

Fused π -extended discotic triangular porphyrinoids

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Dedicated to Professor Emanuel Vogel in memoriam

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ABSTRACT: A novel fused two-dimensionally π -expanded triangular porphyrinoid has been designed. The synthesis is based on facile hexaazatrinaphthalene chemistry in combination with well-established condensation procedures to simultaneously close three porphyrinic cavities. A series of different functionalized π -expanded triangular derivatives were synthesized and their optical and electrochemical properties, as well as their supramolecular organization investigated. Low lying HOMO–LUMO energy gaps between 1.11–1.32 eV were found for the highly π -conjugated planar triangular hexaaza-trinaphthalene derivatives which organize into discotic liquid crystalline columnar stacks. Thereby, derivatives with alkoxy substituents reveal significantly higher order due to their improved flexibility in comparison to their alkyl counterparts.

KEYWORDS: porphyrinoids, π -extended systems, triangular, trinuclear, hexaazatrinaphthalene, supramolecular organization, 2DWAXS.

INTRODUCTION

Nitrogen-containing macrocycles, like porphyrins and their analogs are of wide interest due to their unique chemical and optical properties, as well as their rich coordination chemistry [1]. Recently, considerable attention has been given to the fusion of such macrocycles and creating expanded π -systems with multi-metal sites [2–4]. These planar, sheet-like structures are among the most promising scaffolds as advanced materials for applications such as photodynamic therapy [5], non-linear optics [6] or organic semiconductors [7]. For instance, one-dimensional fused oligoporphyrins are expected to be good conducting molecular wires, due to their ability to transfer electronic charge over macroscopically large distances [8]. Two-dimensional π -expanded synthetically fused porphyrinoids are very challenging and up to date, only one example has been

reported by Osuka et al. in 2006 [3]. They were able to fuse four porphyinic moieties in a square planar fashion. Our interest for creating new expanded π -systems with multi-metal sites is driven by the need to develop highly efficient catalysts for the reduction of oxygen (ORR = oxygen reduction reaction). Macrocyclic metal-N₄ complexes are known to be promising alternatives to platinum-based catalysts for ORR e.g. in fuel cells [9]. Although many efforts involving the design of novel ligands [10], molecular decoration with functional groups [11] and post-heating treatment [12] have been made, limitations regarding catalytic activity, selectivity and stability still exist. In this regard, our concept to develop a highly effective catalyst is to create a maximum density of active metal sites. Therefore, we synthesized a novel triangular trinuclear macrocycle as a new metal-N₄ catalyst which show excellent electrocatalytic activity for ORR (Fig. 1a) [13]. To the best of our knowledge, this is the first example of a *triangular* symmetric π -expanded system with incorporated porphyrinic cavities which are in unprecedented vicinity to each other. The distances

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Fig. 1. (a) The trinuclear macrocycle as catalyst for ORR and (b) its schematic possible stacking alignment

between the centers of the porphyrin-like rings were determined by DFT calculations to be 6.6 Å, which is almost 2 Å smaller than those for linear oligoporphyrins (8.45 Å) or for Osuka's tetrameric porphyrin square (8.32 Å). The recently reported triangular trinuclear $[CoN_4]$ complex possesses structurally defined catalytic sites for ORR and provides a platform for new generation of nonprecious metal catalysts (NPMCs). Further development of this NPMC pointed us to consider network forming through cross-linking by heat treatment in the liquid crystalline phase. Through this approach, even higher density of active sites can be provided resulting in an improved activity. Related two-dimensional alkylsubstituted graphene disks are known to oligomerize and form carbon nano-particles by pyrolysis in the mesophase [14]. Accessorily, we will also take advantage of the presumably improved stability of the [CoN₄] complex after heat treatment, which was already discovered for metal macrocycles by Jahnke et al. [15].

A discotic liquid crystalline phase in which the molecules organize in columnar stacks can be induced by the introduction of flexible side chains around a π -conjugated core (Fig. 1b) [16–18]. These onedimensional (1D) superstructures can serve as charge carrier pathways which can be applied in field-effect transistors (FETs) and solar cells [19, 20]. Among various systems, discotic hexaazatrinapththalenes and porphyrins are well described in the literature [21–23]. In their liquid crystalline phases these molecules reveal high charge carrier mobilites on the local and on macroscopic dimensions [24-26]. Therefore, we considered the investigation of different substituents at the triangular core and to study their self-assembly behavior by twodimensional X-ray wide-angle scattering (2D-WAXS) experiments. Since our design of the π -expanded triangle is based on a facile synthetic strategy a straightforward functionalization at the periphery is possible. Herein, we report the synthesis of a series of planar triangular porphyrinic sheets with different substituents like phenyl or (phenyl)ethynylbenzene moieties with attached linear alkyl, branched alkyl or alkoxy side chains. Furthermore, their optical and electrochemical properties as well as their supramolecular organization in solid state were investigated.

