Electronic Supplementary Material (ESI) for ChemComm.

Memory-Driven Order-Disorder Transition of 3D-Supramolecular Architecture Based on Calix[5]arene and Porphyrin Derivatives

Nunzio Tuccitto,* Giuseppe Trusso Sfrazzetto,* Chiara M. A. Gangemi, Francesco P. Ballistreri, Rosa Maria Toscano, Gaetano A. Tomaselli, Andrea Pappalardo,* and Giovanni Marletta

Electronic Supporting Information

Table of contents

General experimental methods. The NMR experiments were carried out at 27° C on a Varian UNITY Inova 500 MHz spectrometer (^{1}H at 499.88 MHz, ^{13}C NMR at 125.7 MHz) equipped with pulse field gradient module (Z axis) and a tuneable 5 mm Varian inverse detection probe (ID-PFG). ESI mass spectra were acquired on a ES-MS Thermo-Finnigan LCQ-DECA using MeOH (positive ion mode). A JASCO V-560 UV-vis spectrophotometer equipped with a 1 cm path-length cell was used for the measurements. UV-vis band fitting was performed by Origin data treatment software (Originlab) by using Gaussian components and keeping constant centroid positions and full width at half maximum. Luminescence measurements were carried out using a Cary Eclipse Fluorescence spectrophotometer with a λ_{ex} of 410 nm and a 0.5 nm resolution, at room temperature. The emission was recorded at 90° with respect to the exciting line beam using 5:5 slit-widths for all measurements. All chemicals were reagent grade and were used without further purification. PDMS was purchased from Aldrich as SYLGARD 184 Silicone Elastomer Kit and used as received. Thin layer chromatography (TLC) was performed on silica gel 60F_{254} (Merck) pre-coated aluminium sheets. Flash chromatography was carried out using Fluka Silica Gel 60 (230–400 mesh).

Procedure for ^{1}H NMR titrations. Two stock solutions of **PC[5]** and **BHAP** (7.0 x 10^{-3} M) in a mixture $CDCl_3/CD_3OD$ 4:1 were prepared. From these, different solutions with different ratio **PC[5]⊃BHAP** were prepared as reported in the manuscript, and ^{1}H NMR spectra were recorded.

DOSY experiments. Diffusion-Ordered SpectroscopY (DOSY) NMR has been particularly used in host–guest chemistry to give information about the possibility to form higher order species.[1] The samples for DOSY experiments were prepared by mixing an appropriate volume of equimolecular stock solutions (7 x 10^{-3} M in $CDCl_3/CD_3OD$ 4:1) of **PC[5]** and **BHAP** as to reach a 2:1 host/guest ratio at a fixed 1 mM concentration. D value of **PC[5]** is referred to the literature (2.06 ± 0.01 × 10^{-6} cm^2 s^{-1}),[2] while D value of 3D network is 4.27 ± 0.07 × 10^{-7} cm^2 s^{-1}.

Procedure for fluorescence titrations. Two stock solutions of **PC[5]** (host) and **BHAP** (guest) (1.0 x 10^{-3} M) in a mixture $CHCl_3/CH_3OH$ 4:1 were prepared. From these, fluorescence titrations were performed starting from **PC[5]** (1.0 x 10^{-6} M) adding increasing amounts of **DHAP** (λ_{exc} 410 nm, λ_{em} 485 nm). The binding affinity between **PC[5]** and **BHAP** was estimated using HypSpec (version 1.1.33), a software designed to extract equilibrium constants from potentiometric and/or spectrophotometric titration data.[3] HypSpec starts with an assumed complex formation scheme and uses a least-squares approach to derive the spectra of the complexes and the stability constants. χ^2 test (chi-square) was applied, where the residuals follow a normal distribution (for a distribution approximately normal, the χ^2 test value is around 12 or less). In all of the cases, $\chi^2 \leq 10$ were found, as obtained by 3 independent measurements sets.

Synthesis of porphyrin 2. 260 mg (0.370 mmol) of porphyrin **1** were dissolved in 10 mL of DMF under nitrogen. 6-Boc-amino-1-hexylamine (94 µL, 0.427 mmol), HATU (128 mg, 0.336 mmol) and DIPEA (58 µL, 0.336 mmol) were added and the solution was stirred for 24 h. The reaction mixture was poured in water and filtered, thus the crude product was purified through chromatographic column (silica gel, $CHCl_3$/EtOH = 98:2) giving the desired compound as violet powder (49 mg, 0.045 mmol, 32 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.86 (d, *J* = 4.5 Hz, 4H), 8.80 (d, *J* = 4.5 Hz, 4H) 8.28 (d, *J* = 8.0 Hz, 4H), 8.19 (m, 8H), 7.76 (m, 6H) 6.74 (s, 2H), 4.60 (s, 2H) 3.63 (m, 4H), 3.19 (m, 4H), 1.78 (m, 4H), 1.76 (m, 4H), 1.57 (m, 8H), 1.46 (bs, 18H), – 2.78 (s, 2H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 167.5, 156.2, 145.2, 141.9, 134.6, 134.5, 134.2, 127.9, 126.7, 125.3, 120.4, 119.1, 118.3, 117.6, 39.8, 32.8, 30.1, 29.6, 28.4, 26.1, 25.9. ESI-MS: *m/z* 1099.6 $[M+H]^+$. Anal. Calcd. For $C_{68}H_{74}N_8O_6$: C, 74.29; H, 6.78; N, 10.19; O, 8.73. Found: C, 74.24; H, 6.71; N, 10.14.

