View Article Online View Journal

Journal of Materials Chemistry C

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: H. Kayal, M. Ahmida, S. Dufour, H. Taing and H. Eichorn, *J. Mater. Chem. C*, 2013, DOI: 10.1039/C3TC31588F.



This is an *Accepted Manuscript*, which has been through the RSC Publishing peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, which is prior to technical editing, formatting and proof reading. This free service from RSC Publishing allows authors to make their results available to the community, in citable form, before publication of the edited article. This Accepted Manuscript will be replaced by the edited and formatted Advance Article as soon as this is available.

To cite this manuscript please use its permanent Digital Object Identifier (DOI®), which is identical for all formats of publication.

More information about *Accepted Manuscripts* can be found in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics contained in the manuscript submitted by the author(s) which may alter content, and that the standard **Terms & Conditions** and the **ethical guidelines** that apply to the journal are still applicable. In no event shall the RSC be held responsible for any errors or omissions in these *Accepted Manuscript* manuscripts or any consequences arising from the use of any information contained in them.

RSCPublishing

www.rsc.org/materialsC

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxx

ARTICLE TYPE

Cross-linking of discotic tetraazaporphyrin dyes in 2 and 3 dimensions by "click" chemistry

Himadri Kayal,^a Mohamed M. Ahmida,^a Scott Dufour,^a Hi Taing,^a and S. Holger Eichhorn*^a

Received (in XXX, XXX) Xth XXXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX 5 DOI: 10.1039/b000000x

An intrinsic shortcoming of self-organizing materials is their susceptibility to structural changes by mechanical forces and exposure to chemicals and radiation. Cross-linking of the molecules in the desired supramolecular structure is a generally applicable pathway to structurally more stable materials but is difficult to apply to self-organizing materials because the introduction of cross-linkable groups affects

- ¹⁰ their self-organization and the process of cross-linking may alter the supramolecular structure of the preceding phase. Reported here are the synthesis, thermal properties, and cross-linking of octaalkylthio substituted tetraazaporphyrins that contain either eight terminal azide groups or eight terminal acetylene groups. Synthesis of these compounds requires the preparation of the azide and alkyne containing sidechains and their reaction with 1,2-dicyanoethylene-1,2-dithiolate to the corresponding maleodinitrile
- ¹⁵ intermediates. All maleodinitriles are successfully converted to tetraazaporphyrins by the established Mg templated cyclotetramerization in typical yields of 60-70%. Thermal properties of the metal-free and copper(II) metallated tetraazaporphyrins were studied by thermal gravimetric analysis, polarized optical microscopy, differential scanning calorimetry, and variable temperature powder X-ray diffraction measurements. Azide substituted tetraazaporphyrins with trimethylene and hexamethylene spacers as well
- ²⁰ as acetylene derivatives with with trimethylene spacers unexpectedly display columnar mesophases over ranges of temperature from 30 °C to 110 °C. A thermally activated cross-linking of a hexagonal columnar mesophase by cycloaddition at 65 °C is demonstrated for a 1:1 mixture of azide and acetylene derivatives. At this temperatures the reaction progresses for up to 48 hours but renders the mesophase insoluble and stable to above 200 °C. The structure of the mesophase is surprisingly little affected by the cross-coupling

²⁵ process that reaches a conversion of 60% of all azide and acetylene groups based on IR measurements. Conversion of up to 80% of azide and acetylene groups is reached by copper catalysed cross-linking of a 1:1 mixture in solution to generate insoluble polymers. A similar degree of conversion is achieved by copper catalysed cross-linking of a 1:1 mixture as Langmuir film after 3 hours. However, transfer of intact cross-linked Langmuir films onto substrates was not successful.

30 Introduction

Published on 17 September 2013. Downloaded by East Carolina University on 19/09/2013 07:23:17.

First reported in 2002, "click" reactions based on the copper catalyzed azide-alkyne [3+2] cycloaddition (CuAAC) have quickly become a versatile tool in organic, biological, and materials chemistry. CuAAC reactions are tolerant to most ³⁵ functional groups, proceed in high yields with few possible side-

- reactions, and form stable 1,2,3-triazole rings as linker.¹⁻³ Their application in the synthesis and processing of self-organizing and self-assembling materials, however, has been limited to the synthesis of molecular building blocks and the modification of ⁴⁰ self-assembled monolayers⁴ and Langmuir-Blodgett films.⁵
- CuAAC is a particularly powerful reaction for the construction of complex structures through covalent bond formation such as the attachment of large dendrons to a rotaxane core,⁶ the synthesis of oligomeric phthalocyanines,⁷⁻⁹ and the attachment of
- ⁴⁵ dyes to polymers and carbon nanotubes.¹⁰ The 1,2,3-triazole rings that result from the CuAAC may also benefit self-organization

and electronic properties of the generated adducts due to their strong dipole and aromatic character. Both, calamitic,¹¹⁻¹³ polymeric,¹⁴ and discotic¹⁵⁻¹⁷ liquid crystals containing the 1,2,3-⁵⁰ triazole motive have recently been reported.

Surprisingly, neither CuAAC nor thermally activated AAC have been employed for the cross-linking of Langmuir films and mesophases. Cross-linking of Langmuir and Langmuir-Blodgett films is important to stabilize these monolayers and thin films for ⁵⁵ potential applications but have been given relatively little attention. Reported approaches include the photochemical cross-linking of cinnamic acid and acrylate derivatives,^{18, 19} the polymerization of amphiphilic diacetylene derivatives,²⁰ the oxidative polymerization of aniline derivatives,²¹ the ionic ⁶⁰ interaction between ionic amphiphiles and ionic polyelectrolytes of opposite charge,^{22, 23} the polycondenzation at the air-water interface,²⁴ and the linking by sol-gel chemistry of siloxanes.^{25, 26}

Cross-linking of discotic columnar mesophases has been mainly achieved by the polymerization of vinyl groups that are



attached via alkyl spacers. Early work by Ringsdorf and Schumacher was based on liquid crystalline triphenylene derivatives that were photopolymerized in the presence of a radical initiator.^{27, 28} A limitation of this approach is the low 5 discogenic potency of the triphenylene core that limits the number of vinyl groups that can be attached without compromising their mesomorphism. In contrast, the columnar mesomorphism of macrocycles like phthalocyanines can tolerate the attachment of 8 terminal acrylate groups and their columnar 10 mesophases were successfully polymerized by thermally activated radical polymerization.²⁹ Photopolymerization was not successful, most likely because the light was preferentially absorbed by the phthalocyanine core. However, this work has not been pursued much further because the generated materials were 15 contaminated by the required radical initiator, typically AIBN, and the fast progress of the cross-linking reaction generates defects and cracks in the material. Müllen et al. recently

- succeeded in the photochemical and thermal polymerization of a columnar mesophases of an acrylate substituted ²⁰ hexabenzocoronene derivative without the aid of a photoinitiator.³⁰ The same group, together with Thünemann, also developed an alternative approach to the cross-linking of discotic mesophases by combining ionic hexabenzocoronene derivatives with oppositely charged polyelectrolites.^{31, 32}
- Reported here is the synthesis of octaalkylthio substituted tetraazaporphyrins (TAPs) that contain eight terminal azide or acetylene groups and the cross-linking of their 1:1 mixtures *via* CuAAC in solution and as Langmuir monolayers. Also presented is the characterization of their discotic columnar mesophases and ³⁰ the cross-linking of a hexagonal columnar mesophase of a 1:1
- mixture by thermally activated [3+2] cycloaddition.

