform is no longer planar. This C-atom is shifted by 0.740 Å from a least-square plane calculated through the three N atoms and the three six-membered rings (Figure 1, top). The phenyl ring is oriented exactly perpendicular to the platform (dihedral angle: 90°) (Figure 1, top) and is exactly eclipsed to one of the three propyl groups (Figure 1, bottom). However, one can expect that the rotational barrier is rather low and can easily be overcompensated by packing effects (Figure 1, bottom).

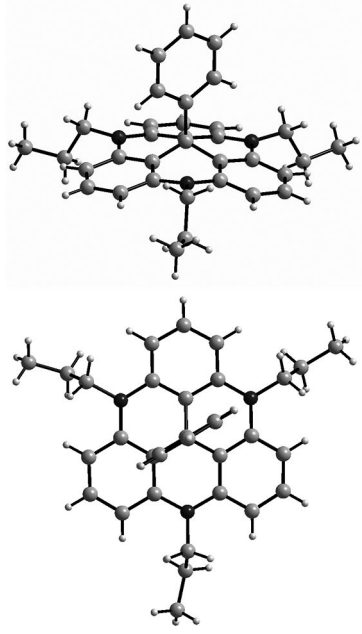


Figure 1. Crystal structure of compound **3a** with view along (top) and onto (bottom) the TATA platform.

Compound **4a** crystallizes monoclinic in space group *C*2/*c* with all atoms located in general positions. As in **3a** the central C-atom is shifted out of the molecular plane (deviation: 0.998 Å). The phenylethynyl substituent is oriented almost perpendicular to the TATA platform and the dihedral angle between this substituent and the platform amounts to 84.7° (Figure 2, top). Moreover, this substituent is nearly eclipsed to one of the three propyl substituents.

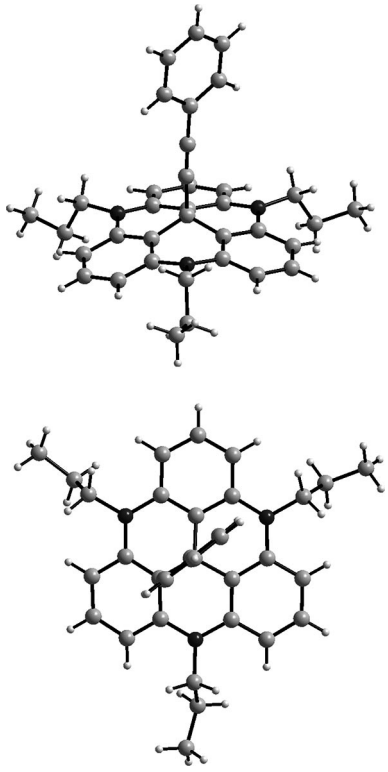


Figure 2. Crystal structure of compound **4a** with view along (top) and onto (bottom) the TATA platform.

Photoswitching

In solution, the isomerization of the azobenzene derivatives **6**–**16a/b** (Figure 3) was observed by UV/Vis and NMR spectroscopy. Upon irradiation with a high pressure mercury lamp and a band-pass filter (365 nm), the π→π* transition band in the UV/Vis spectrum decreases and the n-π* transition band increases, which indicates the formation of the *cis*-isomer.[34–35] The reisomerization was induced by irradiation with light of 440 nm. The conversion, however, is not complete and leads to a photostationary equilibrium.

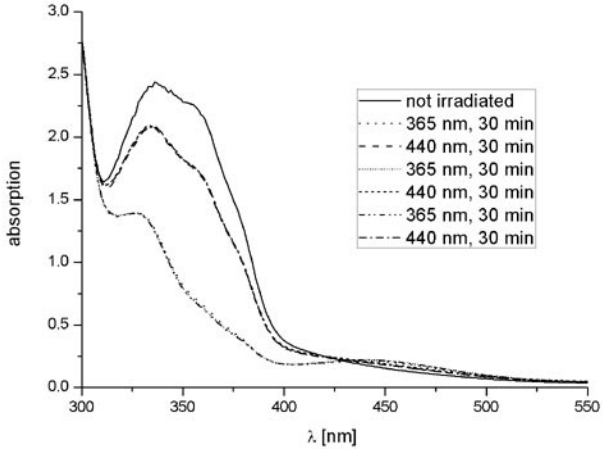


Figure 3. UV/Vis absorption spectra of **6a** in toluene, before and after irradiation with 365 nm and 440 nm, respectively.

In the NMR spectrum, a new set of signals appears after irradiation of the *trans* isomer with 365 nm. Up to 80% *cis*-isomer is formed. The *cis* to *trans* isomer ratio can be easily determined by intergration of the ^{1}H NMR signals of both isomers. The half life of the thermal back isomerization at ambient conditions was determined by following the decrease of the signals of the *cis*-isomer over several days and is shown in Table 1. As expected, the introduction of electron withdrawing as well as electron donating substituents to the azobenzene system in *para* position increases the reaction rate of the thermal back isomerization.[36–41]

Table 1. Percentage of the *cis*-isomers formed by irradiation with 365 nm in the photostationary equilibrium and half life of thermal back isomerization determined by NMR of azobenzene substituted triazatriangulenes in [D_8]toluene at room temperature.

	cis_{max}	$t_{1/2}$ [min]
6a	73%	2771
6b	80%	2999
7b	80%	1486
8a	42%	1135
8b	37%	910
9b	74%	1437
12b	72%	942
15b	47%	2047

Conclusions

In summary, several triazatriangulenes **2**–**16a/b** were synthesized by nucleophilic attack at the central C atom of the TATA cations **1a/b**. Various functionalities, including azobenzenes, with different spacer lengths were attached perpendicular to the plane of the platform like a floor lamp on a pedestal. The reversible photoisomerization of the azobenzene derivatives was proven by UV/Vis and NMR spectroscopy in solution. The TATA platform in combination with the click-type perpendicular attachment of functional groups with different linear spacer groups represents a modular and flexible system to design and prepare sophisticated functional monolayers.[1,23] Preliminary experiments revealed that the Azo TATA molecules form ordered monolayers on Au(111) and retain their switching capability. Details will be published in a forthcoming publication.

Experimental Section

General Remarks: TLC was performed with TLC plates (Polygram Sil G/UV_{254}), Fa. Macherey–Nagel. Column chromatography was performed with silica gel 60 (0.04–0.063 mm) or aluminium oxide 60 basic (0.063–0.2 mm), Fa. Merck. NMR spectra were recorded using a Bruker DRX 500 [^{1}H NMR (500.1 MHz), ^{13}C NMR (125.8 MHz)] with tetramethylsilane (δ_H = 0.00 ppm) and $CDCl_3$ (δ_C = 77.01 ppm) as internal standard. For the assignment of the NMR signals and the numbering of the corresponding carbon atoms see Supporting Information. Mass spectra were recorded on a MAT 8230 (EI, 70 eV), Fa. Finnigan. IR spectra were recorded with a Perkin–Elmer 1600 series FT-IR spectrometer, using a golden-gate-diamond-ATR unit A531-G. UV/Vis spectra were recorded with a Lambda 14 UV/Vis spectrometer, Fa. Perkin–Elmer.

Elemental analysis were recorded with a CHNSO elemental analyser EURO EA 3000 series, Fa. Euro Vector. Photo-irradiation was performed with a UV light source UV-P 250 C, Fa. Panacol-Elosol, using band-pass filters LC-365BP20–25 and LC-440BP10–25, Fa. Laser Components.

Crystal Structure Determination: Data measurements were performed with an imaging plate diffraction system (IPDS-1) with Mo-K_α radiation from STOE & CIE. The structure solutions were done with direct methods using SHELXS-97 and structure refinements were performed against F^2 using SHELXL-97. All non hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were positioned with idealized geometry and were refined with fixed isotropic displacement parameters using a riding model. **3a** contain a small amount of solvent disordered around a center of inversion. Because no reasonable structure model was found the data were corrected for disordered solvent using the SQUEEZE option in Platon (Table 2).

Table 2. Crystallographic data for **3a** and **4a**.

Compound	**3a**	**4a**
Formula	$C_{38}H_{45}N_3O$	$C_{36}H_{35}N_3$
MW [g mol^{-1}]	559.77	509.67
Crystal system	orthorhombic	monoclinic
Space group	*Pnma*	*C*2/*c*
a [Å]	14.473(1)	26.175(2)
b [Å]	14.734(1)	15.096(1)
c [Å]	14.894(1)	18.625(2)
β [°]	–	124.15 (1)
V [Å^3]	3176.1(4)	6090.8(7)
T [K]	170	170
Z	4	8
D_{calc} [g cm^{-3}]	1.171	1.112
μ [mm^{-1}]	0.070	0.065
θ_{max}/deg	28.1	26.0
Measured reflections	25196	18150
Unique reflections	3981	5978
Reflections [$F_o > 4\sigma(F_o)$]	3328	4379
Parameters	212	353
R_{int}	0.0495	0.0391
R_1[a] [$F_o > 4\sigma(F_o)$]	0.0428	0.0486
wR_2[b] [all data]	0.1217	0.1307
GOF	1.034	1.021
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [e Å^{-3}]	0.267–0.227	0.281/–0.255

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

CCDC-775476 (for **3a**) and CCDC-775477 (for **4a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Method 1. Trimethylsilylethynyl-Substituted Azobenzenes:[25] A solution of Oxone® (2 equiv.) in water was added to a solution of the respective aniline (1 equiv.) in dichloromethane. After stirring for 0.5 to 5 h (TLC monitoring) at room temperature, the layers were separated. The aqueous layer was extracted twice with dichloromethane. The combined organic phases (usually green) were washed with 1 N HCl, saturated $NaHCO_3$ solution, H_2O, saturated NaCl solution and dried with $MgSO_4$. Removal of the solvent yielded the corresponding nitrosoarene, which was used in the next step without further purification. An equimolar amount of an aniline derivative was dissolved in 40 mL acetic acid. After adding the nitrosoarene, the mixture was stirred for 2–24 h. The resulting orange precipitate was separated by filtration and recrystallized from ethanol.

General Method 2. Azobenzene-Substituted Triazatriangulenes: Powdered KOH (in excess) was added to a solution of trimethylsilylethynyl-substituted azobenzene (1 equiv.) in 20–40 mL THF under nitrogen. The mixture was sonicated for 20–60 min at 0 °C using a Branson Sonifier W-450. After adding 4,8,12-tri-*n*-propyl-4,8,12-triaza-triangulenium tetrafluoroborate **1a** (1 equiv.) or 4,8,12-tri-*n*-octyl-4,8,12-triazatriangulenium tetrafluoroborate **1b** (1 equiv.) respectively, the mixture was sonicated for a further period of 1.5–5 h at 0 °C. Afterwards, the mixture was poured into 100 mL water. The layers were separated and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried with $MgSO_4$ and filtered. After evaporating the solvents, the residue was dissolved in dichloromethane and filtered through a short column of basic aluminium oxide. The solvent was evaporated and the resulting orange residue recrystallized from diethyl ether or ethanol, respectively.

(*E*)-1-Phenyl-2-{4-[(trimethylsilyl)ethynyl]phenyl}diazene (20): Nitrosobenzene (1.07 g, 10.0 mmol) was added to a solution of 4-[(trimethylsilyl)ethynyl]aniline (**19**) (1.89 g, 10.0 mmol) in 40 mL acetic acid and stirred for 16 h. The resulting precipitate was separated by filtration and recrystallized from ethanol to yield **20** (1.66 g, 60%) as an orange solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.92 (d, ^3J = 8.1 Hz, 2 H, 13-H, 17-H), 7.86 (d, ^3J = 8.8 Hz, 2 H, 7-H, 9-H), 7.60 (d, ^3J = 8.8 Hz, 2 H, 6-H, 10-H), 7.46–7.55 (m, 3 H, 14-H, 15-H, 16-H), 0.28 (s, 9 H, 1-H, 2-H, 3-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 152.63 (C-12), 151.91 (C-8), 132.81 (C-6, C-10), 131.27 (C-15), 129.14 (C-14, C-16), 125.8 (C-11), 122.96 (C-13, C-17), 122.79 (C-7, C-9), 104.64 (C-5), 97.04 (C-4), –0.08 (C-1, C-2, C-3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 278 (93), 263 (17), 201 (16), 173 (100), 158 (50), 143 (23), 105 (22). IR (ATR): $\tilde{\nu}$ = 3057 (w), 2960 (m), 2903 (m), 2149 (s), 1594 (m), 1492 (m), 1482 (m), 1396 (m), 1298 (m), 1247 (s), 1220 (s), 1151 (s), 1105 (m), 1000 (m), 837 (vs), 759 (s), 683 (s), 664 (s), 563 (s), 536 (s), 505 (s) cm^{-1}. UV (toluene): λ_{max} (lg ε) = 451 (3.09), 344 (4.44) nm. $C_{17}H_{18}N_2Si$ (278.12): calcd. C 73.33, H 6.52, N 10.06; found C 73.23, H 6.75, N 9.83.

(*E*)-1-(4-Iodophenyl)-2-{4-[(trimethylsilyl)ethynyl]phenyl}diazene (21): 4-Iodonitrosobenzene[27] (885 mg, 3.80 mmol) was added to a solution of 4-[(trimethylsilyl)ethynyl]aniline (**19**) (718 mg, 3.80 mmol) in 40 mL acetic acid and stirred for 16 h. The resulting precipitate was separated by filtration and recrystallized from ethanol to yield **21** (1.00 g, 65%) as an orange solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.86 (d, ^3J = 8.5 Hz, 2 H, 14-H, 16-H), 7.85 (d, ^3J = 8.4 Hz, 2 H, 7-H, 9-H), 7.64 (d, ^3J = 8.5 Hz, 2 H, 13-H, 17-H), 7.60 (d, ^3J = 8.4 Hz, 2 H, 6-H, 10-H), 0.28 (s, 9 H, 1-H, 2-H, 3-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 152.02 (C-12), 151.81 (C-8), 138.52 (C-14, C-16), 132.95 (C-6, C-10), 126.26 (C-11), 124.62 (C-13, C-17), 122.99 (C-7, C-9), 104.66 (C-5), 98.12 (C-15), 97.51 (C-4), 0.00 (C-1, C-2, C-3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 404 (89), 389 (16), 231 (24), 203 (53), 201 (25), 173 (100), 158 (55), 145 (24), 143 (29). IR (ATR): $\tilde{\nu}$ = 3082 (w), 2957 (m), 2898 (m), 2159 (m), 1593 (m), 1566 (m), 1491 (m), 1473 (m), 1393 (m), 1251 (s), 1225 (s), 1154 (m), 1100 (m), 1050 (m), 1002 (s), 834 (vs), 759 (s), 556 (s) cm^{-1}. UV (toluene): λ_{max} (lg ε) = 448 (3.23), 360 (4.53) nm. $C_{17}H_{17}IN_2Si$ (404.02): calcd. C 50.50, H 4.24, N 6.93; found C 49.68, H 3.89, N 6.71.

