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ORIGINAL ARTICLE

Hydrogen Bonded non-covalent synthesis by reaction of porphyrin appended calix[4]arene with 5,5-diethylbarbituric acid in solution

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Abstract Calix[4]arene, diametrically substituted at the upper rim, with two porphyrin appended melamine units spontaneously form well-defined double rosette in the presence of 5,5-diethylbarbituric acid. This assembly consists of nine components which utilize 36 hydrogen bonds and are quite stable in apolar solvents of up to 10^{-4} M concentration. The formation of assembly between porphyrin appended calix[4]arene and diethylbarbiturate has been broadly studied by UV–visible, fluorescence and ^{1}H NMR spectroscopic techniques. The stoichiometries of proposed aggregates have been analyzed by facile titration of calixarene and barbital. Furthermore, the MALDI-TOF mass measurement is found fully compatible with the observed stoichiometries.

Keywords Non-covalent interaction · Self-assembly · Porphyrin appended calix[4]arene · 5,5-diethylbarbituric acid

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Introduction

The non-covalent synthesis is a dominant synthetic method for the preparation of complex molecular structures to understand the molecular mechanism of multifarious biological reactions in nature and development of newer materials [1, 2]. Multi-hydrogen bond mediated synthesis has been used to understand the photosynthesis, secondary and tertiary structures of biomolecules and formation of newer materials in physical sciences. In particular, hydrogen bonds are considered to be useful for controlling molecular self-assembly due to the reversibility, specificity, directionality, and cooperative strength of this class of interactions [3, 4]. For the last two decades, the supramolecular chemistry has utilized the advantages of self-assembly to control the synthesis of non-covalent structures in solutions [5–7].

The supramolecular organization of functional porphyrin is involved in many important biological systems. The self-assembly of porphyrin derivatives has garnered considerable attention because of their photoelectric properties, as components of nano scale photonic devices and as novel functional materials [8]. Much effort has been applied to the design and synthesis of covalent porphyrinic arrays, analogous to those found in nature for charge separation, electron transport [9, 10], and signal transduction [11–13]. Multi-hydrogen bonds between complementary molecular components are widely used in the fabrication of supramolecular assemblies such as, a linear strand (ribbon or tape) [14–16] and crinkled tape or rosette [17]. The functional porphyrin arrays have been primarily formed by hydrogen bonding [18–21], axial metallo-porphyrin coordination [22–24] and coordination of exocyclic ligands [25–27]. Nevertheless, the other non-covalent interactions, in particular, π–π interaction contribute significantly in the formation of supramolecular porphyrinic structures.

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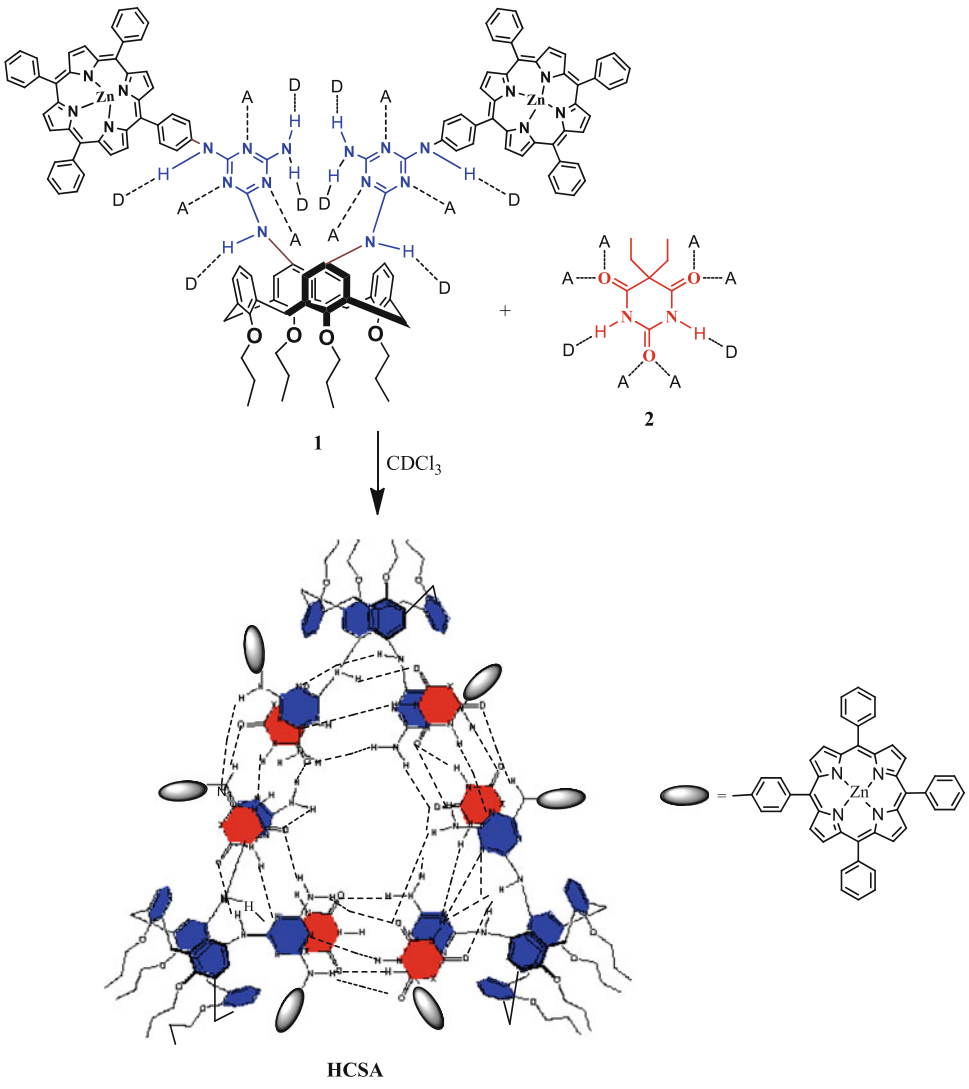
Over the years, calixarenes have been widely used as efficient building blocks in supramolecular chemistry to construct various three-dimensional assembly structures because of their bowl shaped unique constitution and easy functionalization at lower and upper rims [28–30]. A variety of box- or capsules like arrangements with calixarenes were constructed using neutral hydrogen bonds in polar solvent systems [31–33]. In this milieu, it should be pointed out here that the structural diversity at supramolecular level was generated just simply by mixing the various components under thermodynamically controlled conditions.