Experimental

Synthesis

- *Chemicals*: All reagents and solvents were purchased from ³⁵ Sigma-Aldrich and Fluka Chemical Companies and used as received unless otherwise stated. 1-Propanol and methanol were dried over 4 Å and 3 Å molecular sieves, respectively, whereas dry and air-free dichloromethane, tetrahydrofuran, and diethyl ether were obtained from a solvent purification system ⁴⁰ (Innovative Technology Inc. MA, USA, Pure-Solv 400). Silica
- gel 60 (35-70 mesh ASTM, from EM Science, Germany) was used for column chromatography and Silica Gel 60 aluminum backed sheets (EM Science, Germany) for thin layer chromatography.
- ⁴⁵ Instrumentation: ¹H-NMR and ¹³C-NMR spectra were obtained on Bruker NMR spectrometers (DRX 500 MHz and DPX 300 MHz). The residual proton signal of the deuterated solvent (usually chloroform (CDCl₃)) was used as a reference signal and multiplicities of the peaks are given as s = singlet, d = doublet, t =
- ⁵⁰ triplet, and m = multiplet. Coupling constants are given in Hz and only calculated for 1st-order systems. Data are presented in the following order: integration, multiplicity, and coupling constant. Fourier Transform Infrared spectra (FT-IR) were obtained on a Bruker Vector 22 as KBr pellets or thin films on KBr windows.
- s5 Relative peak intensities and shapes in IR are abbreviated as vs = very strong, s = strong, m= medium, w = weak, and br = broad.

Mass spectrometry measurements were performed by Kirk Green at the Regional Center for Mass Spectrometry (McMaster University) and Jiaxi Wang at the Mass Spectrometry and ⁶⁰ Proteomics Unit (Queen's University). UV/VIS absorption spectra were run on a Varian Cary 50 Conc UV-visible spectrophotometer. Elemental analysis was performed on a Perkin Elmer 2400 combustion CHNS analyser at the Centre for Catalysis and Materials Research at the University of Windsor.

⁶⁵ Described below are the synthesis and characterization of all TAP derivatives. Details on the synthesis of all starting materials (Scheme 1) and spectroscopic data for all TAPs are provided as ESI[†].

70 Synthesis of octa-azide and octa-acetylene TAPs (6a-c, 7a-c, 6a-cCu, and 7a-cCu)

Mg powder (24.6 mg, 1 mmol) and 5 mg of iodine crystals were refluxed overnight in 50 mL of dry propan-1-ol under nitrogen until all Mg is reacted to Mg(II) propanolate. Maleodinitrile **4a** ⁷⁵ (1.54 g, 5 mmol) (or **4b** (1.96 g, 5 mmol), **4c** (2.38 g, 5 mmol), **5a** (1.372 g, 5 mmol), **5b** (1.793 g, 5 mmol), **5c** (2.21 g, 5 mmol)) was added and the suspension was heated at reflux for 24 hrs. The resulting greenish-blue suspension was cooled to room temperature, diluted with 50 mL of water, filtered, and the filter ⁸⁰ residue was washed with methanol/water 1:1 until the filtrate remains colourless. The filter residue was dissolved in a mixture

- of 50 mL acetic acid and 10 mL THF and stirred at 80 °C for about 8 hours until demetallation was completed. Progress of the demetallation was monitored by UV-Vis spectroscopy. Water
- $_{\rm 85}$ (100 mL) was added to the now purple solution and the product was extracted with $\rm H_2CCl_2$ (3 x 100 mL). The combined $\rm H_2CCl_2$ layers were dried over anhydrous MgSO₄ and the solvent was removed under vacuum to give the crude TAP. Precipitation of the crude TAP from acetone solution by slow addition of a 2:1
- ⁹⁰ mixture of methanol and water purifies the TAPs to about 90% purity and these samples were further purified by flash chromatography on silica gel with H₂CCl₂/hexane 1:2 as eluent. The purified metal-free TAPs were obtained as dark purple solids.
- ⁹⁵ 2,3,7,8,12,13,17,18-octakis(azidopropylthio)-5,10,15,20-tetraazaporphyrin (6a) (839 mg, 68%): ¹H NMR (300 MHz, CDCl₃, δ): -1.45 (2H, s, NH), 2.18 (16H, tt, J = 6.5 Hz, J = 7.0 Hz), 3.67 (16H, t, J = 6.3 Hz), 4.19 (16H, t, J = 6.6 Hz); ¹³C NMR (130 MHz, HMBC, CDCl₃, δ): 29.21, 34.42, 49.21, 139.82, 151 ¹⁰⁰ (not observed); IR (cm⁻¹): 3290 (m,v(N-H)), 2930 (m, v(C-H)), 2098 (s, v(N₃)); UV/VIS in THF (λ_{max} in nm, ε in dm³ mol⁻¹ cm⁻¹): 344 (44300), 513 (20600), 651 (26100), 712 (34200); EA calcd for C₄₀H₅₀N₃₂S₈: 38.88 %C, 36.28 %N, 4.08 %H; Found: 39.12 %C, 36.00 %N, 4.15 %H.
- ¹⁰⁵ 2,3,7,8,12,13,17,18-octakis(azidohexylthio)-5,10,15,20tetraazaporphyrin (**6b**) (1.098 g, 70%): ¹H NMR (300 MHz, CDCl₃, δ): -1.12 (2H, s, NH), 1.31-1.45 (16H, m), 1.47-1.71 (32H, m), 1.88 (16H, t, J = 6.9 Hz), 3.19 (16H, t, J = 6.6 Hz), 4.09 (16H, t, J = 6.9 Hz); ¹³C NMR (75 MHz, CDCl₃, δ): 26.12,
 ¹¹⁰ 28.63, 28.81, 29.72, 34.89, 49.86, 138.01, 149.93; IR (cm⁻¹): 3285 (m, v(N-H), inner core NH), 2932 (m, v(C-H), CH₂), 2095
- 3285 (m, v(N-H), inner core NH), 2932 (m, v(C-H), CH₂), 2095 (s, v(N₃)); UV/VIS in THF (λ_{max} in nm, ε in dm³ mol⁻¹ cm⁻¹): 342 (44100), 515 (20500), 655 (26200),714 (34200); EA calcd for C₆₄H₉₈N₃₂S₈: 48.89 %C, 28.51 %N, 6.28 %H; Found: 48.80 %C,

