

Supplementary Information for

Dynamic rearrangement of bilayers of porphyrin hetero-dimers at a solid/liquid interface

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1. Statistical analysis

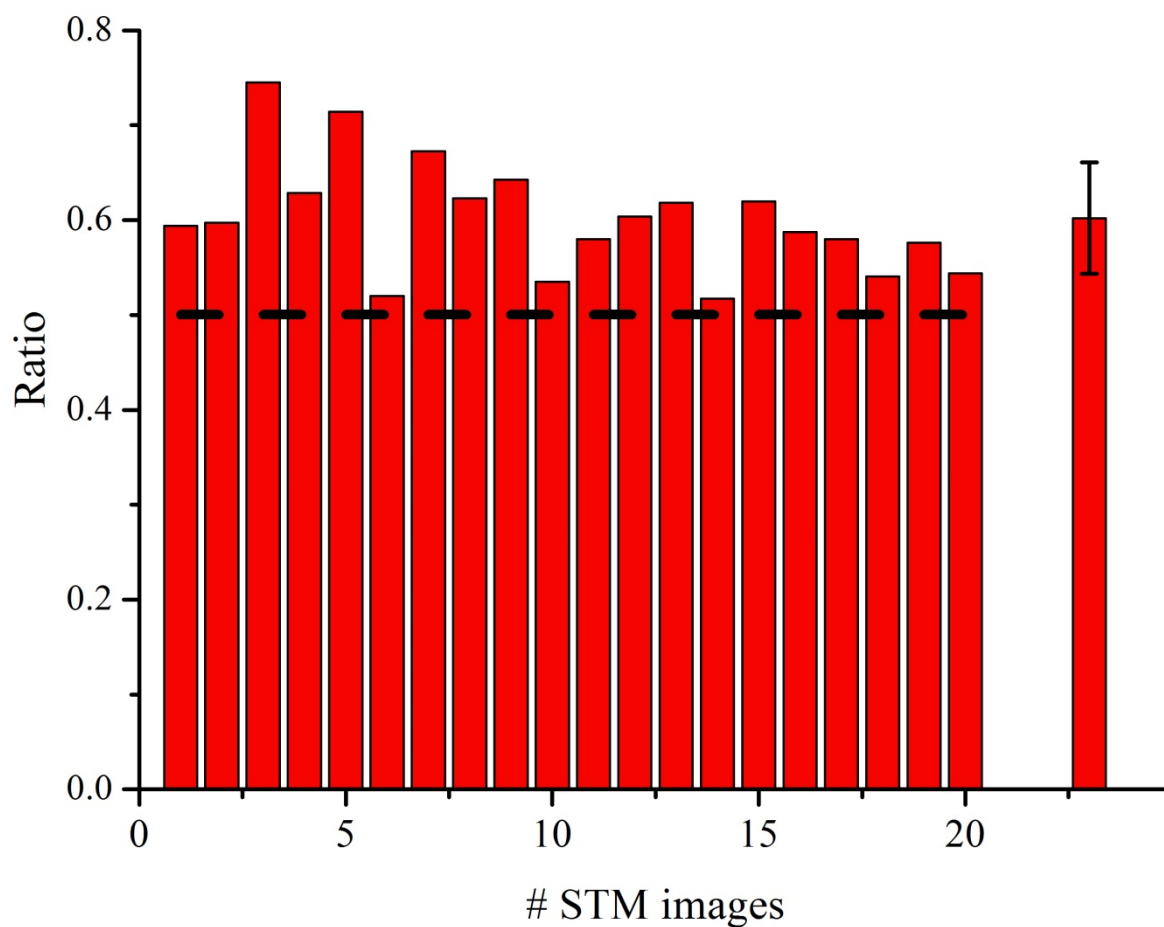


Figure S1. Statistical analysis of 20 consecutive STM images of a bilayer of Cu-Mn porphyrin dimer **2**, in which the number of manganese chloride porphyrin moieties that in the top layer exists as a H-type aggregate is plotted: the last bar shows the average ratio, which is 0.60 ± 0.06 (standard deviation is indicated). The total number of porphyrin dimers counted is 1223, of which 742 MnCl-porphyrins were found to be in a H-type aggregate with respect to the layer below. The black dashed line indicates the normal distribution.