EXPERIMENTAL

General

Commercially available reagents and solvents were used without further purification unless otherwise stated. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AVANCE 300 or Bruker AVANCE III 500 or AVANCE III 700 in CD₂Cl₂ (referenced 5.32 ppm) hexafluoroisopropanol-d₂ (HFIP-d₂, the alcohol or proton signal was referenced to 4.66 ppm) plus 0.1% TFA- d_2 , using a 5 mm broadband probe with z-gradient. The experiments were conducted between 298 K and the temperature was regulated by standard ¹H methanol or glycol NMR samples using the topspin 2.1 software (Bruker). Mass spectra were obtained using FD on a VG Instruments ZAB 2 SE-FPD. MALDI-TOF spectrometry was conducted on a Bruker Reflex IITOF spectrometer, utilizing a 337 nm nitrogen laser. Tetracyanoquinodimethane (TCNQ) was used as the matrix substance for solid state prepared samples. HRESI mass spectrometry was measured on a QT of Ultima 3 Fa. Micromass/Waters. Solution UV-vis spectra were recorded at 298 K on a Perkin-Elmer Lambda 100 spectrophotometer. Cyclic voltammetry was measured on a Princeton Applied Research Parstat 2273 instrument with anhydrous solvents under argon atmosphere. Tetrabutylammonium-hexafluorophosphate was used as conductive salt at a concentration of 0.1 M. A platinum working electrode (0.5 mm diameter), a platinum wire as counter electrode, and a silver wire as quasi-reference electrode were used. The peaks were calibrated vs. the half wave oxidation peak of the internal standard ferrocene (1 mM). The 2D-WAXS experiments were performed by using a copper anode X-ray tube, operated at 35 kV/20 mA, and Osmic confocal Max-Flux with pinhole collimation and a two-dimensional MAR345 image plate detector. A double-graphite monochromator for the CrK α radiation ($\lambda = 0.154$) was used. The samples were prepared as thin filaments of 0.7 mm diameter by filament extrusion using a home-made miniextruder and were positioned perpendicular to the incident X-ray beam and vertical to the 2D detector for the X-ray experiments.

Synthesis

Hexa(1H-pyrrol-yl)hexaazatrinaphthalene (4) [13], 1,2,3-tris(decyloxy)-5-ethynylbenzene (17) [27] and 7-(bromomethyl)pentadecane [28] were synthesized following the literature procedures.

Preparation of 3,4,5-tris(dodecyloxy)benzaldehyde (8). Compound 8 was synthesized according to the literature procedure [29]. 1.0 g (5.8 mmol, 1 eq) 3,4, 5-trihydroxybenzaldehyde (15) and 8.7 g (8.5 mL, 35 mmol, 6 eq) 1-bromododecane (16) were dissolved in 35 mL DMF. To this solution 2.4 g K₂CO₃ (17.4 mmol, 3 eq) and 60 mg KI (0.4 mmol, 0.06 eq) were added. The reaction mixture was heated to 70 °C and stirred for 18 h. After cooling to rt the reaction was quenched with water and extracted with DCM. The organic layer was dried over MgSO₄, filtered and the solvent removed in vacuo. The resulting crude product was purified by column chromatography using hexane:DCM (3:1) as eluent, to obtain 3.5 g (92%) of compound 8 as a colorless solid. ¹H NMR (CD₂Cl₂, 300 MHz, 298 K): δ, ppm 0.88 (m, 9H), 1.28 (m, 48H), 1.38 (m, 6H), 1.72 (m, 6H), 4.03 (m, 6H), 7.08 (s, 2H), 9.82 (s, 1H). ¹³C NMR (CD₂Cl₂, 75 MHz, 298 K): δ, ppm 14.3, 23.1, 26.4, 26.5, 29.7, 29.8, 29.8, 29.9, 30.0, 30.1, 30.1, 30.1, 30.2, 30.8, 32.3, 69.6, 73.9, 107.9, 132.0, 144.3, 154.3, 191.4. HRESI MS (THF 1:1 MeCN): $[C_{43}H_{78}O_4+Na]^+ m/z$ 681.5811 found 681.5798 calcd.

Preparation of 4-dodecylbenzaldehyde (5). Compound **5** was synthesized according to the literature procedure [29]. 1.8 g (5.4 mmol, 1 eq) 1-bromo-4-dodecylbenzene (**10**) was dissolved in 10 mL dry THF under argon atmosphere and was cooled to -78 °C. To this solution 8.5 mL (13.5 mmol, 1.6 M in hexane, 2.5 eq) *n*-BuLi was added slowly and stirred for 1 h at this temperature. Finally, 1 mL (13.5 mmol, 2.5 eq) DMF (dry) was added and the reaction mixture was allowed to warm to rt overnight. The reaction mixture was hydrolyzed at 0 °C by the addition of 1 M aqueous HCl and then diluted with EtOAc. The organic phase was

washed twice with 1 M aqueous NaOH and once with 1 M NaHCO₃ solutions, dried over MgSO₄, filtered, and the solvent removed *in vacuo*. The crude product was purified by column chromatography using hexane:EtOAc (100:2) as eluent to give 1.0 g (70%) of compound **5** as a colorless liquid. ¹H NMR (CD₂Cl₂, 300 MHz, 298 K): δ, ppm 0.87 (m, 3H), 1.29 (m, 18H), 1.63 (m, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 9.65 (s, 1H). ¹³C NMR (CD₂Cl₂, 75 MHz, 298 K): δ, ppm 14.3, 23.1, 29.6, 29.7, 29.8, 29.9, 30.0, 30.1, 31.5, 32.3, 36.5, 129.4, 130.0, 134.9, 150.9, 193.2. HRESI MS (THF 1:1 MeCN): [C₁₉H₂₀O]⁺ *m/z* 275.2375 found 275.2375 calcd.

