Supporting Information

© Wiley-VCH 2008

69451 Weinheim, Germany
Supporting Information

Toroidal Nanoobjects from Supramolecular Rosette Assemblies of Melamine-Linked Oligo(p-phenyleneethynylene)s and Cyanurates

Shiki Yagai*, Sankarapillai Mahesh, Yoshihiro Kikkawa, Kanako Unoike, Takashi Karatsu Akihide Kitamura, Ayyappanpillai Ajayaghosh*

Dr. S. Yagai*, K. Unoike, Prof. Dr. T. Karatsu, Prof. Dr. A. Kitamura
Department of Applied Chemistry and Biotechnology, Faculty of Engineering
Chiba University, 1-33 Yayoi-cho, Inage-ku
Chiba 263-8522, Japan, Fax: (+) 81-43-290-3039
Email: yagai@faculty.chiba-u.jp

Dr. A. Ajayaghosh*, Mr. S. Mahesh
Photosciences and Photonics Group, Chemical Sciences and Technology Division
National Institute of Interdisciplinary Science and Technology (NIST), CSIR
Trivandrum, 695019, India
Fax: (+) 91-471-249-0186
Email: ajayaghosh62@gmail.com.
Webpage: http://w3rrlt.csir.res.in/photo/people/draajayaghosh/Homepage.htm

Dr. Y. Kikkawa
Nanoarchitectonics Research Center
National Institute of Advanced Industrial Science and Technology (AIST)
1-1-1 Higashi, Tsukuba, Ibaraki 305-8562, Japan
# Table of Contents

1. Experimental section .......................................................... S3
2. Synthesis .............................................................................. S3
3. Description of experimental techniques ................................. S9
4. $^1$H NMR Spectra ................................................................. S12
5. Molecular modeling ............................................................... S13
6. Absorption and emission spectroscopic studies .................... S14
7. AFM studies of toroidal nanostructures ................................. S16
8. References ............................................................................ S17
1. Experimental section

General

All reactions were performed under an atmosphere of nitrogen unless stated otherwise. All commercially available reagents and solvents were of reagent grade and used without further purification. Silica gel plates were 250 μm thick, 60 F_{254} grade from Merck. Silica gel was grade 60N (Spherical, Neutral, 60-210 mesh) from Kanto chemicals, Japan. ^1^H NMR spectra were recorded on JEOL LA400 or LA500 spectrometer and chemical shifts were reported in ppm (δ) with the signal of TMS as internal standard. Variable temperature ^1^H NMR spectra were recorded on JEOL LA500 spectrometer and chemical shifts were reported in ppm with the signals of residual solvents as internal standard. ^13^C NMR spectra were recorded on a 300 MHz Bruker Avance DPX Spectrometer. High resolution mass spectra were recorded with a JEOL JMS600. MALDI-TOF MS spectra were measured on a Voyager DE Pro (Applied Biosystems) using α-cyano-4-hydroxy cinnamic acid as the matrix. UV/Vis spectra were measured on a JASCO V660 spectrophotometer. Fluorescence spectra were measured on SPEX-Fluorolog F112X spectrofluorimeter. Molecular modeling calculations were performed on MacroModel version 9.0 (AMBER force field).

2. Synthesis

General procedure for the coupling of terminal alkyne with an aryl halide utilizing a palladium-copper cross-coupling (Sonogashira protocol)

To an oven-dried screw cap tube or a round bottom flask equipped with a magnetic stir bar was added the aryl halide, bis(triphenylphosphine)palladium (II) dichloride (1-10 mol % based on the aryl halide), and copper (I) iodide (1-10 mol % based on the aryl halide). The vessel was then sealed with rubber septum, evacuated and backfilled with nitrogen three times. Triethyl amine or N, N-diisopropylethylamine (Hünig’s base) was added followed by THF to serve as the co-solvent.
After stirring 5 minutes at room temperature, the terminal alkyne was added and the reaction mixture was stirred at ambient temperature (< 60°C) until complete reaction was noted by the TLC. The vessel was cooled to room temperature and the reaction mixture was passed through a short column of celite (CH₂Cl₂ as eluent), the fractions obtained were evaporated under reduced pressure. The crude product was further purified by flash or column chromatography (silica gel).

