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A study on the synthesis, characterization, structural optimization, and conformational behaviors of bromo-substituted pyromelliticdiimidebased [2+2] macrocycle as structural units of covalently linked molecular tubes

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ABSTRACT: Synthesis and structural, photo physical, and conformational behaviors at variable temperature and structural optimization of the pyromellitic diimide-based bromo-substituted [2+2] macrocycles are described. Cyclization of the diamine (3) with dianhydride (4) in THF, followed by dehydration of the resultant amic acids resulted in the isolation of the bromo-substituted [2+2] macrocycle 1 (4.5%). The dynamic temperature-dependent ¹H NMR spectra and MO calculations revealed the presence of two possible conformers for the [2+2] macrocycle 1. The UV/Vis spectrum of 1 reveals the presence of a weak intramolecular CT interaction of electron-withdrawing pyromellitic moiety with the electron-donating hexyloxy-substituted xylyl moiety. The cyclic voltammetric measurement shows two two-electron reversible reduction processes.

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Introduction

Supramolecular structures with spherical and tubular shapes have practical implications in material science and molecular electronics [1]. The discovery of the highest covalent bond containing carbon nanotubes has created a flurry of activity in the design and synthesis of other forms of nanotubes [2]. The tubular structure increases the stability of the molecule by chemical bonding as well as offers synthetic control of the conformations. Encapsulation [3] of atoms or molecules as well as their transportation [4] is also desired in the empty cylindrical cavity of tubular molecules. The tubular molecules known till date are designed by self-assembly, [5] held together by hydrogen bonds, [6] π - π interactions, [7] or van der Waals contacts [8]. We have been investigating a directed and controlled approach for the synthesis of nanotubes held together *via* covalent bonds [9].

Macrocycles with their interesting structures and properties are a promising candidate to build up the supramolecular structure. Till now there exist very little reports in the literature on the covalently linked nanotubes [10] based on macrocycles, presumably due to difficulties in synthesizing suitably tethers macrocyclic precursors and poor solubility of bulkier macrocycles. So, we are interested to incorporate macrocyclic motif into nanotubes framework. For the construction of macrocycles as structural units, we have selected pyromelliticdiimide moiety [11] since this moiety has four connecting sites; two nitrogen atoms for the construction of the macrocycles, and the carbon atoms at the para-positions of the benzene ring for the connection of the macrocycles. In addition to that, pyromelliticdiimide moiety can take the conformation with a deep cavity, in which π -planes of the benzene rings face to the center of the cavity. Pyromelliticdiimides have electron affinity, thus the selective inclusion of an electron-rich guest *via* a charge transfer (**CT**) interaction is also desirable [2, 12]. Furthermore, photo physical and redox properties of pyromelliticdiimide are also interesting and the carbonyl oxygen atoms of the moiety can serve as hydrogen acceptor for the formation of supramolecules [13].

As a part of our continuing effort toward the synthesis of the pyromelliticdiimide-based molecular tube, we aimed to synthesize functionalized macrocycle 1. Synthesis of nanotube can be done by connecting suitable spacer molecules (Sonogashira coupling) with the functionalized pyromelliticdiimide-based macrocycles, followed by connecting the resultant capsule with another macrocycle (Scheme 1). We now report herein the synthesis of bromo-substituted macrocycles as structural units of molecular tubes and their properties, based on the electronic spectra and redox potentials, structural optimization and conformational behavior at variable temperature. The solubility in common organic solvents for attachment of hexyloxy groups to the xylyl moiety will also allow the investigation of electroscopic and electrochemical properties. The introduction of methylene linker between diimide and xylyl moiety should create electron affinity for host-guest chemistry with electronically richer molecules.



Scheme 1. Synthetic strategy toward molecular capsule and tube.

Experimental

Materials and methods

Chemicals were used without further purification unless otherwise, stated. Column chromatography was carried out using Kanto Chemical silica gel 60N. Dry toluene was obtained by refluxing and distillation over CaH₂. Dry THF and Et₂O were prepared according to the literature [14]. The melting point of the product was determined by BUCHI M-565 Melting Point Apparatus. ¹H and ¹³C NMR spectra were recorded using a JEOL ECS-400, ECA-500 or a Bruker AVANCE 600 spectrometer. Chemical shifts are reported (δ -scale) relative to internal tetramethylsilane (TMS). Mass spectra were recorded on a JEOL LMS-HX-110 spectrometer. FAB MS spectra were measured with 3-nitrobenzyl alcohol (NBA) as the matrix. The absorption spectra were recorded using JASCO U-4000 spectrometer. Redox potentials were carried out on a BAS-100B/W electrochemical analyzer. CV measurements were performed using a cell equipped with glassy carbon as the working electrode, platinum wire as the counter electrode, and Ag/AgNO₃ as the reference electrode. All electrochemical measurements were performed under an Ar atmosphere at room temperature in o-dichlorobenzene solution (1 x -4 10 M) containing 0.10 Μ tetra-nbutylammoniumhexafluorophosphate as a supportin electrolyte at a scan rate of 100 mV/s. The ferrocine/ferrocenium (Fc/Fc+) couple was used as an internal standard.