Preparation of 4-(2-hexyldecyl)benzaldehyde (7). 5 g (22 mmol, 1 eq) 2-(4-bromophenyl)-1,3-dioxolane (13) and 200 mg (0.29 mmol, 10%mol) 1,1'-bis(diphenylphosphino)ferrocene]dichloronickel(II) were suspended in 200 mL anhydrous THF. A freshly prepared Grignard solution, made from 0.8 g magnesium (33 mmol, 1.5 eq) and 10 g (33 mmol, 1.5 eq) 7-(bromomethyl) pentadecane in 200 mL anhydrous THF, were transferred via cannula into the suspension. The mixture was stirred at 45 °C for 12 h. The solvent was removed in vacuo and the crude product was purified by column chromatography using hexane as eluent to give 0.8 g (10% over two steps, 2.4 mmol) of compound 7 as a colorless liquid. ¹H NMR (CD₂Cl₂, 300 MHz, 298 K): δ, ppm 0.89 (m, 6H), 1.26 (m, 24H), 1.68 (m, 1H), 2.64 (d, ${}^{3}J = 7.16$ Hz, 2H), 7.35 (d, ${}^{3}J = 8.1$ Hz, 2H), 7.80 (d, ${}^{3}J = 8.1$ Hz, 2H), 9.96 (s, 1H). ¹³C NMR (CD₂Cl₂, 75 MHz, 298 K): δ, ppm 14.2, 14.3, 23.0, 23, 1, 26.9, 29.7, 29.9, 30.3, 32.2, 32.3, 33.5, 33.6, 40.0, 41.2, 129.9, 130.2, 134.8, 150.1, 192.2.

Preparation of 1-dodecyl-4-ethynylbenzene (12). 1.6 g (4.9 mmol, 1 eq) 1-bromo-4-dodecylbenzene (10) was dissolved in 14 mL anhydrous THF under argon atmosphere. To this solution 16 mL diisopropylamine, 30 mg (25 μ mol, 5%mol) Pd(PPh₃)₄ and 10 mg (52 μ mol, 10%mol) CuI were added. The reaction mixture was heated to 60 °C and 1.4 mL ethynyltrimethylsilane was added through a septum. The reaction was strirred for 12 h at this temperature. The reaction mixture was filtered over a silica frit and the solvent removed in vacuo. The crude product was redissolved in THF and 6 mL of a 1 M TBAF solution was added and stirred for 1 h at rt. The solvent was again reduced on a rotary evaporator and the crude product was purified by column chromatography (hexane) affording 330 mg (25% over two steps, 1.22 mmol) of compound 12 as a colorless solid. ¹H NMR $(CD_2Cl_2, 300 \text{ MHz}, 298 \text{ K}): \delta$, ppm 0.88 (t, ${}^{3}J = 6.4 \text{ Hz}$, 3H), 1.26 (m, 18H), 1.59 (m, 2H), 2.60 (t, ${}^{3}J = 8.0$ Hz, 2H), 3.08 (s, 1H), 7.16 (d, ${}^{3}J = 8.2$ Hz, 2H), 7.37 (d, ${}^{3}J = 8.2$ Hz, 2H). ${}^{13}C$ NMR (CD₂Cl₂, 75 MHz, 298 K): δ , ppm 14.3, 23, 1, 29.6, 29.7, 29.8, 29.9, 30.0, 30.1, 31.6, 32.3, 36.2, 76.7, 84.1, 119.5, 128.8, 132.3, 144.6.

Preparation of 4-((4-dodecylphenyl)ethynyl)benzaldehyde (6). 307.5 mg (1.14 mmol, 1 eq) 1-dodecyl-4-ethynylbenzene (12) and 209.3 mg (1.14 mmol, 1 eq) 4-bromobenzaldehyde (11) were dissolved in 4 mL anhydrous THF under argon atmosphere. To this solution 16 mL diisopropylamine, 15 mg (13 µmol, 10%mol) Pd(PPh₃)₄ and 5 mg (26 µmol, 20%mol) CuI were added. The reaction mixture was heated to 60 °C and stirred for 3 h at this temperature. The reaction mixture was filtered over a frit and the solvent removed in vacuo. The crude product was purified by column chromatography using hexane:DCM (2:1) as eluent, affording 255 mg (60%, 0.68 mmol) of compound 6 as a colorless liquid. ¹H NMR $(CD_2Cl_2, 300 \text{ MHz}, 298 \text{ K}): \delta$, ppm 0.88 (t, ${}^{3}J = 7.0 \text{ Hz}$, 3H), 1.27 (m, 18H), 1.61 (m, 2H), 2.63 (t, ${}^{3}J = 8.0$ Hz, 2H), 7.20 (d, ${}^{3}J = 8.2$ Hz, 2H), 7.47 (d, ${}^{3}J = 8.2$ Hz, 2H), 7.67 (d, ${}^{3}J$ = 8.2 Hz, 2H), 7.85 (d, ${}^{3}J$ = 8.2 Hz, 2H), 10.00 (s, 1H). ¹³C NMR (CD₂Cl₂, 75 MHz, 298 K): δ, ppm 14.3, 23.1, 29.6, 29.7, 29.8, 29.9, 30.0, 30.1, 31.6, 32.3, 36.2, 88.3, 93.9, 119.9, 129.0, 129.8, 130.0, 132.0, 132.3, 135.8, 144.9, 191.6.