Synthesis of BHAP. 49 mg (0.045 mmol) of porphyrin **2** were dissolved in 20 mL of CH_2Cl_2 and 250 µL of trifluoroacetic acid were added to the solution. The reaction mixture was stirred at room temperature until the disappearance of the reactant, monitored by TLC analysis ($CHCl_3$/EtOH = 98:2). The solvent was evaporated under vacuum, giving **BHAP** as trifluoracetic salt (43 mg, 0.038 mmol, 85 %). ^{1}H NMR (500 MHz, acetone-d_6): δ 8.86 (bs, 8H), 8.38-8.19 (m, 12H), 7.86 (m, 6H), 3.92 (m, 4H), 3.57 (bs, 4H), 1.92 (m, 4H), 1.78 (m, 4H), 1.59 (m, 8H). ^{13}C NMR (126 MHz, acetone-d_6) δ 151.00, 150.57, 147.09, 144.18, 135.21, 132.62, 128.34 127.88, 127.38, 126.60, 126.14, 121.88, 121.73, 120.60, 120.27, 48.21, 39.96, 28.16, 26.90, 26.72. ESI-MS: *m/z* 899.2 $[M-H]^+$; 450.4 $[M]^{2+}$. Anal. Calcd. For $C_{62}H_{60}F_6N_8O_6$: C, 66.06; H, 5.37; F, 10.11; N, 9.94; O, 8.52. Found: C, 66.03; H, 5.33; F, 10.07; N, 9.89.

Solid matrix embedding procedure. The embedding of 3D-macrostructure, porphyrin alone or mixed with PC[5]-monomers in the hosting PDMS matrix was obtained by dissolving 80 μl of solution of each compound (1×10^{-3} M in $CHCl_3/CH_3OH$ 4:1) in 1g of PMDS pre-polymer. The viscous composite was strongly stirred and gently heated around 70-80 °C for 15 minutes allowing the solvent evaporation. After that, 100 mg of curing agent were added and the composite was strongly mixed. Finally, composite was transferred onto a glass slide and cured at 100°C for 30 minutes. In the specific case of PDMS-based composites prepared by adding first BHAP and subsequently PC[5], 80 μl of solution of BHAP (1×10^{-3} M in $CHCl_3/CH_3OH$ 4:1) were added to 1g of PMDS pre-polymer, stirred and heated around 70-80 °C for 15 minutes allowing the solvent evaporation. Subsequently, 80 μl of solution of PC[5] (1×10^{-3} M in $CHCl_3/CH_3OH$ 4:1) were added strongly mixed and heated around 70-80 °C for 15 minutes allowing, once more, the solvent evaporation. After that, 100 mg of curing agent were added and again strongly mixed. Finally, composite was transferred onto a glass slide and cured at 100°C for 30 minutes.

