

Supporting Information

Role of complementary H-bonding interaction of a cyanurate in the self-assembly and gelation of melamine linked tri(*p*-phenyleneethynylene)s

Sankarapillai Mahesh, Rajasekaran Thirumalai, Shiki Yagai,* Akihide Kitamura, Ayyappanpillai Ajayaghosh*

Dr. A. Ajayaghosh, Mr. S. Mahesh, Mr. R. Thirumalai

Photosciences and Photonics Group, Chemical Sciences and Technology Division,
National Institute of Interdisciplinary Science and Technology (NIIST), 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. S. Yagai, 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

Table of Contents

1. Experimental section	S3
2. Synthesis	S3
3. Description of experimental techniques	S8
4. Absorption and emission spectroscopic studies	S9
5. IR studies	S10
9. References	S10

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 F₂₅₄ grade from Merck. Silica gel was grade 60N (Spherical, Neutral, 60-210 mesh) from Kanto chemicals, Japan. ¹H 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. 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.

2. Synthesis

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

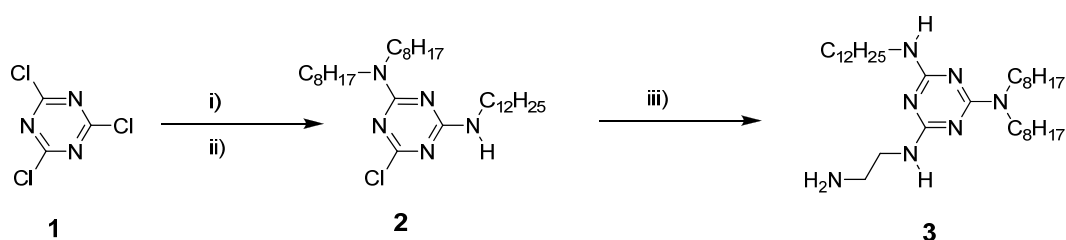
To an oven-dried screw cap tube or a round bottom flask equipped with a magnetic stir bar was added the aryl halide, bis(triphenylphosphine)palladium (II) dichloride (1-10 mol % based on the aryl halide), and copper (I) iodide (1-10 mol % based on the aryl halide). The vessel was then sealed with rubber 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 for 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 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 alkynes and THF, were added followed by KOH in methanol (2 N). 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 two 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.

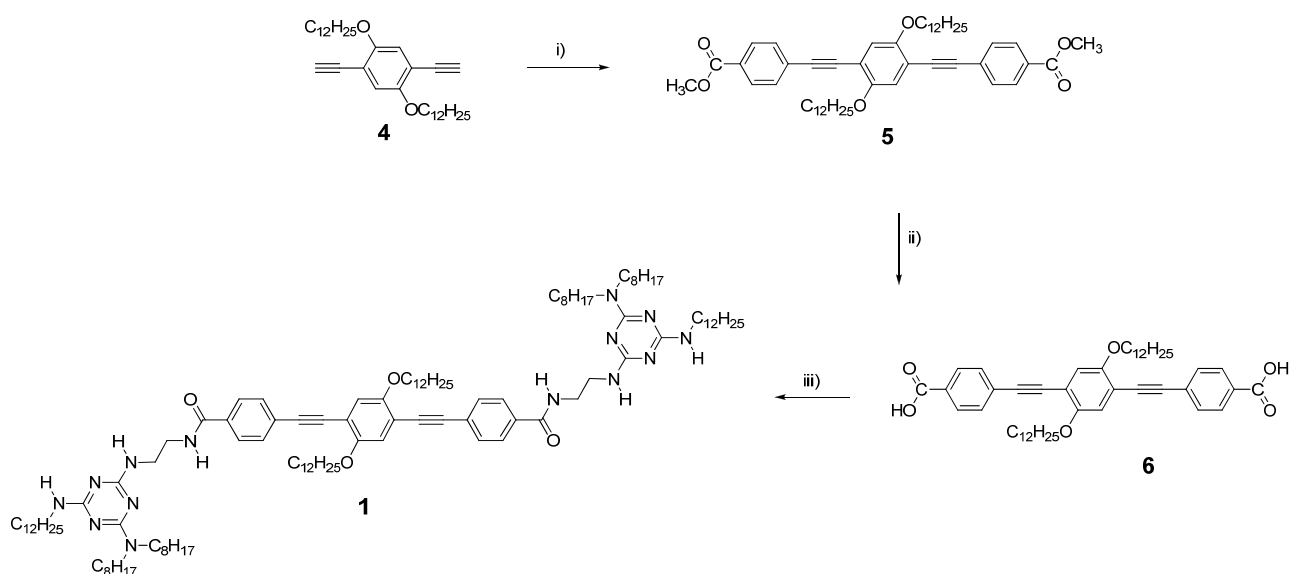
Scheme S1 outlines the synthesis of bismelamine **3** and scheme S2 describes the synthesis of melamine linked OPE **1**. The bisethynyl derivative **4** was prepared from the reaction of 1,4-bis(dodecyloxy)-2,5-diiodobenzene with trimethylsilyl acetylene.^{S1} The synthesis was started from 1,4-bis(dodecyloxy)-2,5-diethynylbenzene. Compound **1** was obtained by the reaction of **6** with bismelamine (**3**).