Preparation of 4-((3,4,5-tris(decyloxy)phenyl)ethynyl)benzaldehyde (9). 382 mg (0.67 mmol, 0.98 eq) 1,2,3-tris(decyloxy)-5-ethynylbenzene (17), 126 mg (0.68 mmol, 1 eq) 4-bromobenzaldehyde (11), 60 mg (51 µmol, 10%mol) Pd(PPh₃)₄ and 30 mg (158 µmol, 20%mol) CuI were dissolved in 5 mL anhydrous THF and 20 mL diisopropylamine. The reaction mixture was heated to 60 °C and stirred for 2 h at this temperature. The reaction mixture was filtered over a frit and the solvent removed in vacuo. The crude product was purified by column chromatography using hexane:EtOAc (6:1) as eluent, affording 355 mg (77%, 0.53 mmol) of compound 9 as a colorless liquid. ¹H NMR (CD₂Cl₂, 300 MHz, 298 K): δ , ppm 0.88 (t, ${}^{3}J$ = 6.6 Hz, 9H), 1.29 (m, 42H), 1.79 (m, 6H), 3.93 (dt, ${}^{3}J = 6.5$ Hz, 6H), 6.77 (s, 2H), 7.66 (d, ${}^{3}J = 8.3$ Hz, 2H), 7.85 (d, ${}^{3}J = 8.3$ Hz, 2H), 10.00 (s, 1H). ¹³C NMR (CD₂Cl₂, 75 MHz, 298 K): δ, ppm 14.3, 23.1, 26.5, 29.7, 29.8, 30.0, 30.1, 30.1, 30.2, 30.7, 32.3, 32.4, 69.5, 73.9, 89.6, 94.2, 110.5, 117.1, 129.8, 129.9, 132.3, 135.9, 136.0, 153.5, 191.6. HRESI MS (THF 1:1 MeCN): $[C_{45}H_{70}O_4+Na]^+ m/z$ 697.5192 found 697.5172 calcd.

General procedure for the preparation of triangular hexa(pyrrol-yl)hexaazatrinaphthalene derivatives 1a–3b. Hexa(1*H*-pyrrol-2-yl)hexaazatrinaphthalene (4) and the corresponding aldehydes 5–9 (4.5 eq) were suspended in 4 mL DCM and 2 mL THF. To this solution 0.5 mL TFA were added and the reaction mixture was degassed. The compounds were reacted under microwave irradiation (3 × 6 h, 85 °C, 50 W). The reaction mixture was concentrated *in vacuo* and the crude product was precipitated from MeOH. The solid was filtered off and purified by Soxhlet extraction with acetone affording the corresponding trinuclear compound 1a–3b.

Hexa(pyrrol-yl)hexaazatrinaphthalene (1a). Prepared from 119 mg (0.15 mmol, 1 eq) hexa(1*H*-pyrrol-2-yl)hexaazatrinaphthalene (4) and 190 mg (0.70 mmol, 4.5 eq) 1-dodecyl-4-ethynylbenzene (5). Yield: 75 mg (0.05 mmol, 32%) of compound 1a as a black solid. UV-vis (CHCl₃, 10⁻⁵ M): λ_{max} , nm 343. ¹H NMR (C₃D₂F₆O plus 0.1% C₂DF₃O₂, 700 MHz, 298 K): δ, ppm 0.74 (m, 9H), 1.14 (m, 54H), 1.50 (m, 6H), 2.54 (m, 6H), 6.09 (d, 6H), 6.15 (d, 6H), 6.62 (s, 6H), 6.92 (d, ³*J* = 7.3 Hz, 6H), 7.11 (d, ³*J* = 7.3 Hz, 6H). ¹³C NMR (C₃D₂F₆O plus 0.1% C₂DF₃O₂, 176 MHz, 298 K): δ, ppm 10.6, 20.3, 26.9, 27.0, 27.1, 27.2, 27.3, 27.4, 27.5, 28.8, 29.8, 33.0, 126.8, 129.4, 129.7, 130.1, 133.7, 135.0, 135.5, 143.2, 143.8, 148.6, 149.1, 149.5. MALDI-TOF (TCNQ): *m/z* found 1538.78; calcd. 1536.88. HRESI MS (THF 1:1 MeCN): [C₁₀₅H₁₀₈N₁₂+2H]²⁺ *m/z* 769.4471 found 769.4488 calcd.

Hexa(pyrrol-yl)hexaazatrinaphthalene (1b). Prepared from 69 mg (0.09 mmol, 1 eq) hexa(1H-pyrrol-2-yl)hexaazatrinaphthalene (4) and 150 mg (0.40 mmol, 4.5 eq) 4-((4-dodecylphenyl)ethynyl)benzaldehyde (6). Yield: 137 mg (0.07 mmol, 82%) of compound 1b as a black solid. UV-vis (CHCl₃, 10^{-5} M): λ_{max} , nm 291. ¹H NMR (C₃D₂F₆O plus 0.1% C₂DF₃O₂, 500 MHz, 298 K): δ, ppm 0.65 (m, 9H), 1.07 (m, 54H), 1.51 (m, 6H), 2.42 (m, 6H), 5.92 (d, ${}^{3}J = 4.7$ Hz, 6H), 5.99 (d, ${}^{3}J = 4.7$ Hz, 6H), 6.40 (s, 6H), 6.88 (d, ${}^{3}J$ = 8.2 Hz, 6H), 7.02 (d, ${}^{3}J = 8.2$ Hz, 6H), 7.24 (d, ${}^{3}J = 8.2$ Hz, 6H), 7.30 (d, ${}^{3}J =$ 8.2 Hz, 6H). ¹³C NMR ($C_3D_2F_6O$ plus 0.1% $C_2DF_3O_2$, 176 MHz, 298 K): δ, ppm 10.6, 20.3, 26.9, 27.1, 27.2, 27.3, 27.3, 27.4, 27.4, 29.0, 29.8, 33.7, 91.5, 96.4, 127.1, 129.0, 129.6, 129.7, 130.3, 131.9, 135.1, 135.2, 143.5, 144.1, 144.5, 144.8, 149.8 1. MALDI-TOF (TCNQ): m/z found 1842.36; calcd. 1843.02. HRESI MS (THF 1:1 MeCN): $[C_{129}H_{120}N_{12}+2H]^{2+} m/z$ 919.4977 found 919.4958 calcd.