(*E*)-4-({4-[(Trimethylsilyl)ethynyl]phenyl}diazenyl)benzonitrile (22): Following the general method 1, a solution of Oxone® (20.8 g, 33.9 mmol) in 150 mL water was added to a solution of 4-aminobenzonitrile (2.00 g, 16.9 mmol) in 40 mL dichloromethane and the mixture was stirred for 2.5 h. The crude product was purified by column chromatography (silica gel, dichloromethane) yielding a yellow solid (1.12 g, 50%).

The nitroso compound (660 mg, 5.00 mmol) was added to a solution of 4-[(trimethylsilyl)ethynyl]aniline (**19**) (945 mg, 5.00 mmol) in 30 mL acetic acid and stirred for 3.5 h. The resulting precipitate was separated by filtration and recrystallized from ethanol to yield **22** (987 mg, 65%) as an orange solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.98 (d, ^3J = 8.7 Hz, 2 H, 13-H, 17-H), 7.90 (d, ^3J = 8.7 Hz, 2 H, 7-H, 9-H), 7.81 (d, ^3J = 8.7 Hz, 2 H, 14-H, 16-H), 7.62 (d, ^3J = 8.7 Hz, 2 H, 6-H, 10-H), 0.28 (s, 9 H, 1-H, 2-H, 3-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 154.49 (C-12), 151.60 (C-8), 133.25 (C-14, C-16), 132.93 (C-6, C-10), 127.15 (C-11), 123.43 (C-13, C-17), 123.25 (C-7, C-9), 118.40 (C-18), 114.23 (C-15), 104.35 (C-5), 98.19 (C-4), –0.13 (C-1, C-2, C-3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 303 (67), 288 (19), 260 (9), 201 (11), 173 (100), 158 (65), 145 (15), 143 (28), 102 (33). IR (ATR): $\tilde{\nu}$ = 3095 (w), 3050 (w), 2959 (m), 2906 (w), 2228 (m), 2158 (m), 1594 (m), 1489 (m), 1449 (m), 1407 (m), 1250 (s), 1227 (s), 1152 (m), 1135 (m), 1101 (m), 1007 (m), 834 (vs), 756 (s), 637 (s), 564 (s), 473 (s) cm^{-1}. UV (toluene): λ_{max} (lg ε) = 457 (3.19), 360 (4.52) nm. $C_{18}H_{17}N_3Si$ (303.12): calcd. C 71.25, H 5.65, N 13.85; found C 71.04, H 5.72, N 14.16.

(*E*)-1-(4-Methylphenyl)-2-{4-[(trimethylsilyl)ethynyl]phenyl}diazene (23): Following the general method 1, a solution of Oxone® (24.6 g, 40.0 mmol) in 120 mL water was added to a solution of 4-methylaniline (2.14 g, 20.0 mmol) in 60 mL dichloromethane and the mixture was stirred for 30 min. The crude product was obtained as a green solid (696 mg, 29%).

The crude nitroso compound (605 mg, 5.00 mmol) was added to a solution of 4-[(trimethylsilyl)ethynyl]aniline (**19**) (945 mg, 5.00 mmol) in 30 mL acetic acid and stirred for 36 h. The resulting precipitate was separated by filtration and recrystallized from ethanol to yield **23** (332 mg, 23%) as an orange solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.84 (d, ^3J = 8.5 Hz, 2 H, 7-H, 9-H), 7.82 (d, ^3J = 8.6 Hz, 2 H, 13-H, 17-H), 7.59 (d, ^3J = 8.3 Hz, 2 H, 6-H, 10-H), 7.31 (d, ^3J = 8.6 Hz, 2 H, 14-H, 16-H), 2.43 (s, 3 H, 18-H), 0.27 (s, 9 H, 1-H, 2-H, 3-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 152.10 (C-8), 150.86 (C-12), 142.00 (C-15), 132.86 (C-6, C-10), 129.87 (C-14, C-16), 125.50 (C-11), 123.05 (C-13, C-17), 122.73 (C-7, C-9), 104.80 (C-5), 96.89 (C-4), 21.61 (C-18), 0.00 (C-1, C-2, C-3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 292 (100), 277 (17), 173 (84), 158 (49), 143 (24), 119 (40). IR (ATR): $\tilde{\nu}$ = 3034 (w), 2957 (m), 2900 (w), 2151 (m), 1602 (m), 1491 (m), 1409 (m), 1247 (s), 1225 (m), 1156 (m), 1107 (m), 1011 (m), 839 (vs), 760 (s), 644 (s), 556 (s), 504 (s) cm^{-1}. UV (toluene): λ_{max} (lg ε) = 447 (3.30), 355 (4.60) nm. $C_{18}H_{20}N_2Si$ (292.14): calcd. C 73.92, H 6.89, N 9.58; found C 74.10, H 6.98, N 9.79.

(*E*)-1-[4-(Trifluoromethyl)phenyl]-2-{4[(trimethylsilyl)ethynyl]-phenyl}diazene (24): Following the general method 1, a solution of Oxone® (24.6 g, 40.0 mmol) in 150 mL water was added to a solution of 4-(trifluoromethyl)aniline (3.22 g, 20.0 mmol) in 40 mL dichloromethane and the mixture was stirred for 1.5 h. The crude product (2.41 g) was added to a solution of 4-[(trimethylsilyl)ethynyl]aniline (**19**) (2.60 g, 13.7 mmol) in 40 mL acetic acid and stirred for 2 h. The resulting precipitate was separated by filtration and recrystallized from ethanol to yield **24** (2.24 g, 32% over two steps) as an orange solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.99 (d, ^3J = 8.7 Hz, 2 H, 13-H, 17-H), 7.89 (d, ^3J = 8.7 Hz, 2 H, 7-H, 9-H), 7.78 (d, ^3J = 8.7 Hz, 2 H, 14-H, 16-H), 7.62 (d, ^3J = 8.7 Hz, 2 H, 6-H, 10-H), 0.28 (s, 9 H, 1-H, 2-H, 3-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 154.37 (C-12), 151.62 (C-8), 132.90 (C-6, C-10), 132.30 (C-15), 126.68 (C-11), 126.36 (C-14, C-16), 124.98 (C-18), 123.11 (C-7, C-9, C-13, C-17), 104.43 (C-5), 97.79 (C-4), –0.09 (C-1, C-2, C-3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 346 (70), 331 (17), 201 (19), 173 (100), 158 (32), 145 (41), 143 (15), 126 (11). IR (ATR): $\tilde{\nu}$ = 3056 (w), 2965 (m), 2904 (m), 2162 (m), 1594 (m), 1490 (m), 1409 (m), 1317 (s), 1255 (s), 1223 (s), 1165 (s), 1128 (s), 1102 (s), 1063 (s), 1011 (s), 837 (vs), 763 (s), 674 (s), 601 (s), 553 (s) cm^{-1}. UV (toluene): λ_{max} (lg ε) = 453 (3.14), 346 (4.49) nm. $C_{18}H_{17}F_3N_2Si$ (346.11): calcd. C 62.41, H 4.95, N 8.09; found C 62.82, H 5.20, N 8.10.

(*E*)-1-(4-Hexylphenyl)-2-{4-[(trimethylsilyl)ethynyl]phenyl}diazene (25): Following the general method 1, a solution of Oxone® (19.5 g, 31.7 mmol) in 160 mL water was added to a solution of 4-[(trimethylsilyl)ethynyl]aniline (**19**) (3.00 g, 15.9 mmol) in 60 mL dichloromethane and the mixture was stirred for 5 h. The crude product was purified by column chromatography (silica gel, cyclohexane/dichloromethane, 3:1) yielding a green solid (1.01 g, 31%).

The nitroso compound **33** (227 mg, 1.12 mmol) was added to a solution of 4-hexylaniline (90%, 220 mg, 1.12 mmol) in 20 mL acetic acid and stirred for 16 h. The solvent was removed in vacuo and the residue was purified by column chromatography (silica gel, cyclohexane/dichloromethane, 5:1) to yield **25** (227 mg, 56%) as an orange solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.84 (d, ^3J = 8.3 Hz, 2 H, 7-H, 9-H), 7.83 (d, ^3J = 8.3 Hz, 2 H, 13-H, 17-H), 7.59 (d, ^3J = 8.3 Hz, 2 H, 6-H, 10-H), 7.31 (d, ^3J = 8.2 Hz, 2 H, 14-H, 16-H), 2.68 (t, ^3J = 7.7 Hz, 2 H, 18-H), 1.65 (quint, ^3J = 7.5 Hz, 2 H, 19-H), 1.39–1.33 (m, 2 H, 20-H), 1.33–1.26 (m, 4 H, 21-H, 22-H), 0.89 (t, ^3J = 7.0 Hz, 3 H, 23-H), 0.27 (s, 9 H, 1-H, 2-H, 3-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 152.14 (C-8), 151.03 (C-12), 147.04 (C-15), 132.85 (C-6, C-10), 129.22 (C-14, C-16), 125.48 (C-11), 123.05 (C-13, C-17), 122.72 (C-7, C-9), 104.81 (C-5), 96.87 (C-4), 36.01 (C-18), 31.77 (C-21), 31.30 (C-19), 29.02 (C-20), 22.67 (C-22), 14.15 (C-23), 0.00 (C-1, C-2, C-3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 362 (60), 350 (34), 173 (37), 161 (100), 105 (9). IR (ATR): $\tilde{\nu}$ = 3024 (w), 2958 (m), 2921 (s), 2852 (m), 2150 (s), 1601 (m), 1490 (m), 1447 (m), 1411 (m), 1245 (s), 1221 (s), 1155 (m), 1008 (m), 835 (vs), 753 (s), 645 (s), 571 (s), 506 (s) cm^{-1}. UV (toluene): λ_{max} (lg ε) = 449 (3.26), 355 (4.57) nm. $C_{23}H_{30}N_2Si$ (362.22): calcd. C 76.19, H 8.34, N 7.73; found C 76.52, H 8.85, N 7.87.

(*E*)-1-(3,5-Dimethylphenyl)-2-{4-[(trimethylsilyl)ethynyl]phenyl}-diazene (26): 3,5-Dimethylnitrosobenzene[27] (351 mg, 2.60 mmol) was added to a solution of 4-[(trimethylsilyl)ethynyl]aniline (**19**) (491 mg, 2.60 mmol) in 20 mL acetic acid and stirred for 14 h. The solvent was removed in vacuo and the remaining oil was purified by column chromatography (silica gel, cyclohexane/dichloromethane, 3:1) to yield **26** (325 mg, 41%) as an orange solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.84 (d, ^3J = 8.7 Hz, 2 H, 7-H, 9-H), 7.59 (d, ^3J = 8.7 Hz, 2 H, 6-H, 10-H), 7.53 (s, 2 H, 13-H, 17-H), 7.13 (s, 1 H, 15-H), 2.41 (s, 6 H, 18-H, 19-H), 0.27 (s, 9 H, 1-H, 2-H, 3-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 152.87 (C-12), 152.02 (C-8), 138.82 (C-14, C-16), 133.01 (C-15), 132.80 (C-6, C-10), 125.55 (C-11), 122.68 (C-7, C-9), 120.75 (C-13, C-17), 104.70 (C-5), 96.90 (C-4), 21.26 (C-18, C-19), –0.07 (C-1, C-2, C-3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 306 (96), 291 (10), 263 (9), 201 (11), 173 (77), 158 (29), 143 (12), 133 (14), 105 (100). IR (ATR): $\tilde{\nu}$ = 3041 (w), 3009 (w), 2954 (m), 2919 (m), 2858 (w), 2159 (m), 1611 (m), 1492 (m), 1442 (m), 1401 (m), 1246 (s), 1148 (m), 838 (vs), 760 (s), 679 (s), 531 (s) cm^{-1}. UV (toluene): λ_{max} (lg ε) = 450 (3.19), 346 (4.53) nm. $C_{19}H_{22}N_2Si$ (306.16): calcd. C 74.46, H 7.24, N 9.14; found C 74.24, H 7.78, N 9.19.

(*E*)-1-(3,5-Di-*tert*-butylphenyl)-2-{4-[(trimethylsilyl)ethynyl]phenyl}-diazene (27): Following the general method 1, a solution of Oxone® (19.5 g, 31.7 mmol) in 160 mL water was added to a solution of 4-[(trimethylsilyl)ethynyl]aniline (**19**) (3.00 g, 15.9 mmol) in 60 mL

dichloromethane and the mixture was stirred for 5 h. The crude product was purified by column chromatography (silica gel, cyclohexane/dichloromethane, 3:1) to yield a green solid (1.01 g, 31%).