**General procedure for the deprotection of a trimethylsilyl (TMS)-protected alkyne.**

To a round bottom flask equipped with a magnetic stir bar was added the TMS-protected alkyne and THF, followed by KOH in methanol (2N). The reaction vessel was sealed with a rubber septum and then filled with nitrogen. The reaction was allowed to go to completion for around 3 hours and solvent is removed under vacuum. The solid obtained was dissolved in water. The mixture was extracted with chloroform and organic layer was dispersed three times with brine, and to times with water. The extracts were combined and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure. The crude product obtained was further purified by column chromatography.

Scheme S1 outlines the synthesis of melamine linked OPE 1. Melamine 1 was prepared from the reaction of \(N, N'-(p\text{-iodophenyl})\text{-triaminotriazine} (8)\) with 3,4,5–tridodecylbenzyloxy substituted ethynyltolan (7). The synthesis was started from 3,4,5-tri(n-dodecan-1-xyloxy)benzylchloride.\(^{[S1]}\)
Reagents and Conditions: i) K₂CO₃, dry DMF, 4-iodophenol, 120°C, 12 hrs; ii) TMS-acetylene, Pd(PPh₃)₂Cl₂, CuI, dry TEA, 40 °C, 8 hrs; iii) KOH/MeOH, dry THF, RT; iv) 1-iodo-4-(trimethylsilylethynyl) benzene, Pd(PPh₃)₂Cl₂, CuI, dry TEA, 12 hrs, 50°C; v) KOH/MeOH, dry THF, RT; vi) 7, Pd(PPh₃)₂Cl₂, CuI, TEA, dry THF, reflux, 24 hrs.

Synthesis of 1,2,3-tris(dodecyloxy)-5-((4-iodophenoxy)methyl)benzene (3)

To a solution of 4-iodophenol (4.89 g, 22.09 mmol) in dry DMF, K₂CO₃ (10.15 g, 73.6 mmol) was added followed by 2 (10 g, 14.72 mmol) and reaction mixture was heated to 120°C for 12 hrs. After the completion of the reaction, the mixture was poured to ice-cold water and the precipitate formed was filtered. The residue was then dissolved in chloroform and washed two times with brine and three times with water. The organic fractions were combined and dried over anhydrous sodium sulphate, solvent was removed under reduced pressure. The brown solid thus obtained was then purified by column chromatography (hexane as the eluent) to give 3 as white solid (4.89 g, yield
\(78.8\%\).

**\(^1\)H NMR** (400 MHz, CDCl\(_3\), TMS) : \(\delta = 7.55-7.53\) (d, \(J = 8\) Hz, 2H, aromatic), 6.74-6.72 (d, \(J = 8\) Hz, 2H, aromatic), 6.58 (s, 2H, aromatic), 4.89 (s, 2H, OCH\(_2\)), 3.97-3.92 (m, 6H, OCH\(_2\)), 1.80 (m, 6H), 1.48 (m, 6H), 0.87 (t, 9H).

**\(^13\)C NMR** (75 MHz, CDCl\(_3\), TMS): \(\delta = 14.09, 22.68, 26.08, 29.35, 29.40, 29.63, 29.68, 30.32, 31.91, 69.18, 70.50, 73.44, 106.14, 117.31, 131.37, 138.22, 153.34, 153.14.\)

**MS (FAB)**: [M]\(^+\) calcd for C\(_{49}\)H\(_{83}\)IO\(_4\), 862.53; found: 862.81.

**Synthesis of trimethyl((4-(3,4,5-tris(dodecyloxy)benzyloxy)phenyl)ethynyl)silane (4)**

To a solution of 3 (3 g, 3.476 mmol) in dry triethylamine (50 mL), CuI (0.033 g, 0.174 mmol), Pd(PPh\(_3\))\(_2\)Cl\(_2\) (0.1220 g, 0.174 mmol) were added and followed by dry THF (50 mL) as the co-solvent. The mixture was cooled in an ice bath and (trimethylsilyl) acetylene (0.6237 mL, 4.52 mmol) was added slowly. The reaction mixture was then stirred at room temperature for 30 minutes and temperature was raised to 50°C for 12 hours. After the completion of the reaction, the mixture was passed through a short celite column using dichloromethane as the eluent. The fractions were combined and solvent was removed under reduced pressure. The crude product obtained was further purified by column chromatography (EtOAc/Hexane = 1:9) to give 4 (2.69 g, 93% yield).