2. Additional STM images and energy profile of the bilayer dynamics of Cu-Mn porphyrin dimer 2

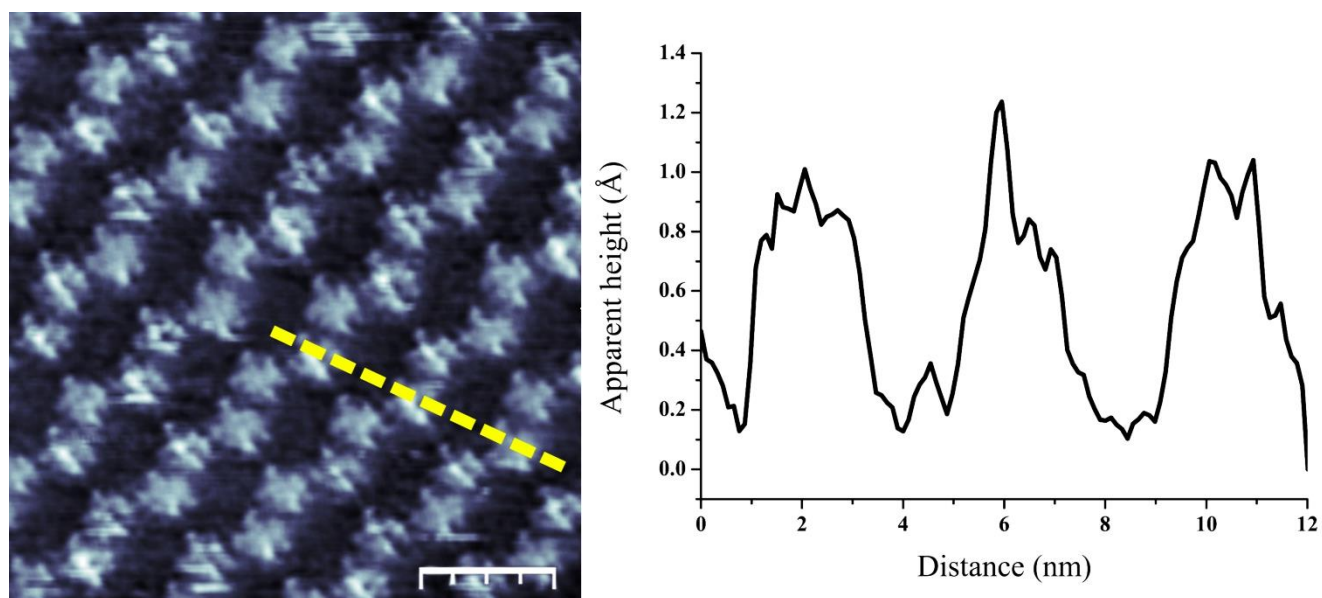


Figure S2. STM image (left) and apparent height profile (right) of a monolayer of Cu-Mn-porphyrin dimers at the HOPG/1-phenyloctane interface ($V_b = -450$ mV, $I_s = 5$ pA, scale bar 5 nm).