2,3,7,8,12,13,17,18-octakis(azidononylthio)-5,10,15,20-

- tetraazaporphyrin (6c) (1.259 g, 66%): ¹H NMR (300 MHz, CDCl₃, δ): -1.06 (2H, s, NH), 1.28 (64H, m), 1.59 (32H, m), ⁵ 1.97(16H, m), 3.20 (16H, broad), 4.12 (16H, broad); ¹³C NMR (75 MHz, CDCl₃, δ): 26.71, 28.84, 28.96, 29.15, 29.26, 29.44, 30.54, 35.32, 51.45, 140.63, 153.43; IR (cm⁻¹): 3283 (m,v(N-H)), 2920 (m, v(C-H)), 2100 (s, v(N₃)); UV/VIS in THF (λ_{max} in nm, ϵ in dm³ mol⁻¹ cm⁻¹): 344 (44 300), 510 (21 000), 651 (25 900), 713
- 10 (34115); HRMS-MALDI (m/z): calcd for $C_{88}H_{146}N_{32}S_8 + H:$ 1908.0252; Found: 1908.0242 $[M + H]^+$; EA calcd for $C_{88}H_{146}N_{32}S_8$: 55.37 %C, 23.48 %N, 7.71 %H; Found: 55.25 %C, 23.31 %N, 7.84 %H.

2,3,7,8,12,13,17,18-octakis(pent-4-yn-1-ylthio)-5,10,15,20-

- ¹⁵ tetraazaporphyrin (**7a**) (770 mg, 70%): ¹H NMR (300 MHz, CDCl₃, δ):-1.30 (2H, s, NH), 1.90 (8H, s), 2.08 (16H, tt appears as p, J = 6.9 Hz), 2.52 (16H, t, J = 2.1 Hz), 4.18 (16H, t, J = 7.2 Hz); ¹³C NMR (75 MHz, CDCl₃, δ): 17.72, 29.28, 34.00, 69.33, 83.43, 140.59, 153.35; IR (cm⁻¹): 3290 (s, v(C-H) alkyne and w,
- ²⁰ v(N-H)), 2917, 2850 (m, v(C-H), CH₂), 2115 (w, v(C=C)); UV/VIS in THF (λ_{max} in nm, ϵ in dm³ mol⁻¹ cm⁻¹): 355 (43090), 565 (18940), 645 (26470), 710 (34200); HRMS-MALDI (m/z): calcd for C₅₆H₅₈N₈S₈+H: 1099.2625; Found: 1099.2646 [M+H]⁺. 2,3,7,8,12,13,17,18-octakis(oct-7-yn-1-ylthio)-5,10,15,20-
- ²⁵ tetraazaporphyrin (**7b**) (976 mg, 68%): ¹H NMR (300 MHz, CDCl₃, δ):-1.13 (2H, s, NH), 1.38-1.72 (48H, m), 1.79-1.96 (24H, m), 2.04-2.19 (16H, m), 4.08 (16H, t, J = 7.2 Hz); ¹³C NMR (75 MHz, CDCl₃, δ): 18.37, 28.39, 28.45, 29.75, 30.41, 35.24, 68.26, 84.49, 140.63, 153.2; IR (cm⁻¹): 3290 (s, v(C-H) alkyne and w,
- $_{30}$ v(N-H)), 2930, 2854 (m, v(C-H), CH₂), 2115 (w, v(C=C)); UV/VIS in THF (λ_{max} in nm, ϵ in dm³ mol⁻¹ cm⁻¹): 355 (43030), 562 (19091), 642 (26060), 710 (33333); HRMS-MALDI (m/z): calcd for C₈₀H₁₀₆N₈S₈+H: 1435.6384; Found: 1435.6380 [M+H]⁺. 2,3,7,8,12,13,17,18-octakis(undeca-10-yn-1-ylthio)-5,10,15,20-
- ³⁵ tetraazaporphyrin (7c) (1.241 g, 70%): ¹H NMR (300 MHz, CDCl₃, δ): -1.09 (2H, s, NH), 1.2-1.3 (64H, m), 1.42 (16H, m), 1.60 (16H, m), 1.89 (24H, broad), 2.10 (16H, broad), 4.10 (16H, broad); ¹³C NMR (75 MHz, CDCl₃, δ): 18.33, 28.40, 28.68, 28.78, 28.90, 29.04, 29.26, 30.49, 35.28, 68.05, 84.65, 140.42
 (IMDC at 120 MHz) 151 (cat characad); M (cat characad);
- ⁴⁰ (HMBC at 130 MHz), 151 (not observed); IR (cm⁻¹): 3300 (s, v(C-H) alkyne and w, v(N-H)), 2933, 2845 (m, v(C-H), CH₂), 2113 (w, v(C=C)); UV/VIS in THF (λ_{max} in nm, ϵ in dm³ mol⁻¹ cm⁻¹): 360 (43100), 565 (18965), 645 (26500), 712 (34200); EA calcd for C₁₀₄H₁₅₄N₈S₈: 70.46 %C, 6.32 %N, 8.76 %H; Found: 45 70.19 %C, 6.15 %N, 8.91 %H.

Synthesis of octa-azide and octa-acetylene copper TAPs (6acCu and 7a-cCu)

- Metal-free TAP **6a** (617 mg, 0.5 mmol) (or **6b** (785 mg, 0.5 mmol), **6c** (954 mg, 0.5 mmol), **7a** (550 mg, 0.5 mmol), **7b** (718 mg, 0.5 mmol), **7c** (886 mg, 0.5 mmol)) was stirred in a solution of copper(II) acetyl acetonate (262 mg, 1.0 mmol) in THF (50 mL) at 60 °C for 6-8 hrs. Progress and completion of the metallation with copper(II) was monitored by UV-VIS
- ⁵⁵ spectroscopy. Ethyl acetate (100 mL) was added and the mixture was then extracted with an aqueous solution of ammonium chloride (5% w/w, 3 x 100 mL) and finally with water (2 x 100 mL). The organic layer was dried over anhydrous MgSO₄,

concentrated, and filtered through a small amount of silica gel ⁶⁰ with ethyl acetate/hexane 1:3 to generate the purified copper TAPs as dark blue solids.