Scheme S1



Reagents and Conditions: i) $C_{12}H_{25}NH_2$, DIPEA (N, N-Diisopropylethylamine), 8h, 4 °C; ii) $(C_8H_{17})_2N$, DIPEA, 8h, RT; iii) ethylenediamine, DIPEA, Reflux, 12 h

Scheme S2



Reagents and Conditions: i) 4-Iodobenzoate, Pd(PPh₃)₂Cl₂, CuI, dry TEA, 50 °C, 12 hrs; ii) KOH/MeOH, THF, reflux, 3 hrs; iii) **3**, N-Ethyl-N'-(3-dimethylaminopropyl)-carbodiimide(WSC), DCM, RT, 8 hrs.

Synthesis of dimethyl 4,4'-(2,5-bis(dodecyloxy)-1,4-phenylene)bis(ethyne-2,1-diyl)dibenzoate (5)

To a solution of **4** (0.250 g, 0.500 mmol) in triethylamine (20 mL), Pd(PPh₃)₂Cl₂ (0.082 g, 0.116 mmol), CuI (0.022 g, 0.116 mmol) were added followed by dry THF (5 mL) as the co-solvent. 4-Iodobenzoate (0.262 g, 0.116 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 CH₂Cl₂ as the eluent. The fractions were collected and solvent was removed under reduced pressure. The crude product obtained was further purified by column chromatography (3% EtOAc/Hexane) to give compound **6** as a yellow solid (Yield, 78 %).

¹H NMR (400 MHz, CDCl₃) : δ = 8.03-8.01 (d, *J* = 8 Hz, 4H, aromatic), 7.79-7.75 (d, 4H, aromatic), 7.03-6.99 (d, 2H, aromatic), 4.06-4.02 (m, 4H, OCH₂), 3.97 (s, 6H, OCH₃), 1.87 (m, 6H), 1.55 (m, 8H), 1.37 (m, 22H), 0.87 (m, 10H).

HRMS-FAB: [M]⁺ Calcd for C₅₀H₆₆O₆, 762.49; found:763.01

Synthesis of 4,4'-(2,5-bis(dodecyloxy)-1,4-phenylene)bis(ethyne-2,1-diyl)dibenzoic acid(6)

To a solution of **5** (0.500g, 0.650 mmol) in THF, 20% KOH in methanol was added and refluxed for 3 hours, then it was checked for completion of the reaction. After that the reaction mixture was poured into 10% HCl, the precipitate formed was filtered, dried and used for the next step (Yield, 61 %).

¹H NMR (400 MHz, CDCl₃): δ = 8.05-8.03 (d, J = 8 Hz, 4H, aromatic), 7.60-7.57 (d, J = 8 Hz, 4H, aromatic), 7.03-6.99 (d, 2H, aromatic), 4.04-4.01 (m, 4H, OCH₂), 1.85 (m, 4H), 1.35 (m, 32H), 0.85 (t, 12H)

HRMS-FAB: [M]⁺ Calcd for C₄₈H₆₂O₆, 734.65; found: 734.02

Synthesis of 4'-(2,5-bis(dodecyloxy)-1,4-phenylene)bis(ethyne-2,1-diyl)bis-

(N-(2-(4-(dioctylamino)-6-(dodecylamino)-1,3,5-triazin-2-ylamino)ethyl)benzamide) (1)