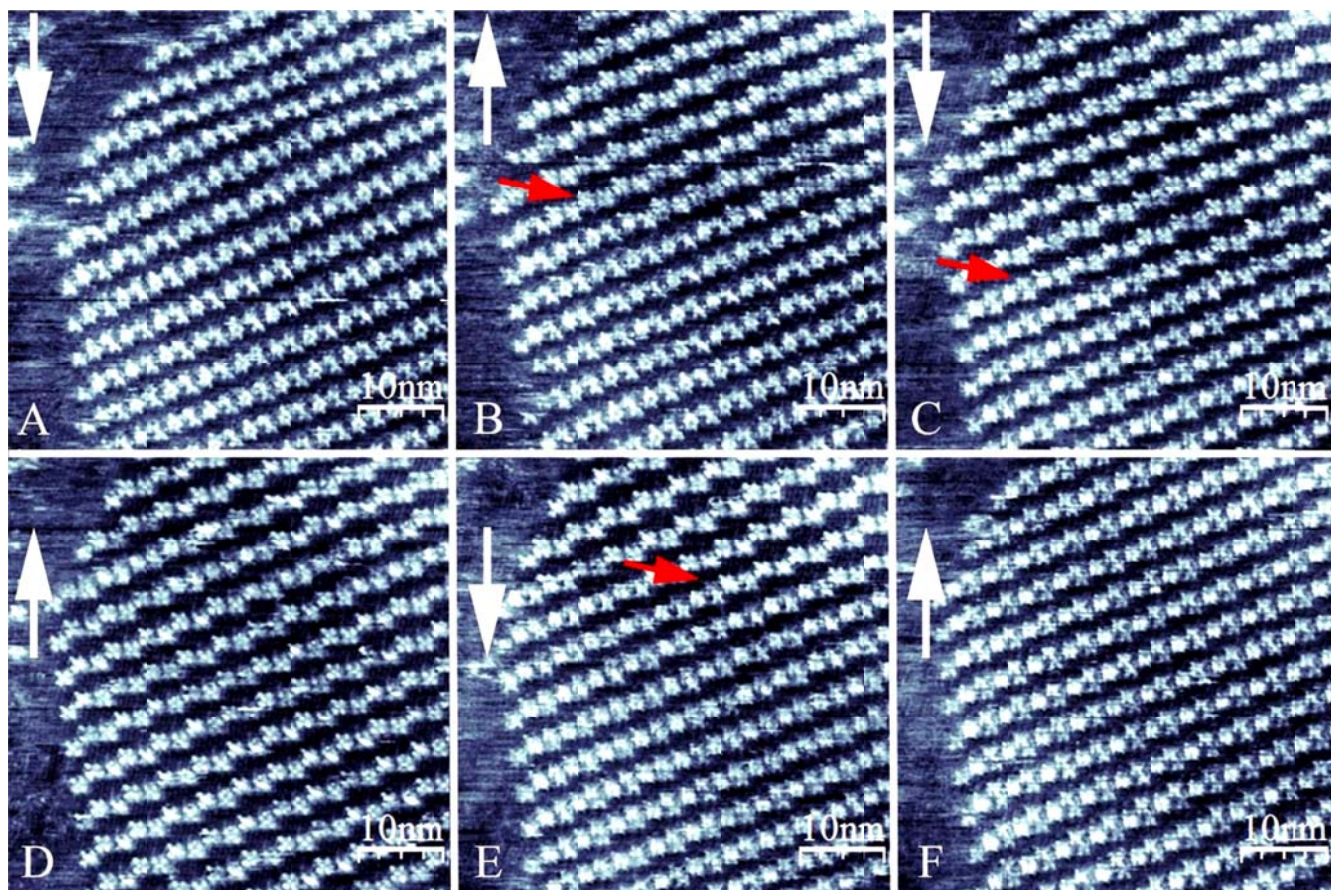


Figure S3. Six consecutive STM images of a bilayer of Cu-Mn porphyrin dimer **2** at the HOPG/1-phenyloctane interface ($V_b = -450$ mV, $I_s = 5$ pA), showing the full repositioning of the top layer. The white arrows indicate the scanning direction. **(A)** Porphyrin dimers are stacked in an offset position. **(B)** During the upward scan the top layer is gradually transformed into a H-type aggregate. The red arrow shows the start of the H-type aggregation packing. **(C)** The downward scan shows that more porphyrins have adopted the H-type packing. The red arrow indicates where the porphyrin dimers are still stacked in an offset-type fashion. **(D)** All porphyrin dimers are stacked in a H-type packing. **(E)** The downward scan shows that the porphyrin dimers transform again, from a H-type packing into an offset-type packing (indicated by the red arrow). **(F)** The upward scan shows that all the porphyrin dimers have adopted their new offset-type packing, which is however different from the packing observed in **(A)**.