Scheme 2. Synthesis of $Br_4[2+2]$ MC 1.

Preparation and characterization

Synthesis of 1,4-bis(aminomethyl)-2,5bis(hexyloxy)benzene 3: 1,4-Bis(hexyloxy)benzene 3(a): To a mixture of hydroquinone (66.0 g, 0.6 mol) in degassed acetone (1200 mL), were added K_2CO_3 (248.8 g, 1.8 mol) and n-bromohexane (210.0 mL, 1.5 mol). The suspension was then stirred at 80 °C for 3d. The reaction mixture was then allowed to attain the

room temperature and solid was filtered off and washed several times with EtOAc. Solvent was removed under reduced pressure in the rotary evaporator and the crude product was poured into ice cold water (500 mL), extracted with ethyl acetate. The organic extract was washed with saturated brine solution (200 mL). The organic layer was dried over Na₂SO₄, and solvent was removed to get the crude product as a brown solid. It was separated by column chromatography on silica gel with hexane as eluent to get the desired product, 1,4-Bis(hexyloxy)benzene 3(a) (155.0 g, 0.55 mol, 93%)asa colorless solid: mp 41-42 °C; ¹H NMR (CDCl₃, 500 MHz) δ 6.82 (s, 4H), 3.90 (t, J = 6.6 Hz, 4H), 1.75 (quint, J = 7.2 Hz, 4H), 1.45 (quint, J = 7.2 Hz, 4H), 1.33 (quint, J = 3.6 Hz, 8H), 0.90(t, J = 6.6 Hz, 6H); ¹³C NMR (CDCl₃, 125) MHz) δ 153.2, 115.4, 68.6, 31.6, 29.4, 25.7, 22.6, 14.1; HRMS (FAB-MS, NBA-positive) calcd. for $C_{18}H_{30}O_2$ (M^{+}) : 278.2246, found: 278.2254. Anal.Calcd for C₁₈H₃₀O₂: C, 77.65; H, 10.86. Found: C, 76.90; H, 10.78.

1,4-Dibromo-2,5-bis(hexyloxy)benzene 3(b): To a mixture of 1,4-Bis(hexyloxy)benzene (139.0 g, 0.5 mol) and I₂ (1.27 g, 5.0 mmol) in CH₂Cl₂ (800 mL), was added Br₂ (71.3 mL, 1.25 mol) at 0 °C. The mixture was then stirred at room temperature for 12 h. Excess bromine in the reaction mixture was then destroyed by slow addition of saturated aqueous solution of NaOH, until the red color disappears. The mixture was then extracted with CH_2Cl_2 (3 x 200 mL). The organic extract was washed with saturated brine solution (200 mL). The organic layer was dried over Na_2SO_4 , and solvent was removed to get the crude product as a white solid. It was separated by column chromatography on silica gel with hexane as eluent to the desired product, 1,4-Dibromo-2,5get bis(hexyloxy)benzene 3(b) (213.0 g, 0.49 mol, 98%)asa colorless solid: mp 61-62 °C; ¹H NMR $(CDCl_3, 500 \text{ MHz}) \delta 7.08 \text{ (s, 2H)}, 3.94 \text{ (t, } J = 6.6 \text{ Hz},$ 4H), 1.79 (quint, J = 7.2 Hz, 4H), 1.48 (quint, J = 7.2Hz, 4H), 1.33 (quint, J = 3.5 Hz, 8H), 0.90 (t, J = 6.6Hz, 6H); ¹³C NMR (CDCl₃, 125 MHz) δ 149.9, 118.2, 111.0, 70.2, 31.4, 29.0, 25.6, 22.5, 14.0; HRMS (FAB-MS, NBA-positive) calcd. for C₁₈H₂₈O₂Br₂ (M⁺): 434.0456, found: 434.0454. Anal.Calcd

forC₁₈H₂₈O₂Br₂: C, 49. 56; H, 6.47. Found: C, 49.47; H, 6.44.