To a solution of **6** (0.150 g, 0.205 mmol) and alkyl substituted melamine (0.240 g, 0.428 mmol) in dry DCM, followed by N-Ethyl-N'-(3-dimethylaminopropyl)-carbodiimide(WSC) (0.196 g, 1.024 mmol) dissolved in 30 mL dry DCM was added drop wise in cold condition and then the reaction mixture was stirred at room temperature for 8 hours. The reaction mixture was then checked for completion and poured into water (500 mL) and extracted with dichloromethane. The organic fractions were collected and dried with anhydrous sodium sulphate. The crude product was purified by column chromatography (EtoAc: Hexane) followed by repeated precipitation from methanol (Yield, 53 %).

¹H NMR (400 MHz, CDCl₃): δ = 7.70-7.68 (d, J = 8 Hz, 4H, aromatic), 7.52-7.50 (d, J = 8 Hz, 4H, aromatic), 6.99 (s, 2H, aromatic), 4.96(s, 2H), 4.63 (s, 2H), 4.04(m, 4H, OCH₂), 3.62 (s, 8H), 3.43-3.32 (m, 12H), 1.85-1.82 (m, 5H), 1.54 (m, 24H), 1.25(m, 99H), 0.86(m, 26H).

MALDI-TOF: [M+H]⁺ Calcd for C₁₁₄H₁₉₂N₁₄O₄, 1821.53; found:1822.93

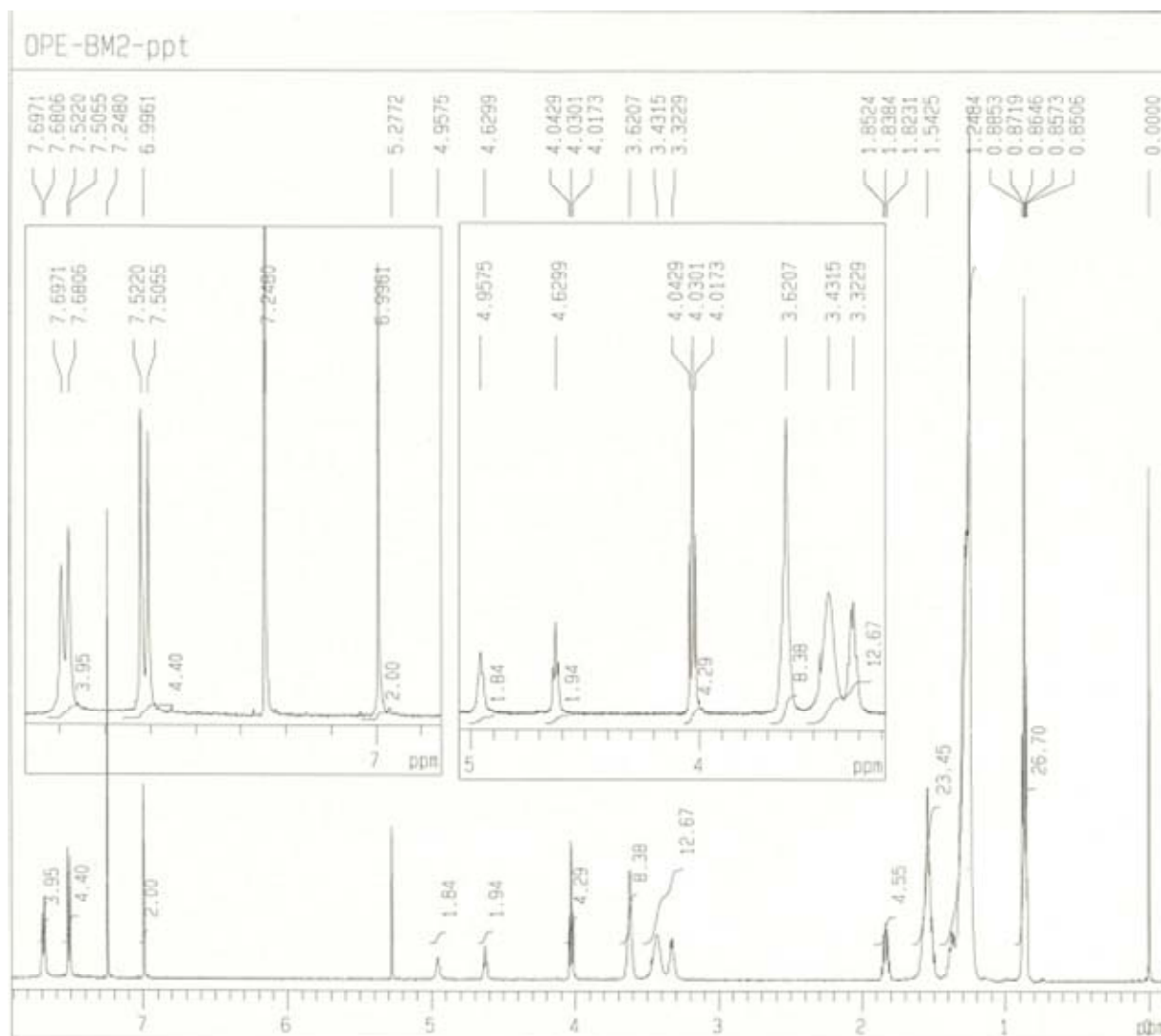


Figure S1. ^1H NMR spectra of **1** in CDCl_3 (400 MHz)

3. Description of experimental techniques

i) Atomic force microscopy (AFM)

AFM images were acquired under ambient conditions using SII Nano Navigator 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. 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. The samples were prepared by drop casting the diluted gel samples (**1** or **1-dCA** in methylcyclohexane) at a concentration of $c = 1 \times 10^{-5}$ M on a freshly cleaved highly oriented pyrolytic graphite (HOPG). The samples were dried under vacuum for 24 hours after the spin coating.

ii) 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 drop casting the diluted gel samples (**1** or **1-dCA** in methylcyclohexane) at a concentration of $c = 1 \times 10^{-5}$ M on to carbon coated copper grids (400 mesh). TEM images were obtained after drying the sample in vacuum for 24 hours.