The nitroso compound **33** (345 mg, 1.70 mmol) was added to a solution of 3,5-(di-*tert*-butyl)aniline (349 mg, 1.70 mmol) in 20 mL acetic acid and stirred for 16 h. The solvent was removed in vacuo and the residue was recrystallized from ethanol to yield **27** (406 mg, 61%) as an orange solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.86 (d, ^3J = 8.6 Hz, 2 H, 7-H, 9-H), 7.78 (d, ^4J = 1.8 Hz, 2 H, 13-H, 17-H), 7.61 (d, ^3J = 8.6 Hz, 2 H, 6-H, 10-H), 7.58 (d, ^4J = 1.8 Hz, 1 H, 15-H), 1.40 (s, 18 H, 19-H, 20-H, 21-H, 23-H, 24-H, 25-H), 0.28 (s, 9 H, 1-H, 2-H, 3-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 152.59 (C-12), 152.16 (C-8), 151.89 (C-14, C-16), 132.79 (C-6, C-10), 125.65 (C-15), 125.35 (C-11), 122.66 (C-7, C-9), 117.43 (C-13, C-17), 104.76 (C-5), 96.77 (C-4), 35.13 (C-18, C-22), 31.46 (C-19, C-20, C-21, C-23, C-24, C-25), –0.04 (C-1, C-2, C-3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 390 (61), 375 (8), 347 (7), 189 (100), 180 (19), 173 (47), 158 (27), 143 (10), 133 (22). IR (ATR): $\tilde{\nu}$ = 3076 (w), 2961 (m), 2900 (m), 2868 (m), 2157 (m), 1604 (m), 1476 (m), 1458 (m), 1363 (m), 1250 (s), 1221 (m), 1170 (m), 839 (vs), 759 (s), 697 (s), 538 (s) cm^{-1}. UV (toluene): λ_{max} (lg ε) = 348 (4.52) nm. $C_{25}H_{34}N_2Si$ (390.25): calcd. C 76.87, H 8.77, N 7.17; found C 76.50, H 9.13, N 7.20.

(*E*)-1-(4-Methoxyphenyl)-2-{4-[(trimethylsilyl)ethynyl]phenyl}-diazene (34): Following the general method 1, a solution of Oxone® (19.5 g, 31.7 mmol) in 160 mL water was added to a solution of 4-[(trimethylsilyl)ethynyl]aniline (**19**) (3.00 g, 15.9 mmol) in 60 mL dichloromethane and the mixture was stirred for 5 h. The crude product was purified by column chromatography (silica gel, cyclohexane/dichloromethane, 3:1) yielding a green solid (1.01 g, 31%).

The nitroso compound **33** (860 mg, 4.24 mmol) was added to a solution of 4-methoxyaniline (522 mg, 4.24 mmol) in 40 mL acetic acid and stirred for 16 h. The resulting precipitate was separated by filtration and recrystallized from ethanol to yield **34** (342 mg, 26%) as an orange solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.92 (d, ^3J = 9.0 Hz, 2 H, 13-H, 17-H), 7.82 (d, ^3J = 8.6 Hz, 2 H, 7-H, 9-H), 7.58 (d, ^3J = 8.6 Hz, 2 H, 6-H, 10-H), 7.01 (d, ^3J = 9.0 Hz, 2 H, 14-H, 16-H), 3.89 (s, 3 H, 18-H), 0.27 (s, 9 H, 1-H, 2-H, 3-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 162.33 (C-15), 152.09 (C-8), 147.06 (C-12), 132.78 (C-6, C-10), 125.04 (C-11), 124.93 (C-13, C-17), 122.50 (C-7, C-9), 114.29 (C-14, C-16), 104.81 (C-5), 96.62 (C-4), 55.61 (C-18), –0.06 (C-1, C-2, C-3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 308 (74), 293 (9), 173 (26), 158 (29), 143 (16), 135 (54), 107 (100). IR (ATR): $\tilde{\nu}$ = 3076 (w), 2995 (m), 2955 (m), 2897 (m), 2838 (m), 2156 (m), 1599 (m), 1582 (m), 1497 (m), 1461 (m), 1439 (m), 1414 (m), 1323 (m), 1298 (m), 1244 (s), 1178 (m), 1151 (m), 1140 (m), 1106 (m), 1031 (s), 1010 (m), 835 (vs), 756 (s), 560 (s) cm^{-1}. UV (toluene): λ_{max} (lg ε) = 365 (4.67) nm. $C_{18}H_{20}N_2OSi$ (308.13): calcd. C 70.09, H 6.54, N 9.08; found C 70.35, H 6.75, N 9.07.

(*E*)-1-[4-([D$_3$]Methoxy)phenyl]-2-{4-[(trimethylsilyl)ethynyl]phenyl}-diazene (35): Following the general method 1, a solution of Oxone® (19.5 g, 31.7 mmol) in 160 mL water was added to a solution of 4-[(trimethylsilyl)ethynyl]aniline (**19**) (3.00 g, 15.9 mmol) in 60 mL dichloromethane and the mixture was stirred for 5 h. The crude product was purified by column chromatography (silica gel, cyclohexane/dichloromethane, 3:1) to yield a green solid (1.01 g, 31%).

The nitroso compound **33** (1.00 g, 4.93 mmol) was added to a solution of 4-([D$_3$]methoxy)aniline (610 mg, 4.93 mmol) in 40 mL acetic acid and stirred for 16 h. The solvent was evaporated and the resulting residue recrystallized from ethanol to yield **35** (690 mg, 45%) as an orange solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.91 (d, ^3J = 9.0 Hz, 2 H, 13-H, 17-H), 7.82 (d, ^3J = 8.6 Hz, 2 H, 7-H, 9-H), 7.58 (d, ^3J = 8.6 Hz, 2 H, 6-H, 10-H), 7.01 (d, ^3J = 9.0 Hz, 2 H, 14-H, 16-H), 0.27 (s, 9 H, 1-H, 2-H, 3-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 162.39 (C-15), 152.15 (C-8), 147.10 (C-12), 132.84 (C-6, C-10), 125.09 (C-11), 124.99 (C-13, C-17), 122.55 (C-7, C-9), 114.33 (C-14, C-16), 104.87 (C-5), 96.67 (C-4), 54.86 (C-18), 0.00 (C-1, C-2, C-3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 311 (69), 296 (8), 173 (27), 158 (27), 143 (16), 138 (61), 110 (100). IR (ATR): $\tilde{\nu}$ = 3073 (w), 3054 (w), 2955 (m), 2897 (m), 2250 (m), 2155 (m), 2071 (m), 1597 (m), 1580 (m), 1491 (m), 1414 (m), 1322 (m), 1298 (m), 1249 (s), 1153 (m), 1142 (m), 1103 (s), 992 (m), 954 (m), 836 (vs), 758 (s), 560 (s) cm^{-1}. UV (toluene): λ_{max} (lg ε) = 367 (4.61) nm. $C_{18}H_{17}D_3N_2OSi$ (311.15): calcd. C 69.41, H 7.44, N 8.99; found C 69.69, H 6.65, N 9.11.

(*E*)-1-Phenyl-2-(4-{4-[(trimethylsilyl)ethynyl]phenyl}phenyl)diazene (40): Nitrosobenzene (282 mg, 2.64 mmol) was added to a solution of 4-amino-4′-[(trimethylsilyl)ethynyl]-1,1′-biphenyl (**39**) (700 mg, 2.64 mmol) in 40 mL acetic acid and stirred for 16 h. The resulting precipitate was separated by filtration and recrystallized from ethanol to yield **40** (567 mg, 61%) as an orange solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 8.00 (d, ^3J = 8.6 Hz, 2 H, 14-H, 16-H), 7.94 (d, ^3J = 8.2 Hz, 2 H, 19-H, 23-H), 7.74 (d, ^3J = 8.6 Hz, 2 H, 13-H, 17-H), 7.61 (d, ^3J = 8.5 Hz, 2 H, 7-H, 9-H), 7.56 (d, ^3J = 8.5 Hz, 2 H, 6-H, 10-H), 7.55–7.46 (m, 3 H, 20-H, 21-H, 22-H), 0.28 (s, 9 H, 1-H, 2-H, 3-H) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$, 25 °C): δ = 152.73 (C-18), 151.94 (C-15), 142.74 (C-12), 140.08 (C-8), 132.51 (C-6, C-10), 131.07 (C-21), 129.12 (C-20, C-22), 127.67 (C-13, C-17), 126.92 (C-7, C-9), 123.45 (C-14, C-16), 122.90 (C-19, C-23), 122.69 (C-11), 104.81 (C-5), 95.44 (C-4), –0.01 (C-1, C-2, C-3) ppm. IR (ATR): $\tilde{\nu}$ = 3064 (w), 3040 (w), 2956 (m), 2897 (w), 2153 (m), 1594 (m), 1487 (m), 1399 (m), 1245 (s), 1196 (m), 1154 (m), 1071 (m), 1018 (m), 1002 (m), 825 (vs), 757 (s), 687 (s), 542 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 354 (77), 339 (9), 249 (100), 234 (41), 169 (6), 117 (8), 105 (14). UV (toluene): λ_{max} (lg ε) = 355 (4.63) nm. $C_{23}H_{22}N_2Si$ (354.16): calcd. C 77.92, H 6.25, N 7.90; found C 77.88, H 6.64, N 8.11.

12*c*-Ethynyl-4,8,12-tri-*n*-propyl-4,8,12-triazatriangulene (2a): Under nitrogen atmosphere, sodium (200 mg, 8.70 mmol) was added to anisole (50 mL) and heated to 110 °C. Acetylene was bubbled through the mixture for about 2 h until a white suspension occurred. 4,8,12-Tri-*n*-propyl-4,8,12-triazatriangulenium tetrafluoroborate (**1a**) (300 mg, 0.61 mmol) was added and acetylene was bubbled through the mixture for 4 h. After 14 h of strirring at 110 °C the mixture was carefully quenched with water. The layers were separated and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried with $MgSO_4$ and filtered. The solvent was removed in vacuo and the obtained residue was recrystallized from diethyl ether to yield **2a** (110 mg, 41%) as a light pink solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.19 (t, ^3J = 8.2 Hz, 3 H, 5-H, 11-H, 17-H), 6.52 (d, ^3J = 8.3 Hz, 6 H, 4-H, 6-H, 10-H, 12-H, 16-H, 18-H), 3.86 (t, ^3J = 8.0 Hz, 6 H, 20-H, 23-H, 26-H), 2.32 (s, 1 H, 30-H), 1.84 (sext, ^3J = 7.9 Hz, 6 H, 21-H, 24-H, 27-H), 1.05 (t, ^3J = 7.4 Hz, 9 H, 22-H, 25-H, 28-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 140.35 (C-3, C-7, C-9, C-13, C-15, C-19), 128.47 (C-5, C-11, C-17), 109.45 (C-2, C-8, C-14), 104.94 (C-4, C-6, C-10, C-12, C-16, C-18), 87.55 (C-29), 71.82 (C-30), 48.18 (C-20, C-23, C-26), 27.31 (C-1), 19.01 (C-21, C-24, C-27), 11.15 (C-22, C-25, C-28) ppm. MS (EI, 70 eV): *m*/*z* (%) = 433 (33), 408 (100), 390 (17), 365 (13), 293 (20), 280 (19). IR (ATR): $\tilde{\nu}$ = 3292 (m), 3098 (w), 3028 (w), 2963 (m), 2911 (m), 2874 (m), 1609 (s), 1576 (s), 1478 (s), 1454 (s), 1388 (s), 1362 (s), 1270 (s), 1226 (s), 1164 (m), 1145 (s), 1100 (m), 975 (m), 919 (m), 888 (m), 764 (s), 709 (s), 656 (s), 637 (m) cm^{-1}. UV (toluene): λ_{max}

(lg ε) = 330 (4.03), 296 (4.56) nm. $C_{30}H_{31}N_3$ (433.25): calcd. C 83.10, H 7.21, N 9.69; found C 82.68, H 7.39, N 9.60.

12*c*-Ethynyl-4,8,12-tri-*n*-octyl-4,8,12-triazatriangulene (2b): Under nitrogen atmosphere, sodium (600 mg, 26.1 mmol) was added to anisole (150 mL) and heated to 110 °C. Acetylene was bubbled through the mixture for about 3 h until a white suspension occurred. 4,8,12-Tri-*n*-octyl-4,8,12-triazatriangulenium tetrafluoroborate (**1b**) (900 mg, 1.28 mmol) was added and acetylene was bubbled through the mixture for 1.5 h at 110 °C. The mixture was carefully quenched with water. The layers were separated and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried with $MgSO_4$. After filtration the solvent was removed in vacuo. The obtained residue was dissolved in dichloromethane and filtered through a short column of basic aluminium oxide. The solvent was evaporated and the resulting residue recrystallized from diethyl ether to yield **2b** (370 mg, 45%) as a light pink solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.19 (t, ^3J = 8.2 Hz, 3 H, 5-H, 11-H, 17-H), 6.53 (d, ^3J = 8.3 Hz, 6 H, 4-H, 6-H, 10-H, 12-H, 16-H, 18-H), 3.90 (t, ^3J = 7.9 Hz, 6 H, 20-H, 28-H, 36-H), 2.31 (s, 1 H, 45-H), 1.81 (quint, ^3J = 7.4 Hz, 6 H, 21-H, 29-H, 37-H), 1.46 (quint, ^3J = 7.3 Hz, 6 H, 22-H, 30-H, 38-H), 1.38 (quint, ^3J = 7.5 Hz, 6 H, 23-H, 31-H, 39-H), 1.35–1.25 (m, 18 H, 24-H, 25-H, 26-H, 32-H, 33-H, 34-H, 40-H, 41-H, 42-H), 0.89 (t, ^3J = 6.8 Hz, 9 H, 27-H, 35-H, 43-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 140.26 (C-3, C-7, C-9, C-13, C-15, C-19), 128.48 (C-5, C-11, C-17), 109.24 (C-2, C-8, C-14), 104.84 (C-4, C-6, C-10, C-12, C-16, C-18), 87.50 (C-44), 71.83 (C-45), 46.57 (C-20, C-28, C-36), 31.85 (C-25, C-33, C-41), 29.39 (C-23, C-31, C-39), 29.37 (C-24, C-32, C-40), 27.26 (C-1), 27.02 (C-22, C-30, C-38), 25.60 (C-21, C-29, C-37), 22.68 (C-26, C-34, C-42), 14.13 (C-27, C-35, C-43) ppm. MS (EI, 70 eV): *m*/*z* (%) = 643 (100), 618 (91), 530 (24), 505 (25), 393 (11), 321 (20), 294 (22), 280 (15), 97 (15). IR (ATR): $\tilde{\nu}$ = 3263 (m), 3096 (w), 3028 (w), 2950 (m), 2921 (s), 2851 (m), 1614 (s), 1578 (vs), 1482 (s), 1457 (vs), 1397 (vs), 1372 (m), 1272 (m), 1246 (s), 1169 (s), 1148 (m), 974 (m), 910 (m), 766 (s), 748 (m), 715 (vs), 666 (m), 649 (m) cm^{-1}. UV (toluene): λ_{max} (lg ε) = 332 (4.06), 296 (4.56) nm. $C_{45}H_{61}N_3$ (643.49): calcd. C 83.93, H 9.55, N 6.53; found C 84.34, H 9.82, N 6.42.