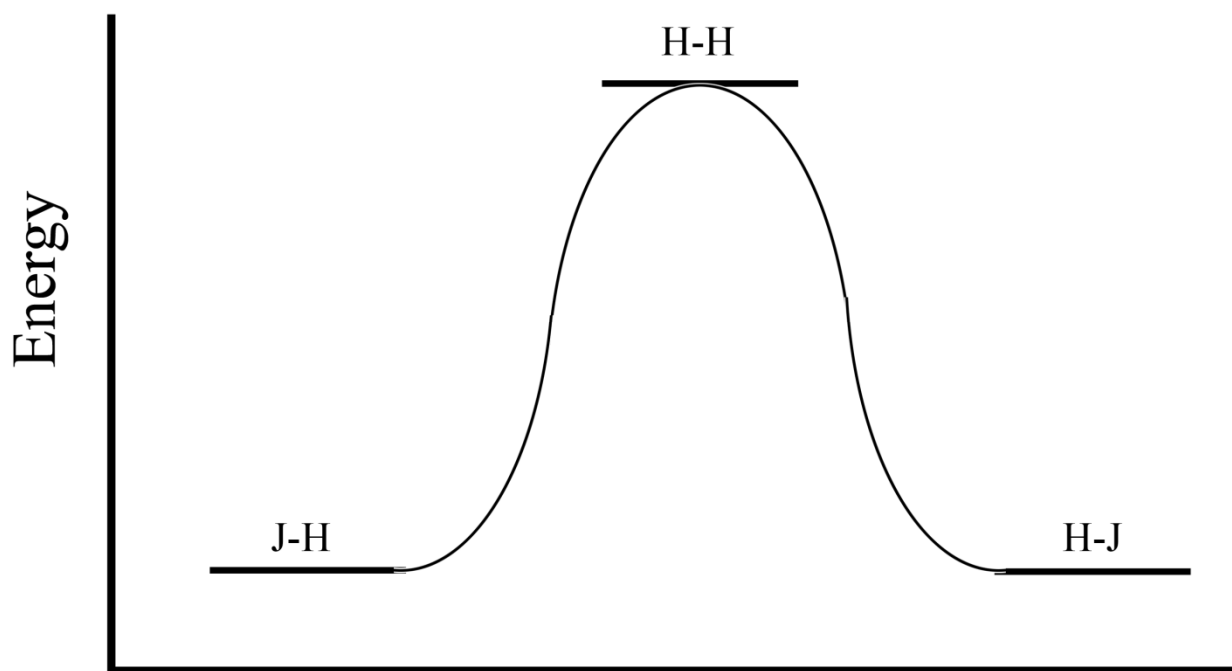


Figure S4. Schematic representation of an energy diagram corresponding to the transformation process observed in the bilayer of Cu-Mn porphyrin dimer **2**, where J-H indicates that one porphyrin of a dimer in the top layer is oriented in a J-type geometry and the other porphyrin in a H-type geometry with respect to the porphyrins of a dimer in the bottom layer. The initial orientation of the top layer of the porphyrin dimers reorganises itself into an energetically less favourable H-H type orientation, and finally reorients itself in a bilayer with an H-J-type geometry.