**\(^1\)H NMR** (400 MHz, CDCl\(_3\), TMS) : \(\delta = 7.42-7.40\) (d, \(J = 8\) Hz, 2H), 6.89-6.87 (d, \(J = 8\) Hz, 2H), 6.59 (s, 2H), 4.93 (s, 2H), 3.97-3.92 (m, 6H), 1.80 (m, 6H), 1.48 (m, 6H), 1.27 (m, 48H), 0.86 (t, 9H), 0.23 (s, 9H).

**\(^13\)C NMR** (75 MHz, CDCl\(_3\), TMS): \(\delta = 0.039, 14.09, 22.67, 26.08, 29.40, 29.63, 29.68, 29.74, 30.32, 31.92, 69.17, 70.39, 73.43, 106.15, 114.71, 115.56, 133.45, 153.32.\)

**MS (FAB)**: [M]\(^+\) calcd for C\(_{54}\)H\(_{92}\)O\(_4\)Si, 832.68; found: 833.01.

**Synthesis of 1,2,3-tris(dodecyloxy)-5-((4-ethynylphenoxy)methyl)benzene (5)**
To a solution of 4 (2.65 g, 3.19 mmol) in dry THF (50 mL), 2N KOH in methanol was added and stirred at room temperature for 3 hours. After the completion of the reaction solvent was removed under reduced pressure. The solid obtained was dissolved in water. The mixture was then extracted with chloroform, washed two times with brine followed by two times with distilled water and the organic layer was combined, dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure to get the crude product. The crude product was further purified by column chromatography (EtOAc/Hex = 1:9) give the compound 5 as brown solid (2.10 g, yield 87%).

$^1$H NMR (400 MHz, CDCl$_3$, TMS) : $\delta = 7.43$-$7.41$ (d, $J = 8$ Hz, 2H), 6.92-$6.90$ (d, $J = 8$ Hz, 2H), 6.59 (s, 2H), 4.93 (s, 2H), 3.98-$3.92$ (m, 6H), 3.1 (s, 1H), 1.81 (m, 6H), 1.47 (m, 6H) 1.26 (m, 48H), 0.87 (t, 9H).

$^{13}$C NMR (75 MHz, CDCl$_3$, TMS): $\delta = 14.08$, 22.67, 26.09, 29.12, 29.35, 29.40, 29.63, 29.69, 30.33, 31.92, 69.18, 70.43, 73.43, 106.18, 114.84, 114.47, 131.37, 133.58, 138.13, 153.34, 159.14.

MS (FAB): $[M]^+$ calcd for C$_{51}$H$_{84}$O$_4$, 760.64; found: 760.80.

Synthesis of trimethyl((4-((4-(3,4,5-tris(dodecyloxy)benzyloxy)phenyl)ethynyl)phenyl)ethynyl)silane (6)

To a solution of 5 (1.10 g, 1.5 mmol) in triethylamine (50 mL), Pd(PPh$_3$)$_2$Cl$_2$ (0.055 g, 0.0788 mmol), CuI (0.03 g, 0.1577 mmol) were added followed by THF (15 mL) as the co-solvent. 1-ioddo-4(trimethylsilylethynyl)benzene (0.473 g, 1.577 mmol) was then added and the reaction mixture was kept at ambient temperature(50 °C) for 12 hours. After the completion of the reaction, the mixture was passed through short celite column using CH$_2$Cl$_2$ as the eluent. The fractions were collected and solvent was removed under reduced pressure. The crude product obtained was further purified by column chromatography (EtOAc/Hexane = 1:9) to give compound 6 as a pale yellow solid (1.05g, yield 78%).
1H NMR (400 MHz, CDCl3, TMS) : δ = 7.46-7.44 (d, J = 8 Hz, 2H), 7.42 (s, 4H), 6.95-6.93 (d, J = 8 Hz, 2H), 6.60 (s, 2H), 4.96 (s, 2H), 3.98-3.92 (m, 6H), 1.80 (m, 6H), 1.48 (m, 6H), 1.26 (m, 48H), 0.86 (t, 9H), 0.24 (t, 9H).

13C NMR (75 MHz, CDCl3, TMS): δ = 0.08, 14.09, 22.68, 26.10, 29.36, 29.41, 29.65, 29.70, 30.34, 31.93, 69.19, 70.47, 73.45, 104.73, 106.20, 114.97, 131.19, 131.40, 131.86, 133.09, 153.35, 159.14.

MS (FAB): [M]+ calcd for C62H96O4Si, 932.71; found: 933.91.