12*c*-Phenyl-4,8,12-tri-*n*-propyl-4,8,12-triazatriangulene (3a): Under nitrogen atmosphere, *n*-Butyllithium (1.47 mmol, 0.59 mL of a 2.5 M solution in hexane) was added to a solution of bromobenzene (231 mg, 1.47 mmol) in 30 mL THF at –78 °C and the mixture was stirred for 1 h. 4,8,12-Tri-*n*-propyl-4,8,12-triazatriangulenium tetrafluoroborate (**1a**) (300 mg, 0.61 mmol) was added and the mixture was sonicated for 1.5 h at 0 °C using a Branson Sonifier W-450. The mixture was quenched with water, the layers were separated and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried with $MgSO_4$ and the solvents were removed in vacuo. The obtained residue was dissolved in dichloromethane and filtered through a short column of basic aluminium oxide. The solvent was evaporated and the resulting residue recrystallized from diethyl ether to yield **3a** (140 mg, 47%) as colorless crystals. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.16 (t, ^3J = 8.2 Hz, 3 H, 5-H, 11-H, 17-H), 7.00–6.91 (m, 3 H, 31-H, 32-H, 33-H), 6.86 (dd, ^3J = 8.4, ^4J = 1.4 Hz, 2 H, 30-H, 34-H), 6.52 (d, ^3J = 8.2 Hz, 6 H, 4-H, 6-H, 10-H, 12-H, 16-H, 18-H), 3.78 (t, ^3J = 8.1 Hz, 6 H, 20-H, 23-H, 26-H), 1.81 (sext, ^3J = 7.7 Hz, 6 H, 21-H, 24-H, 27-H), 0.96 (t, ^3J = 7.4 Hz, 9 H, 22-H, 25-H, 28-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 148.99 (C-29), 140.86 (C-3, C-7, C-9, C-13, C-15, C-19), 127.98 (C-31, C-33), 127.79 (C-5, C-11, C-17), 125.91 (C-32), 125.50 (C-30, C-34), 112.95 (C-2, C-8, C-14), 104.67 (C-4, C-6, C-10, C-12, C-16, C-18), 48.28 (C-20, C-23, C-26), 36.81 (C-1), 19.04 (C-21, C-24, C-27), 11.10 (C-22, C-25, C-28) ppm. MS (EI, 70 eV): *m*/*z* (%) = 485 (2), 408 (100), 365 (5), 293 (7), 280 (7), 204 (8). IR (ATR): $\tilde{\nu}$ = 3098 (w), 3054 (w), 3014 (w), 2960 (m), 2870 (m), 1614 (s), 1579 (s), 1482 (s), 1455 (s), 1395 (s), 1270 (m), 1251 (m), 1230 (s), 1167 (m), 1143 (s), 897 (m), 760 (s), 715 (s), 692 (s), 656 (m), 638 (m) cm^{-1}. UV (toluene): λ_{max} (lg ε) = 327 (3.98), 298 (4.39) nm. $C_{34}H_{35}N_3$ (485.28): calcd. C 84.08, H 7.26, N 8.65; found C 84.19, H 7.21, N 8.72.

12*c*-Phenyl-4,8,12-tri-*n*-octyl-4,8,12-triazatriangulene (3b): Under nitrogen atmosphere, *n*-Butyllithium (1.72 mmol, 0.69 mL of a 2.5 M solution in hexane) was added to a solution of bromobenzene (270 mg, 1.72 mmol) in 30 mL THF at –78 °C and the mixture was stirred for 1 h. 4,8,12-Tri-*n*-octyl-4,8,12-triazatriangulenium tetrafluoroborate (**1b**) (600 mg, 0.86 mmol) was added and the mixture was sonicated for 4 h at 0 °C using a Branson Sonifier W-450. The mixture was quenched with water, the layers were separated and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried with $MgSO_4$ and the solvents were removed in vacuo. The obtained residue was dissolved in dichloromethane and filtered through a short column of basic aluminium oxide. The solvent was evaporated and the resulting residue recrystallized from diethyl ether to yield **3b** (170 mg, 28%) as a colorless solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.16 (t, ^3J = 8.2 Hz, 3 H, 5-H, 11-H, 17-H), 6.99–6.89 (m, 3 H, 46-H, 47-H, 48-H), 6.87–6.83 (m, 2 H, 45-H, 49-H), 6.52 (d, ^3J = 8.3 Hz, 6 H, 4-H, 6-H, 10-H, 12-H, 16-H, 18-H), 3.82 (t, ^3J = 7.9 Hz, 6 H, 20-H, 28-H, 36-H), 1.78 (quint, ^3J = 7.3 Hz, 6 H, 21-H, 29-H, 37-H), 1.39–1.24 (m, 30 H, 22-H, 23-H, 24-H, 25-H, 26-H, 30-H, 31-H, 32-H, 33-H, 34-H, 38-H, 39-H, 40-H, 41-H, 42-H), 0.89 (t, ^3J = 6.9 Hz, 9 H, 27-H, 35-H, 43-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 149.01 (C-44), 140.81 (C-3, C-7, C-9, C-13, C-15, C-19), 127.97 (C-46, C-48), 127.76 (C-5, C-11, C-17), 125.93 (C-47), 125.46 (C-45, C-49), 112.91 (C-2, C-8, C-14), 104.60 (C-4, C-6, C-10, C-12, C-16, C-18), 46.59 (C-20, C-28, C-36), 36.78 (C-1), 31.88 (C-25, C-33, C-41), 29.39 (C-23, C-31, C-39), 29.36 (C-24, C-32, C-40), 27.07 (C-22, C-30, C-38), 25.73 (C-21, C-29, C-37), 22.70 (C-26, C-34, C-42), 14.15 (C-27, C-35, C-43) ppm. MS (EI, 70 eV): *m*/*z* (%) = 695 (1), 618 (100), 505 (5), 393 (1), 348 (3), 309 (10), 280 (2). IR (ATR): $\tilde{\nu}$ = 3053 (w), 3024 (w), 2951 (m), 2921 (s), 2869 (m), 2851 (m), 1613 (s), 1580 (vs), 1483 (s), 1456 (vs), 1397 (vs), 1374 (s), 1268 (s), 1247 (s), 1166 (s), 1147 (m), 896 (m), 762 (vs), 716 (vs), 694 (s), 657 (m), 640 (m) cm^{-1}. UV (toluene): λ_{max} (lg ε) = 328 (4.04), 294 (4.62) nm. $C_{49}H_{65}N_3$ (695.52): calcd. C 84.55, H 9.41, N 6.04; found C 84.68, H 9.69, N 6.09.

12*c*-Phenylethynyl-4,8,12-tri-*n*-propyl-4,8,12-triazatriangulene (4a): Under nitrogen atmosphere, *n*-butyllithium (1.22 mmol, 0.48 mL of a 2.5 M solution in hexane) was added to a solution of phenylacetylene (124 mg, 1.22 mmol) in 50 mL THF and the mixture was stirred for 3 h at 0 °C. At room temperature, 4,8,12-tri-*n*-propyl-4,8,12-triazatriangulenium tetra-fluoroborate (**1a**) (250 mg, 0.51 mmol) was suspended in the mixture and stirred for 3 d. The mixture was quenched with water, the layers were separated and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried with $MgSO_4$ and the solvents were removed in vacuo. Recrystallization of the resulting residue from diethyl ether yielded **4a** (168 mg, 65%) as light pink crystals. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.17 (t, ^3J = 8.2 Hz, 3 H, 5-H, 11-H, 17-H), 7.08–7.10 (m, 5 H, 32-H, 33-H, 34-H, 35-H, 36-H), 6.53 (d, ^3J = 8.3 Hz, 6 H, 4-H, 6-H, 10-H, 12-H, 16-H, 18-H), 3.88 (t, ^3J = 7.8 Hz, 6 H, 20-H, 23-H, 26-H), 1.86 (sext, ^3J = 7.7 Hz, 6 H, 21-H, 24-H, 27-H), 1.04 (t, ^3J = 7.4 Hz, 9 H, 22-H, 25-H, 28-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 140.58 (C-3, C-7, C-9, C-13, C-15, C-19), 131.54 (C-32, C-36), 128.12 (C-5, C-11, C-17), 127.69 (C-33, C-35), 127.22 (C-34), 124.08 (C-31), 110.44

(C-2, C-8, C-14), 104.99 (C-4, C-6, C-10, C-12, C-16, C-18), 93.53 (C-29), 83.56 (C-30), 48.09 (C-20, C-23, C-26), 27.99 (C-1), 19.24 (C-21, C-24, C-27), 11.19 (C-22, C-25, C-28) ppm. MS (EI, 70 eV): *m*/*z* (%) = 509 (66), 466 (29), 408 (100), 365 (32), 293 (15), 280 (13), 102 (57). IR (ATR): $\tilde{\nu}$ = 3028 (w), 2953 (m), 2868 (m), 2186 (w), 1900 (w), 1612 (s), 1576 (s), 1482 (s), 1453 (s), 1394 (s), 1229 (s), 1143 (s), 1115 (m), 917 (m), 891 (m), 751 (s), 687 (s), 657 (m) cm^{-1}. UV (toluene): λ_{max} (lg ε) = 335 (4.05) nm. $C_{36}H_{35}N_3$ (509.28): calcd. C 84.83, H 6.92, N 8.24; found C 84.54, H 7.12, N 8.19.

12*c*-Phenylethynyl-4,8,12-tri-*n*-octyl-4,8,12-triazatriangulene (4b): Under nitrogen atmosphere, *n*-Butyllithium (1.25 mmol, 0.50 mL of a 2.5 M solution in hexane) was added to a solution of phenylacetylene (132 mg, 1.29 mmol) in 10 mL THF at 0 °C. After 30 min 4,8,12-tri-*n*-octyl-4,8,12-triazatriangulenium tetrafluoroborate **1b** (300 mg, 0.43 mmol) was added and the mixture was sonicated for 3 h at 0 °C using a Branson Sonifier W-450. The mixture was quenched with water, the layers were separated and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried with $MgSO_4$ and the solvents were removed in vacuo. The obtained residue was dissolved in dichloromethane and filtered through a short column of basic aluminium oxide. The solvent was evaporated and the resulting residue recrystallized from diethyl ether to yield **4b** (241 mg, 79%) as a light pink solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.18 (t, ^3J = 8.2 Hz, 3 H, 5-H, 11-H, 17-H), 7.12–7.07 (m, 5 H, 47-H, 48-H, 49-H, 50-H, 51-H), 6.53 (d, ^3J = 8.3 Hz, 6 H, 4-H, 6-H, 10-H, 12-H, 16-H, 18-H), 3.91 (t, ^3J = 7.8 Hz, 6 H, 20-H, 28-H, 36-H), 1.82 (quint, ^3J = 7.3 Hz, 6 H, 21-H, 29-H, 37-H), 1.45 (quint, ^3J = 7.2 Hz, 6 H, 22-H, 30-H, 38-H), 1.36 (quint, ^3J = 7.1 Hz, 6 H, 23-H, 31-H, 39-H), 1.33–1.22 (m, 18 H, 24-H, 25-H, 26-H, 32-H, 33-H, 34-H, 40-H, 41-H, 42-H), 0.88 (t, ^3J = 6.8 Hz, 9 H, 27-H, 35-H, 43-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 140.48 (C-19), C-3, C-7, C-9, C-13, C-15, 131.60 (C-47, C-51), 128.13 (C-5, C-11, C-17), 127.64 (C-48, C-50), 127.23 (C-49), 124.01 (C-46), 110.21 (C-2, C-8, C-14), 104.87 (C-4, C-6, C-10, C-12, C-16, C-18), 93.42 (C-44), 83.60 (C-45), 46.53 (C-20, C-28, C-36), 31.87 (C-25, C-33, C-41), 29.42 (C-23, C-31, C-39), 29.34 (C-24, C-32, C-40), 27.91 (C-1), 27.03 (C-22, C-30, C-38), 25.86 (C-21, C-29, C-37), 22.66 (C-26, C-34, C-42), 14.13 (C-27, C-35, C-43) ppm. MS (EI, 70 eV): *m*/*z* (%) = 719 (58), 618 (100), 606 (13), 505 (78), 359 (14), 309 (12), 293 (10), 280 (9), 202 (12), 102 (77). IR (ATR): $\tilde{\nu}$ = 3078 (w), 3027 (w), 2953 (m), 2921 (s), 2851 (m), 1615 (s), 1579 (s), 1484 (s), 1457 (s), 1395 (s), 1373 (m), 1266 (m), 1246 (s), 1166 (s), 1148 (m), 912 (m), 753 (vs), 722 (m), 701 (s), 690 (s), 658 (m) cm^{-1}. UV (toluene): λ_{max} (lg ε) = 335 (4.07) nm. $C_{51}H_{65}N_3$ (719.52): calcd. C 85.07, H 9.10, N 5.84; found C 85.23, H 9.41, N 5.93.