3. Magnifications of the figures in the paper

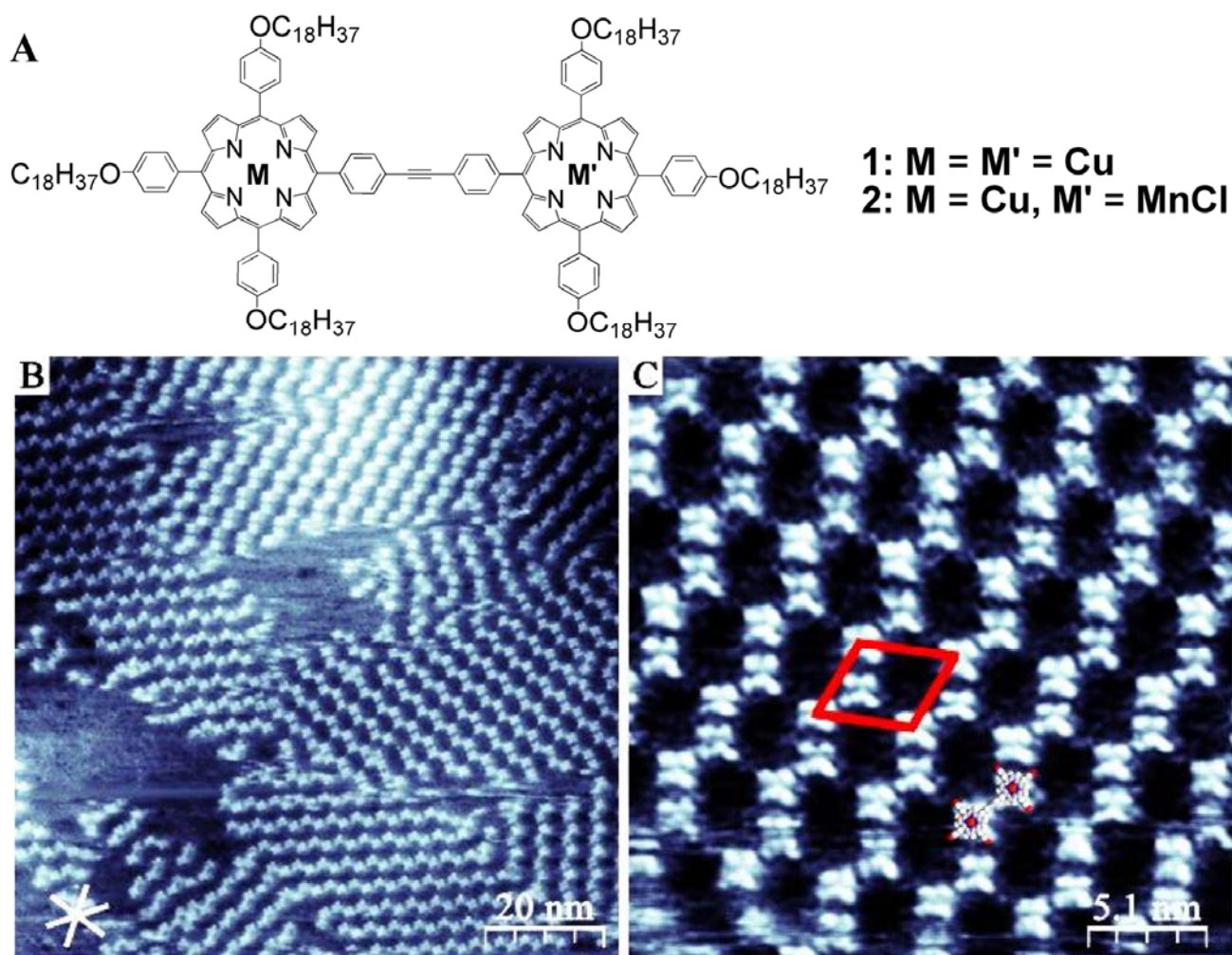


Fig. 1 (A) Molecular structures of Cu-Cu porphyrin dimer **1** and Cu-Mn porphyrin dimer **2**. (B) STM image of a self-assembled monolayer of **1** at the graphite/1-phenyloctane interface. The white asterisk represents the symmetry directions of the underlying graphite lattice. $V_{\text{bias}} = -450$ mV and $I_{\text{set}} = 3$ pA. (C). Magnification, with a molecular model of the conjugated parts of **1** superimposed and the unit cell drawn in.