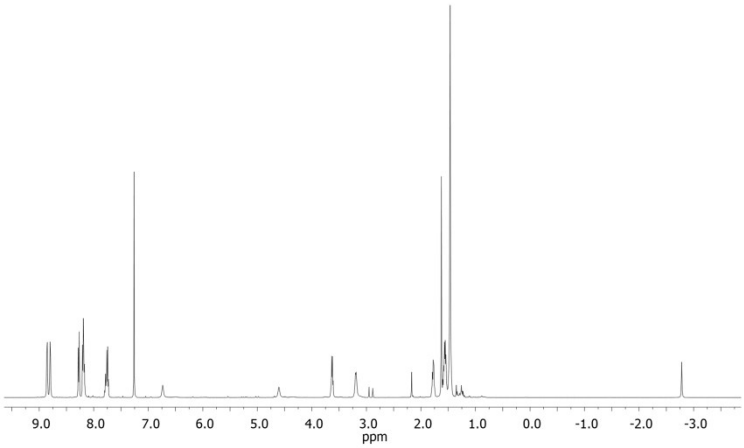


Figure S1. ^{1}H-NMR of compound **2** in $CDCl_3$

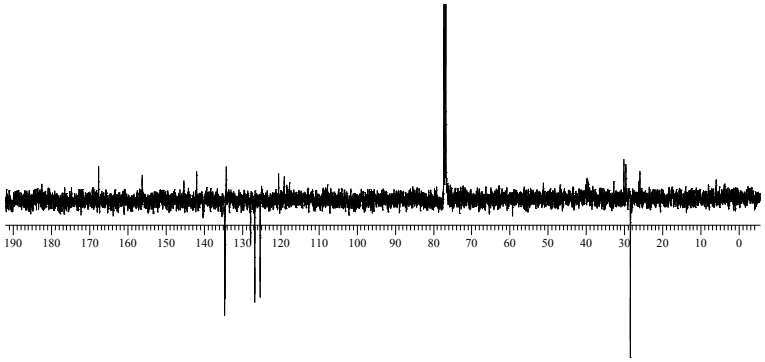


Figure S2. APT of compound **2** in $CDCl_3$

Figure S3. ESI-MS of compound **2**.