- 2,3,7,8,12,13,17,18-octakis(azidopropylthio)-5,10,15,20tetraazaporphyrinato-copper (**6aCu**) (571 mg, 88%): IR (cm⁻¹): 2917, 2849 (m, v(C-H), CH₂), 2093 (s, v(N₃), azide); UV/VIS in
- ⁶⁵ THF (λ_{max} in nm, ε in dm³ mol⁻¹ cm⁻¹): 362 (21820), 500 (7576), 667 (30606); EA calcd for C₄₀H₄₈CuN₃₂S₈: 37.04 %C, 34.56 %N, 3.73 %H; Found: 36.79 %C, 34.35 %N, 3.91 %H. 2,3,7,8,12,13,17,18-octakis(azidohexylthio)-5,10,15,20-
- 2,3,7,8,12,13,17,18-octakis(azidonexyitnio)-5,10,15,20tetraazaporphyrinato-copper (**6bCu**) (653 mg, 81%):_, MW: IR 70 (cm⁻¹): 2929, 2853 (m, v(C-H), CH₂), 2094 (s, v(N₃), azide); UV/VIS in THF (λ_{max} in nm, ε in dm³ mol⁻¹ cm⁻¹): 365 (21970),
- 505 (7758), 670 (30667); HRMS-MALDI (m/z): calcd for $C_{64}H_{96}CuN_{32}S_8$ +H: 1632.5635; Found: 1632.5630 [M+H]⁺. 2,3,7,8,12,13,17,18-octakis(azidononylthio)-5,10,15,20-
- ⁷⁵ tetraazaporphyrinato-copper(**6cCu**) (788 mg, 80%); IR (cm⁻¹): 2915, 2851 (m, v(C-H), CH₂), 2090 (s, v(N₃), azide); UV/VIS in THF (λ_{max} in nm, ϵ in dm³ mol⁻¹ cm⁻¹): 365 (24857), 504 (8354), 670 (30616); HRMS-MALDI (m/z): calcd for C₈₈H₁₄₄CuN₃₂S₈+H: 1968.9391; Found: 1968.9329 [M+H]⁺.
- ⁸⁰ 2,3,7,8,12,13,17,18-octakis(pent-4-yn-1-ylthio)-5,10,15,20tetraazaporphyrinato-copper (**7aCu**) (493 mg, 85%): IR (cm⁻¹): 3353, 3295 (s, v(C-H) alkyne), 2930, 2853 (s, v(C-H), CH₂), 2116 (w, v(C≡C)); UV/VIS in THF (λ_{max} in nm, ε in dm³ mol⁻¹ cm⁻¹): 360 (25151), 500 (8667), 665 (29090); HRMS-MALDI (m/z): c calcd_for_C_H_CuN S ±H: 1160 1767; Found: 1160 1754
- ss calcd for $C_{56}H_{56}CuN_8S_8$ +H: 1160.1767; Found: 1160.1754 $[M+H]^+$.

2,3,7,8,12,13,17,18-octakis(oct-7-yn-1-ylthio)-5,10,15,20tetraazaporphyrinato-copper (**7bCu**) (600 mg, 80%): IR (cm⁻¹): 3352, 3300 (s, v(C-H) alkyne), 2930, 2853 (s, v(C-H), CH₂), 2117

 $_{90}$ (w, v(C≡C)); UV/VIS in THF (λ_{max} in nm, ε in dm³ mol⁻¹ cm⁻¹): 365 (24850), 503 (8364), 670 (30606); HRMS-MALDI (m/z): calcd for C₈₀H₁₀₄CuN₈S₈+H: 1496.5523; Found: 1496.5552 [M+H]⁺.

2,3,7,8,12,13,17,18-octakis(undeca-10-yn-1-ylthio)-5,10,15,20-

⁹⁵ tetraazaporphyrinato-copper(**17cCu**) (726 mg, 82%); IR (cm⁻¹): 3300, 3350 (s, v(C-H) alkyne), 2928, 2850 (s, v(C-H), CH₂), 2110 (w, v(C=C)); UV/VIS in THF (λ_{max} in nm, ε in dm³ mol⁻¹ cm⁻¹): 365 (21975), 505 (7760), 670 (30655); EA calcd for C₁₀₄H₁₅₂CuN₈S₈: 68.09 %C, 6.11 %N, 8.35 %H; Found: 67.83 ¹⁰⁰ %C, 5.99 %N, 8.42 %H.

Results and Discussion

Synthesis

Synthesis of maleonitriles 4-5 required the preparation of azide and acetylene terminated alkanes that contain a leaving group at 105 their other terminal position (Scheme 1). Azide terminated bromoalkanes 1 have previously been prepared in 46-65% yield by a statistical mono-substitution of dibromoalkanes with sodium azide in DMF at 80 °C.33-35 Reported here is an alternative approach based on the selective substitution of OH by N₃ in 110 bromoalkanols Mitsunobu-type *via* a reaction with diisopropylazodicarboxylate (DIAD) and diphenylphosphorylazide (DPPA).³⁶ This methodology avoids the tedious chromatographic separation of mono- and di-azide products but the removal of DIAD, DPPA, and their sideproducts still required chromatographic separations to generate the products in only slightly higher yields of 60%-70%.

Alkyne **2a** was also obtained in one step by converting the commercially available 4-pentyne-1-ol to its methylsulfonate.³⁷⁻⁴⁰

⁵ A different approach is required for alkynes 2b-c, which were prepared by statistical nucleophilic substitution of 1,6-dibromohexane and 1,9-dibromononane with 1.5 eq. of TMS-acetylene.⁴¹ The obtained product mixtures of about 80% 2b-c and 20% disubstituted compounds were used for the following reactions with 3 without prior separation. Compound 3 only reacts with the mono-acetylides 2b-c and the chromatographic removal of the di-acetylides from maleonitriles 5b-c was straightforward. Previously reported preparations of unprotected 2b-c are lower yielding and some require fractionated ¹⁵ distillation.⁴²



Published on 17 September 2013. Downloaded by East Carolina University on 19/09/2013 07:23:17.

 Scheme 1
 Reaction conditions and yields: (a) THF, PPh₃, DIAD, DPPA,

 0-20 °C, 24 hrs; 60%-70%. (b) MsCl, Et₃N, H₂CCl₂, 0 °C, 5 hrs; 90%. (c)

 1.5 eqiv. trimethylsilylacetylene, BuLi, HMPA, THF, -78-20 °C, 15 hrs;

 20

 about 56% 2b,c and 14% disubstituted product. (d) For 4a-c and 5a:

 NaI_{cat}, MeOH, 20 °C, 5-24 hrs; 65-70%. For 5b-c: first Na₂CO₃, MeOH,

 20 °C, 5 hrs; then addition of 3 and NaI_{cat}, 20 °C, 24 hrs; 60%. (e)

 Mg(OC₃H₇)₂, HOC₃H₇, refl., 24 hrs; not purified. (f) AcOH/MeOH 5:1,

 refl., 8 hrs.; 60-70% for both steps. (g) CuAcAc, THF, 60 °C, 8 hrs.;

 25

Compounds **1** and **2a** readily reacted with 1,2dicyanoethylene-1,2-dithiolate **3** to give maleodinitriles **4** and **5a** but, unexpectedly, reactions of **2b-c** with **3** generated complex product mixtures. The observed side-reactions were apparently ³⁰ caused by the TMS group since the problem was resolved when the TMS groups were removed (in situ) prior to the addition of **3**. Compound **3** was prepared by the method of Davison and Holm and can be stored for weeks in a freezer under argon if sufficiently pure.⁴³