The rosette formation by three-point intermolecular hydrogen-bonding interactions between substituted triazines and barbituric acid derivatives has been reported previously by us [34]. Inspired by the earlier report by Reindhoudt et al. [35] together with our high interest in self-assembly [36, 37] and non-covalent interactions [38–41], herein we report the synthesis of 5,17-*N,N'*-Bis [4-amino-6-[5-(4′-aminophenyl)porphinatozinc(II)]-1,3,5-triazin-2-yl]diamino-25,26,27,28-tetrakis(propyloxy)calix[4]arene. Further, the formation of hetero-composite self-assembly (HCSA) of synthesized derivative with barbital has been studied using UV–visible, fluorescence, ^{1}H NMR and MALDI-MS techniques in solution. The supramolecular assembly is fashioned due to the development of complementary hydrogen bonds between the donor-acceptor-donor (DAD) arrays of calix[4]arene dimelamine derivative and the acceptor-donor-acceptor (ADA) array of barbituric acid building block (Scheme 1).

Experimental

Materials and methods

All the reagents and chemicals for synthesis were obtained commercially and suitably purified when required. Solvents



Scheme 1 Schematic presentation of hetero-composite self-assembly (HCSA)

used were dried and distilled before use. The solid compounds were dried under vacuum in the presence of P_2O_5. Column chromatography was carried out using silica gel (60–120 mesh and 230–400 mesh) of Spectrochem. The ^1H (300 MHz) and ^{13}C NMR (75 MHz) were recorded on Bruker Avance-300 spectrometer using tetramethylsilane (TMS) as internal standard. The chemical shifts (δ ppm) are referenced to the respective solvents and splitting patterns are designed as *s*(singlet), *d*(doublet), *m*(multiplet), *br*(broad) and *bs*(broad singlet). The UV–visible spectra were recorded on a Perkin-Elmer (Lambda 35) spectrophotometer with a quartz cuvette (path length =1 cm) at 298.2 ± 0.1 K and the absorption maxima (λ_{max}) are expressed in nanometers. The FTIR spectra were recorded on Perkin-Elmer spectrum FT-2000 spectrometer and ν_{max} are expressed in cm^{-1}. Matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF-MS) was performed on a Bruker Ultraflex TOF mass spectrometer equipped with a 337 nm UV nitrogen laser. The matrix used in MALDI-TOF-MS was 2,5-dihydroxybenzoic acid (DHB). The ESI-MS were recorded on LC-TOF (KC-455) mass spectrometer of Waters. Fluorescence spectra were recorded on Shimadzu RF-5301 spectrophotometer.

General methods to study the rosette formation between compounds 1 and 2

All experiments were carried out at 298.2 ± 0.1 K, unless otherwise mentioned. The stock solutions of 5,17-*N,N'*-Bis[4-amino-6-[5-(4′-aminophenyl) porphinatozinc(II)]-1,3,5-triazin-2-yl]diamino-25,26,27,28-tetrakis(propyloxy) calix[4] arene, **1** (2.2 mg, 1.0 μmol) and 5,5-diethylbarbituric acid, **2** (1.84 mg, 10 μmol) were prepared by dissolving in $CHCl_3$ (5 mL and 50 mL) in different volumetric flasks. The 500 μL solution of **1** in chloroform (2.0 mL) was placed in a quartz cell and titrated with increasing amount of **2**. After each addition of 100 μL solution of **2**, UV–visible spectra was recorded and the changes in absorbance and shift in wavelength were measured. A similar procedure was employed for the fluorescent spectroscopic titrations.