1, 4-Dicyano-2, 5-bis(hexyloxy)benzene 3(c): A mixture of 1,4-Dibromo-2,5-bis(hexyloxy)benzene (109.0 g, 0.25 mol) and CuCN (89.5 g, 1.0 mol) in DMF (800 mL) was heated at 150 °C for 24 h. The reaction mixture was then allowed to attain the room temperature. Into that mixture was added slowly a solution of FeCl₃.6H₂O (135.0 g, 0.5 mol) in 800 ml 1.6 N HCl and stirred at room temperature for 12 h in a hood with very good ventilation. Solid was filtered off and washed several times with water. Solid was then taken in CH₂Cl₂ (500 mL) and was poured into ice cold water (500 mL), extracted with CH₂Cl₂ (3 x 200 mL). The organic extract was washed with saturated brine solution (200 mL). The organic layer was dried over Na₂SO₄, and solvent was removed to get the crude product as a brown solid. It was separated by column chromatography on silica gel with CH₂Cl₂ as eluent to get the desired product, 1,4-Dicyano-2,5bis(hexyloxy)benzene 3(c) (66.7 g, 0.20 mol, 81%) as a colorless solid: mp 150-151 °C; ¹H NMR (CDCl₃, 500 MHz) δ 7.13 (s, 2H), 4.03 (t, J = 6.6 Hz, 4H), 1.84 (quint, J = 7.2 Hz, 4H), 1.48 (quint, J = 7.2 Hz, 4H), 1.33 (quint, J = 3.5 Hz, 8H), 0.91 (t, J = 6.6 Hz, 6H); ¹³C NMR (CDCl₃, 125 MHz) δ 154.1, 116.8, 114.9, 106.9, 70.0, 31.3, 28.7, 25.4, 22.4, 14.0; (FAB-MS, HRMS NBA-positive) calcd. for $C_{20}H_{28}O_2N_2$ (M⁺): 328.2151, found: 328.2152. Anal.Calcd forC₂₀H₂₈O₂N₂: C, 73. 14; H, 8.59; N, 8.53. Found: C, 72. 96; H, 8.53; N, 8.56.

1,4- Bis(aminomethyl)-2,5-bis(hexyloxy)benzene 3: To а solution 1,4-Dicyano-2,5of bis(hexyloxy)benzene(3.38 g, 0.01 mol) in dry toluene (100 mL) was added diisobutylaluminium hydride (1.0 M toluene solution, 50 mL, 0.05 mol) at room temperature. The mixture was then heated at 100 °C for 4 h. The reaction mixture was then allowed to attain the room temperature and poured to an ice-cold aqueous solution of KF (9.5 g, 0.25 mol). Solid was filtered off and washed several times with Et₂O. The filtrate was extracted with Et₂O (3 x 50 mL). The organic extract was washed with saturated brine solution (200 mL). The organic layer was dried over Na₂SO₄, and solvent was removed to get the crude product as a yellow liquid (3.22 g, 9.6 mmol, 96%). It was then used for next cyclization reaction without further purification. ¹H NMR (CDCl₃, 500 MHz) δ 6.77 (s, 2H), 3.95 (t, *J* = 6.6 Hz, 4H), 3.78 (s, 4H), 1.78 (quint, *J* = 7.2 Hz, 4H), 1.61 (bs, 4H), 1.46 (quint, *J* = 7.2 Hz, 4H), 1.34 (quint, *J* = 3.5 Hz, 8H), 0.90 (t, *J* = 7.2 Hz, 6H); ¹³C NMR (CDCl₃, 125 MHz) δ 150.5, 130.9, 112.4, 68.5, 42.7, 31.5, 29.4, 25.8, 22.5, 13.9; HRMS (FAB-MS, NBA-positive) calcd. for C₂₀H₃₆O₂N₂ (M⁺): 336.2777, found: 336.2777.

3, 6-Dibromodurene 4 (a): A solution of durene 12 (26.8 g, 200.0 mmol) and I_2 (1.0 g, 4.0 mmol) in CH₂Cl₂ (350 mL) were added Br₂ (26 mL, 500.0 mmol) in CH₂Cl₂ (50 mL) at room temperature. After adding the Br₂, the reaction mixture was refluxed for overnight. After cooling to room temperature, the mixture was quenched saturated aqueous NaHCO₃ to color disappearing, and the resultant mixture was extracted with CH_2Cl_2 (20 mL \times 3) and the combined extracts were dried over sodium sulfate and filtered. The solutions evaporated to leave a residue, which was recrystallized from CH₂Cl₂-methanol (5:1) to give 3, 6-Dibromodurenecolorless needle crystals; yield 51.4 g (88%); mp 208-209 °C; ¹H NMR (CDCl₃, 600 MHz) δ 2.48 (s, 12H); ¹³C NMR (CDCl₃, 150 MHz) δ 22.27, 128.13, 135.03; FAB-MS (NBA, positive): m/z calcd for C₁₀H₁₂Br₂N₂ 292.00 (M⁺), found 292.01 (M^+), peak ration of ⁷⁹Br and ⁸¹Br isotopes (1 : 1).