12*c*-(4-Cyanophenyl)ethynyl-4,8,12-tri-*n*-octyl-4,8,12-triazatriangulene (5b): Following the general method 2, KOH (300 mg, 5.36 mmol) was added to a solution of 4-[(trimethylsilyl)ethynyl]-benzonitrile[26] (86 mg, 0.43 mmol) in 40 mL THF. After 20 min of sonication, **1b** (300 mg, 0.43 mmol) was added and the mixture was sonicated for 5 h. After recrystallization from diethyl ether, **5b** (129 mg, 40%) was obtained as a light pink solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.37 (d, ^3J = 8.3 Hz, 2 H, 48-H, 50-H), 7.20 (t, ^3J = 8.2 Hz, 3 H, 5-H, 11-H, 17-H), 7.16 (d, ^3J = 8.3 Hz, 2 H, 47-H, 51-H), 6.54 (d, ^3J = 8.3 Hz, 6 H, 4-H, 6-H, 10-H, 12-H, 16-H, 18-H), 3.91 (t, ^3J = 7.9 Hz, 6 H, 20-H, 28-H, 36-H), 1.81 (quint, ^3J = 7.5 Hz, 6 H, 21-H, 29-H, 37-H), 1.44 (quint, ^3J = 7.7 Hz, 6 H, 22-H, 30-H, 38-H), 1.36 (quint, ^3J = 7.3 Hz, 6 H, 23-H, 31-H, 39-H), 1.32–1.20 (m, 18 H, 24-H, 25-H, 26-H, 32-H, 33-H, 34-H, 40-H, 41-H, 42-H), 0.88 (t, ^3J = 6.9 Hz, 9 H, 27-H, 35-H, 43-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 140.47 (C-3, C-7, C-9, C-13, C-15, C-19), 132.13 (C-47, C-51), 131.38 (C-48, C-50), 128.97 (C-46), 128.44 (C-5, C-11, C-17), 118.67 (C-52), 110.46 (C-49), 109.43 (C-2, C-8, C-14), 104.97 (C-4, C-6, C-10, C-12, C-16, C-18), 98.20 (C-44), 82.37 (C-45), 46.47 (C-20, C-28, C-36), 31.83 (C-25, C-33, C-41), 29.38 (C-23, C-31, C-39), 29.32 (C-24, C-32, C-40), 28.36 (C-1), 26.98 (C-22, C-30, C-38), 25.77 (C-21, C-29, C-37), 22.65 (C-26, C-34, C-42), 14.11 (C-27, C-35, C-43) ppm. MS (MALDI-TOF, Cl-CCA): *m*/*z* = 744 $[M]^+$. IR (ATR): $\tilde{\nu}$ = 3095 (w), 3025 (w), 2952 (m), 2922 (s), 2851 (m), 2226 (m), 1615 (s), 1579 (vs), 1483 (s), 1456 (vs), 1396 (vs), 1374 (s), 1267 (s), 1246 (s), 1166 (s), 1147 (m), 983 (m), 840 (m), 767 (s), 721 (s), 657 (m), 554 (m) cm^{-1}. $C_{52}H_{64}N_4$ (744.51): calcd. C 83.82, H 8.66, N 7.52; found C 83.54, H 8.84, N 7.42.

(*E*)-12*c*-[4-(Phenyldiazenyl)phenyl]ethynyl-4,8,12-tri-*n*-propyl-4,8,12-triazatriangulene (6a): Following the general method 2, KOH (300 mg, 5.36 mmol) was added to a solution of **20** (169 mg, 0.61 mmol) in 40 mL THF. After 20 min of sonication, **1a** (300 mg, 0.61 mmol) was added and the mixture was sonicated for 5 h. After recrystallization from diethyl ether, **6a** (246 mg, 66%) was obtained as an orange solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.84 (d, ^3J = 8.2 Hz, 2 H, 38-H, 42-H), 7.68 (d, ^3J = 8.7 Hz, 2 H, 33-H, 35-H), 7.49–7.41 (m, 3 H, 39-H, 40-H, 41-H), 7.23 (d, ^3J = 8.8 Hz, 2 H, 32-H, 36-H), 7.19 (t, ^3J = 8.2 Hz, 3 H, 5-H, 11-H, 17-H), 6.55 (d, ^3J = 8.3 Hz, 6 H, 4-H, 6-H, 10-H, 12-H, 16-H, 18-H), 3.90 (t, ^3J = 7.8 Hz, 6 H, 20-H, 23-H, 26-H), 1.87 (sext, ^3J = 7.7 Hz, 6 H, 21-H, 24-H, 27-H), 1.05 (t, ^3J = 7.4 Hz, 9 H, 22-H, 25-H, 28-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 152.68 (C-37), 151.18 (C-34), 140.60 (C-3, C-7, C-9, C-13, C-15, C-19), 132.32 (C-32, C-36), 130.98 (C-40), 129.05 (C-39, C-41), 128.27 (C-5, C-11, C-17), 126.94 (C-31), 122.82 (C-38, C-42), 122.37 (C-33, C-35), 110.17 (C-2, C-8, C-14), 105.07 (C-4, C-6, C-10, C-12, C-16, C-18), 96.28 (C-29), 83.50 (C-30), 48.09 (C-20, C-23, C-26), 28.28 (C-1), 19.24 (C-21, C-24, C-27), 11.18 (C-22, C-25, C-28) ppm. MS (EI, 70 eV): *m*/*z* (%) = 613 (10), 408 (63), 365 (100), 323 (19), 293 (23), 280 (20), 206 (66), 129 (24), 105 (20), 101 (78). IR (ATR): $\tilde{\nu}$ = 3014 (w), 2956 (m), 2922 (m), 2867 (m), 1608 (s), 1577 (s), 1480 (s), 1453 (s), 1377 (s), 1227 (s), 1167 (s), 1132 (s), 987 (m), 918 (m), 841 (m), 748 (s), 698 (s), 682 (s), 550 (m) cm^{-1}. UV (toluene): λ_{max} (lg ε) = 356 (4.54), 336 (4.59) nm. $C_{42}H_{39}N_5$ (613.32): calcd. C 82.19, H 6.40, N 11.41; found C 82.11, H 6.75, N 11.17.

(*E*)-12*c*-[4-(Phenyldiazenyl)phenyl]ethynyl-4,8,12-tri-*n*-octyl-4,8,12-triazatriangulene (6b): Following the general method 2, KOH (300 mg, 5.36 mmol) was added to a solution of **20** (167 mg, 0.60 mmol) in 30 mL THF. After 20 min of sonication, **1b** (423 mg, 0.60 mmol) was added and the mixture was sonicated for 4 h. After recrystallization from diethyl ether, **6b** (344 mg, 70%) was obtained as an orange solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.84 (d, ^3J = 8.4 Hz, 2 H, 53-H, 57-H), 7.67 (d, ^3J = 8.4 Hz, 2 H, 48-H, 50-H), 7.49–7.40 (m, 3 H, 54-H, 55-H, 56-H), 7.23 (d, ^3J = 8.4 Hz, 2 H, 47-H, 51-H), 7.20 (t, ^3J = 8.3 Hz, 3 H, 5-H, 11-H, 17-H), 6.55 (d, ^3J = 8.3 Hz, 6 H, 4-H, 6-H, 10-H, 12-H, 16-H, 18-H), 3.93 (t, ^3J = 7.7 Hz, 6 H, 20-H, 28-H, 36-H), 1.83 (quint, ^3J = 7.2 Hz, 6 H, 21-H, 29-H, 37-H), 1.46 (quint, ^3J = 7.4 Hz, 6 H, 22-H, 30-H, 38-H), 1.37 (quint, ^3J = 7.0 Hz, 6 H, 23-H, 31-H, 39-H), 1.33–1.22 (m, 18 H, 24-H, 25-H, 26-H, 32-H, 33-H, 34-H, 40-H, 41-H, 42-H), 0.87 (t, ^3J = 6.8 Hz, 9 H, 27-H, 35-H, 43-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 152.66 (C-52), 151.14 (C-49), 140.53 (C-3, C-7, C-9, C-13, C-15, C-19), 132.41 (C-47, C-51), 130.99 (C-55), 129.06 (C-54, C-56), 128.29 (C-5, C-11, C-17), 126.95 (C-46), 122.82 (C-53, C-57), 122.36 (C-48, C-50), 109.97 (C-2, C-8, C-14), 104.97 (C-4, C-6, C-10, C-12, C-16, C-18), 96.24 (C-44), 83.54 (C-45), 46.53 (C-20, C-28, C-36), 31.88 (C-25, C-33, C-41), 29.44 (C-23, C-31, C-39), 29.36 (C-24, C-32, C-40), 28.24 (C-1), 27.04 (C-22, C-30, C-38), 25.87 (C-21, C-29, C-37), 22.68 (C-

26, C-34, C-42), 14.15 (C-27, C-35, C-43) ppm. MS (EI, 70 eV): *m*/*z* (%) = 823 (4), 618 (10), 505 (9), 206 (100), 176 (22), 151 (18), 129 (67), 105 (25), 101 (97). IR (ATR): $\tilde{\nu}$ = 3102 (w), 3028 (w), 2951 (m), 2924 (s), 2852 (m), 1613 (s), 1577 (s), 1480 (s), 1455 (s), 1388 (s), 1368 (s), 1242 (s), 1224 (s), 1168 (s), 1151 (s), 847 (s), 767 (m), 752 (s), 724 (m), 701 (m), 685 (s), 629 (m), 555 (m) cm^{-1}. UV (toluene): λ_{max} (lg ε) = 352 (4.51), 336 (4.55), 297 (4.68) nm. $C_{57}H_{69}N_5$ (823.56): calcd. C 83.06, H 8.44, N 8.50; found C 83.37, H 8.78, N 8.59.

(*E*)-12*c*-[4-(4-Iodophenyldiazenyl)phenyl]ethynyl-4,8,12-tri-*n*-propyl-4,8,12-triazatriangulene (7a): Following the general method 2, KOH (300 mg, 5.36 mmol) was added to a solution of **21** (246 mg, 0.61 mmol) in 40 mL THF. After 20 min of sonication, **1a** (300 mg, 0.61 mmol) was added and the mixture was sonicated for 5 h. After recrystallization from diethyl ether, **7a** (232 mg, 51%) was obtained as an orange solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.82 (d, ^3J = 8.8 Hz, 2 H, 39-H, 41-H), 7.67 (d, ^3J = 8.8 Hz, 2 H, 33-H, 35-H), 7.57 (d, ^3J = 8.8 Hz, 2 H, 38-H, 42-H), 7.23 (d, ^3J = 8.8 Hz, 2 H, 32-H, 36-H), 7.19 (t, ^3J = 8.2 Hz, 3 H, 5-H, 11-H, 17-H), 6.55 (d, ^3J = 8.3 Hz, 6 H, 4-H, 6-H, 10-H, 12-H, 16-H, 18-H), 3.90 (t, ^3J = 7.8 Hz, 6 H, 20-H, 23-H, 26-H), 1.87 (sext, ^3J = 7.7 Hz, 6 H, 21-H, 24-H, 27-H), 1.05 (t, ^3J = 7.4 Hz, 9 H, 22-H, 25-H, 28-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 151.99 (C-37), 151.01 (C-34), 140.62 (C-3, C-7, C-9, C-13, C-15, C-19), 138.35 (C-39, C-41), 132.40 (C-32, C-36), 128.30 (C-5, C-11, C-17), 127.38 (C-31), 124.43 (C-38, C-42), 122.50 (C-33, C-35), 110.14 (C-2, C-8, C-14), 105.09 (C-4, C-6, C-10, C-12, C-16, C-18), 101.10 (C-40), 96.63 (C-29), 83.49 (C-30), 48.10 (C-20, C-23, C-26), 28.90 (C-1), 19.25 (C-21, C-24, C-27), 11.19 (C-22, C-25, C-28) ppm. MS (EI, 70 eV): *m*/*z* (%) = 739 (8), 696 (5), 408 (46), 365 (69), 332 (82), 323 (14), 293 (17), 280 (15), 231 (23), 203 (48), 129 (44), 101 (100). IR (ATR): $\tilde{\nu}$ = 3018 (w), 2955 (m), 2864 (m), 1607 (s), 1577 (s), 1479 (s), 1451 (s), 1376 (s), 1227 (s), 1166 (s), 1131 (s), 1003 (m), 918 (m), 840 (s), 750 (s), 700 (s), 654 (m), 547 (m) cm^{-1}. UV (toluene): λ_{max} (lg ε) = 364 (4.50), 339 (4.45) nm. $C_{42}H_{38}IN_5$ (739.22): calcd. C 68.20, H 5.18, N 9.47; found C 68.10, H 5.10, N 9.37.

(*E*)-12*c*-[4-(4-Iodophenyldiazenyl)phenyl]ethynyl-4,8,12-tri-*n*-octyl-4,8,12-triazatriangulene (7b): Following the general method 2, KOH (300 mg, 5.36 mmol) was added to a solution of **21** (242 mg, 0.60 mmol) in 30 mL THF. After 20 min of sonication, **1b** (423 mg, 0.60 mmol) was added and the mixture was sonicated for 4 h. After recrystallization from diethyl ether, **7b** (377 mg, 66%) was obtained as an orange solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.81 (d, ^3J = 8.7 Hz, 2 H, 54-H, 56-H), 7.66 (d, ^3J = 8.6 Hz, 2 H, 48-H, 50-H), 7.57 (d, ^3J = 8.7 Hz, 2 H, 53-H, 57-H), 7.22 (d, ^3J = 8.6 Hz, 2 H, 47-H, 51-H), 7.20 (t, ^3J = 8.2 Hz, 3 H, 5-H, 11-H, 17-H), 6.55 (d, ^3J = 8.3 Hz, 6 H, 4-H, 6-H, 10-H, 12-H, 16-H, 18-H), 3.93 (t, ^3J = 7.9 Hz, 6 H, 20-H, 28-H, 36-H), 1.83 (quint, ^3J = 7.5 Hz, 6 H, 21-H, 29-H, 37-H), 1.46 (quint, ^3J = 7.5 Hz, 6 H, 22-H, 30-H, 38-H), 1.36 (quint, ^3J = 7.1 Hz, 6 H, 23-H, 31-H, 39-H), 1.31–1.21 (m, 18 H, 24-H, 25-H, 26-H, 32-H, 33-H, 34-H, 40-H, 41-H, 42-H), 0.87 (t, ^3J = 6.9 Hz, 9 H, 27-H, 35-H, 43-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 151.94 (C-52), 150.93 (C-49), 140.51 (C-3, C-7, C-9, C-13, C-15, C-19), 138.32 (C-54, C-56), 132.45 (C-47, C-51), 128.30 (C-5, C-11, C-17), 127.34 (C-46), 124.41 (C-53, C-57), 122.46 (C-48, C-50), 109.90 (C-2, C-8, C-14), 104.96 (C-4, C-6, C-10, C-12, C-16, C-18), 97.65 (C-55), 96.55 (C-44), 83.51 (C-45), 46.52 (C-20, C-28, C-36), 31.87 (C-25, C-33, C-41), 29.43 (C-23, C-31, C-39), 29.35 (C-24, C-32, C-40), 28.26 (C-1), 27.03 (C-22, C-30, C-38), 25.85 (C-21, C-29, C-37), 22.67 (C-26, C-34, C-42), 14.13 (C-27, C-35, C-43) ppm. MS (MALDI-TOF, Cl-CCA): *m*/*z* = 949 [M]$^+$. IR (ATR): $\tilde{\nu}$ = 3098 (w), 3025 (w), 2951 (m), 2922 (s), 2852 (m), 1613 (s), 1579 (s), 1482 (s), 1456 (s), 1392 (s), 1372 (s), 1266 (m), 1243 (s), 1166 (s), 1005 (m), 844 (m), 792 (m), 751 (s), 705 (s), 551 (m) cm^{-1}. UV (toluene): λ_{max} (lg ε) = 365 (4.60), 337 (4.56), 296 (4.74) nm. $C_{57}H_{68}IN_5$ (949.45): calcd. C 72.06, H 7.21, N 7.37; found C 71.61, H 7.58, N 7.64.