In the ^1H NMR experiment, the stock solutions were prepared by dissolving **1** (8.8 mg, 4 μmol) and **2** (3.68 mg, 20 μmol) in 1 and 5 mL of $CDCl_3$ respectively. The 0.5 mL solutions of **1** and **2** were transferred to the separate NMR tubes and the spectra were recorded. Further, the $CDCl_3$ solution of **1** (200 μL) and **2** (400 μL) were mixed together and ^1H NMR spectra were recorded. The changes in each resonance were carefully measured.

In MALDI-TOF-MS experiment, the stock solutions were prepared by dissolving **1** (2.2 mg, 1 μmol) and **2** (1.84 mg, 10 μmol) in $CHCl_3$ (1 and 10 mL respectively). Solutions of **1** (100 μL) and **2** (200 μL) were taken from stock solutions and mixed thoroughly with CH_3CN (1 mL). Later, 1 μL of the resulting mixture was spotted on the MALDI-TOF plate and spectrum was recorded.

Synthesis

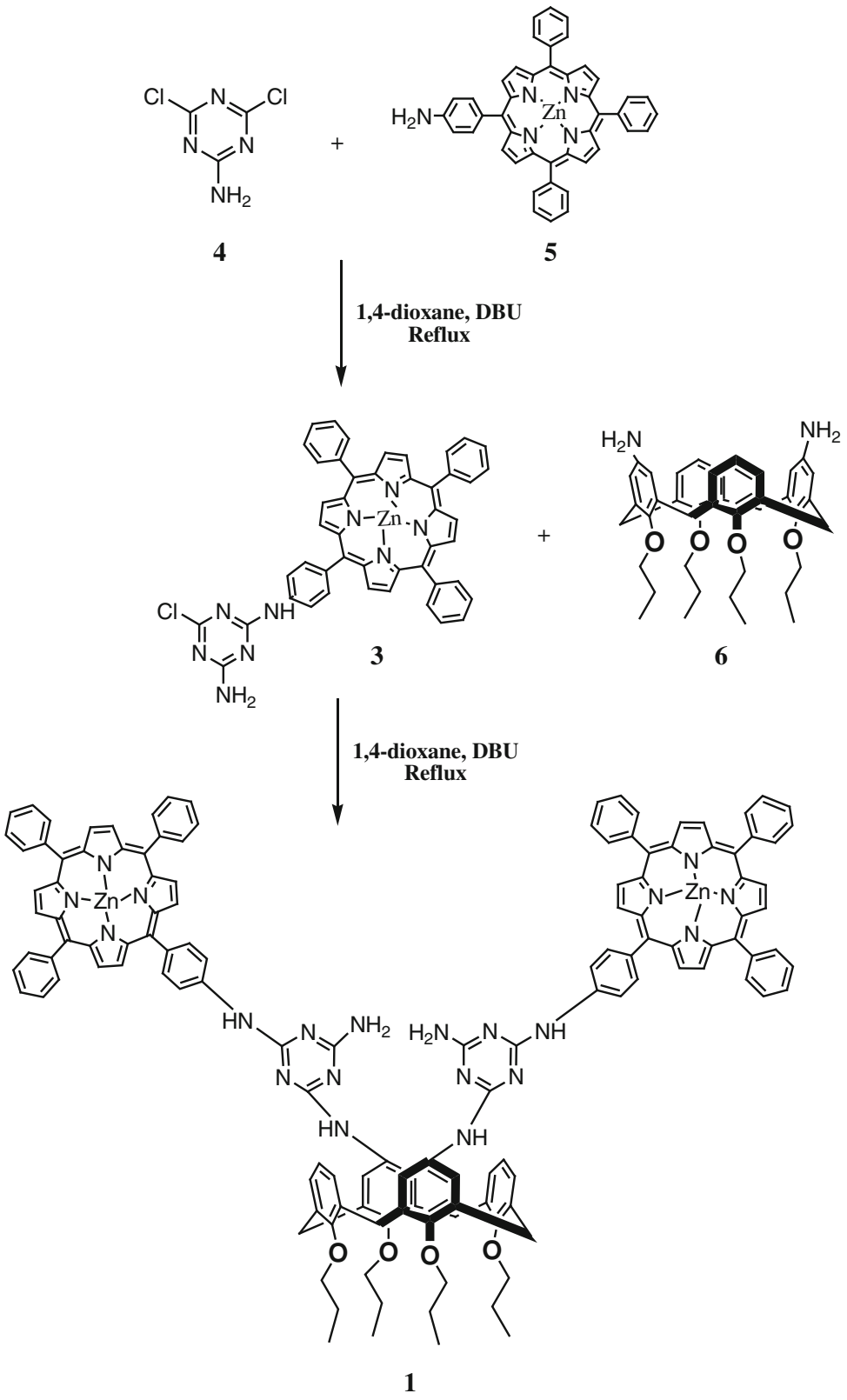
The 5,5-diethylbarbituric acid, **2** was synthesized as described previously [42]. The reaction of cyanuric chloride with ammonia gave 2-amino-4,6-dichloro-1,3,5-triazine which on reaction with 5-(4′-aminophenyl)-10,15,20-triphenylporphyrinatozinc(II) in the presence of DBU in 1,4-dioxane resulted in the formation of 2-amino-4-chloro-6-[5-(4′-aminophenyl)-10,15,20-triphenylporphyrinatozinc(II)]-1,3,5-triazine, **3** along with a dimer in appreciable quantity. Further, the reaction of **3** with 5,17-Diamino-25,26,27,28-tetrapropoxycalix[4]arene **6** in the presence of DBU in 1,4-dioxane resulted in **1** in appreciable yield (Scheme 2).