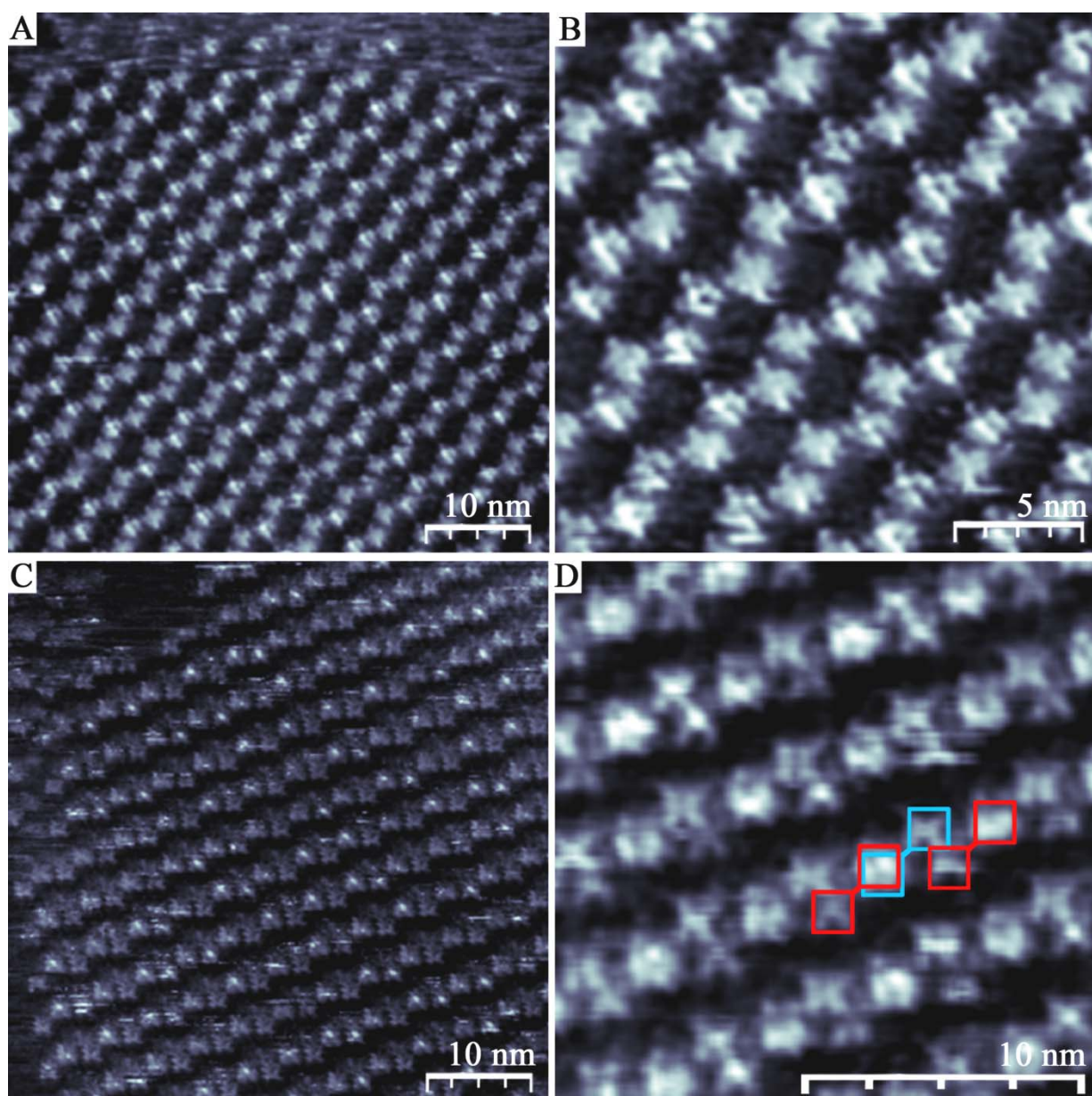


Fig. 2 (A) STM image of a monolayer of Cu-Mn porphyrin dimer **2** at the graphite/1-phenyloctane interface. $V_{\text{bias}} = -450$ mV and $I_{\text{set}} = 5$ pA. (B) Magnification of the STM image in (A). (C) STM image of a bilayer of **2**, recorded under the same conditions as the monolayer in (A). (D) Magnification of the STM image in (B). The red squares represent porphyrin dimers in the top layer and the blue squares represent porphyrins in the bottom layer.