Synthesis of 3,6-dibromo-1,2,4,5-Benzenetetracarboxylic acid 4 (b): To a 3L four necked round bottom flask fitted with refluxed condenser and mechanical stirrer, were added 1,4dibromotetramethylbenzene (30g, 102.73 mmol), pridine (1250 ml) and water (180 ml). The reaction mixture was heated at 100°C with constant stirring. To this reaction mixture, KMnO₄ (82.5g, 522.15 mmol) was added in small aliquots in 45 min. After complete addition the reaction mixture was refluxed for next 5h. The hot solution was filtered to remove MnO₂ from reaction mixture and the solvent concentration of at vacuo. To the residual solid were added water (1500 ml) and NaOH (70 g). The reaction mixture was stirred and heated at 100°C. KMnO₄ (82.5 g, 522.15 mmol) was added in small aliquots in 1h. The reaction mixture was refluxed for next 5h. Excess of KMnO₄ was destroyed by caution addition of ethanol (60ml). The hot solution was filtered to separate MnO₂. The filtrate was acidified with aqueous HCl (5N). After solvent was removed under reduced pressure, colorless compound obtained. Acetone was added to this solution and stirred for 40 min. It was filtered to remove NaCl and filtrate was concentrated under reduced pressure to obtain 20g (47%) product. The colorless powder from acetone .¹³C-NMR (Acetone-d₆, 75 MHz) δ = 116.41m (CBr), 138.39 (C-COOH), 165.87 (C=O).

3, 6-Dibromopyromellitic dianhydride 4: Though preparation of this compound is already known, we here describe our own procedure. A suspension of 3, 6-dibromopyromellitic acid (4.12 g, 0.01 mol) in Ac₂O (19 mL) was heated at 100 °C for 2 h. The reaction mixture was allowed to attain the room temperature slowly and further cooled by dipping the flask in ice. The precipitate was collected by filtration and was washed with dry Et₂O (3 x 10 ml). The solid was dried under reduced pressure at 90 °C to obtain crude product as a white solid (2.63 g, 7.0 mmol, 70%). It was then used for next cyclization reaction without further purification: mp > 300 °C; 13 C NMR (CDCl₃, 125 MHz) & 158.5, 138.3, 116.8; HRMS (FAB-MS, NBA-positive) calcd. for $C_{10}H_6Br_2$ (M⁺): 373.8062, found: 373.8047. Anal.Calcd for C₁₀H₆Br₂: C, 31. 95. Found: C, 31.91.

Tetrabromo [2+2] pyromelliticdiimide-based macrocycle 1: To 100 mL dry THF were simultaneously added a solution of the diamine 3 (3.38 g, 0.01 mol) and the dianhydride 4 (3.76 g, 0.01 mol) both in dry THF (200 mL) over a period of 4 h at 60 °C. The mixture was then heated at 70 °C for 24 h. The reaction mixture was then allowed to attain room temperature and solvent was completely removed under reduced pressure to get a yellow color mixture of amic acids. The solid was taken in a mixture of Ac₂O (50.0 ml) and NaOAc (8.2 g, 0.1 mol) and heated at 110 °C for 2 h. The reaction mixture was then allowed to attain the room temperature and poured to water. The resultant solid was filtered off and washed with water and then air-dried. The collected precipitate was extracted continuously with CH₂Cl₂ (400 mL). The solvent was removed to get the crude product as red solid. It was separated by column chromatography on silica gel with hexane-EtOAc (20:1, v/v) as the eluent and followed by separation with recyclic HPLC (GPC column, CHCl₃) to obtain the [2+2] macrocycle **1** (0.20 g, 0.148 mmol, 4.5%) as a red solid: mp 214-215 °C. ¹H NMR (CDCl₃, 600 MHz) δ 6.76 (s, 2H), 4.78 (s, 2H), 3.78 (t, *J* = 6.3 Hz, 4H), 1.72 (quint, *J* = 7.2 Hz, 4H), 1.42 (quint, *J* = 7.2 Hz, 4H), 1.28 (quint, *J* = 3.5 Hz, 8H), 0.84 (t, *J* = 7.2 Hz, 6H); ¹³C NMR (CDCl₃, 150 MHz) δ 161.4, 149.6, 135.2, 123.8, 114.9, 113.4, 68.5, 36.3, 31.0, 30.4, 28.6, 24.7, 13.1; HRMS (FAB-MS, NBA-positive) calcd. for C₆₀H₆₄O1₂N₄ Br₄ (M⁺): 1348.1254, found: 1348.1329.

Computational methods

All calculations were done with the Gaussian software package. After computing the optimized structure, the molecular orbital calculations were conducted using B3LYP/6-31G (d) level of theory for analyzing the HOMO–LUMO energies. The HF/6-31G* minimization of [2+2] cp was carried out as well. The distances between two benzene rings and two pyromelliticdiimide motifs are 9.859A° and 7.026 A°, respectively. The cavity size in [2+2] macrocycle, which is suitable for inclusion of pyrrol and anisole, toluene, xylene and so on as per6-31G minimization by using Gaussian program.

Results and Discussion

The temperature-dependent ¹H NMR spectra of **1** in CD_2Cl_2 show no shifts but a broadening of some signals until -20 °C; however, below -30 °C, a slight shift and coalescence of the signals were observed. These observations are presumably due to the presence of two conformers of **1** (Figure 1). The MO calculations (B3LYP/6-31G (d)) of **1** suggested that *anti*-**1** and *syn*-**1** have similar stability (Figure 2). The HF/6-31G optimized structure [2+2] macrocycle along with cavity size were calculated to understand the types of guest molecules it can accommodate (Figure 4).