4. Absorption and fluorescence spectroscopic studies of **1**

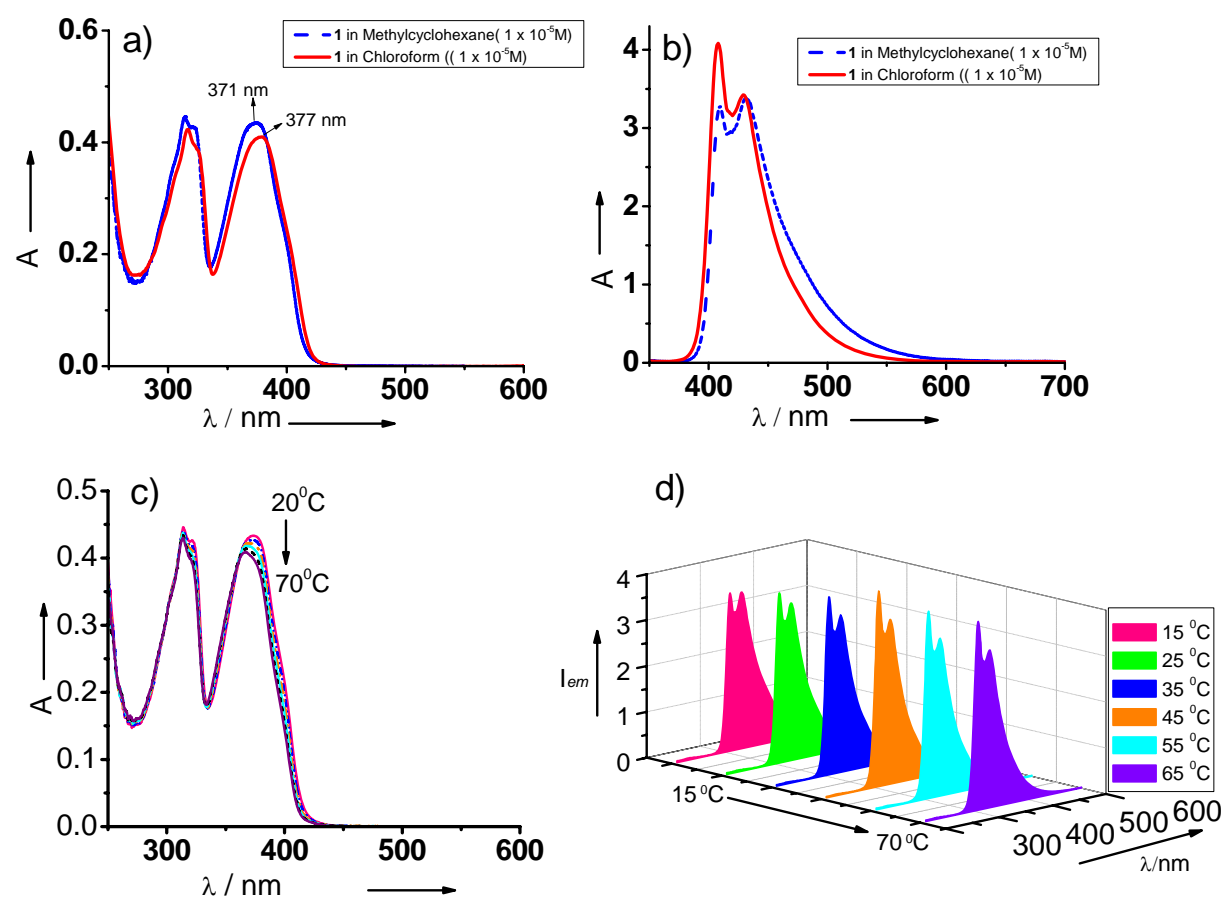


Figure S2. a) Absorption and b) fluorescence spectra of **1** in CHCl_3 (Red curve, $c = 1.0 \times 10^{-5} \text{ M}$) and **1** in and in methylcyclohexane alone (Blue curve, $c = 1.0 \times 10^{-5} \text{ M}$) in chloroform. Variable temperature