Synthesis of 1,2,3-tris(dodecyloxy)-5-((4-((4-ethynylphenyl)ethynyl)phenoxy)methyl)benzene (7)

To a solution of 6 (0.50 g, 0.5356 mmol) in dry THF, 2N KOH in methanol was added and stirred at room temperature for 2 hours. After the completion of the reaction, the solvent was removed under vacuum and solid obtained was dissolved in water. It was then extracted with chloroform, washed two times with brine followed by two times with distilled water and the organic layer was combined, dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure to give the crude product. Which was further purified by column chromatography (EtOAc/Hex = 1:9) to give 7 as pale yellow solid (0.407 g, yield 87%).

1H NMR (400 MHz, CDCl3, TMS) : δ = 7.43 (m, 6H), 6.92-6.89 (d, J = 9 Hz, 2H), 6.55 (s, 2H), 4.94 (s, 2H) 3.97-3.92 (m, 6H), 3.1 (s, 1H), 1.80 (m, 6H), 1.48 (m, 6H), 1.26 (m, 48H), 0.87 (t, 9H).

13C NMR (75 MHz, CDCl3, TMS): δ = 14.04, 22.63, 26.04, 26.08, 29.30, 29.36, 29.59, 29.64, 29.68, 29.69, 30.28, 31.87, 69.13, 70.41, 73.39, 83.29, 87.68, 91.37, 106.13, 114.91, 115.26, 121.46, 124.06, 131.22, 131.33, 131.97, 133.06, 133.96, 138.07, 153.29, 158.99.


Synthesis of 1

To a solution of 7 (0.10 g, 0.1162 mmol) in dry triethylamine (50 mL), co-solvent THF
(50mL) was added followed by 8 (0.03, 0.057 mol) and deoxygenated for 30 minutes. The flask was then filled with nitrogen after adding Pd (PPh₃)₂Cl₂ (0.0039 g, 0.00566 mmol), CuI (0.0005 g, 0.00566 mmol) and stirred at ambient temperature (50°C) for 24 hours. After the completion of the reaction, mixture was passed through celite column using dichloromethane as the eluent. The fractions were collected and solvent was removed under reduced pressure. The crude product obtained was further purified by column chromatography (EtOAc/Hex = 3:7) to give the compound 1 as solid (0.60 g, yield 25.8 %).

¹H NMR (500 MHz, CDCl₃, TMS) : δ = 7.61-7.59 (d, J = 8 Hz, 4H), 7.51-7.46 (m, 16H), 6.96-6.94 (d, 4H), 6.93 (br-s, 2H), 6.61 (s, 4H), 5.02 (br-s, 2H), 4.95 (s, 4H), 3.99-3.95 (m, 12H), 1.81-1.70 (m, 12H), 1.40-1.50 (m, 12H), 1.40-1.20 (m, 96H), 0.85 (m, 18H).


3. Description of experimental techniques

i) Sample preparation for measurements

Decane solutions of toroidal assemblies were prepared by mixing chloroform solution of 1 and chloroform/methanol mixed solution of 2 with a 1:1 molar stoichiometry and the solvent was evaporated thoroughly. The resulting solid was easily dissolved in decane by gentle heating to give decane solutions of toroidal assemblies. In another method, compounds 1 and 2 were took in 1:1 molar ratio ($c = 1 \times 10^{-2}$ M in 1 mL) in a screw capped vial and dissolved in a mixture of chloroform and methanol (1:1) by sonication followed by heating. It was then flushed with nitrogen gas to remove the solvent and further dried in vacuum for 36 hours. It was then dissolved in decane and diluted to different concentrations for each measurement.

ii) Dynamic light scattering (DLS)

Dynamic light scattering measurements were conducted on Beckmann Coulter N5 particle analyzer equipped with 25 mW He-Ne laser. The sample solutions were filtered with Millipore membrane filter (pore size = 0.2 μm) before measurements to remove dust. The temperature was kept at 25°C and scattering angle was set to 90° C.

iii) Atomic force microscopy (AFM)