Figure 1. Possible *syn* - and *anti*-conformers of Br₄



Figure 2. Optimized structures of 1 (*syn*-1, left and *anti*-1, right) by B3LYP/6-31G*(d) level of MO calculations



Figure 3. HOMO (left) and LUMO (right) orbitals of the macrocycle **1** by B3LYP/6-31G*(d) level of theory



Figure 4.HF/6-31G*optimized structure of [2+2] MC 1

VT ¹H NMR spectrum behavior of Br_4 [2+2] MC 1 in CD₂Cl₂ and the existence of two conformers along with the comparable thermodynamic stability of the two isomers is expected. Two conformational isomers, syn and anti, are possible (Figure 1) in relation to the overlapping mode of the facing bis(hexyloxy)benzene moieties. The benzylic proton signal at 4.86 ppm ($H_g+H_{g'}$) appears as a broad singlet at room temperature in CD₂Cl₂, indicating free rotation of the bis(hexyloxy)benzene moieties between synand anti-conformers (Figure 5). The sharp singlet of the aromatic proton signals (H_h and $H_{h'}$) of the bis(hexyloxy)benzene moiety of 1 also supports rapid rotation of the bis(hexyloxy)benzene moieties at room temperature (Figure 6). The singlet due to the benzylic proton at 4.86 ppm ($H_g+H_{g'}$) at room temperature significantly broadens as the temperature lowers, and then the signal begins to split and becomes two double doublets below -70 °C, indicating that the rotation of the bis(hexyloxy)benzene moiety is frozen. As a result, two conformers exist and the comparable thermodynamic stability of the two isomers is expected.



Figure 5. The temperature-dependent ¹H NMR spectra (recorded at rt to -90°C) of Br_4 [2+2] MC **1** in CD_2Cl_2



Figure 6. The temperature-dependent ¹H NMR spectra of the benzylic proton signal of Br_4 [2+2] MC **1** in CD_2Cl_2

UV/Vis spectrum of the macrocycle **1** was measured in CHCl₃. The spectrum shows three absorption maxima (λ_{max}) over 250 nm [303.5 (loge) 0.88), 352.5 (loge) 0.63), 367.5 nm (loge) 0.68)] (Figure 7 and Table 1). The absorption bands at 352.5 and 367.5 nm were presumably due to short and long axis polarized π - π * transitions at the pyromellitic moiety. For long axis polarized π - π * transition, the corresponding absorption coefficient 0.68) is slightly higher than that of the short axis polarized π - π * transition (0.63). The UV/Vis spectrum over 380 nm (Figure 7) shows the tail of the longer absorption band in 1. This tail is assigned for out-of-plane polarized n- π^* transition (390-410 nm), enter into the visible region (> 400 nm). This may be due to a weak intramolecular CT interaction of electron-withdrawing pyromelliticdiimide moiety with the electron-donating hexyloxy-substituted xylyl moiety. The intramolecular CT interaction is also supported by MO calculations (B3LYP/6-31G*). The calculation showed the HO-MO and LUMO orbitals of 1 to be localized in the xylyl andpyromelliticdiimide moieties, respectively, through the methylene linker (Figure 3).

Table 1

UV/Vis absorption bands of the macrocycles 1 and their parent compounds in CHCl₃

	λ_{\max} (loge)
Br ₄ [2+2] 1	303.5 (0.88), 352.5 (0.63), 367.5 (0.68)
[2+2]	307 (0.79)
- 2.5 2.5 1.5 1.5 0.5 250	Br4[2+2] [2+2] 300 350 400 450 500

Wavelength / nm

Figure 7. UV/Vis absorption bands of **MC 1** and their parent compounds in CHCl₃

The cyclic voltammetric traces of the macrocycle **1** were recorded in *o*-dichlorobenzene solution with tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte (Figure 8). The macrocycle **1** exhibited first two-electron reduction process, followed by the second two-electron reduction. Each reduction process was split into two waves (Table 2). Pyromelliticdiimide moiety generally shows two reversible one electron reductions. The first and second waves are due to radical anion and dianion species, respectively. The splitting of the first two-electron reduction is due to electronic repulsion between radi-

cal anion and neutral species and then second twoelectron reduction splitting is due to electronic repulsion between radical anion and dianion species.Surprisingly, long distance between two pyromelliticdiimide π -faces (ca. 7.1 Å) has not make barrier for making weak electronic interaction between the radical anion and neutral diimide moiety. The first radical anion for one pyromelliticdiimide moiety increases the electron density on the other diimide moiety. So, another one-electron reduction of the radical anion species become harder compare to the first oneelectron reduction.