6-7 TAPs were prepared by the established cvclotetramerization of 2.3-bis(alkylthio)maleonitrile drivatives 4-5 in a suspension of magnesium propanolate in propanol at reflux temperature. The initially obtained Mg containing TAPs were demetallated in situ under acidic conditions to give the 40 metal-free macrocycles 6-7. Overall yields of 60-70% for cyclization and demetallation are equal to yields previously reported for cyclotetramerizations of other 2.3bis(alkylthio)maleonitrile derivatives.⁴⁴⁻⁴⁶ Clearly, the presence of terminal alkyne and azide groups does not affect the cyclization 45 and both functional groups are surprisingly stable to the reaction conditions. Perhaps this is not an unexpected result since both, azide and acetylene groups, have been previously shown to be compatible with the lithium alcoholate mediated synthesis of phthalocyanines.⁴⁷⁻⁴⁹ Metallation of TAPs 6-7 with Cu(II) was ⁵⁰ achieved with CuAcAc in THF solution in >80% yield.

Mesomorphism

65

The thermal stability of TAPs **6** and **7** is limited by the stability of their alkynyl and alkylazide chains and was studied by thermal gravimetric analysis under He (Tab. S1 in ESI†). Least stable are ⁵⁵ the TAPs with azide groups and propyl spacers (**6a** and **6aCu**) that start to decompose between 110-120 °C. All other TAPs decompose between 140-160 °C, which is still significantly lower than the reported 240 °C for analogous octa-alkenyl substituted TAPs.⁴⁵ Differences in thermal stability between metal-free and ⁶⁰ copper containing TAPs are small and non-systematic.

6a Cry 53.2 (-0.83) 48.3 (0.52)	lso 6aCu Cry <u>€8.3 (-1.75)</u> 52.3 (1.56) Col _h >120 dec.
6b Cry <u>47.6 (-36.99)</u> <u>₹</u> <u>25.2 (40.99)</u>	Iso 6bCu Cry $\underbrace{41.9 (-45.10)}_{8.9 (46.09)}$ Col $\underbrace{73 (POM)}_{68 (POM)}$ Iso
6c Cry <u>43.5 (-39.67)</u> <u>₹</u> <u>18.9 (30.99)</u>	lso 6cCu Cry 34.4 (-13.46) 11.1 (13.18) Iso
7a Cry $\frac{68.7 (-14.96)^a}{53.6 (15.68)^a}$	Col _r ∡ 2 Iso 143.5 (6.79)
	7aCu Cry
7b Cry <u>45.8 (-3.80)</u> <u>−0.3 (3.74)</u>	lso 7bCu amorph. solid — ^{39 (POM)} ► Iso
7c Cry 37.1 (-16.75) 4.3 (8.71)	Iso 7cCu Iso at 0 °C, no transition in DSC

Scheme 2 Phase behaviour of TAPs as determined by POM, DSC, and XRD. Transition temperatures are given in °C (peak temperatures of 2nd heating and 1st cooling runs) and enthalpies (in brackets) in kJ/mol.
 Transition temperatures not observed by DSC were determined by POM

(POM). Col_h and Col_r are columnar mesophases of hexagonal and rectangular symmetry, respectively. ^aTwo overlapping transitions.

All twelve TAPs were studied by polarized optical microscopy 70 (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD) to probe their mesomorphism (Scheme 2). POM images, DSC curves, and XRD data are provided as ESI[†]. All TAPs with hexamethylene and nonamethylene spacers are not liquid crystalline except for **6bCu** that displays a Col mesophase 75 of probably rectangular symmetry over a temperature range of 30 Published on 17 September 2013. Downloaded by East Carolina University on 19/09/2013 07:23:17.

^oC on heating. TAPs with nonamethylene spacers either melt just above room temperature or are isotropic liquids at room temperature (**7cCu**). In fact, compound **7cCu** does not show any transition in DSC down to -50 °C and is an isotropic liquid down ⁵ to 0 °C based on POM, which is rather unusual for TAPs⁴⁶ and porphyrins in general.⁵⁰

All Cu metallated and one metal-free TAP (7a) with trimethylene spaces display liquid crystal phases. Particularly surprising is the Col_r mesophase displayed by 7a over a ¹⁰ temperature range of 80 °C. Only few metal-free octaalkylthio-substituted TAPs have been reported to display columnar mesophases, in contrast to their metallated analogues, and the temperature ranges of their mesophases are below 20 °C.⁵¹ Another evidence of the high stability of the mesophase of 7a is ¹⁵ the large enthalpy of its clearing transition when compared to the

clearing enthalpy of the Col_h mesophases of **7aCu**, although a larger enthalpy can be reasoned with the higher order of a Col_r mesophase. Nematic discotic mesophases that have been reported for metal-free TAPs with alkene terminated aliphatic chains have ²⁰ not been observed for TAPs **6** and **7**.⁵¹

A comparison of the Col_h mesophases of TAPs **6aCu** and **7aCu** reveals similar melting points but a higher clearing point of TAP **6aCu**. This and the mesomorphism of **6bCu** suggest that the attachment of terminal azide groups is less detrimental to the ²⁵ mesomorphism of octaalkylthio substituted TAPs than terminal acetylene groups. However, a comparison of the mesomorphism of TAPs **6** and **7** with the mesomorphism of analogous octaalkenyl substituted TAPs⁴⁵ shows that terminal alkenes are better accommodated by their columnar mesophases than terminal ³⁰ azides and alkynes. All three terminal functional groups destabilize mesophases in comparison to TAPs with eight alkylthio chains of comparable length.⁵¹

Thermally activated AAC of columnar mesophase

1:1 Mixtures of any of the azide TAPs **6** and alkyne TAPs **7** can ³⁵ be cross-linked in solution by standard CuAAC to give amorphous insoluble polymers of the dyes. Conversions of azide and acetylene groups based on the decrease of the overlapping IR stretching absorptions of the acetylene and azide groups reach values of 60 to 80%, similar to the IR measurements shown in

⁴⁰ Figure 1. However, detailed studies of cross-linking in solution have not been pursued because the formation of insoluble amorphous polymers was not our objective and they are difficult to characterize.

More intriguing to us was the cross-linking of TAPs in their ⁴⁵ columnar mesophases, especially when conducted under thermal activation without the use of a catalyst. A 1:1 mixture of TAPs **6aCu** and **7aCu** was chosen for this experiment because it does not crystallize and its Col_h mesophase is stable from below -50 to above 100 °C. The absence of any transitions in this temperature

⁵⁰ range was confirmed by DSC (Fig. S29 in ESI[†]) and the presence of a Col_h mesophase was verified by POM and XRD studies. In fact, the defect texture observed by POM shows only minor changes even at 200 °C (Fig. 2), although partial decomposition cannot be excluded at these high temperatures. This high thermal

 $_{\rm 55}$ stability of the Col_h mesophase is reasoned with a fast cross-linking process at temperatures above 100 °C.