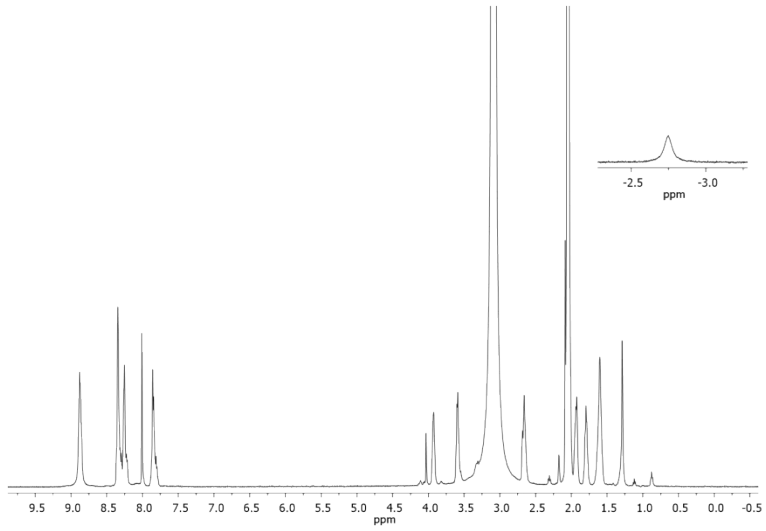


Figure S4. ^{1}H-NMR of **BHAP** in acetone-d_6

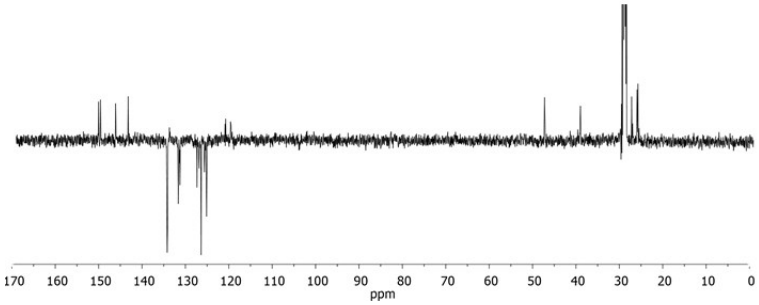


Figure S5. APT of **BHAP** in acetone-d_6

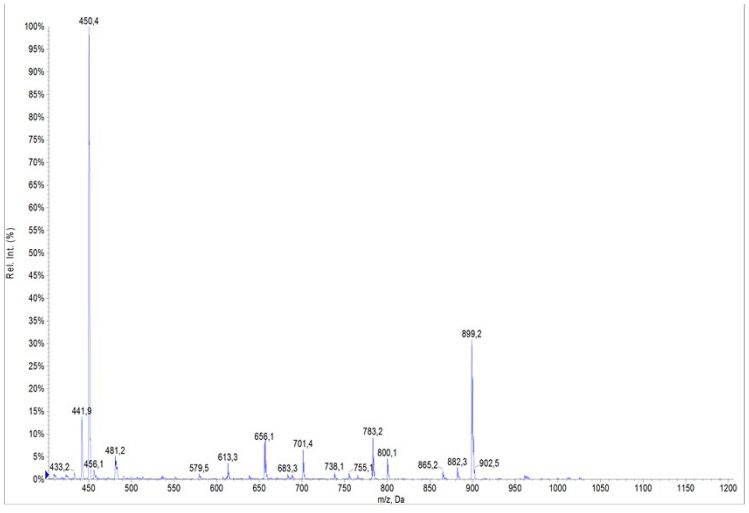


Figure S6. ESI-MS of **BHAP**

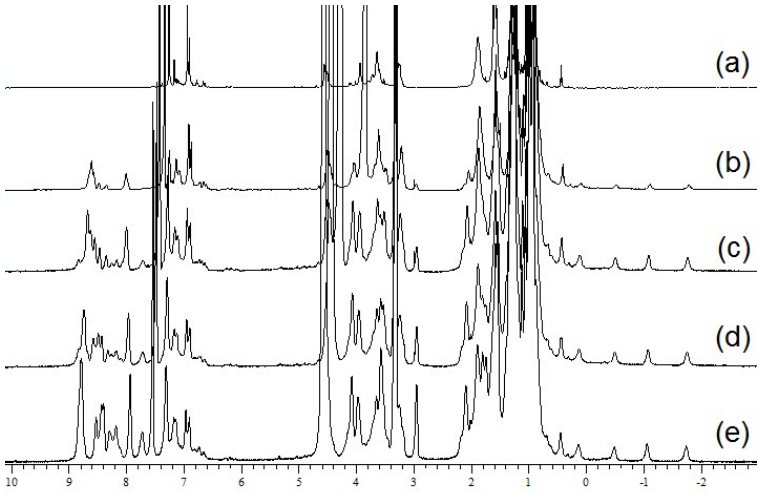


Figure S7. ^{1}H NMR titration between **PC[5]** and **BHAP** in $CDCl_3/CD_3OD$ (4/1). (a) **PC[5]** (1.00×10^{-3} M); (b) [**BHAP**]/[**PC5**] = 0.5; (c) [**BHAP**]/[**PC5**] = 1.0; (d) [**BHAP**]/[**PC5**] = 1.5; (e) [**BHAP**]/[**PC5**] = 2.0.

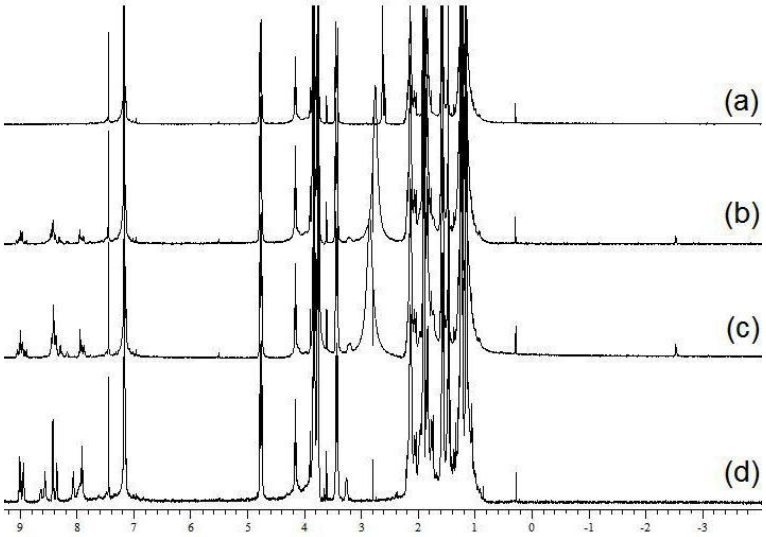


Figure S8. ^{1}H NMR titration between **PC[5]** and **BHAP** in THF-d_8. (a) **PC[5]** (1.00×10^{-3} M); (b) [**BHAP**]/[**PC5**] = 0.5; (c) [**BHAP**]/[**PC5**] = 1.0; (d) [**BHAP**]/[**PC5**] = 1.5; (e) [**BHAP**]/[**PC5**] = 2.0. The absence of signals at ppm < 0 suggests the lack of 3D network formation.

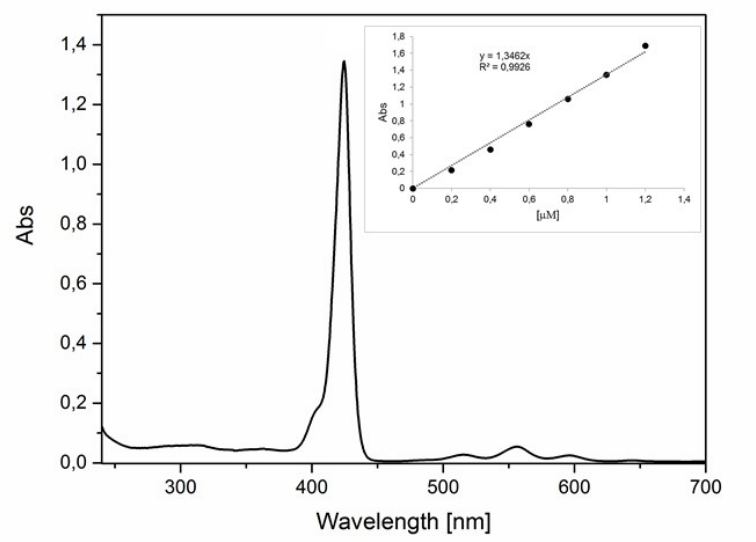


Figure S9. UV-Vis spectrum of **BHAP** 1 µM $CHCl_3/CH_3OH$ 4/1. Inset shows plot for ε determination (ε = 1.35 x 10^5 M^{-1} cm^{-1}).