Hexa(pyrrol-yl)hexaazatrinaphthalene (2a). Prepared from 100 mg (0.13 mmol, 1 eq) hexa(1*H*-pyrrol-2-yl)hexaazatrinaphthalene (4) and 191 mg (0.58 mmol, 4.5 eq) 4-(2-hexyldecyl)benzaldehyde (7). Yield: 117 mg (0.06 mmol, 52%) of compound 2a as a black solid. UV-vis (CHCl₃, 10⁻⁵ M): λ_{max} , nm 344. ¹H NMR (C₃D₂F₆O plus 0.1% C₂DF₃O₂, 700 MHz, 298 K): δ , ppm 0.81 (m, 18H), 1.22 (m, 72H), 1.63 (m, 3H), 2.58 (d, ³J = 6.6 Hz, 6H), 6.18 (d, ³J = 4.5 Hz, 6H), 6.23 (d, ³J = 4.5 Hz, 6H), 6.70 (s, 6H), 7.01 (d, ³J = 7.7 Hz, 6H), 7.20 (d, ³J = 7.7 Hz, 6H). MALDI-TOF (TCNQ): *m/z* found 1707.27; calcd. 1705.07. HRESI MS (THF 1:1 MeCN): [C₁₁₇H₁₃₂N₁₂+2H]²⁺ *m/z* 853.5408 found 853.5427 calcd.

Hexa(pyrrol-yl)hexaazatrinaphthalene (3a). Prepared from 100 mg (0.13 mmol, 1 eq) hexa(1*H*-pyrrol-2-yl)hexaazatrinaphthalene (4) and 383 mg (0.56 mmol, 4.5 eq) 3,4,5-tris(dodecyloxy)benzaldehyde (8). Yield: 250 mg (0.09 mmol, 71%) of compound **3a** as a black solid. UV-vis (CHCl₃, 10⁻⁵ M): λ_{max} , nm 364. ¹H NMR (C₃D₂F₆O plus 0.1% C₂DF₃O₂, 500 MHz, 298 K): δ , ppm 0.84 (t, 27H, ²J = 6.8 Hz), 1.24 (m, 144H), 1.43 (m, 18H), 1.75 (m, 18H), 3.89 (t, 12H, ²J = 6.1 Hz), 4.12 (t, 6H, ²J = 6.8 Hz), 6.12 (d, 6H, ³J = 4.7 Hz), 6.18 (d, 6H, ³J = 4.7 Hz), 6.37 (s, 6H), 6.59 (s, 6H). ¹³C NMR (C₃D₂F₆O plus 0.1% C₂DF₃O₂, 176 MHz, 298 K): δ , ppm 10.7, 20.4, 23.8, 23.9, 26.9, 27.1, 27.3, 27.4, 27.6, 27.9, 29.9, 74.0, 107.7, 128.9, 130.3, 133.8, 135.0, 135.1, 138.7, 143.6, 144.1, 146.8, 149.8, 151.0. MALDI-TOF (TCNQ): m/z found 2693.08; calcd. 2696.01. HRESI MS (THF 1:1 MeCN): $[C_{177}H_{252}N_{12}O_9+2H]^{2+}$ m/z 1345.9829 found 1345.9893 calcd.

Hexa(pyrrol-yl)hexaazatrinaphthalene (3b). Prepared from 66 mg (0.08 mmol, 1 eq) hexa(1*H*-pyrrol-2-yl)hexaazatrinaphthalene (4) and 260 mg (0.39 mmol, 4.9 eq) 4-((3,4,5-tris(decyloxy)phenyl)ethynyl)benzaldehyde (9). Yield: 213 mg (0.077 mmol, 97%) of compound 3b as a black solid. UV-vis (CHCl₃, 10⁻⁵ M): λ_{max} , nm 321. ¹H NMR (C₃D₂F₆O plus 0.1% C₂DF₃O₂, 700 MHz, 298 K): δ, ppm 0.76 (m, 27H), 1.34 (m, 126H), 1.78 (m, 18H), 3.95 (m, 18H), 5.99 (d, 6H), 6.12 (d, 6H), 6.50 (s, 6H), 6.97 (d, ³J = 7.8 Hz, 6H), 7.34 (d, ³J = 8.5 Hz, 6H). MALDI-TOF (TCNQ): *m/z* found 1707.27; calcd. 1705.07. HRESI MS (THF 1:1 MeCN): [C₁₈₃H₂₂₈N₁₂O₉]⁺ *m/z* 1369.8903 found 1369.8954 calcd.