*2-amino-4,-Chloro-6-[5-(4′-aminophenyl)porphyrinatozinc(II)]-1,3,5-triazine (**3**)*

In a 100 mL round bottomed flask, equipped with an efficient condenser were taken 2-amino-4,6-dichloro-1,3,5-triazine, **4** (13 mg, 0.08 mmol) and 5-(4′-aminophenyl)porphyrinatozinc(II), **5** (80 mg, 0.17 mmol) in dry 1,4-dioxane (30 mL) and thoroughly mixed. To this solution, DBU (30 μL, 0.20 mmol) was added with vigorous stirring and reaction mixture was allowed to reflux at 110 °C for 6 h under nitrogen. After cooling, distilled water (150 mL) was poured into the reaction mixture. The precipitate was filtered on suction pump, washed with water (3 × 30 mL) and air dried. The crude was column chromatographed on silica gel (60–120 mesh). The elution of column with chloroform: petroleum ether (1:4, v/v) afforded monomer **3** and dimer in appreciable yields. 32 mg, 42 %; UV–Visible (λ_{max}, $CHCl_3$, log ε): 416 (2.9), 545 (1.56), 582 (0.084); IR ν_{max}, (Nujol)/cm^{-1}: 3342, 3076, 2854, 1598, 1512, 1487, 1440, 1344, 1296, 1200, 1172, 1104, 1073, 989, 862, 843, 792, 747, 715, 702, 654; ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 8.96 (s, 4H, β-pyrrole), 8.80 (d, *J* = 5.2 Hz, 2H, β-pyrrole), 8.67 (d, *J* = 5.3 Hz, 2H, β-pyrrole), 8.50 (d, *J* = 8.1 Hz, 2H, phenyl), 8.22 (d, *J* = 8.1 Hz, 2H, phenyl), 8.10 (d, *J* = 8.1 Hz, 6H, phenyl), 7.87–7.95 (m, 9H, phenyl), 7.78 (br, 1H, NH), 4.36 (s, 2H, NH_2); ESI–MS (m/z, positive ion): 842.2009 $[M(Cl^{35})+Na]^+$ (100 %), 844.5614 $[M(Cl^{37})+Na]^+$ (33 %).

Dimer: 48 mg, 50 %; UV-Visible (λ_{max}, $CHCl_3$, log ε): 419 (4.42), 548 (3.31), 587 (2.32); ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 8.98 (d, *J* = 5 Hz, 4H, β-pyrrole), 8.96 (s, 8H, β-pyrrole), 8.84 (d, *J* = 5 Hz, 4H, β-pyrrole), 8.64 (d, *J* = 8 Hz, 4H, phenyl), 8.41 (d, *J* = 8 Hz, 4H, phenyl), 8.22 (m, 12H, o-phenyl), 7.77 (m, 18H, m- and p-phenyl), 7.75 (s, broad 2H, -NH-), 4.21 (s, 2H, amino).; ESI-MS (m/z, positive ion):1501.3534 $[M^+Na]^+$

Scheme 2 Synthesis of bisporphyrin-melamine appended calix[4]arene **1**



*Synthesis of 5,17-N,N'-Bis[4-amino-6-[5-(4′-aminophenyl) porphinatozinc(II)]-1,3,5-triazin-2-yl]diamino-25,26,27, 28-tetrakis(propyloxy)calix[4]arene (**1**)*

A solution of 2-amino-4,-Chloro-6-[5-(4′-aminophenyl)porphinatozinc(II)]-1,3,5-triazine, **3** (163 mg, 0.2 mmol) and 5,17-diamino-25,26,27,28-tetrakis(propyloxy)calix[4]arene, **6** (63 mg, 0.1 mmol) in THF (50 mL) was refluxed for 16 h in the presence of DBU (2 equiv). After completion of reaction, the mixture was evaporated to dryness. The residue so obtained was dissolved in CH_2Cl_2 (50 mL), washed with H_2O (3 × 25 mL) followed by brine (25 mL) and dried over anhydrous Na_2SO_4. The compound was purified by column chromatography on silica gel (60-120 mesh). Elution of column with chloroform: methanol (95:5, v/v) gave porphyrin appended calix[4]arene, **1** as purple solid. Yield: 136 mg, 62 %; UV–Visible (λ_{max}, $CHCl_3$, log ε): 421 (1.24), 542 (0.86), 596 (0.62); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 9.38 (s, 8H, β-pyrrole), 8.81 (d, *J* = 4.8 Hz, 2H, β-pyrrole), 8.69 (d, *J* = 4.8 Hz, 4H, β-pyrrole), 8.51 (d, *J* = 7.8 Hz, 4H, phenyl), 8.23 (d, *J* = 7.8 Hz, 4H, phenyl), 8.16 (d, *J* = 8.1 Hz, 12H, phenyl), 7.92 (m, 18H, phenyl), 7.80 (s, 2H, NH), 7.75 (s, 2H, NH), 7.62 (s, 4H, $phenyl_{calix}$), 7.10 (d, *J* = 8.0 Hz, 4H, $phenyl_{calix}$), 6.89 (t, 2H, $phenyl_{calix}$), 4.40 (s, 2H, NH_2), 4.42 (d, 4H, $ArCH_2Ar$), 3.81 (t, 8H, OCH_2), 3.11 (d, 4H, $ArCH_2Ar$), 2.15(m, 8H, CH_2), 0.98 (t, 12H, CH_3); ESI-MS (m/z, positive ion): 2230.7658 $[M+Na]^+$.