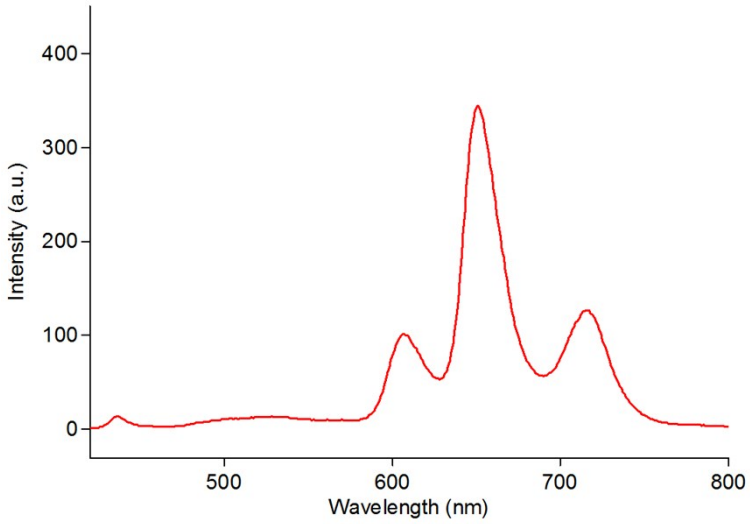


Figure S10. Fluorescence spectrum of **BHAP** 1 µM $CHCl_3/CH_3OH$ 4/1 (λ_{exc} 410 nm)

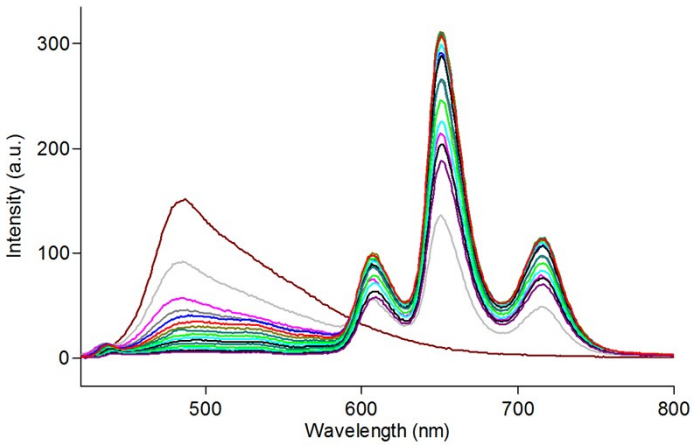
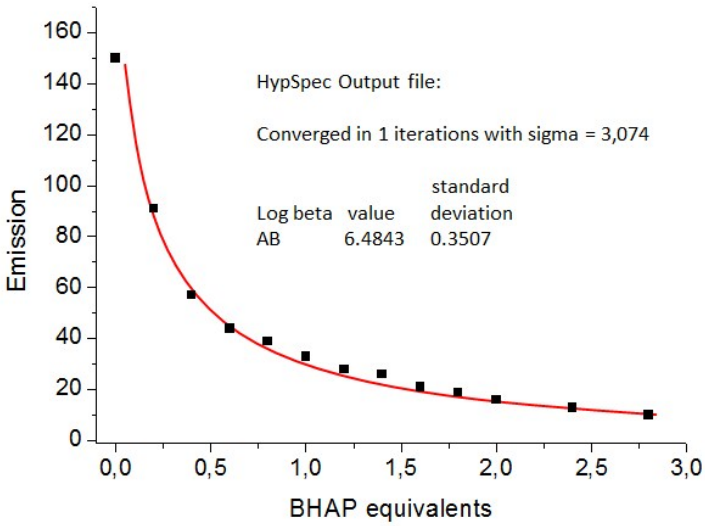


Figure S11. Fluorescence titration between **PC[5]** (1 μM) and progressive amounts of **BHAP** (0-3 equivalents) in $CHCl_3/CH_3OH$ (4/1) (λ_{exc} 410 nm).