(*E*)-12*c*-[4-(4-Cyanophenyldiazenyl)phenyl]ethynyl-4,8,12-tri-*n*-propyl-4,8,12-triazatriangulene (8a): Following the general method 2, KOH (300 mg, 5.36 mmol) was added to a solution of **22** (185 mg, 0.61 mmol) in 30 mL THF. After 20 min of sonication, **1a** (300 mg, 0.61 mmol) was added and the mixture was sonicated for 3 h. After two recrystallizations from ethanol, **8a** (146 mg, 38%) was obtained as an red solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.90 (d, ^3J = 8.7 Hz, 2 H, 39-H, 41-H), 7.75 (d, ^3J = 8.7 Hz, 2 H, 38-H, 42-H), 7.70 (d, ^3J = 8.7 Hz, 2 H, 33-H, 35-H), 7.25 (d, ^3J = 8.7 Hz, 2 H, 32-H, 36-H), 7.20 (t, ^3J = 8.3 Hz, 3 H, 5-H, 11-H, 17-H), 6.55 (d, ^3J = 8.3 Hz, 6 H, 4-H, 6-H, 10-H, 12-H, 16-H, 18-H), 3.90 (t, ^3J = 7.8 Hz, 6 H, 20-H, 23-H, 26-H), 1.87 (sext, ^3J = 7.7 Hz, 6 H, 21-H, 24-H, 27-H), 1.05 (t, ^3J = 7.4 Hz, 9 H, 22-H, 25-H, 28-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 154.47 (C-37), 150.82 (C-34), 140.55 (C-3, C-7, C-9, C-13, C-15, C-19), 133.16 (C-39, C-41), 132.47 (C-32, C-36), 128.34 (C-5, C-11, C-17), 126.33 (C-31), 123.29 (C-38, C-42), 122.84 (C-33, C-35), 118.40 (C-43), 113.85 (C-40), 109.88 (C-2, C-8, C-14), 105.05 (C-4, C-6, C-10, C-12, C-16, C-18), 97.26 (C-29), 83.39 (C-30), 48.06 (C-20, C-23, C-26), 28.40 (C-1), 19.14 (C-21, C-24, C-27), 11.19 (C-22, C-25, C-28) ppm. MS (EI, 70 eV): *m*/*z* (%) = 638 (3), 596 (2), 408 (21), 365 (22), 231 (49),129 (24), 118 (41), 101 (100). IR (ATR): $\tilde{\nu}$ = 3101 (w), 3024 (w), 2960 (m), 2930 (m), 2873 (m), 2229 (m), 1613 (s), 1578 (s), 1482 (s), 1455 (s), 1393 (s), 1271 (m), 1230 (s), 1173 (m), 1142 (s), 1100 (m), 918 (m), 858 (s), 756 (s), 726 (m), 687 (m), 566 (s) cm^{-1}. UV (toluene): λ_{max} (lg ε) = 368 (4.21), 336 (4.19), 296 (4.39) nm. $C_{43}H_{38}N_6$ (638.32): calcd. C 80.85, H 6.00, N 13.16; found C 80.39, H 6.36, N 13.15.

(*E*)-12*c*-[4-(4-Cyanophenyldiazenyl)phenyl]ethynyl-4,8,12-tri-*n*-octyl-4,8,12-triazatriangulene (8b): Following the general method 2, KOH (300 mg, 5.36 mmol) was added to a solution of **22** (130 mg, 0.43 mmol) in 30 mL THF. After 20 min of sonication, **1b** (300 mg, 0.43 mmol) was added and the mixture was sonicated for 4 h. After recrystallization from ethanol/dichloromethane (1:1), **8b** (151 mg, 41%) was obtained as a red solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.90 (d, ^3J = 8.7 Hz, 2 H, 53-H, 57-H), 7.76 (d, ^3J = 8.7 Hz, 2 H, 54-H, 56-H), 7.69 (d, ^3J = 8.7 Hz, 2 H, 48-H, 50-H), 7.25 (d, ^3J = 8.0 Hz, 2 H, 47-H, 51-H), 7.20 (t, ^3J = 8.2 Hz, 3 H, 5-H, 11-H, 17-H), 6.55 (d, ^3J = 8.3 Hz, 6 H, 4-H, 6-H, 10-H, 12-H, 16-H, 18-H), 3.93 (t, ^3J = 7.8 Hz, 6 H, 20-H, 28-H, 36-H), 1.83 (quint, ^3J = 7.5 Hz, 6 H, 21-H, 29-H, 37-H), 1.46 (quint, ^3J = 7.7 Hz, 6 H, 22-H, 30-H, 38-H), 1.36 (quint, ^3J = 7.4 Hz, 6 H, 23-H, 31-H, 39-H), 1.32–1.21 (m, 18 H, 24-H, 25-H, 26-H, 32-H, 33-H, 34-H, 40-H, 41-H, 42-H), 0.87 (t, ^3J = 6.9 Hz, 9 H, 27-H, 35-H, 43-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 154.50 (C-52), 150.83 (C-49), 140.52 (C-3, C-7, C-9, C-13, C-15, C-19), 133.17 (C-54, C-56), 132.53 (C-47, C-51), 128.34 (C-5, C-11, C-17), 128.30 (C-46), 123.28 (C-53, C-57), 122.81 (C-48, C-50), 118.48 (C-58), 113.86 (C-55), 109.82 (C-2, C-8, C-14), 104.98 (C-4, C-6, C-10, C-12, C-16, C-18), 97.26 (C-44), 83.41 (C-45), 46.50 (C-20, C-28, C-36), 31.86 (C-25, C-33, C-41), 29.41 (C-23, C-31, C-39), 29.33 (C-24, C-32, C-40), 28.34 (C-1), 27.02 (C-22, C-30, C-38), 25.86 (C-21, C-29, C-37), 22.65 (C-26, C-34, C-42), 14.11 (C-27, C-35, C-43) ppm. MS (MALDI-TOF, Cl-CCA): *m*/*z* = 848 [M]$^+$. IR (ATR): $\tilde{\nu}$ = 3097 (w), 3028 (w), 2953 (m), 2922 (s), 2852 (m), 2227 (m), 1614 (s), 1579 (s), 1482 (s), 1455 (s), 1393 (s), 1373 (s), 1266 (m), 1242 (s), 1167 (s), 1141 (m), 851 (s), 758 (s), 726 (s), 688 (s), 564 (s) cm^{-1}. UV (toluene): λ_{max} (lg ε) = 368 (4.56), 338 (4.52), 296

(4.71) nm. $C_{58}H_{68}N_6$ (848.55): calcd. C 82.03, H 8.07, N 9.90; found C 82.16, H 8.45, N 9.99.

(*E*)-12*c*-[4-(4-Methylphenyldiazenyl)phenyl]ethynyl-4,8,12-tri-*n*-octyl-4,8,12-triazatriangulene (9b): Following the general method 2, KOH (300 mg, 5.36 mmol) was added to a solution of **23** (126 mg, 0.43 mmol) in 30 mL THF. After 20 min of sonication, **1b** (300 mg, 0.43 mmol) was added and the mixture was sonicated for 4 h. After 2 recrystallizations from diethyl ether, **9b** (130 mg, 36%) was obtained as an orange solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.75 (d, ^3J = 8.3 Hz, 2 H, 53-H, 57-H), 7.65 (d, ^3J = 8.7 Hz, 2 H, 48-H, 50-H), 7.26 (d, ^3J = 8.3 Hz, 2 H, 54-H, 56-H), 7.22 (d, ^3J = 8.7 Hz, 2 H, 47-H, 51-H), 7.20 (t, ^3J = 8.2 Hz, 3 H, 5-H, 11-H, 17-H), 6.55 (d, ^3J = 8.3 Hz, 6 H, 4-H, 6-H, 10-H, 12-H, 16-H, 18-H), 3.93 (t, ^3J = 7.8 Hz, 6 H, 20-H, 28-H, 36-H), 2.40 (s, 3 H, 58-H), 1.83 (quint, ^3J = 7.5 Hz, 6 H, 21-H, 29-H, 37-H), 1.46 (quint, ^3J = 7.6 Hz, 6 H, 22-H, 30-H, 38-H), 1.37 (quint, ^3J = 7.4 Hz, 6 H, 23-H, 31-H, 39-H), 1.32–1.22 (m, 18 H, 24-H, 25-H, 26-H, 32-H, 33-H, 34-H, 40-H, 41-H, 42-H), 0.87 (t, ^3J = 6.9 Hz, 9 H, 27-H, 35-H, 43-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 151.20 (C-49), 150.76 (C-52), 141.57 (C-55), 140.50 (C-3, C-7, C-9, C-13, C-15, C-19), 132.41 (C-47, C-51), 129.71 (C-54, C-56), 128.25 (C-5, C-11, C-17), 126.59 (C-46), 122.80 (C-53, C-57), 122.21 (C-48, C-50), 109.96 (C-2, C-8, C-14), 104.93 (C-4, C-6, C-10, C-12, C-16, C-18), 96.00 (C-44), 83.55 (C-45), 46.51 (C-20, C-28, C-36), 31.86 (C-25, C-33, C-41), 29.41 (C-23, C-31, C-39), 29.34 (C-24, C-32, C-40), 28.19 (C-1), 27.02 (C-22, C-30, C-38), 25.84 (C-21, C-29, C-37), 22.66 (C-26, C-34, C-42), 21.49 (C-58), 14.18 (C-27, C-35, C-43) ppm. MS (MALDI-TOF, Cl-CCA): *m*/*z* = 837 $[M]^+$. IR (ATR): $\tilde{\nu}$ = 3098 (w), 3026 (w), 2952 (m), 2922 (s), 2851 (m), 1613 (s), 1579 (vs), 1480 (s), 1455 (vs), 1393 (s), 1370 (s), 1244 (s), 1168 (s), 1153 (s), 848 (m), 768 (m), 751 (m), 725 (m), 696 (m), 555 (m) cm^{-1}. UV (toluene): λ_{max} (lgε) = 355 (4.53), 337 (4.54), 296 (4.70) nm. $C_{58}H_{71}N_5$ (837.57): calcd. C 83.11, H 8.54, N 8.36; found C 82.85, H 8.78, N 8.39.

(*E*)-12*c*-{4-[4-(Trifluoromethyl)phenyldiazenyl]phenyl}ethynyl-4,8,12-tri-*n*-octyl-4,8,12-triazatriangulene (10b): Following the general method 2, KOH (300 mg, 5.36 mmol) was added to a solution of **24** (149 mg, 0.43 mmol) in 30 mL THF. After 20 min of sonication, **1b** (300 mg, 0.43 mmol) was added and the mixture was sonicated for 4 h. After recrystallization from ethanol, **10b** (200 mg, 52%) was obtained as an orange solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.92 (d, ^3J = 8.3 Hz, 2 H, 53-H, 57-H), 7.73 (d, ^3J = 8.5 Hz, 2 H, 54-H, 56-H), 7.70 (d, ^3J = 8.7 Hz, 2 H, 48-H, 50-H), 7.25 (d, ^3J = 8.0 Hz, 2 H, 47-H, 51-H), 7.20 (t, ^3J = 8.2 Hz, 3 H, 5-H, 11-H, 17-H), 6.55 (d, ^3J = 8.3 Hz, 6 H, 4-H, 6-H, 10-H, 12-H, 16-H, 18-H), 3.93 (t, ^3J = 7.8 Hz, 6 H, 20-H, 28-H, 36-H), 1.83 (quint, ^3J = 7.5 Hz, 6 H, 21-H, 29-H, 37-H), 1.46 (quint, ^3J = 7.7 Hz, 6 H, 22-H, 30-H, 38-H), 1.37 (quint, ^3J = 7.5 Hz, 6 H, 23-H, 31-H, 39-H), 1.32–1.22 (m, 18 H, 24-H, 25-H, 26-H, 32-H, 33-H, 34-H, 40-H, 41-H, 42-H), 0.87 (t, ^3J = 6.9 Hz, 9 H, 27-H, 35-H, 43-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 154.41 (C-52), 150.88 (C-49), 140.51 (C-3, C-7, C-9, C-13, C-15, C-19), 132.48 (C-47, C-51), 131.99 (C-55), 128.31 (C-5, C-11, C-17), 127.84 (C-46), 126.25 (C-54, C-56), 122.94 (C-53, C-57), 122.65 (C-48, C-50), 109.85 (C-2, C-8, C-14), 104.96 (C-4, C-6, C-10, C-12, C-16, C-18), 96.86 (C-44), 83.42 (C-45), 46.50 (C-20, C-28, C-36), 31.86 (C-25, C-33, C-41), 29.42 (C-23, C-31, C-39), 29.34 (C-24, C-32, C-40), 28.28 (C-1), 27.02 (C-22, C-30, C-38), 25.84 (C-21, C-29, C-37), 22.66 (C-26, C-34, C-42), 14.12 (C-27, C-35, C-43) ppm. MS (MALDI-TOF, Cl-CCA): *m*/*z* = 891 $[M]^+$. IR (ATR): $\tilde{\nu}$ = 3102 (w), 3028 (w), 2954 (m), 2923 (s), 2852 (m), 1614 (s), 1579 (s), 1481 (s), 1456 (s), 1393 (s), 1320 (vs), 1244 (s), 1166 (vs), 1128 (vs), 1101 (s), 1064 (s), 1012 (m), 852 (s), 763 (s), 751 (s), 703 (s), 598 (m) cm^{-1}. UV (toluene): λ_{max} (lgε) = 362 (4.44), 337 (4.47), 297 (4.63) nm. $C_{58}H_{68}F_3N_5$ (891.54): calcd. C 78.08, H 7.68, N 7.85; found C 77.90, H 7.98, N 8.02.