Table 2

Reduction potentials for $Br_4[2+2]MC$ in *o*-di chlorobenzene (0.1 mM in *o*-dichlorobenzene; 0.1 M nBu_4NPF_6 supporting electrolyte; scan rate 100 mVs⁻¹)



Figure 8: Cyclic voltammetric traces and reversible sequential reduction processes of the $Br_4[2+2]MC$ in *o*- dichlorobenzene (0.1 mM in *o*-dichlorobenzene; 0.1 M nBu_4NPF_6 supporting electrolyte; scan rate 100 mVs⁻¹)

Conclusions

Synthesis of the dibromo-substituted [2+2] macrocycle has been accomplished by cyclocondensation of corresponding diamine with dianhydride. The [2+2] macrocycle is a precursor forcovalently linked nanotubes based on macrocycles. The temperaturedependent ¹H NMR spectra and MO calculations suggested the presence of two possible conformers for the macrocycle. The MO calculations also showed the HOMO and LUMO orbitals of the macrocycle to be localized in the xylyl and pyromelliticdiimide moie-

ties, respectively. The UV/Vis spectrum revealed the presence of a weak intramolecular CT interaction between electron-withdrawing pyromelliticdiimidemoiety with the electron-donating hexyloxy-substituted xylyl moiety. The cyclic voltammetric measurement shows two two-electron reduction processes. Moreover, VT ¹H NMR spectrum behavior of Br₄[2+2] MC 2 in CD_2Cl_2 gives us idea about not only the existence of two conformers but also the comparable thermodynamic stability of the two isomers at lower temperature. These new findings could be applied for the conformational study, free and restricted rotation in a molecule when the NMR- temperature is varied. Our study towards covalently bonded organic nanotubes based on pyromelliticdiimidecyclophane is in progress and the results will be reported soon.

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References

[1] (a) J.-M. Lehn, In Supramolecular Chemistry: Concepts and Perspectives, WILEY-VCH (1995). (b) J.W. Steed, J.L. Atwood, In Supramolecular Chemistry, John Wiley & Sons (2000). (c) D.M. Bassani, Molecular wires get connected, Nature, 480 (2011) 326-327.

[2] (a) P. J. F. Harris, In Carbon Nanotubes and Related Structures: New Materials for the Twenty-First Century, Cambridge University Press (1999). (b) V. Sgarlata V.G. Organo, D.M. Rudkevich, A procedure for filling calixarene nanotubes, Chem Commun. (2005) 5630-5632.

[3] (a) A. Harada, J. Li, M. Kamachi, Synthesis of a tubular polymer from threaded cyclodextrins, Nature 364 (1993) 516-518. (b) V.G. Organo, A.V. Leontiev, V. Sgarlata, H.V.R Dias, D.M.

Rudkevich, Supramolecular features of calixarenebased synthetic nanotubes, Angew. Chem. Int. Ed. 44 (2005) 3043-3047. (c) K. Koga, G.T. Gao, H. Tanaka, X.C. Zeng, Formation of ordered ice nanotubes inside carbon nanotubes, Nature 421 (2001) 802-805. (d) O. Vostrowsky, A. Hirsch, Molecular peapods as supramolecular carbon allotropes, Angew. Chem., Int. Ed. 43 (2004) 2326-2329.(e) O.O. Adisa, B.J. Cox, J.M. Hill, Encapsulation of methane molecules into carbon nanotubes, Physica B 406 (2011), 88-93. (f) I. Oueslati, P. Thuery, O. Shkurenko, K. Suwinska, J.M. Harrowfield, R. Abidi, J. Vicens, Calix[4]azacrowns: selfassembly and effect of chain length and O-alkylation on their metal ion-binding properties, Tetrahedron 63 (2007) 62-70.

[4] For guest transport in organic solids, see: (a) J.L. Atwood, L.J. Barbour, A. Jerga, B.L. Schottel, Guest transport in a nonporous organic solid via dynamic van der Waals cooperativity, Science 298 (2002) 1000-1002. (b) O. Ohmori, M. Kawano, M. Fujita, Crystal-to-crystal guest exchange of large organic molecules within a 3d coordination network, J. Am. Chem. Soc. 126 (2004) 16292-16293.(c) S.J. Dalgarno, P.K. Thallapally, L.J. Barbour, J.L. Atwood, Engineering void space in organic van der Waals crystals: calixarenes lead the way, Chem. Soc. Rev. 36 (2007) 236-245.

[5] For self-assembling nanotubes, see: (a) M.R. Ghadiri, J.R. Granja, R.A. Milligan, D.E. McRee, N.Khazanovich, Self-assembling organic nanotubes based on a cyclic peptide architecture, Nature 366 (1993) 324-327. (b) M.R. Ghadiri, J.R. Granja, L.K.Buehler, Artificial transmembrane ion channels from self-assembling peptide nanotubes, Nature 369 (1994) 301-304. (c) J.R. Granja, M.R. Ghadiri, Channel-Mediated Transport of Glucose across Lipid Bilayers, J. Am. Chem. Soc. 116 (1994) 10785-10786. (d) D.T. Bong, T.D. Clark, J.R. Granja, M.R. Ghadiri, Self-assembling organic nanotubes, Angew. Chem. Int. Ed. 40 (2001), 988-1011.(e) R.S. Lokey, B.L. Iverson, Synthetic molecules that fold into a pleated secondary structure in solution, Nature, 375 (1995) 303-305.