Results and discussion

Spectral characterization

The structures of all synthesized derivatives (Scheme 2) were unambiguously confirmed by different spectroscopic techniques. The UV–visible spectrum of **3** exhibited a Soret band at 416 nm and two Q bands at 545 and 582 nm. The ^{1}H NMR spectra of **3** showed three signals resonating at δ 8.80 (d, 2H), 8.68 (d, 2H) and 8.95 ppm (s, 4H) which were assigned to the eight β-pyrrolic protons. Two doublets at δ 8.53 and 8.22 ppm, integrated to two protons each, were assigned to the protons on the phenyl ring attached to the triazine unit. In addition, two broad resonances at δ 7.78 and 4.23 ppm were assigned to the −NH and $-NH_2$ protons respectively. The ESI-MS spectra of **3** showed a sodiated peak at 842.2009 Da $[\mathbf{10Cl^{35}}+Na]^+$ along with an isotopic peak at 844.5614 Da $[\mathbf{10Cl^{37}}+Na]^+$ in 3:1 ratio which indicated the presence of the halogen atom.

The ^{1}H NMR spectrum of **1** showed two broad resonances at δ 7.70 and 7.80 ppm for different NHs while a signal at δ 4.40 ppm was assigned due to free NH_2 protons. Interestingly, the phenyl protons of calixarene scaffold appeared upfield relative to other phenyl protons. Furthermore, the distereotropic protons of methylene bridge appeared as two doublets resonating at δ 4.5 and 3.1 ppm, indicative of the cone conformation of calix[4]arene. The remaining signals for sixteen β-pyrrolic protons and the propyl chain appeared as usual and were assigned with ease. The ESI mass spectrum of **1** gave singly charged, mono-sodiated peak at 2230.7651 Da for $[M+Na]^+$.

UV–visible and Fluorescence spectroscopy

The assembly pattern of porphyrin appended calix[4]arene, **1** with barbital, **2** was initially studied by UV–Visible spectroscopy, the most appropriate technique to study the porphyrin-based systems. The UV–visible spectrum of **1** exhibits a characteristic Soret band, corresponding to the porphyrin B transition, at 421 nm. The gradual addition of **2** (2×10^{-5} to 2×10^{-4} M) to the solution of **1** (~2×10^{-4} M) resulted in pronounced UV–visible spectral changes. Specifically, upon successive addition of aliquots of **2** to the solution of **1**, the Soret band at 421 nm progressively decreased and experienced a bathochromic shift by 2–4 nm together with consistent broadening. The analogous bathochromic shift (~3–4 nm) and broadening was also recognized in visible bands, corresponding to the Q transitions, of the porphyrins. At the end point of titration, the soret band get splitted and