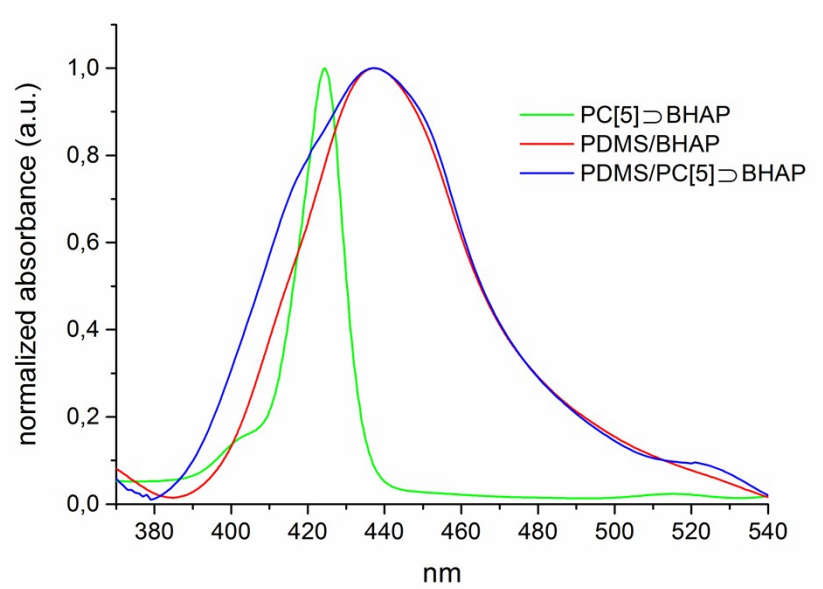


Figure S12. UV-vis spectra of **PC[5]⊃BHAP** assembled in a mixture of $CHCl_3/CH_3OH$ 4:1 (green line), and after transferred in solid matrix **PDMS/3D-PC[5]⊃BHAP** (blue line). UV-vis spectra of **BHAP** embedded in PDMS (red line).

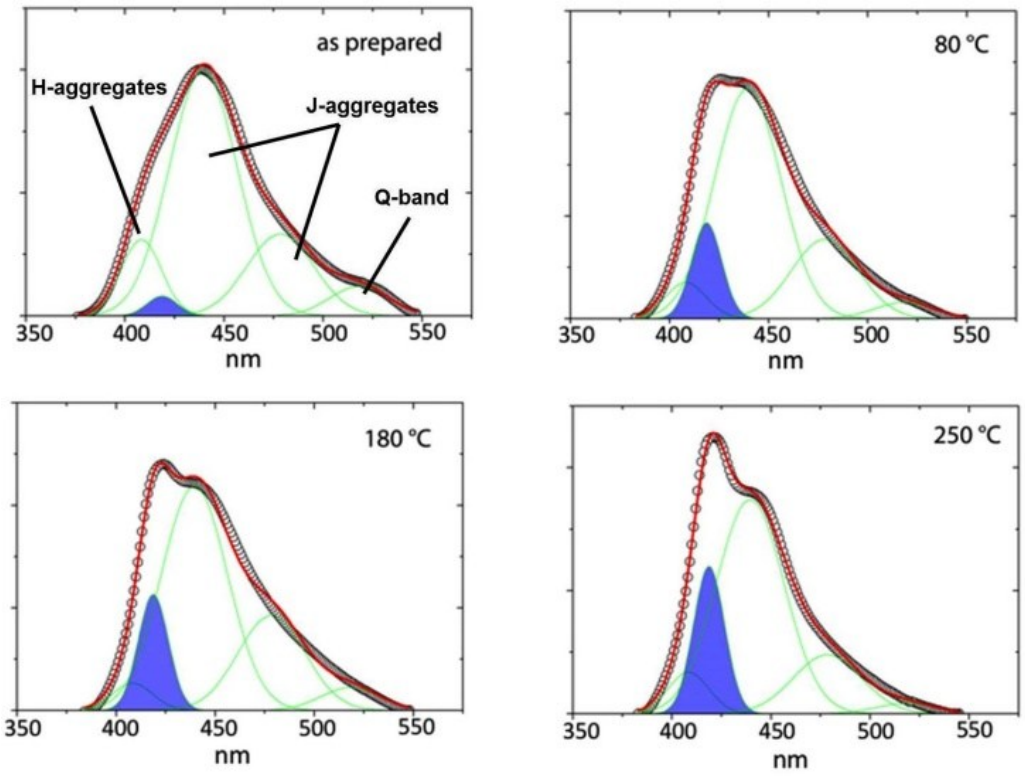


Figure S13. Soret band fitting of UV-vis spectra of a) **PDMS/3D-PC[5]⊃BHAP** as prepared and at increasing thermal shocks temperatures: b) 80 °C, c) 180 °C and d) 250 °C. The treatment time is in any case of 120 seconds. The blue area corresponds to the non-aggregates porphyrins.