[6] For reviews of hydrogen-bonded assemblies, see: (a) M.M. Conn, J.Jr. Rebek, Self-Assembling Capsules, Chem. Rev. 97 (1997) 1647-1668. (b) J. Jr. Rebek, Reversible encapsulation and its consequences

in solution, Acc. Chem. Res. 32 (1999) 278-286. (c) J.Jr. Rebek, Host–guest chemistry of calixarene capsules, Chem. Commun. (2000) 637-643. (d) L.M. Greig, D. Philp, Applying biological principles to the assembly and selection of synthetic superstructures, Chem. Soc. Rev. 30 (2001) 287-302. (e) L.J. Prins, D. Reinhoudt, P. Timmerman, Noncovalent Synthesis Using Hydrogen Bonding, Angew. Chem., Int. Ed.40 (2001) 2382-2426.

[7] (a) K. Balakrishnan, A. Datar, W. Zhang, X. Yang, T. Naddo, J. Huang, J. Zuo, M. Yen, J.S. Moore, L. Zang, Nanofibril self-assembly of an arylene ethynylene macrocycle, J. Am. Chem. Soc.128 (2006) 6576-6577. (b) M. Tominaga, H. Masu, I. Azumaya, Construction and charge-transfer complexation of adamantane-based macrocycles and a cage with aromatic ring moieties, J. Org. Chem. 74 (2009) 8754-8760.

[8] B.K. Saha, A. Nangia, Self-assembled organic tubular host for van der Waals guest inclusion, Cryst. Eng. Comm. 8 (2006) 440-443.

[9] Molecular tubes and capsules, part 9. For part 1-8, see: (a) T. Iwanaga, R. Nakamoto, M. Yasutake, H. Takemura, K. Sako, T. Shinmyozu, Cyclophanes within cyclophanes: the synthesis of a pyromelliticdiimide-based macrocycle as a structural unit in a molecular tube and its inclusion phenomena, Angew. Chem. Int. Ed. 45 (2006) 3643-3647. (b) S.-I. Kato, T. Matsumoto, K. Ideta, T. Shimasaki, K. Goto, T. Shinmyozu, Supramolecular assemblies and redox modulation of pyromelliticdiimide-based cyclophane via noncovalent interactions with naphthol¹, J. Org. Chem. 71 (2006) 4723-4733. (c) S.I. Kato, T. Nakagaki, T. Shimasaki, T. Shinmyozu, The first Xray crystallographic evidence of a cyclic aniline trimer via self-complementary N–H··· π interactions: the aniline inclusion both inside and outside the macrocyclic cavity, Cryst. Eng. Comm. 10 (2008) 483-486. (d) S.I. Kato, Y. Nonaka, T. Shimasaki, K. Goto, T. Shinmyozu, Novel pyromelliticdiimide-based macrocycle with a linear π -electronic system and bis(phenylethynyl)pyromelliticdiimide: syntheses, structures, photophysical properties, and redox characteristics, J. Org. Chem. 73 (2008) 4063-4075. (e) T. Nakagaki, S.I. Kato, A. Harano, T. Shinmyozu, Molecular recognition of polymethoxybenzenes by host molecule comprised of two pyromelliticdiimides and two dialkoxynaphthalenes, Tetrahedron 66 (2010) 976-985. (f) T. Nakagaki, A. Harano, Y. Fuchigami, E. Tanaka, S. Kidoaki, T. Okuda, T. Iwanaga, K. Goto, T. Shinmyozu, Formation of nanoporous fibers by the self-assembly of a pyromelliticdiimide-based macrocycle, Angew. Chem., Int. Ed. 49 (2010) 9676–9679. (g) A.Harano, M. Tanaka, T. Nakagaki, M. Annaka, K. Ideta, K. Goto, T. Shinmyozu, Changing the volume of a giant macrocycle: the swelling of the macrocycle with organic solvents, Org. Biomol. Chem. 9 (2011), 3611-3614.