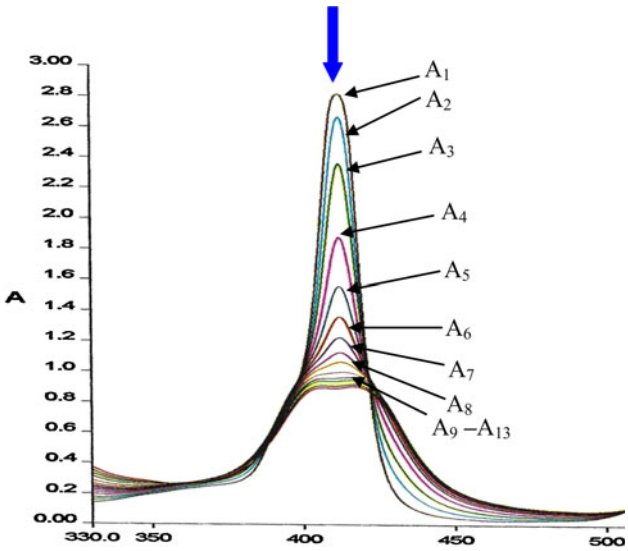


Fig. 1 Study of rosette formation by electronic transition spectra; $\mathbf{A_1}$ = **1** (2×10^{-4} M); $\mathbf{A_2}$ = **1** (2×10^{-4} M) and **2** (0.2×10^{-4} M); $\mathbf{A_3}$ = **1** (1.98×10^{-4} M) and **2** (0.39×10^{-4} M); $\mathbf{A_4}$ = **1** (1.97×10^{-4} M) and **2** (0.59×10^{-4} M); $\mathbf{A_5}$ = **1** (1.97×10^{-4} M) and **2** (0.78×10^{-4} M); $\mathbf{A_6}$ = **1** (1.96×10^{-4} M) and **2** (0.98×10^{-4} M); $\mathbf{A_7}$ = **1** (1.96×10^{-4} M) and **2** (1.17×10^{-4} M); $\mathbf{A_8}$ = **1** (1.95×10^{-4} M) and **2** (1.38×10^{-4} M); $\mathbf{A_9}$ = **1** (1.95×10^{-4} M) and **2** (1.57×10^{-4} M); $\mathbf{A_{10}}$ = **1** (1.94×10^{-4} M) and **2** (1.77×10^{-4} M); $\mathbf{A_{11}}$ = **1** (1.94×10^{-4} M) and **2** (1.96×10^{-4} M) $\mathbf{A_{12}}$ = **1** (1.93×10^{-4} M) and **2** (2.16×10^{-4} M); $\mathbf{A_{13}}$ = **1** (1.93×10^{-4} M) and **2** (2.36×10^{-4} M)

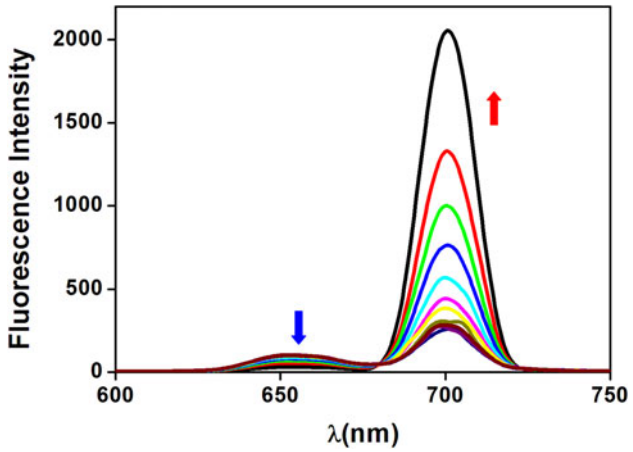


Fig. 2 Fluorescence spectroscopic titrations of **1** (2×10^{-4} M) with 5,5-diethylbarbituric acid **2** (2×10^{-5} M) at 298 K

broadened into two minor but observable peaks at 417 and 423 nm (Fig. 1), a 'hallmark' for self-assembly between two components [43]. It is reasonable because the rotational conformations of **1** are restricted to an eclipsed state such that the effective cross-section per porphyrin is significantly reduced. The binding stoichiometry between two components was determined by Job's method and the assembly showed a 1:2 binding pattern.

Spectrofluorometry is another important tool for the studies of aggregated porphyrins in solutions and accordingly used in our studies as well. In particular, the fluorescence spectrum of **1** (2×10^{-4} M) in $CHCl_3$ showed a characteristic fluorescent peak at 665 nm. Upon addition of aliquots of **2** (2×10^{-5} M) to the solution of **1**, the fluorescence peak decreased with the concomitant formation of new peak at 700 nm (Fig. 2). The significant bathocromic