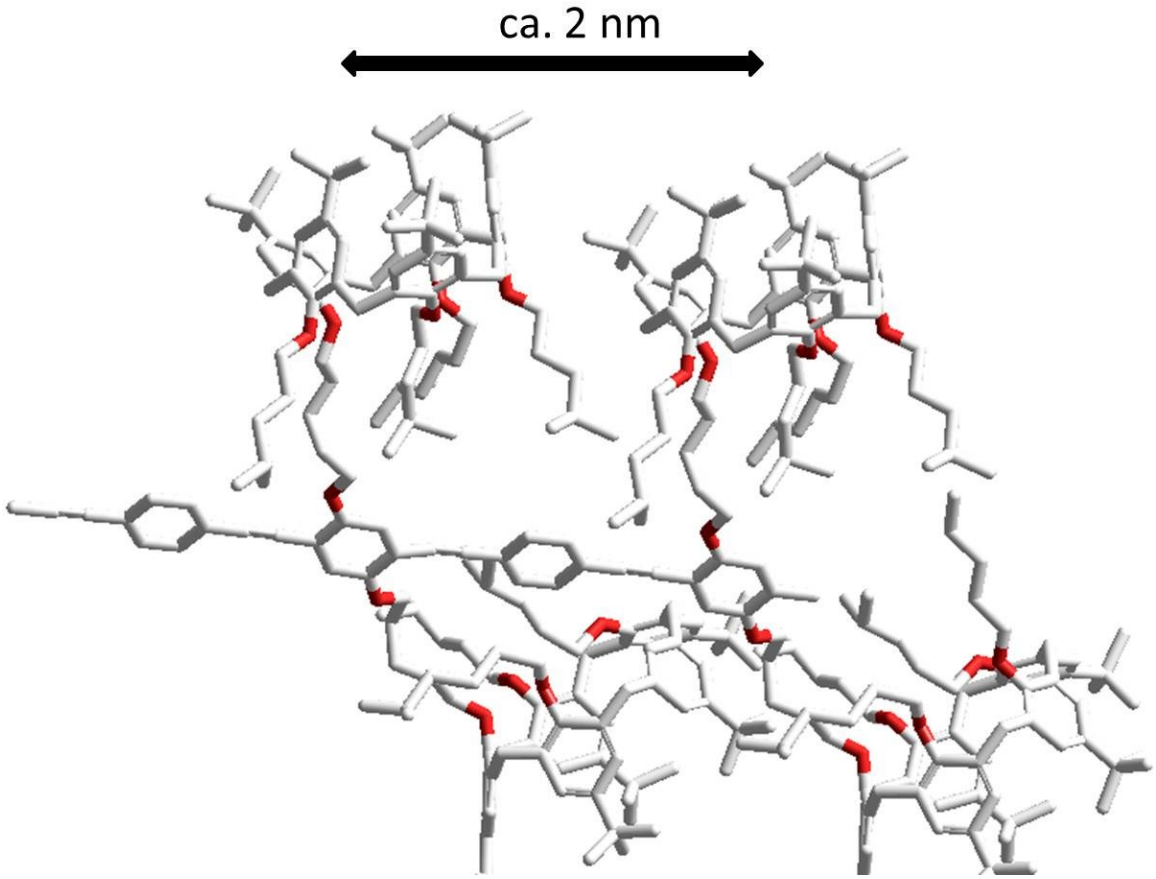


Figure S14. Optimized structure of **PC[5]** sub-unit: hydrogens and aliphatic chains of PPE are omitted for clarity.

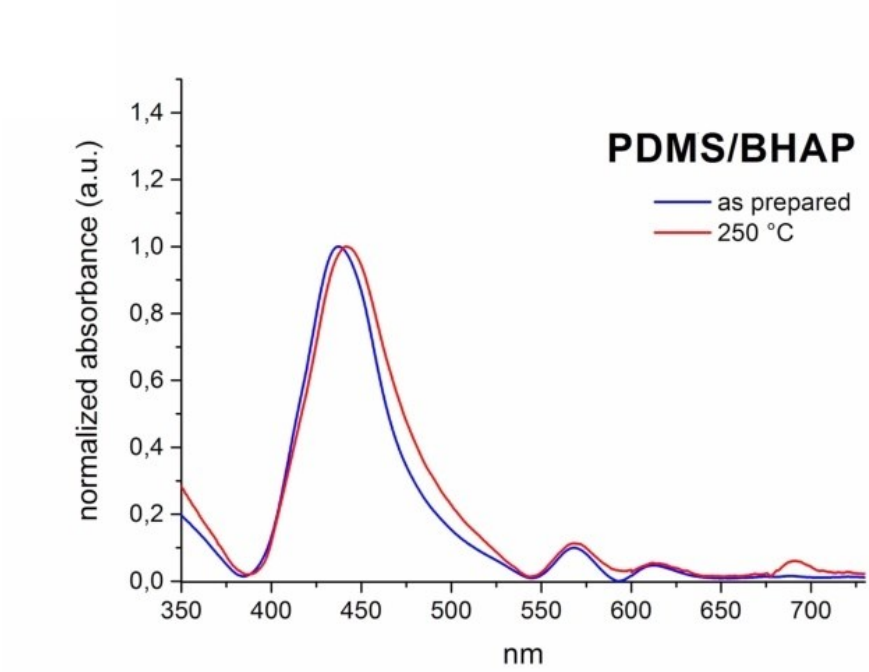


Figure S15. UV-vis spectra of PDMS/**BHAP** as prepared and after various thermal shocks (RT to high temperature within 120 s and back to RT within 240 s).