AFM images of the toroids were acquired under ambient conditions using Digital Instruments, Multimode Nanoscope IIIa (Veeco Instruments, Santa Barbara, CA) in tapping mode with different set points. Silicon cantilevers (OMCL-AC160TS-C2) with a spring constant of 42 N/m and frequency of 300 kHz (nominal value, Olympus, Japan) were used for the AFM observations in air. The scan rate was varied from 1 to 2 Hz. Variations of the tapping force can be achieved by changing the driving amplitude ($A_0$) and set-point amplitude ($A_{sp}$) ratio. Simultaneous registration was performed for height and phase images. The samples were prepared by spin coating (3000 rpm) from equimolar mixture of 1 and 2 ($c = 5 \times 10^{-5}$ M) on a freshly cleaved highly oriented...
pyrolytic graphite (HOPG). The samples were dried under vacuum for 24 hours after the spin coating. The tip broadening was calculated according to the equation (1) where R is the radius of the tip and h is the mean height of the toroids.

\[ 2\Delta = 2[h(2R-h)]^{1/2} \quad (1) \]

Radius of the tip (OLYMPUS OMCL-AC series cantilevers, Model: OMCL-AC160TS-C2) is 6.8 nm. The average height of the toroids formed from the \( c = 5 \times 10^{-5} \) M solution is 3.2 ± 0.3, the tip broadening factor \( 2\Delta = 11.54 \pm 0.3 \). The actual diameter obtained after subtracting from the observed diameter is 8.46 nm.

Samples on mica and silicon substrates were imaged by an SII NanoNavi station (SII Nanotechnology Inc, Japan) with an SPA-400 Probe unit operated with dynamic force mode. Silicon cantilevers (SII) with average resonance frequency of 140 kHz were used.

**iv) Transmission electron microscopy (TEM)**

Transmission electron microscopic studies were performed by using JEOL JEM1011 transmission electron microscope operating at 80 kV accelerating voltage. The samples were prepared by dipping the carbon coated copper grids (400 mesh) to an equimolar mixture of 1 and 2 in decane \( (c = 5 \times 10^{-5} \) M). TEM images were obtained after staining with RuO_4 vapors followed by drying the sample in vacuum for 24 hours. The samples were stained by placing the TEM grids above the aqueous solution of RuO_4 for 15-30 minutes in a closed chamber.
4. $^1$H NMR Spectra

Figure S1. $^1$H NMR spectra of a) 1 in CDCl$_3$, b) 2 in DMSO-$d_6$, and c) the equimolar mixture of 1 and 2 in CDCl$_3$ ($c = 5.0 \times 10^{-3}$ M). Insets show the magnified spectra.
5. Molecular modeling

**Figure S2.** Molecular modeled structure of rosette $1_3 2_3$. The gyration diameter of the rosette is approximately 8 nm.

**Figure S3.** Top and side views of molecular-modeled rosette $1_3 2_3$ highlighting the OPE segments (orange).
6. Absorption and fluorescence spectroscopic studies

Figure S4. a) Absorption and b) fluorescence spectra of 1 in the presence of 1 equivalent of 2 (solid curves, $c = 1.0 \times 10^{-2}$ M, 0.01 mm quartz cuvette) and 1 alone (dashed curves, $c = 1.0 \times 10^{-5}$ M, 1 cm quartz cuvette) in chloroform. Excitation wavelength in the emission spectra is 300 nm. Fluorescence spectra of the mixture were measured by front face illumination setup using 1 mm quartz cuvette.
Figure S5. Temperature-dependent (20−70°C) absorption (a,c) and emission spectra (b,d) of 1 (c = 1.0 × 10^{-5} M) in the presence (a,b) and the absence of 1 equivalent of 2 (c,d) in decane. Excitation wavelength in the emission spectra is 300 nm. Arrows indicate the changes upon increasing temperature. Melamine 1 alone also shows absorption and fluorescence spectra characteristic for the H-type aggregation of OPE chromophores in decane at 20°C, probably due to the self-aggregation of melamines^{[5e,52]} However, self-aggregates of 1 showed clear aggregate-to-monomer transitions upon increasing temperature because of their low stabilities.
Figure S6. AFM height (a,c,d) and phase (b,d,f) images of toroidal nanostructures formed from 1 and 2 in decane ($c = 5.0 \times 10^{-5}$ M), spin-coated (3000 rpm) onto HOPG. Tapping force: $A_{ap} / A_0 = 0.7$. 
Figure S7. Deformation of an isolated toroid by multiple AFM scans. Tapping force: $A_{sp} / A_0 = 0.3$

Figure S8. AFM phase images of toroidal nanostructures (cast from decane solution of $c = 5.0 \times 10^{-5}$ M) on mica (a) and silicon substrates (b).

8. References