A more quantitative investigation of the cross-linking process was conducted by DSC and IR measurements. DSC heating runs

of a freshly prepared 1:1 mixture of TAPs **6aCu** and **7aCu** to 100 °C showed an increase in slope of the baseline when the temperature surpassed 70 °C (Fig. S29 in ESI[†]). Measurements to 200 °C revealed that this increase in slope is actually the onset of an irreversible exothermic transition of 293 J/g (approximately 360 kJ/mol_{TAP}) (Fig. S30 in ESI[†]). This peak is interpreted as the

⁶⁵ heat generated by the AAC reaction, although the measured enthalpy may represent only a part of the total reaction enthalpy as the reported exothermic standard reaction enthalpy is 188-230 kJ/mol per pair of azide and acetylene.¹ Consequently, a total reaction enthalpy of about 800 kJ per mole of TAP is expected if ⁷⁰ four groups per TAP react.

A slow cross-linking of the columnar mesophase by AAC at 65 °C was chosen to minimize structural changes to the film and columnar mesophase. The progress of the AAC reaction was studied by isothermal DSC measurements at 65 °C and IR 75 spectroscopy. Isothermal DSC measurements show a constant exothermic slope of the baseline for the first 700 minutes that is followed by a slow decrease in slope (Fig. S31 in ESI†). The end point of the reaction is difficult to determine by this method but the slope of the baseline approaches 0 after about 22 hours.

More sensitive to the progress of the reaction is the decrease of the azide/alkyne absorptions at 2100 cm⁻¹ (decrease in area) observed by IR spectroscopy. A thin film of the 1:1 mixture of TAPs **6aCu** and **7aCu** was coated onto a KBr window and kept at 65 °C for 3 days and IR spectra were taken after 4, 12, 24, 48, so and 72 hours (Fig. 1). No further decrease of the combined azide/alkyne absorption peak was observed after 48 hours and the majority of the cross-linking had occurred after 24 hours, which overall agrees with the DSC data.



90 Fig. 1 IR spectra of the Col_h mesophase of a 1:1 mixture of TAPs 6aCu and 7aCu as thin film on a KBr disk after heat treatment at 65 °C for specific periods of time. No further change was observed for heat treatments longer than 48 hrs.

After 48 hours the area of the azide/alkyne absorption peak ⁹⁵ was decreased to 40% of its original area. This is equivalent to a conversion of 60% of the azide and acetylene groups or 4.8 azide/alkyne groups per TAP. A conversion of only a fraction of all azide and alkyne groups is reasonable because some azide and alkyne groups will not be able to reach each other once the ¹⁰⁰ molecules are locked into place after the first groups have reacted. Sufficient for the formation of insoluble polymers is likely the conversion of only 2 azide/alkyne groups per TAP (25%) and, indeed, the thin films are completely insoluble in organic solvents after 12-16 hours at 65 °C.

Observation of a thin film of the 1:1 mixture of TAPs **6aCu** ⁵ and **7aCu** on glass by POM at 65 °C for 3 days revealed only minor changes to the texture (Fig. 2). The absence of structural changes to the Col_h mesophase during the cross-linking by AAC was independently confirmed by powder XRD measurements (Fig. 2). In fact, the cross-linking process hardly affects the ¹⁰ columnar mesophase despite the formation of relatively bulky and polar triazole rings. What is observed by XRD is a small decrease in intensity of the (10) reflection and its gradual shift to smaller lattice spacings by 0.2 Å over 44 hours. The former change indicates a small decrease in columnar packing order ¹⁵ while the latter change is explained with the expected shrinkage of the intercolumnar packing distance during cross-linking.²⁷

Published on 17 September 2013. Downloaded by East Carolina University on 19/09/2013 07:23:17.





7aCu kept at 65 °C for up to 48 hours. The top left image shows the freshly prepared sample (less than 30 minutes after mixing) at 65 °C, the top centre image shows the same area after 48 hours at 65 °C for, and the top right image shows the same area (after 48 hours at 65 °C) at 200 °C.

- ²⁵ Cross-linking of the mesophase probably occurs both within columnar stacks to generate 1,5-disubstituted 1,2,3-triazole linkers and between columnar stacks to generate 1,4-disubstituted 1,2,3-triazole linkers. Both types of cycloadditions are thermally allowed, in contrast to CuAAC that exclusively ³⁰ generates 1,4-disubstituted 1,2,3-triazoles. Also, each columnar
- stack likely consists of a 1:1 mixture of TAPs **6aCu** and **7aCu** since all data are consistent with the formation of one phase. The unlikely possibility of a mixture of columnar stacks that contain either just **6aCu** or just **7aCu** is excluded as it should generate a ³⁵ more complex XRD pattern and the average d-spacing of the (10)
- reflection should be at about 15.0 Å. Columnar mesophases of

pure 6aCu and 7aCu have d-spacings of the (10) reflections at 14.6 Å and 15.8 Å, respectively.

CuAAC in Langmuir Film

- ⁶⁵ The overall low amphiphilicity of TAPs **6** and **7** is a disadvantage for the formation of Langmuir films. Monolayers of reasonable quality were obtained for TAPs **6b** and **7a** and their 1:1 mixture served as model systems for testing their cross-linking by CuAAC at the air-water interface.
- Both TAPs 6b and 7a are crystalline at room temperature but 140 their surface pressure versus area $(\pi - A)$ isotherms are rather different (Fig. S32 in ESI⁺). The isotherm of 6b is featureless and the pressure exponentially increases with decreasing surface area until the film collapses at a pressure of 45 mN m⁻¹ and a limiting ¹⁴⁵ area per molecule of 138 Å². In contrast, the L-film of **7a** shows a distinct step in its π -A isotherm. A first steep increase in surface pressure occurs at a limiting area per molecule of 152 $Å^2$ and briefly falls off to 23.5 mN m⁻¹ after reaching a surface pressure of 26 mN m⁻¹. Upon further compression the surface pressure 150 again increases exponentially until the final collapse pressure of 44.5 mN m⁻¹ at a limiting area per molecule of 113 Å² is reached. The in-between decrease in surface pressure to 23.5 mN m⁻¹ may indicate the intermediate formation of 3-dimensional structures but was not studied in more detail. Also uncertain remains the 155 exact orientation of the TAPs at the air-water interface but the observed surface areas per molecule agree with a more face-on orientation of the macrocycle while an edge-on orientation would result in surface areas well below 100 Å².46, 52



⁹⁰ Fig. 3 π–A isotherm of a 1:1 mixture of TAPs **6b** and **7a** spread from chloroform solution onto pure water as subphase (solid line). Change of surface pressure over time of the same mixture at constant surface area (135 Å^2) on pure water (triangles) and on water containing copper (II) acetate (0.638 x 10⁻³ M) and sodium ascorbate (1.92 x 10⁻³ M) (circles).