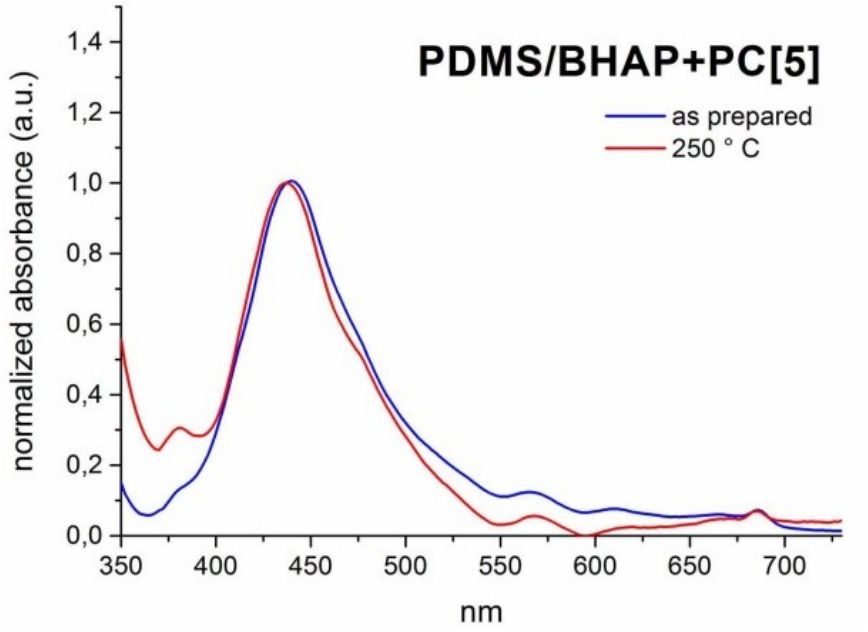


Figure S16. UV-vis spectra of PDMS/**BHAP** + **PC[5]** as prepared (blue line) and after thermal shock at 250 °C (red line).

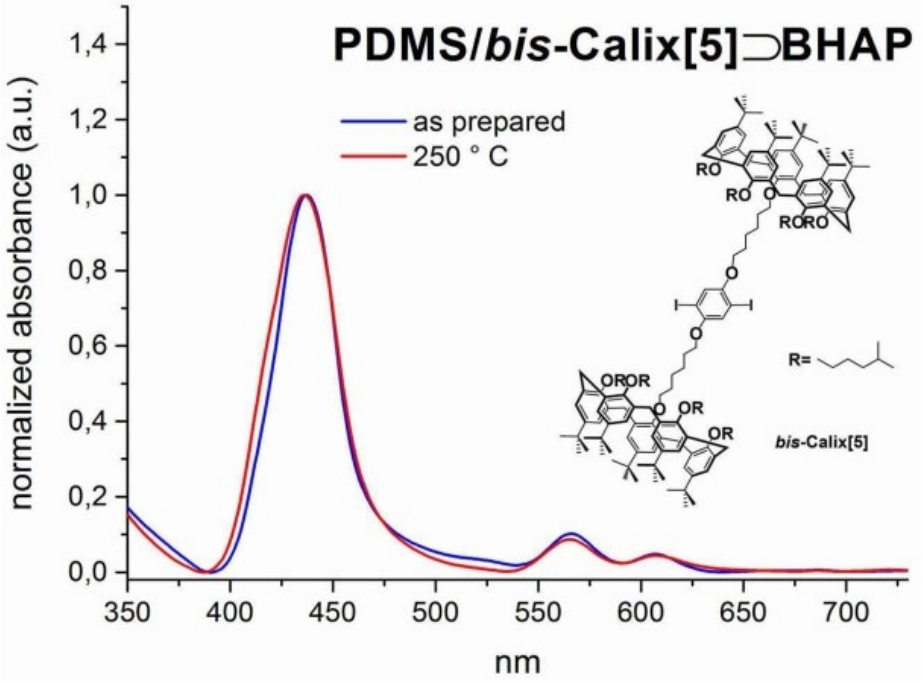


Figure S17. UV-vis spectra of PDMS/bis-Calix[5]⊃DHAP composites, as prepared (blue line) and after thermal shock at 250 °C (red line).

[1] (a) R. Evans, Z. Deng, A. K. Rogerson, A. S. McLachlan, J. J. Richards, M. Nilsson, G. A. Morris, *Angew. Chem., Int. Ed.*, 2013, **52**, 3199–3102; (b) M. L. Giuffrida, E. Rizzarelli, G. A. Tomaselli, C. Satriano, G. Trusso Sfrazzetto, *Chem. Commun.*, 2014, **50**, 9835–9838.

[2] A. Pappalardo, F. P. Ballistreri, G. Li Destri, P. G. Mineo, G. A. Tomaselli, R. M. Toscano, G. Trusso Sfrazzetto, *Macromolecules* 2012, **45**, 7549–7556.

[3] (a) P. Gans, A. Sabatini, A. Vacca, *Talanta* 1996, **43**, 1739–1753; (b) S. Kumar, S. Maji, M. Joseph, K. Sankaran, *J. Lumin.* 2015, **161**, 123–128.