c) Absorption and d) Fluorescence spectra of **1** ($1 \times 10^{-5} \text{ M}$). Excitation wavelength is 370 nm.

5. IR studies of **1** and **1·dCA**

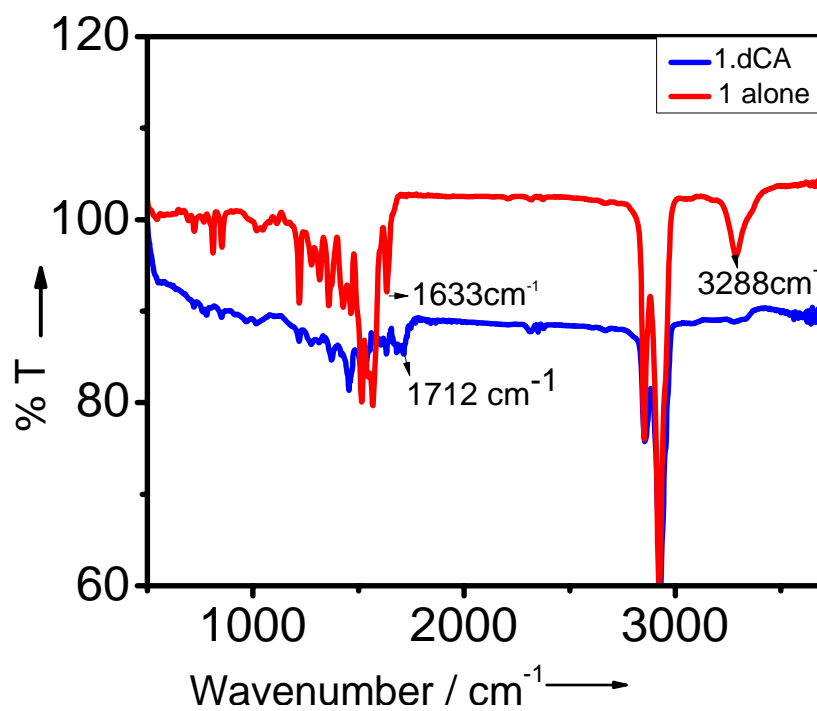


Figure S3. IR spectra of **1** and **1.dCA**

6. References

- [S1] A. Ajayaghosh, R. Varghese, V. K. Praveen, S. Mahesh, *Angew.Chem. Int. Ed.* 2006, 45, 3261 – 3264.