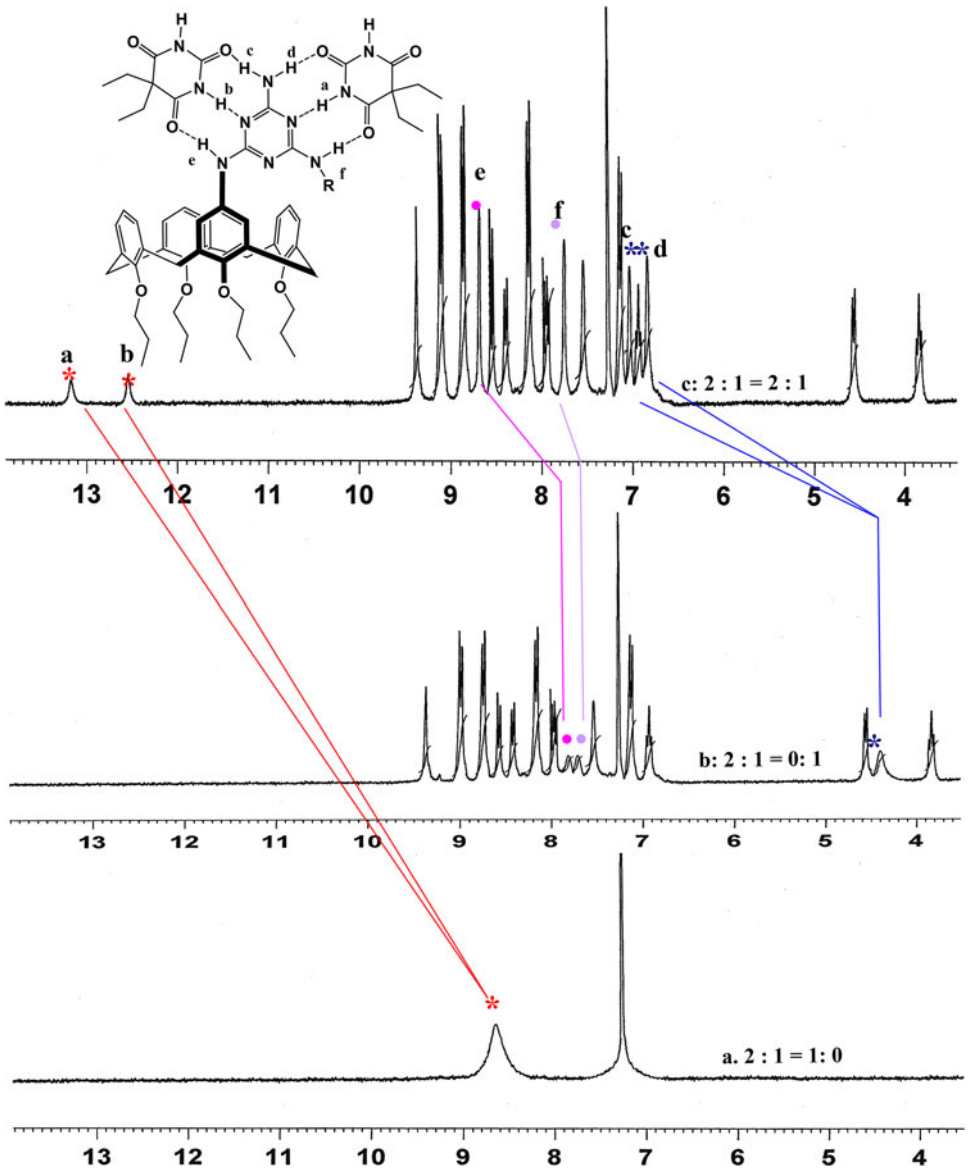


Fig. 3 ^{1}H NMR spectra of **a** 5,5-diethylbarbturic acid **2**, **b** bisporphyrinmelamine appended calix[4]arene **1** and **c** after mixing 1:2 molar solution of **1** and **2**

shifting ($\sim$ 35 nm) as well as a 20 fold increase in the intensity of new peak at the end point of the titration clearly indicated the formation of super structure (the proposed cyclic motifs) between porphyrin appended calix[4]arene and barbiturates.

^{1}H NMR spectroscopy

The ^{1}H NMR spectroscopy can provide a means of monitoring the homo and hetero-composite hydrogen bonded self-assembly of variety of supramolecular architectures. In this context, the doubly rosette formation with calixarene scaffold has been conveniently characterized by ^{1}H NMR spectroscopy [44]. Accordingly, $CDCl_3$ solution of **2** (4 mM) was titrated against $CDCl_3$ solution of **1** (2 mM) at room temperature.

Upon the addition of two equivalents of **2** into the $CDCl_3$ solution of **1**, two new signals originated at δ 12.8 (**a**) and 13.2 (**b**) ppm which were easily assigned to the hydrogen bonded NH protons of diethylbarbituric acid, **2**, in the proposed assembly. The appearance of these signals at different chemical shifts in the ^{1}H NMR spectra is the diagnostic for box-like assembly (double rosette) formation [45, 46]. Reasonably, it is due to unsymmetrical substitution of the melamine units. In line with this, the significant downfield shifting of NHs of **2** further indicates the involvement of theses protons in intermolecular hydrogen bonding (Fig. 3). A similar participation in intermolecular hydrogen bonding was also recognized for two NHs of **1** which experienced a downfield shifting from δ 7.62 and 7.75 ppm to 7.82 (**f**) and 8.72 (**e**) ppm respectively.

The careful examination of spectrum of assembly $\mathbf{1}_3{\cdot}\mathbf{2}_6$ in $CDCl_3$ clearly reveals that the assembly exists exclusively as one single conformational isomer (the *D*3 isomer) [47]. It is worth mentioning here that in their earlier research work, Whitesides et al. presented a model rosette motif which is formed by combining melamine, having small substituents, and alkylated cyanuric acid. However, this rosette motif was found quite unstable at the concentration of less than 4.0 mM in chloroform solution [46]. Nevertheless, the our current studies clearly revealed that the new rosettes, assembled from **1** and **2** are more stable relative to the model system and dictate that the large