RESULTS AND DISCUSSION

Design and synthesis

Hexaazatrinaphthalene was chosen as a basis for the design of the target triangle hexa(pyrrol-yl)hexaazatrinaphthalene disk (Fig. 2). For the creation of porphyrin-like centers, two additional nitrogen atoms are required in each of the three corners. In this regard, the attachment of six pyrrole moieties in the periphery of hexaazatrinaphthalene provides the possibility to create



Fig. 2. Design concept for two-dimensionally triangular porphyrinoid

simultaneously three N₄-rings. Two pyrroles can easily undergo a condensation reaction with an aldehyde at the α positions and in this case close the porphyrinoids. From a design point of view these porphyrinic cavities are as close as possible and well conjugated *via* the central hexaazatrinaphthalene plane. Nevertheless, the three nitrogen containing cycles are not truly porphyrinic ones and contain only one pyrrolic and three imine-type nitrogens. Common porphyrins favor the *trans*-NHtautomers including two pyrrolic and two pyrrolenic nitrogens [30]. In the triangle case, only one nitrogen in each cycle is bearing a free hydrogen atom, consequently, each porphyrin-like ring acts as a monoanion and overall the triangular tricycle as a trianion in coordination chemistry.

All hexa(pyrrol-yl)hexaazatrinaphthalene derivatives (**1a–3b**) were synthesized by an acid catalyzed condensation of the key intermediate **4** and the corresponding arylaldehydes **5–9** (Scheme 1). Hexa(1*H*-pyrrol-yl)hexaazatrinaphthalene (**4**) was synthesized as recently reported by our group [13].

For the preparation of the arylaldehydes 5–9, typical literature methods were used starting with the corresponding precursors (Table 1). 4-dodecylbenzaldehyde (5) was obtained by halogen-metal exchange using n-BuLi followed by quenching with DMF 4-((4-dodecylphenyl)ethynyl)benzaldehyde (6) [31]. 4-((3,4,5-tris(decyloxy)phenyl)ethynyl)benzaland dehyde (9) were synthesized by the reaction of 4-bromobenzaldehyde (11) and the corresponding acetylenes 12 or 17 under Sonogashira-Hagihara crosscoupling reaction conditions [32]. Williamson-ether reaction conditions used achieve were to 3,4,5-tris(dodecyloxy)benzaldehyde (8) [29]. A Kumada coupling towards 4-(2-hexyldecyl)benzaldehyde (7) was performed by using 2-(4-bromophenyl)-1,3dioxolane (13) and a freshly prepared Grignard solution made from 7-(bromomethyl)pentadecane [28].

All aldehydes were then reacted with hexa(1Hthe pyrrol-yl)hexaazatrinaphthalene 4 to give corresponding triangular trinuclear compound 1a-3b (Table 1). The resulting tricycles spontaneously dehydrogenate to the conjugated structures as shown in Scheme 1, which was proven for the first time by HRESI mass spectrometry. The meso-positions are oxidized under work-up conditions. Therefore, unlike previously reported [13] no use of an oxidizing agent such as DDQ was required. All compounds are moderately soluble in THF, dichloromethane or chloroform. Their structures were characterized by NMR spectroscopy, MALDI-TOF and HRESI mass spectrometry.

NMR spectroscopy

Hexaazatrinaphthalene derivatives are known to show line-broadening effects in halogenated solvents most probably arising from aggregation [33]. Therefore



Scheme 1. Synthesis of hexa(pyrrol-yl)hexaazatrinaphthalene derivatives 1a-3b from hexa(1H-pyrrol-yl)hexaazatrinaphthalene 4

Table 1. Overview of starting materials, resulting target compounds and corresponding yield

Entry	Starting materials	Aryl aldehyde	Yield, %	Condensation with 4 results in the target compounds	Yield, %
#1	$Br - C_{12}H_{25}$ 10	0 C ₁₂ H ₂₅ 5	70	1a	32
#2	$ \begin{array}{c} O \\ \hline \\ \hline \\ 11 \end{array} \begin{array}{c} Br \\ \hline \\ 12 \end{array} \begin{array}{c} C_{12}H_{25} \\ \hline \\ 12 \end{array} $	0 6 C ₁₂ H ₂₅	60	1b	82
#3	$ \begin{array}{c} O \\ O \\ \hline \\ 13 \end{array} \begin{array}{c} B^{r} \\ B^{r} \\ C_{6}H_{13} \end{array} \begin{array}{c} B^{r} \\ C_{6}H_{13} \end{array} $	OC ₆ H ₁₃ C ₈ H ₁₇ 7	10 ^a	2a	52
#4	$OH \\ OH \\ OH \\ Br-C_{12}H_{25} \\ 15 OH $ 16	OC ₁₂ H ₂₅ OC ₁₂ H ₂₅ 8 OC ₁₂ H ₂₅	92	3a	71
# 5	$\begin{array}{c} O \\ O $	OC ₁₀ H ₂₁ OC ₁₀ H ₂₁ 9 OC ₁₀ H ₂₁	77	3b	97

^a Over two steps.

hexafluoroisopropanol- d_2 (HFIP) with the addition of 0.1% of TFA- d_2 was used as a solvent to avoid aggregation of the hexa(pyrrol-yl)hexaazatrinaphthalene derivatives. Unfortunately, by using deuterated alcohols the NH protons are exchanged to deuterium and thus cannot be

observed by ¹H NMR spectroscopy. Nevertheless, it can be shown by NMR experiments in non-deuterated HFIP, that the pyrrole proton resonates downfield at 18 ppm [13]. The aromatic proton signals become sharp due to aggregate dissociation induced by the solvent mixture



Fig. 3. ¹H NMR spectrum of hexa(pyrrol-yl)hexaazatrinaphthalene 3a

(Fig. 3, Table 2). The C₃-symmetry of the molecule is in favor with the NMR spectral results, where the signals are reduced to only two doublets for the pyrrolic β -protons (AB-system) and one singlet for the phenylene protons.