(*E*)-12*c*-[4-(4-Hexylphenyldiazenyl)phenyl]ethynyl-4,8,12-tri-*n*-propyl-4,8,12-triazatriangulene (11a): Following the general method 2, KOH (200 mg, 3.57 mmol) was added to a solution of **25** (90 mg, 0.25 mmol) in 30 mL THF. After 30 min of sonication, **1a** (124 mg, 0.25 mmol) was added and the mixture was sonicated for 4 h. After recrystallization from diethyl ether, **11a** (120 mg, 69%) was obtained as an orange solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.76 (d, ^3J = 8.4 Hz, 2 H, 38-H, 42-H), 7.65 (d, ^3J = 8.7 Hz, 2 H, 33-H, 35-H), 7.27 (d, ^3J = 8.5 Hz, 2 H, 39-H, 41-H), 7.22 (d, ^3J = 8.7 Hz, 2 H, 32-H, 36-H), 7.19 (t, ^3J = 8.3 Hz, 3 H, 5-H, 11-H, 17-H), 6.54 (d, ^3J = 8.3 Hz, 6 H, 4-H, 6-H, 10-H, 12-H, 16-H, 18-H), 3.90 (t, ^3J = 7.8 Hz, 6 H, 20-H, 23-H, 26-H), 2.65 (t, ^3J = 7.7 Hz, 2 H, 43-H) 1.87 (sext, ^3J = 7.7 Hz, 6 H, 21-H, 24-H, 27-H), 1.63 (quint, ^3J = 7.3 Hz, 2 H, 44-H), 1.36–1.27 (m, 6 H, 45-H, 46-H, 47-H), 1.05 (t, ^3J = 7.4 Hz, 9 H, 22-H, 25-H, 28-H), 0.87 (t, ^3J = 7.0 Hz, 3 H, 48-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 151.26 (C-34), 150.92 (C-37), 146.64 (C-40), 140.56 (C-3, C-7, C-9, C-13, C-15, C-19), 132.31 (C-32, C-36), 129.08 (C-39, C-41), 128.25 (C-5, C-11, C-17), 126.57 (C-31), 122.82 (C-38, C-42), 122.23 (C-33, C-35), 110.09 (C-2, C-8, C-14), 105.03 (C-4, C-6, C-10, C-12, C-16, C-18), 96.04 (C-29), 83.54 (C-30), 48.08 (C-20, C-23, C-26), 35.89 (C-43), 31.69 (C-46), 31.22 (C-44), 28.93 (C-45), 28.23 (C-1), 22.59 (C-47), 19.17 (C-21, C-24, C-27), 14.08 (C-48), 11.20 (C-22, C-25, C-28) ppm. MS (EI, 70 eV): *m*/*z* (%) = 697 (1), 408 (54), 365 (71), 290 (74), 161 (100), 101 (71). IR (ATR): $\tilde{\nu}$ = 3017 (w), 2950 (m), 2922 (m), 2854 (m), 2360 (s), 1608 (s), 1578 (s), 1480 (s), 1453 (s), 1389 (s), 1229 (s), 1132 (s), 844 (s), 749 (s), 695 (s), 557 (m) cm^{-1}. UV (toluene): λ_{max} (lgε) = 346 (4.61) nm. $C_{48}H_{51}N_5$ (697.41): calcd. C 82.60, H 7.37, N 10.03; found C 82.53, H 7.51, N 10.12.

(*E*)-12*c*-[4-(4-Hexylphenyldiazenyl)phenyl]ethynyl-4,8,12-tri-*n*-octyl-4,8,12-triazatriangulene (11b): Following the general method 2, KOH (300 mg, 5.36 mmol) was added to a solution of **25** (156 mg, 0.43 mmol) in 30 mL THF. After 20 min of sonication, **1b** (300 mg, 0.43 mmol) was added and the mixture was sonicated for 4 h. After recrystallization from ethanol, **11b** (150 mg, 38%) was obtained as an orange solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.76 (d, ^3J = 8.4 Hz, 2 H, 53-H, 57-H), 7.65 (d, ^3J = 8.6 Hz, 2 H, 48-H, 50-H), 7.27 (d, ^3J = 8.5 Hz, 2 H, 54-H, 56-H), 7.22 (d, ^3J = 8.6 Hz, 2 H, 47-H, 51-H), 7.20 (t, ^3J = 8.3 Hz, 3 H, 5-H, 11-H, 17-H), 6.55 (d, ^3J = 8.3 Hz, 6 H, 4-H, 6-H, 10-H, 12-H, 16-H, 18-H), 3.94 (t, ^3J = 7.8 Hz, 6 H, 20-H, 28-H, 36-H), 2.65 (t, ^3J = 7.7 Hz, 2 H, 58-H), 1.83 (quint, ^3J = 7.5 Hz, 6 H, 21-H, 29-H, 37-H), 1.63 (quint, ^3J = 7.4 Hz, 2 H, 59-H), 1.45 (quint, ^3J = 7.7 Hz, 6 H, 22-H, 30-H, 38-H), 1.40–1.33 (m, 6 H, 23-H, 31-H, 39-H), 1.33–1.22 (m, 24 H, 24-H, 25-H, 26-H, 32-H, 33-H, 34-H, 40-H, 41-H, 42-H, 60-H, 61-H, 62-H), 0.87 (t, ^3J = 6.8 Hz, 12 H, 27-H, 35-H, 43-H, 63-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 151.27 (C-49), 150.96 (C-52), 146.60 (C-55), 140.52 (C-3, C-7, C-9, C-13, C-15, C-19), 132.36 (C-47, C-51), 129.11 (C-54, C-56), 128.25 (C-5, C-11, C-17), 126.59 (C-46), 122.81 (C-53, C-57), 122.21 (C-48, C-50), 110.02 (C-2, C-8, C-14), 104.95 (C-4, C-6, C-10, C-12, C-16, C-18), 96.02 (C-44), 83.57 (C-45), 46.53 (C-20, C-28, C-36), 35.90 (C-58), 31.86 (C-25, C-33, C-41), 31.69 (C-61), 31.22 (C-59), 29.41 (C-23, C-31, C-39), 29.34 (C-24, C-32, C-40), 28.93 (C-60), 28.22 (C-1), 27.03 (C-22, C-30, C-38), 25.87 (C-21, C-29, C-37), 22.66 (C-26, C-34, C-42), 22.59 (C-62), 14.12 (C-27, C-35, C-43), 14.07 (C-63) ppm. MS (MALDI-TOF, Cl-CCA): *m*/*z* = 907 $[M]^+$. IR (ATR): $\tilde{\nu}$ = 3031 (w), 2954 (m), 2923 (s), 2852 (m), 1614 (s), 1579 (vs), 1481 (s), 1456 (vs), 1393 (s), 1371 (s), 1264 (m), 1244 (s),

1168 (s), 1153 (s), 849 (s), 753 (s), 723 (s), 697 (s), 563 (m) cm^{-1}. UV (toluene): λ_{max} (lgε) = 357 (4.62), 345 (4.62), 296 (4.72) nm. $C_{63}H_{81}N_5$ (907.65): calcd. C 83.30, H 8.99, N 7.71; found C 83.26, H 9.53, N 7.79.

(*E*)-12*c*-[4-(4-Methoxyphenyldiazenyl)phenyl]ethynyl-4,8,12-tri-*n*-octyl-4,8,12-triazatriangulene (12b): Following the general method 2, KOH (600 mg, 10.7 mmol) was added to a solution of **34** (265 mg, 0.86 mmol) in 40 mL THF. After 20 min of sonication, **1b** (600 mg, 0.86 mmol) was added and the mixture was sonicated for 4 h. After recrystallization from ethanol, **12b** (397 mg, 54%) was obtained as an orange solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.84 (d, ^3J = 9.1 Hz, 2 H, 53-H, 57-H), 7.62 (d, ^3J = 8.6 Hz, 2 H, 48-H, 50-H), 7.21 (d, ^3J = 8.7 Hz, 2 H, 47-H, 51-H), 7.19 (t, ^3J = 8.3 Hz, 3 H, 5-H, 11-H, 17-H), 6.96 (d, ^3J = 9.1 Hz, 2 H, 54-H, 56-H), 6.55 (d, ^3J = 8.3 Hz, 6 H, 4-H, 6-H, 10-H, 12-H, 16-H, 18-H), 3.93 (t, ^3J = 7.8 Hz, 6 H, 20-H, 28-H, 36-H), 3.86 (s, 3 H, 58-H), 1.83 (quint, ^3J = 7.6 Hz, 6 H, 21-H, 29-H, 37-H), 1.46 (quint, ^3J = 7.6 Hz, 6 H, 22-H, 30-H, 38-H), 1.36 (quint, ^3J = 7.5 Hz, 6 H, 23-H, 31-H, 39-H), 1.32–1.21 (m, 18 H, 24-H, 25-H, 26-H, 32-H, 33-H, 34-H, 40-H, 41-H, 42-H), 0.87 (t, ^3J = 6.7 Hz, 9 H, 27-H, 35-H, 43-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 162.08 (C-55), 151.28 (C-49), 147.06 (C-52), 140.52 (C-3, C-7, C-9, C-13, C-15, C-19), 132.35 (C-47, C-51), 128.24 (C-5, C-11, C-17), 126.23 (C-46), 124.72 (C-53, C-57), 122.05 (C-48, C-50), 114.20 (C-54, C-56), 110.05 (C-2, C-8, C-14), 104.95 (C-4, C-6, C-10, C-12, C-16, C-18), 95.84 (C-44), 83.61 (C-45), 55.57 (C-58), 46.53 (C-20, C-28, C-36), 31.86 (C-25, C-33, C-41), 29.42 (C-23, C-31, C-39), 29.34 (C-24, C-32, C-40), 28.20 (C-1), 27.03 (C-22, C-30, C-38), 25.88 (C-21, C-29, C-37), 22.66 (C-26, C-34, C-42), 14.12 (C-27, C-35, C-43) ppm. MS (MALDI-TOF, Cl-CCA): *m*/*z* = 853 $[M]^+$. IR (ATR): $\tilde{\nu}$ = 3095 (w), 3025 (w), 2954 (m), 2923 (s), 2851 (s), 1613 (s), 1579 (vs), 1481 (s), 1455 (vs), 1391 (s), 1370 (s), 1245 (vs), 1168 (s), 1149 (s), 1138 (s), 1103 (m), 1028 (m), 848 (s), 836 (m), 748 (s), 731 (m), 695 (m), 603 (m), 556 (s) cm^{-1}. UV (toluene): λ_{max} (lgε) = 368 (4.54), 336 (4.46), 296 (4.70) nm. $C_{58}H_{71}N_5O$ (853.57): calcd. C 81.55, H 8.38, N 8.20; found C 81.00, H 8.85, N 8.37.

(*E*)-12*c*-{4-[4-([D$_3$]Methoxy)phenyldiazenyl]phenyl}ethynyl-4,8,12-tri-*n*-octyl-4,8,12-triazatriangulene (13b): Following the general method 2, KOH (600 mg, 10.7 mmol) was added to a solution of **35** (268 mg, 0.86 mmol) in 40 mL THF. After 20 min of sonication, **1b** (600 mg, 0.86 mmol) was added and the mixture was sonicated for 4 h. After two recrystallizations from ethanol, **13b** (413 mg, 56%) was obtained as an orange solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.84 (d, ^3J = 9.0 Hz, 2 H, 53-H, 57-H), 7.62 (d, ^3J = 8.5 Hz, 2 H, 48-H, 50-H), 7.21 (d, ^3J = 8.6 Hz, 2 H, 47-H, 51-H), 7.19 (t, ^3J = 8.3 Hz, 3 H, 5-H, 11-H, 17-H), 6.96 (d, ^3J = 9.0 Hz, 2 H, 54-H, 56-H), 6.55 (d, ^3J = 8.3 Hz, 6 H, 4-H, 6-H, 10-H, 12-H, 16-H, 18-H), 3.93 (t, ^3J = 7.7 Hz, 6 H, 20-H, 28-H, 36-H), 1.83 (quint, ^3J = 7.0 Hz, 6 H, 21-H, 29-H, 37-H), 1.46 (quint, ^3J = 7.3 Hz, 6 H, 22-H, 30-H, 38-H), 1.37 (quint, ^3J = 7.5 Hz, 6 H, 23-H, 31-H, 39-H), 1.32–1.21 (m, 18 H, 24-H, 25-H, 26-H, 32-H, 33-H, 34-H, 40-H, 41-H, 42-H), 0.87 (t, ^3J = 6.7 Hz, 9 H, 27-H, 35-H, 43-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 162.08 (C-55), 151.28 (C-49), 147.04 (C-52), 140.52 (C-3, C-7, C-9, C-13, C-15, C-19), 132.35 (C-47, C-51), 128.25 (C-5, C-11, C-17), 126.22 (C-46), 124.73 (C-53, C-57), 122.05 (C-48, C-50), 114.19 (C-54, C-56), 110.03 (C-2, C-8, C-14), 104.95 (C-4, C-6, C-10, C-12, C-16, C-18), 95.84 (C-44), 83.62 (C-45), 46.53 (C-20, C-28, C-36), 31.87 (C-25, C-33, C-41), 29.42 (C-23, C-31, C-39), 29.35 (C-24, C-32, C-40), 28.19 (C-1), 27.03 (C-22, C-30, C-38), 25.88 (C-21, C-29, C-37), 22.67 (C-26, C-34, C-42), 14.13 (C-27, C-35, C-43) ppm. MS (MALDI-TOF, Cl-CCA): *m*/*z* = 856 $[M]^+$. IR (ATR): $\tilde{\nu}$ = 3079 (w), 3031 (w), 2954 (m), 2924 (s), 2852 (m), 2069 (w), 1614 (s), 1579 (vs), 1482 (vs), 1455 (vs), 1392 (s), 1266 (s), 1244 (s), 1168 (s), 1150 (s), 1101 (s), 990 (m), 847 (s), 797 (m), 759 (m), 746 (m), 729 (s), 693 (m), 598 (m), 554 (m) cm^{-1}. UV (toluene): λ_{max} (lgε) = 367 (4.58), 336 (4.51), 296 (4.78) nm. $C_{58}H_{68}D_3N_5O$ (856.58): calcd. C 81.26, H 8.70, N 8.17; found C 80.79, H 8.79, N 8.37.