[10] For covalently linked nanotubes, see: (a) A. Harada, J. Li, M. Kamachi, Synthesis of a tubular polymer from threaded cyclodextrins, Nature 364 (1993) 516-518. (b) A. Ikeda, S. Shinkai, Multiple connection of 1,3-alternate-calix[4]arenes. An approach to synthetic'nano-tubes', J. Chem. Soc. Chem. Commun. (1994) 2375-2376. (c) A. Ikeda, M. Kawaguchi, S. Shinkai, Syntheses of multiply-connected 1,3-alternate-calix[4]arenes. A novel approach to synthetic 'nano-tubes', Quim. Anal. Int. Ed. 93 (1997)408-414. (d) J.-A. Perez-Adelmar, H. Abraham, C. Sanchez, K. Rissanen, P. Prados, J. Mendoza,

calix[4]arene in 1,3-alternate А double а conformation, Angew. Chem. Int. Ed. Engl. 35 (1996) 1009-1011. (e) S.K. Kim, W. Sim, J. Vicens, J.S. Kim, Modular chemistry. Double- and multi-1,3-alternatecalixcrowns, Tetrahedron Lett. 44 (2003), 805-809. (f) S.K. Kim, J. Vicens, K.-M. Park, S.S. Lee, J.S. Kim, Complexation chemistry. Double- and multi-1,3alternate-calixcrowns, Tetrahedron Lett. 44 (2003) 993-997. (g) Y. Kim, M.F. Mayer, S.C. Zimmerman, A new route to organic nanotubes from porphyrin dendrimers, Angew. Chem. Int. Ed. 42 (2003) 1121-1126.(h) V.G. Organo, A.V. Leontiev, V. Sgarlata, H.V.R. Dias, D.M. Rudkevich, Supramolecular features of calixarene-based synthetic nanotubes, Angew. Chem. Int. Ed. 44 (2005) 3043-3047.

[11] (a) D.G. Hamilton, J.K.M. Sanders, J.E. Davies, W. Clegg, S.J. Teat, Neutral [2]catenanes from oxidative coupling of π -stacked components,Chem. Commun,(1997) 897-898. (b) H.M. Colquhoun, D.J. Williams, Z. Zhu, Macrocyclic aromatic ether-imidesulfones: versatile supramolecular receptors with extreme thermochemical and oxidative stability, J. Am. Chem. Soc.124 (2002) 13346-13347. (c) Y. Nakamura, S. Minami, K. Iizuka, J. Nishimura, Preparation of neutral [60]fullerene-based [2]catenanes and

[2]rotaxanes bearing an electron-deficient aromatic diimide moiety, Angew. Chem., Int. Ed.42 (2003) 3158-3162. (d) S.A. Vignon, T. Jarrosson, T. Iijima, H.-R. Tseng, J.K.M. Sanders, J.F. Stoddart, Switchable neutral bistablerotaxanes, J. Am. Chem. Soc. 126(2004) 9884-9885.(e) T. Iijima, S.A. Vignon, H.-R. Tseng, T. Jarrosson, J.K.M. Sanders, F. Marchioni, M. Venturi, E. Apostoli, V. Balzani, J.F. Stoddart, Controllable donor-acceptor neutral [2]rotaxanes, Chem. Eur. J.10 (2004) 6375-6392. (f) D. G. Hamilton, N. Feeder, L. Prodi, S.J. Teat, W. Clegg, J.K.M. Sanders, Tandem hetero-catenation: templating and self-assembly in the mutual closure of two different interlocking rings, J. Am. Chem. Soc.120 (1998) 1096-1097.(g) Z. Dong, X. Liu, G.P.A. Yap, J.M. Fox, Two-dimensional scaffolds for the parallel alignment of rod-shaped conjugated molecules, J. Org. Chem.72 (2007) 617-625.

[12] (a) J. Jazwinski, A.J. Blacker, J.-M. Lehn, M. С. Cesario, J. Guilhem, Pascard, Cyclobisintercalands: synthesis and structure of an intercalative inclusion complex, and anion binding properties, Tetrahedron Lett. 28(1987) 6057-6060. (b) Q.-Z. Zhou, M.-X. Jia, X.-B. Shao, L.-Z. Wu, X.-K. Jiang, Z.-T. Li, G.-J. Chen, Self-assembly of a novel series of hetero-duplexes driven by donor-acceptor interac-Tetrahedron61 (2005) 7117-7124.(c) G. tion, Koshkakaryan, K. Parimal, J. He, X. Zhang, Z. Abliz, A.H. Flood, Y. Liu, π -Stacking enhanced dynamic and redox-switchable self-assembly of donor-acceptor metallo-[2]catenanes from diimide derivatives and crown ethers, Chem.Eur. J.14 (2008) 10211-10218.

[13] Q.-Z. Zhou, X.-K. Jiang, X.-B. Shao, G.-J. Chen, M.-X. Jia, Z.-T. Li, First zipper-featured molecular duplexes driven by cooperative donor-acceptor interaction, Org. Lett. 5 (2003) 1955-1958.

[14] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals; Pergamon Press: New York (1988).

Highlights

Journal Pre-proof

- Bromo-substituted pyromelliticdiimide-based [2+2] macrocycle has been synthesized.
- The macrocycle structure has been elucidated by NMR, HRMS and elemental analyses.
- The conformational behavior has been studied by variable temperature NMR.
- The macrocycle structure has been optimized by computational method.
- HOMO and LUMO orbitals were calculated by B3LYP/6-31G*(d) level of theory.

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The authors have no conflict of interest regarding this research.

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