The signals of the pyrrolic β -protons are shifted upfield compared to single porphyrins [34] and linear oligoporphyrins [35] which could be attributed to an attenuated diatropic ring current. This finding is also in agreement with the downfield resonance of the NH protons. On the other hand the β -proton signals are in the same region as for Osuka's two-dimensional tetrameric fused porphyrin sheet [3].

Optical properties

The optical absorptions of all hexa(pyrrol-yl) hexaazatrinaphthalene derivatives (1a-3b) were

investigated in solution (CHCl₃, 10^{-5} M) and thin film (Figs 4a–4b).

In dilute solution the absorption spectra of all triangular derivatives exhibit similar behavior with considerably broadened absorption bands. They show a main Soret-like absorption maximum in the near ultraviolet region of 300–400 nm and second maxima between 535 and 545 nm which could be identified as broad Q-band like absorption (Fig. 4a; Table 3). Porphyrins usually exhibit defined Q-bands in the visible region of 600–800 nm, which is not the case for the triangular compounds. These molecules feature very broad structureless bands over the whole region of 600–1000 nm. If linear alkyl side chains (**1a**) are compared to branched ones (**2a**), almost no change in the absorption spectra can be found. A bathochromic shift of 21 nm can be observed by exchanging linear alkyl chains (**1a**) to alkoxy chains



Fig. 4. (a) Electronic absorption spectra in $CHCl_3$ (10⁻⁵ M) and (b) in film (spincoated on a glass substrate from a 10⁻³ M THF solution, thickness ~50 nm)

Compound	$\lambda_{\text{soln}}(abs),nm$	log ε	$\lambda_{\text{film}}(abs),nm$	E ^{Homo} , eV	E ^{Lumo} , eV	E _g ^{ec} , eV ^b
# 1a	343	3.65	340	a	_	
# 2a	344	3.71	343	-4.54	-3.43	1.11
# 3a	364	3.88	334	-4.58	-3.26	1.32
# 1b	291	4.10	309	-4.56	-3.38	1.18
# 3b	321	4.05	322	-4.60	-3.28	1.31

Table 3. Summary of optical and electrochemical properties

^a Not soluble in THF at the concentration required for the measurement. ^b DFT quantum mechanical calculations (B3LYP/6-31G*).

(3a) indicating the stronger electron-donating ability of the alkoxy unit. The introduction of ethynyl spacers causes hypsochromic shifts of around 50 nm (for 1a–1b: 52 nm and for 3a–3b: 43 nm) and can be explained by the electron withdrawing properties of the ethynyl groups [1]. In general, in addition to a shift in the absorption spectra induced by electron-donating groups, the molar absorption coefficients are increased, which is the case for compounds 3a, 3b, and 1b [36]. The absorption spectra in thin film show similar trends to those in solutions with even more broadened and structureless bands (Fig. 4b).

Electrochemical properties and DFT calculations

The cyclic voltammograms of all derivatives **1a–3b** were recorded in THF (1 mM, scan rate 25 mV.s⁻¹) and exhibit similar redox behavior (Fig. 5).

The HOMO and LUMO energy levels were estimated from the first oxidation or reduction onsets, respectively (indicated by the red arrows, Fig. 5), and determined according to the empirical formula $E^{\text{HOMO/LUMO}} = -[4.8 - E^{FOC} + E^{\text{ox/red}}_{onset}]$ [37] (Table 3). E^{FOC} is the half-wave potential of ferrocene as the standard. The LUMO level



Fig. 5. Cyclic voltammogram of hexa(pyrrol-yl)hexaazatrinaphthalene 3a in THF at a scan rate of 25 mV.s⁻¹ (1 mM); the red arrows indicate the first oxidation and reduction onset respectively

of compound **3a** (-3.26 eV), bearing alkoxy groups in the periphery, is 0.17 eV higher than that of 2a (-3.43 eV) carrying alkyl chains as substituents. Hence, by the replacement of alkyl with alkoxy side chains the electron affinity is decreased. The same trend can be observed for compounds 1b and 3b and can be explained by the stronger electron-donating ability of the alkoxy groups compared to alkyl groups. Overall, the LUMO energy levels of all compounds are slightly higher than those of common hexaazatrinaphthalene derivatives (-3.54 eV) [38] but much lower than those of unsubstituted porphyrins (-2.23 eV) [39]. Furthermore, the HOMO levels are higher than those for hexaazatrinaphthalene (-5.97 eV) or porphyrins (-5.15 eV) resulting in smaller energy gaps in the range of 1.11 to 1.32 eV. The significant decrease in energy can be attributed to the increase of conjugation due to the planarization upon ring closure and extended π -electron delocalization.