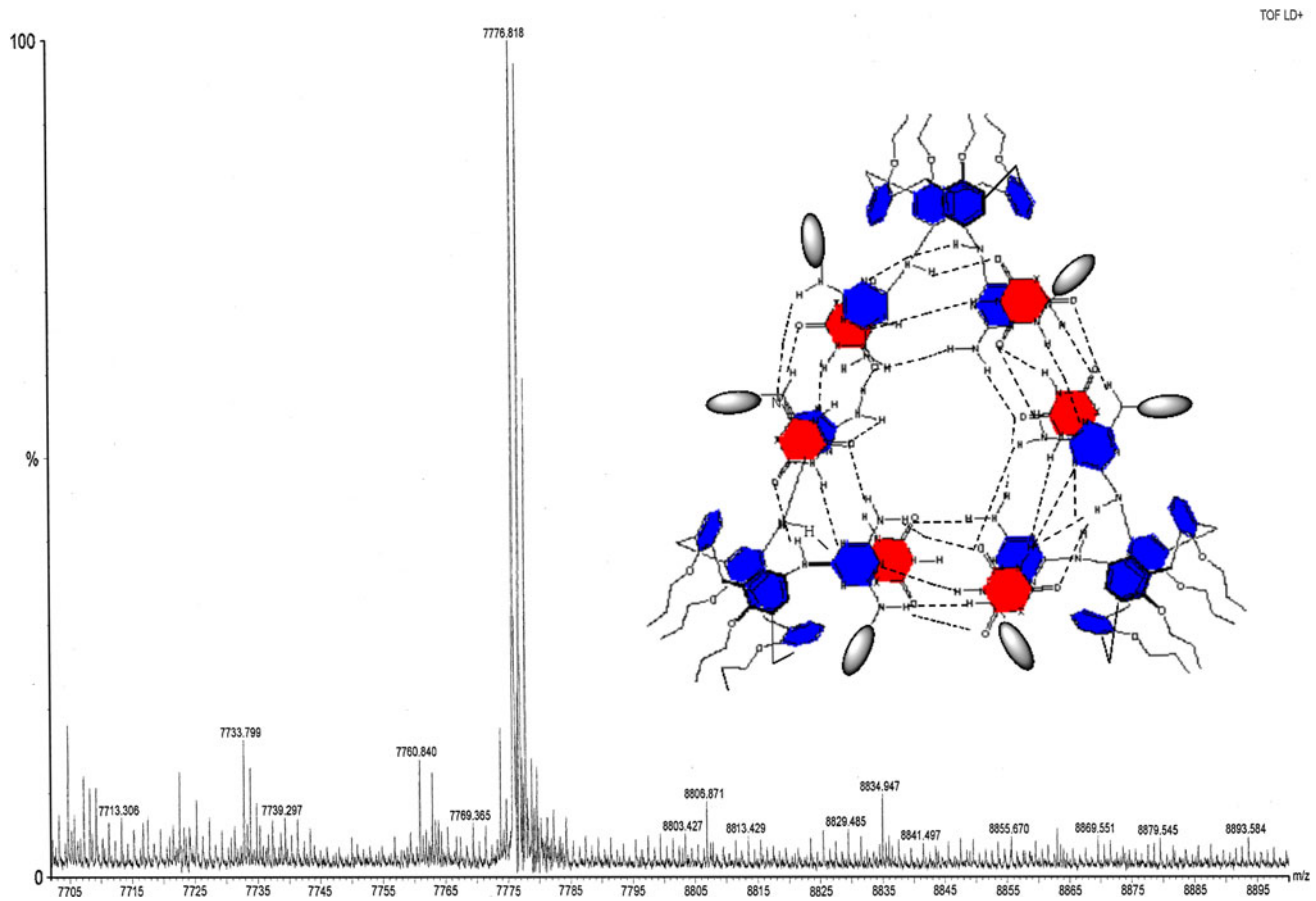


Fig. 4 MALDI-MS spectrum of self-assembled architecture (HCSA)

porphyrin moiety in **1** can facilitate the formation of the rosette motif effectively.

Mass spectrometry

In order to get more insight on assembly formation, finally, the matrix assisted laser desorption ionization–time of flight–mass spectrometry (MALDI–TOF–MS) was used. In particular, the MALDI–TOF mass spectra of 5,17-*N,N'*-Bis[4-amino-6-[5-(4′-aminophenyl)porphinatozinc(II)]-1,3,5-triazin-2-yl] diamino-25,26, 27,28-tetrakis(propyloxy)calix[4]arene, **1** and barbital, **2** (1:2) (3.0×10^{-3} mol L^{-1} in $CHCl_3$ and diluted by acetonitrile) gave doubly charged complexation peak. The mass spectrum of self-assembled architecture exhibited a peak at 7776.818 Da which was assigned to $[\mathbf{1_3}.\mathbf{2_6}+2Na]^{2+}$. A monosodiated peak corresponding to 7733.799 Da $[\mathbf{1_3}.\mathbf{2_6}+Na]^{+}$ was also observed in MALDI–TOF (Fig. 4). The measured *m/z* values were found in good agreement with the calculated mass.

Conclusions

In conclusion, doubly rosette formation ($\mathbf{1_3}.\mathbf{2_6}$) between three moles of 5,17-*N,N'*-Bis[4-amino-6-[5-(4′-aminophenyl)porphinatozinc(II)]-1,3,5-triazin-2-yl]diamino-25,26,27,28-tetrakis(propyloxy)calix[4]arene **1** and six moles of diethylbarbituric acid **2** has been recognized in solution and adequately characterized by UV–visible, fluorescence and MALDI-MS spectroscopic techniques. The exact binding mode between well-defined aggregates in solution could be determined by ^{1}H NMR spectroscopy with ease. The fact that no higher or lower order oligomers were obtained in mass spectrum clearly suggests that the predominant form under the experimental conditions is indeed (3+6) species.

We have shown that just by simple switching of smaller substituents from melamines or alkylated cyanuric acids to larger and hindered one, for instance porphyrins, the formation of super structures could also changed from tape to cyclic one.

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