The π -A isotherm of the 1:1 mixture of TAPs **6b** and **7a** used for the cross-linking by CuAAC has a shape similar to the isotherm of **7a** but the surface areas per molecule shifted to larger molecular areas (Fig. 3). This increase in surface area indicates an overall looser and less compressible packing of the TAP mixture, ¹¹⁵ which agrees with the observed overall flattening of the π -A isotherm and the decreases in transition and collapse pressures by 12 mN m⁻¹. However, the observed limiting area per molecule of

Journal of Materials Chemistry C Accepted Manuscri

151 Å² at a surface pressure of 16.5 mN m⁻¹ used for the crosslinking experiment suggests a predominantly face-on orientation of the macrocycles, which is expected to bring most azide and alkyne groups in contact with the catalyst in the aqueous s subphase.

L-films of the 1:1 mixture on an aqueous solution of copper (II) acetate and sodium ascorbate become insoluble in organic solvents after about 1 hour for the concentrations given in Fig. 3. Progress of the cross-linking of the TAPs by CuAAC was ¹⁰ monitored by the decrease in surface pressure at a constant area and the point at which the surface pressure remains constant is interpreted as the completion of the CuAAC reaction (after about 190 min for the example given in Fig. 3).

The occurrence of CuAAC and its completion was ¹⁵ independently confirmed by ATR-FTIR measurements on parts of the Langmuir film removed from the water surface (Fig. 4). Integrations of the overlapping azide/alkyne absorptions at 2100 cm⁻¹ reveal an astonishing 78% conversion of all azide/alkyne groups, which is 18% more than in the Col_h mesophase and equal ²⁰ to the maximum conversions obtained by CuAAC in solution.





UV-Vis spectra of cross-linked films transferred onto quartz slides verify that the TAP macrocycle is not affected by the cross-³⁰ linking and remains metal-free (Fig. 5). The spectra also reveal a red-shift of the Q-bands in the Langmuir and transferred films that indicate a J-type aggregate structure before and after the cross-linking process. However, the transfer of intact cross-linked mono-layers has not yet been achieved; instead the films rupture ³⁵ and buckle during transfer to generate 3-dimensional structures as

confirmed by AFM measurements on the transferred films (Fig. S33 in ESI⁺).



Fig. 5 UV-Vis spectra of a 1:1 mixture of TAPs **6b** and **7a** as LB films on quartz transferred right after spreading and after cross-linking by CuAAC (0.638 x 10⁻³ M copper (II) acetate and 1.92 x 10⁻³ M sodium ascorbate) for 200 minutes. A solution spectrum is shown for comparison.

Conclusions

60

Octaalkylthio substituted TAPs that contain either eight terminal ⁸⁵ azide or acetylene groups can be prepared based on the established Mg templated cyclization of maleodinitriles. Several TAPs with shorter alkyl spacers display columnar mesophases over surprisingly wide ranges of temperature. Overall, terminal azide groups appear to be more compatible with self-organization ⁹⁰ into columnar mesophases than terminal acetylene groups but both groups are less compatible than terminal vinyl groups.

Demonstrated for the first time is the cross-linking of Langmuir films by CuAAC and of columnar mesophases by thermally activated azide-alkyne cycloaddition (AAC). A 1:1 135 mixture of azide and alkyne TAPs was successfully cross-linked via CuAAC as Langmuir film to reach surprisingly high conversions of almost 80% of all alkyne and azide groups within 3 hours. Thermally activated AAC in a columnar mesophase of a 1:1 mixture of azide and alkyne TAPs reached about 60% 140 conversion of all azide and acetylene groups after 48 hours. The structure of the columnar mesophase is surprisingly little affected by the slow cross-linking process while detailed structural studies on the Langmuir films were not possible because cross-linked films fractured and buckled when removed from the water 145 surface. This shortcoming may be overcome by the design of more amphiphilic TAPs that contain fewer azide and acetylene groups.

Acknowledgements

MMA thanks the Libyan Ministry of Education for scholarship ⁹⁰ awards and SHE acknowledges financial support by NSERC, CFI, and OIT. HK thanks the University of Windsor for a partial tuition scholarship.

Notes and references

^a Department of Chemistry & Biochemistry, University of Windsor, 90 Windsor, Ontario, Canada. Fax: 519-973-7098; Tel: 519-253-3000

x3990; E-mail: eichhorn@uwindsor.ca

75

80

90 39

95 41.

42

43.

44.

45.

47.

49

115 50.

120

105 46

100

† Electronic Supplementary Information (ESI) available: Synthesis and characterization, POM, DSC, and XRD data of mesophases, DSC and IR of columnar mesophase of 1:1 mixture of TAPs 6aCu and 7aCu, π -A isotherms of TAPs 6b and 7a, IR and UV-Vis of L-film. See 5 DOI: 10.1039/b000000x/

- 1. P. Wu and V. V. Fokin, Aldrichimica Acta, 2007, 40, 7-17.
- 2. C. J. Hawker, V. V. Fokin, M. G. Finn and K. B. Sharpless, Aust. J. Chem., 2007, 60, 381-383.
- 10 3. J. A. Johnson, M. G. Finn, J. T. Koberstein and N. J. Turro, Macromol. Rapid Commun., 2008, 29, 1052-1072.
- 4. N. K. Devaraj and J. P. Collman, QSAR Comb. Sci., 2007, 26, 1253-1260
- 5. J. C. Niehaus, M. Hirtz, M. K. Brinks, A. Studer, H. Fuchs and L. Chi, Langmuir, 2010, 26, 15388-15393. 15
- 6. I. Aprahamian, T. Yasuda, T. Ikeda, S. Saha, W. R. Dichtel, K. Isoda, T. Kato and J. F. Stoddart, Angew. Chem., Int. Ed., 2007, 46, 4675-4679.
- U. Hahn and T. Torres, J. Porphyrins Phthalocyanines, 2011, 7. 15, 364-372. 20
- H. Yoshiyama, N. Shibata, T. Sato, S. Nakamura and T. Toru, 8. Org. Biomol. Chem., 2008, 6, 4498-4501.
- 9. D. D. Diaz, J. J. Cid, P. Vazquez and T. Torres, Chem.--Eur. J., 2008, 14, 9261-9273.
- 25 10 S. Campidelli, B. Ballesteros, A. Filoramo, D. D. Diaz, I. T. G. de, T. Torres, G. M. A. Rahman, C. Ehli, D. Kiessling, F. Werner, V. Sgobba, D. M. Guldi, C. Cioffi, M. Prato and J.-P. Bourgoin, J. Am. Chem. Soc., 2008, 130, 11503-11509
- 11. D. Srividhya, S. Manjunathan and S. Thirumaran, E-J. Chem., 2009, 6, 928-937.

Published on 17 September 2013. Downloaded by East Carolina University on 19/09/2013 07:23:17.