To gain additional insight into the optical and electronic properties, the geometric and electronic structures of triply closed hexa(pyrrol-yl)hexaazatrinaphthalene were determined using density functional theory calculation (DFT, B3LYP/6-31G* [40–42]). Substituents were omitted for clarity and calculation time reasons. These calculations revealed the fully planar and conjugated structure of the molecule (Fig. 6). The HOMO is mainly distributed in the outer peripheric ring and the LUMO in C₃-symmetric fashion starting from the electron deficient core. The energies of the corresponding HOMO (-4.57 eV) and LUMO (-3.13 eV) molecular orbitals and the calculated energy gaps ($\Delta E = 1.44 \text{ eV}$) are in good agreement with the data derived from cyclovoltammetric measurements.

Supramolecular organization in the solid-state

The influence of the substituents on the organization of the triangular trinuclear molecules in the solidstate was investigated for extruded fibers by twodimensional X-ray wide-angle scattering (2D-WAXS). Various conjugated macrocycles with flexible alkyl and alkoxy side chains are known to form liquid crystalline columnar phases [43–46]. In this case, all compounds reveal neither a phase transition in the differential



Fig. 6. (a) LUMO, (b) HOMO orbitals and (c) geometric structure of the triangular core

scanning calorimetry (DSC) nor a change in organization at different temperatures observed by 2D-WAXS. Interestingly, the alkoxy substituted derivatives **3a** and **3b** possess significantly higher order in comparison to their alkyl counterparts **1a**, **1b** and **2b**. The 2D-WAXS patterns of **3a** and **3b** are presented in Figs 7a and 7b.

Compound **3a** is organized in a characteristic discotic liquid crystalline phase over the whole investigated temperature range in which the molecules are π -stacked with a distance of 0.36 nm within the columns as indicated by the meridional reflection in the pattern (see schematic illustration in Fig. 7c). Only few discotics show such broad temperature range for the liquid crystalline state. Typically, phenyls as substituents are known to induce this extended thermotropic behavior. For compound 3a the distinct, anisotropic equatorial reflections point towards a pronounced orientation of these stacks along the fiber axis. From the positions of these scattering intensities a hexagonal unit cell with $a_{hex} = 4.20$ nm is derived. As expected, the extension of the substituents to phenyl-ethynylbenzene for 3b enlarges the hexagonal unit cell parameter to $a_{hex} = 5.28$ nm. At the same time, the peripheral steric demand increases, which lowers the molecular interactions and dramatically decreases the order as evident from the relative isotropic reflections and the strong amorphous halo in the pattern (Fig. 7b). Nevertheless, reflections related to the π -stacking distance of 0.36 nm are still obvious in the meridional plane of the pattern, however, significantly weaker than for **3a**.

Surprisingly, the alkyl substituted compounds 1a, 1b and 2a show the lowest order (Fig. 8). Only one isotropic small-angle reflection, which is attributed to the formation of columnar structures, appears for all three compounds. This is astonishing, since, **1a** and **1b** carry only one side chain on each phenyl and generally alkyls are less sterically demanding and lead to better packing. The improved order of **3a** and **3b** can be related to their viscous (wax-like) phases which origin from the higher chain flexibility and allow better molecular arrangement and columnar alignment in the solid-state. In this context, we expect the metal (e.g. cobalt(II)) complex of compound 3a to show improved catalytic activity compared to the previously reported alkyl substituted catalyst [13] due to its better molecular organization. Complexation of 3a and further investigation in view of organization behavior and catalytic activity are currently under progress.





Fig. 7. 2D-WAXS of (a) **3a** and (b) **3b**, (c) schematic illustration of the molecular organization in the columnar structures. Due to simplicity the side chains are omitted, but the substituent attachment is indicated by the grey sticks. It has to be noted that in the liquid crystalline phase the molecules perform a lateral rotation around the columnar axis (indicated by red arrow) and are not stacked on top of each other as illustrated in Fig. 7c



Fig. 8. 2D-WAXS of (a) 1a, (b) 1b, and (c) 2a

CONCLUSION

In conclusion, we have proven the introduction of five different substituents onto a triply fused porphyrinoid. triangular two-dimensional The synthesis of the key intermediate hexa(1H-pyrrol-2-yl)hexaazatrinaphthalene 4, by using well-known hexaazatrinaphthalene chemistry, opens an easy access to functionalize the periphery by facile condensation procedures. Five hexa(pyrrol-yl)hexaazatrinaphthalene derivatives with different substituents have been synthesized and their optical and electrochemical properties as well as their supramolecular organization have been studied. For the first time, the structure of the triangular trinuclear compound in its dehydrogenated from could be verified by HRESI mass spectrometry. Low energy gaps have been determined for all derivatives, which are derived from highly delocalized π -conjugation of the planar triangle. The structure analysis by fiber 2D-WAXS has confirmed the formation of a well-arranged discotic columnar liquid crystalline phase for the alkoxy substituted derivatives, while the compounds with alkyl side chains show surprisingly low order. The improvement in organization of the alkoxy carrying compounds is attributed to the reduced viscosity of the solid-state which is induced by the side chains. This underlines the importance of a welltuned liquid crystalline state for the self-assembly of the hexa(pyrrol-yl)hexaazatrinaphthalenes into highly ordered pathways for charge carriers. Therefore, we consider alkoxy substituted compound 3a to show best results in future catalytic tests. Complexation of compound 3a and the study of its supramolecular organization are currently under progress. By and large, we proved mesophase formation for the novel triangular trinuclear hexaazatrinaphthalene and are now ready to do further investigations for network formation by cross linking though mild pyrolysis.

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