(*E*)-12*c*-[4-(3,5-Dimethylphenyldiazenyl)phenyl]ethynyl-4,8,12-tri-*n*-propyl-4,8,12-triazatriangulene (14a): Following the general method 2, KOH (200 mg, 3.57 mmol) was added to a solution of **26** (187 mg, 0.61 mmol) in 20 mL THF. After 60 min of sonication, **1a** (300 mg, 0.61 mmol) was added and the mixture was sonicated for 5 h. After recrystallization from diethyl ether, **14a** (250 mg, 64%) was obtained as an orange solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.65 (d, ^3J = 8.6 Hz, 2 H, 33-H, 35-H), 7.46 (s, 2 H, 38-H, 42-H), 7.22 (d, ^3J = 8.6 Hz, 2 H, 32-H, 36-H), 7.19 (t, ^3J = 8.2 Hz, 3 H, 5-H, 11-H, 17-H), 7.08 (s, 1 H, 40-H), 6.54 (d, ^3J = 8.3 Hz, 6 H, 4-H, 6-H, 10-H, 12-H, 16-H, 18-H), 3.90 (t, ^3J = 7.8 Hz, 6 H, 20-H, 23-H, 26-H), 2.37 (s, 6 H, 43-H, 44-H), 1.87 (sext, ^3J = 7.6 Hz, 6 H, 21-H, 24-H, 27-H), 1.05 (t, ^3J = 7.4 Hz, 9 H, 22-H, 25-H, 28-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 152.86 (C-37), 151.24 (C-34), 140.56 (C-3, C-7, C-9, C-13, C-15, C-19), 138.72 (C-39, C-41), 132.73 (C-40), 132.32 (C-32, C-36), 128.26 (C-5, C-11, C-17), 126.72 (C-31), 122.26 (C-33, C-35), 120.61 (C-38, C-42), 110.08 (C-2, C-8, C-14), 105.03 (C-4, C-6, C-10, C-12, C-16, C-18), 96.13 (C-29), 83.52 (C-30), 48.09 (C-20, C-23, C-26), 28.23 (C-1), 21.22 (C-43, C-44), 19.17 (C-21, C-24, C-27), 11.19 (C-22, C-25, C-28) ppm. MS (MALDI-TOF, Cl-CCA): *m*/*z* = 641 $[M]^+$. IR (ATR): $\tilde{\nu}$ = 3018 (w), 2956 (m), 2864 (m), 1611 (s), 1578 (s), 1482 (s), 1455 (s), 1390 (s), 1228 (s), 1168 (s), 1143 (s), 986 (m), 918 (m), 840 (m), 752 (s), 707 (s), 684 (m), 659 (s), 531 (m) cm^{-1}. UV (toluene): λ_{max} (lgε) = 358 (4.55), 336 (4.58) nm. $C_{44}H_{43}N_5$ (641.35): calcd. C 82.34, H 6.75, N 10.91; found C 82.63, H 6.94, N 10.75.

(*E*)-12*c*-[4-(3,5-Di-*tert*-butylphenyldiazenyl)phenyl]ethynyl-4,8,12-tri-*n*-propyl-4,8,12-triazatriangulene (15a): Following the general method 2, KOH (300 mg, 5.36 mmol) was added to a solution of **27** (238 mg, 0.61 mmol) in 30 mL THF. After 20 min of sonication, **1a** (300 mg, 0.61 mmol) was added and the mixture was sonicated for 4 h. After recrystallization from diethyl ether, **15a** (206 mg, 47%) was obtained as an orange solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.71 (d, ^4J = 1.8 Hz, 2 H, 38-H, 42-H), 7.67 (d, ^3J = 8.5 Hz, 2 H, 33-H, 35-H), 7.53 (t, ^4J = 1.8 Hz, 1 H, 40-H), 7.23 (d, ^3J = 8.5 Hz, 2 H, 32-H, 36-H), 7.19 (t, ^3J = 8.3 Hz, 3 H, 5-H, 11-H, 17-H), 6.55 (d, ^3J = 8.3 Hz, 6 H, 4-H, 6-H, 10-H, 12-H, 16-H, 18-H), 3.90 (t, ^3J = 7.8 Hz, 6 H, 20-H, 23-H, 26-H), 1.87 (sext, ^3J = 7.7 Hz, 6 H, 21-H, 24-H, 27-H), 1.36 (s, 18 H, 44-H, 45-H, 46-H, 48-H, 49-H, 50-H), 1.05 (t, ^3J = 7.4 Hz, 9 H, 22-H, 25-H, 28-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 152.59 (C-37), 151.79 (C-39, C-41), 151.37 (C-34), 140.57 (C-3, C-7, C-9, C-13, C-15, C-19), 132.32 (C-32, C-36), 128.26 (C-5, C-11, C-17), 126.53 (C-31), 125.37 (C-40), 122.24 (C-33, C-35), 117.29 (C-38, C-42), 110.10 (C-2, C-8, C-14), 105.04 (C-4, C-6, C-10, C-12, C-16, C-18), 95.98 (C-29), 83.54 (C-30), 48.10 (C-20, C-23, C-26), 35.08 (C-43, C-47), 31.43 (C-44, C-45, C-46, C-48, C-49, C-50), 28.23 (C-1), 19.18 (C-21, C-24, C-27), 11.21 (C-22, C-25, C-28) ppm. MS (EI, 70 eV): *m*/*z* (%) = 725 (3), 408 (7), 365 (3), 318 (39), 189 (100), 133 (32), 101 (42). UV (toluene): λ_{max} (lgε) = 352 (4.50), 336 (4.53), 296 (4.71) nm. IR (ATR): $\tilde{\nu}$ = 3098 (w), 3028 (w), 2962 (m), 2873 (m), 1614 (s), 1579 (s), 1482 (s), 1456 (s), 1392 (s), 1364 (m), 1270 (m), 1230 (s), 1170 (s), 1145 (s), 1098 (m), 988 (m), 918 (m), 889 (m), 843 (m), 754 (s), 710 (s), 654 (m), 539 (m) cm^{-1}. $C_{50}H_{55}N_5$ (725.45): calcd. C 82.72, H 7.64, N 9.65; found C 82.63, H 7.46, N 9.82.

(*E*)-12*c*-[4-(3,5-Di-*tert*-butylphenyldiazenyl)phenyl]ethynyl-4,8,12-tri-*n*-octyl-4,8,12-triazatriangulene (15 b): Following the general method 2, KOH (300 mg, 5.36 mmol) was added to a solution of **27** (157 mg, 0.43 mmol) in 30 mL THF. After 20 min of sonication, **1b** (300 mg, 0.43 mmol) was added and the mixture was sonicated for 4 h. After recrystallization from diethyl ether, **15b** (196 mg, 49%) was obtained as an orange solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.70 (d, ^4J = 1.8 Hz, 2 H, 53-H, 57-H), 7.67 (d, ^3J = 8.6 Hz, 2 H, 48-H, 50-H), 7.52 (t, ^4J = 1.8 Hz, 1 H, 55-H), 7.23 (d, ^3J = 8.7 Hz, 2 H, 47-H, 51-H), 7.20 (t, ^3J = 8.3 Hz, 3 H, 5-H, 11-H, 17-H), 6.55 (d, ^3J = 8.3 Hz, 6 H, 4-H, 6-H, 10-H, 12-H, 16-H, 18-H), 3.93 (t, ^3J = 7.8 Hz, 6 H, 20-H, 28-H, 36-H), 1.87 (quint, ^3J = 7.6 Hz, 6 H, 21-H, 29-H, 37-H), 1.46 (quint, ^3J = 7.9 Hz, 6 H, 22-H, 30-H, 38-H), 1.36 (s, 18 H, 59-H, 60-H, 61-H, 63-H, 64-H, 65-H), 1.33–1.22 (m, 24 H, 23-H, 24-H, 25-H, 26-H, 31-H, 32-H, 33-H, 34-H, 39-H, 40-H, 41-H, 42-H), 0.87 (t, ^3J = 6.9 Hz, 9 H, 27-H, 35-H, 43-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 152.60 (C-52), 151.76 (C-54, C-56), 151.35 (C-49), 140.51 (C-3, C-7, C-9, C-13, C-15, C-19), 132.34 (C-47, C-51), 128.25 (C-5, C-11, C-17), 126.52 (C-46), 125.32 (C-55), 122.21 (C-48, C-50), 117.25 (C-53, C-57), 110.01 (C-2, C-8, C-14), 104.94 (C-4, C-6, C-10, C-12, C-16, C-18), 95.93 (C-44), 83.57 (C-45), 46.52 (C-20, C-28, C-36), 35.06 (C-58, C-62), 31.87 (C-25, C-33, C-41), 31.41 (C-59, C-60, C-61, C-63, C-64, C-65), 29.41 (C-23, C-31, C-39), 29.34 (C-24, C-32, C-40), 28.23 (C-1), 27.02 (C-22, C-30, C-38), 25.86 (C-21, C-29, C-37), 22.66 (C-26, C-34, C-42), 14.12 (C-27, C-35, C-43) ppm. MS (MALDI-TOF, Cl-CCA): *m*/*z* = 935 $[M]^+$. IR (ATR): $\tilde{\nu}$ = 3098 (w), 3028 (w), 2955 (m), 2922 (s), 2852 (m), 1615 (s), 1579 (vs), 1480 (s), 1456 (vs), 1393 (s), 1372 (s), 1262 (m), 1244 (s), 1212 (m), 1168 (s), 1144 (m), 848 (m), 757 (s), 713 (s), 699 (m), 654 (m) cm^{-1}. UV (toluene): λ_{max} (lgε) = 352 (4.52), 337 (4.55), 296 (4.68) nm. $C_{65}H_{85}N_5$ (935.68): calcd. C 83.37, H 9.15, N 7.48; found C 82.89, H 9.53, N 7.65.

(*E*)-12*c*-{4-[4-(Phenyldiazenyl)phenyl]phenyl}ethynyl-4,8,12-tri-*n*-octyl-4,8,12-triazatriangulene (16b): Following the general method 2, KOH (300 mg, 5.36 mmol) was added to a solution of **40** (152 mg, 0.43 mmol) in 30 mL THF. After 20 min of sonication, **1b** (300 mg, 0.43 mmol) was added and the mixture was sonicated for 5 h. After recrystallization from ethanol, **16b** (269 mg, 69%) was obtained as an orange solid. ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ = 7.93 (d, ^3J = 8.5 Hz, 2 H, 54-H, 56-H), 7.91 (d, ^3J = 8.2 Hz, 2 H, 59-H, 63-H), 7.63 (d, ^3J = 8.5 Hz, 2 H, 53-H, 57-H), 7.53–7.44 (m, 3 H, 60-H, 61-H, 62-H), 7.40 (d, ^3J = 8.3 Hz, 2 H, 48-H, 50-H), 7.20 (t, ^3J = 8.2 Hz, 3 H, 5-H, 11-H, 17-H), 7.19 (d, ^3J = 8.2 Hz, 2 H, 47-H, 51-H), 6.55 (d, ^3J = 8.3 Hz, 6 H, 4-H, 6-H, 10-H, 12-H, 16-H, 18-H), 3.93 (t, ^3J = 7.8 Hz, 6 H, 20-H, 28-H, 36-H), 1.84 (quint, ^3J = 7.5 Hz, 6 H, 21-H, 29-H, 37-H), 1.46 (quint, ^3J = 7.7 Hz, 6 H, 22-H, 30-H, 38-H), 1.37 (quint, ^3J = 7.4 Hz, 6 H, 23-H, 31-H, 39-H), 1.33–1.23 (m, 18 H, 24-H, 25-H, 26-H, 32-H, 33-H, 34-H, 40-H, 41-H, 42-H), 0.87 (t, ^3J = 6.9 Hz, 9 H, 27-H, 35-H, 43-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 152.73 (C-58), 151.73 (C-55), 143.00 (C-52), 140.49 (C-3, C-7, C-9, C-13, C-15, C-19), 138.78 (C-49), 132.13 (C-47, C-51), 130.97 (C-61), 129.08 (C-60, C-62), 128.18 (C-5, C-11, C-17), 127.48 (C-53, C-57), 126.35 (C-48, C-50), 123.71 (C-46), 123.34 (C-54, C-56), 122.85 (C-59, C-63), 110.14 (C-2, C-8, C-14), 104.91 (C-4, C-6, C-10, C-12, C-16, C-18), 94.72 (C-44), 83.39 (C-45), 46.51 (C-20, C-28, C-36), 31.87 (C-25, C-33, C-41), 29.42 (C-23, C-31, C-39), 29.34 (C-24, C-32, C-40), 28.07 (C-1), 27.03 (C-22, C-30, C-38), 25.86 (C-21, C-29, C-37), 22.66 (C-26, C-34, C-42), 14.11 (C-27, C-35, C-43) ppm. MS (MALDI-TOF, Cl-CCA): *m*/*z* = 899 $[M]^+$. IR (ATR): $\tilde{\nu}$ = 3028 (w), 2953 (m), 2919 (s), 2850 (s), 1612 (s), 1579 (vs), 1483 (vs), 1455 (vs), 1392 (s), 1368 (s), 1265 (m), 1244 (s), 1165 (s), 1139 (m), 991 (m), 915 (m), 822 (s), 761 (vs), 721 (s), 686 (s), 542 (m) cm^{-1}. UV (toluene): λ_{max} (lgε) = 355 (4.65) nm. $C_{63}H_{73}N_5$ (899.59): calcd. C 84.05, H 8.17, N 7.78; found C 84.08, H 8.68, N 7.94.

Supporting Information (see also the footnote on the first page of this article): Numbered structures of the synthesized molecules for the assignment of NMR signals.

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