- 12. H. Gallardo, A. J. Bortoluzzi and O. S. D. M. P. De, Liq. Cryst., 2008, 35, 719-725.
- 13. H. Gallardo, F. Ely, A. Bortoluzzi and G. Conte, Liq. Cryst., 2005, 32, 667-671.
- 35 14. D. Srividhya, S. Manjunathan, S. Nithyanandan, -S Balamurugan and S. Senthil, Chin. J. Polym. Sci., 2009, 27, 110 48 761-770.
 - 15. M.-H. Ryu, J.-W. Choi, H.-J. Kim, N.-J. Park and B.-K. Cho, Angew. Chem., Int. Ed., 2011, 50, 5737-5740.
- 40 16. D. Basak, S. Christensen, S. K. Surampudi, C. Versek, D. T. Toscano, M. T. Tuominen, R. C. Hayward and D. Venkataraman, Chem. Commun., 2011, 47, 5566-5568.
- 17. M.-H. Ryu, J.-W. Choi and B.-K. Cho, J. Mater. Chem., 2010, 20, 1806-1810.
- 45 18. T. Hayashi, M. Mabuchi, M. Mitsuishi, S. Ito, M. Yamamoto and W. Knoll, Macromolecules, 1995, 28, 2537-2543.
- 19. A. Dubault, C. Casagrande and M. Veyssie, The Journal of Physical Chemistry, 1975, 79, 2254-2259.
- 20. R. Steitz, I. R. Peterson, I. Voigt-Martin and H. Möhwald, 50 Thin Solid Films, 1989, 178, 289-304.
 - 21. L. J. Kloeppner and R. S. Duran, J. Am. Chem. Soc., 1999, 121.8108-8109.
 - Y. Wang, E. Stedronsky and S. L. Regen, Langmuir, 2008, 24, 22. 6279-6284
- 55 23. B. J. Lee and T. Kunitake, Langmuir, 1994, 10, 557-562.
 - A. Takahashi and H. Yamamoto, Polym J, 1980, 12, 79-85. 24.
- 25. R. Matmour, T. J. Joncheray, Y. Gnanou and R. S. Duran, J. Colloid Interface Sci., 2007, 311, 315-321.
- 26. M. Kunitake, T. Nishi, H. Yamamoto, K. Nasu, O. Manabe and N. Nakashima, Langmuir, 1994, 10, 3207-3212.
- 27. A. Bacher, C. H. Erdelen, W. Paulus, H. Ringsdorf, H. W. Schmidt and P. Schuhmacher, Macromolecules, 1999, 32, 4551-4557
- H. Bengs, H. Finkelmann, J. Kupfer, H. Ringsdorf and P. 28. Schuhmacher, Makromol. Chem.-Rapid, 1993, 14, 445-450.
- 29. J. F. van der Pol, E. Neeleman, J. C. Vanmiltenburg, J. W. Zwikker, R. J. M. Nolte and W. Drenth, Macromolecules, 1990. 23, 155-162.
- 30. M. Kastler, W. Pisula, R. J. Davies, T. Gorelik, U. Kolb and K. Müllen, Small, 2007, 3, 1438-1444.
- 31. A. F. Thünemann, S. Kubowicz, C. Burger, M. D. Watson, N. Tchebotareva and K. Mullen, J. Am. Chem. Soc., 2003, 125, 352-356.

- 32. A. F. Thünemann, D. Ruppelt, S. Ito and K. Müllen, J. Mater. Chem., 1999, 9, 1055-1057.
- 33. C. Decroocq, D. Rodriguez-Lucena, V. Russo, B. T. Mena, M. C. Ortiz and P. Compain, Chem.--Eur. J., 2011, 17, 13825-13831, S13825/13821-S13825/13827.
- C. Papin, G. Doisneau and J.-M. Beau, Chem.--Eur. J., 2009, 34. 15, 53-57 35.
 - C. Romuald, E. Busseron and F. Coutrot, J. Org. Chem., 2010, 75, 6516-6531.
- D. F. Taber, P. B. Deker, H. M. Fales, T. H. Jones and H. A. 36. Lloyd, The Journal of Organic Chemistry, 1988, 53, 2968-2971
- 37. G. L. Bundy, C. H. Lin and J. C. Sih, Tetrahedron, 1981, 37, 4419-4429
- J. Flahaut and P. Miginiac, Helv. Chim. Acta, 1978, 61, 2275-38. 2285
 - J. Han, B. Xu and G. B. Hammond, Org. Lett., 2011, 13, 3450-3453
- C. L. Le, A.-L. Girard, J. Aubertin, F. Radvanyi, C. Benoist-40. Lasselin, A. Jonquoy, E. Mugniery, L. Legeai-Mallet, P. Busca and M. Y. Le, Org. Biomol. Chem., 2010, 8, 2164-2173.
 - K. Mori, Y. Shikichi, S. Shankar and J. Y. Yew, Tetrahedron, 2010, 66, 7161-7168
 - H. Goto, X. Dai, T. Ueoka and K. Akagi, Macromolecules, 2004, 37, 4783-4793.
 - A. Davison and R. H. Holm, Inorganic Chemistry, 1967, 10, 8-26
 - F. Lelj, G. Morelli, G. Ricciardi, A. Roviello and A. Sirigu, Liq. Cryst., 1992, 12, 941-960.
 - S. Belviso, G. Ricciardi and F. Lelj, J. Mater. Chem., 2000, 10, 297-304
 - S. H. Eichhorn, D. W. Bruce, D. Guillon, J. L. Gallani, T. Fischer, J. Stumpe and T. Geue, J. Mater. Chem., 2001, 11, 1576-1584.
 - G. Bottari, D. D. Diaz and T. Torres, J. Porphyrins Phthalocyanines, 2006, 10, 1083-1100.
 - J. E. Lyons and P. E. Ellis, Jr., Appl. Catal., A, 1992, 84, L1-L6.
 - I. Lopez-Duarte, M. V. Martinez-Diaz, E. Schwartz, M. Koepf, P. H. J. Kouwer, A. E. Rowan, R. J. M. Nolte and T. Torres, ChemPlusChem, 2012, 77, 700-706.
 - A. Nowak-Król, D. Gryko and D. T. Gryko, Chem. Asian J., 2010. 5. 904-909.
- S. Kumar, Chemistry of discotic liquid crystals, CRC Press, 51. Boca Raton, London, New York, 2011.
- 52. M. Ahmida, S. Dufour, H.-S. Li, H. Kayal, R. Schmidt, C. E. DeWolf and S. H. Eichhorn, Soft Matter, 2013, 9, 811-819.

Published on 17 September 2013. Downloaded by East Carolina University on 19/09/2013 07:23:17.

Graphical contents entry

Cross-linking of discotic tetraazaporphyrins in Langmuir films by "click" chemistry and in columnar mesophases by thermally activated azide-alkyne cycloaddition.