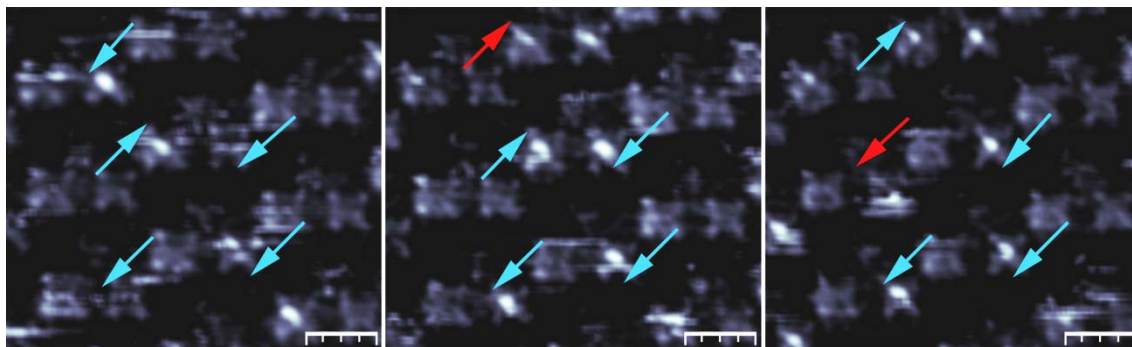


Fig. 3 Three consecutive STM images ($V_b = -450$ mV, $I_s = 5$ pA, $\Delta t = 5$ min, scale bar 3 nm) of a bilayer of Cu-Mn porphyrin dimer **2** at the same location at the graphite/1-phenyloctane interface, revealing the dynamics between the two layers. The arrows point from the Cu to the MnCl centre within a dimer. Dimers that reoriented with respect to the previous scan are indicated by a red arrow.

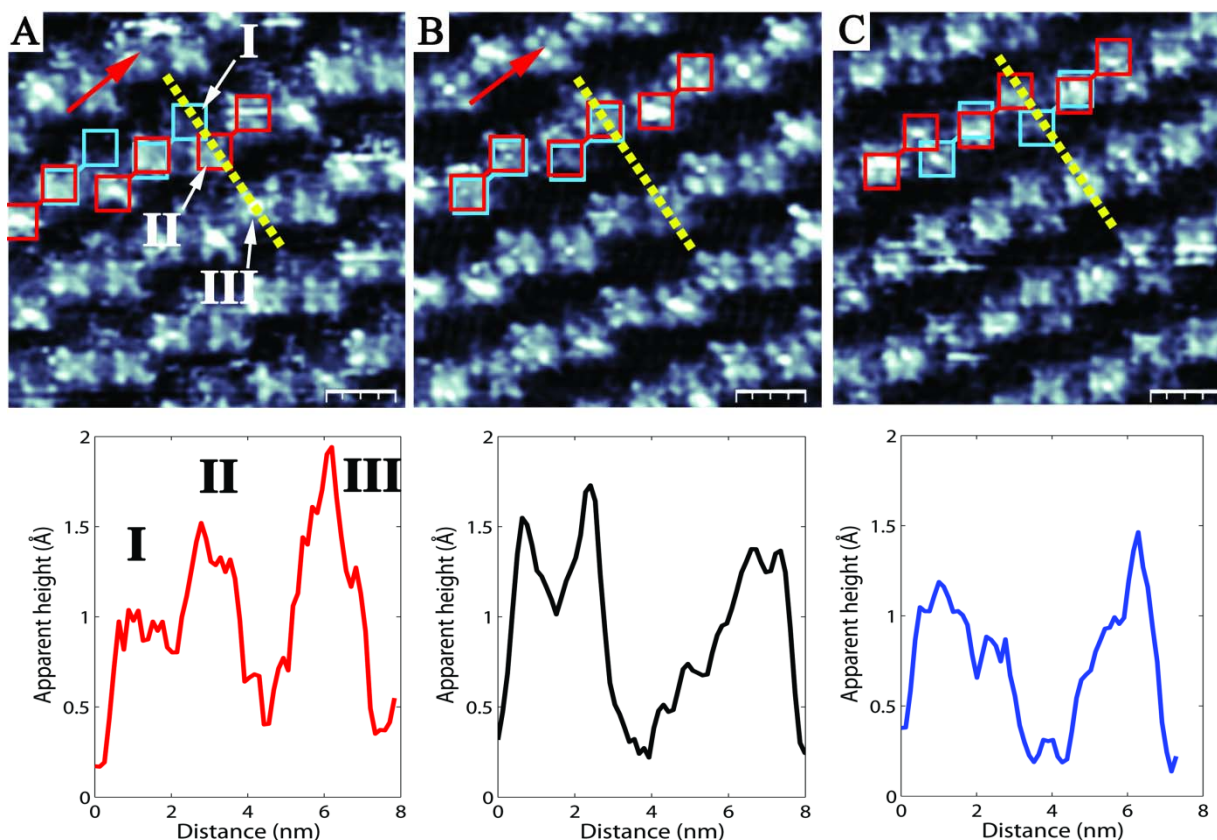


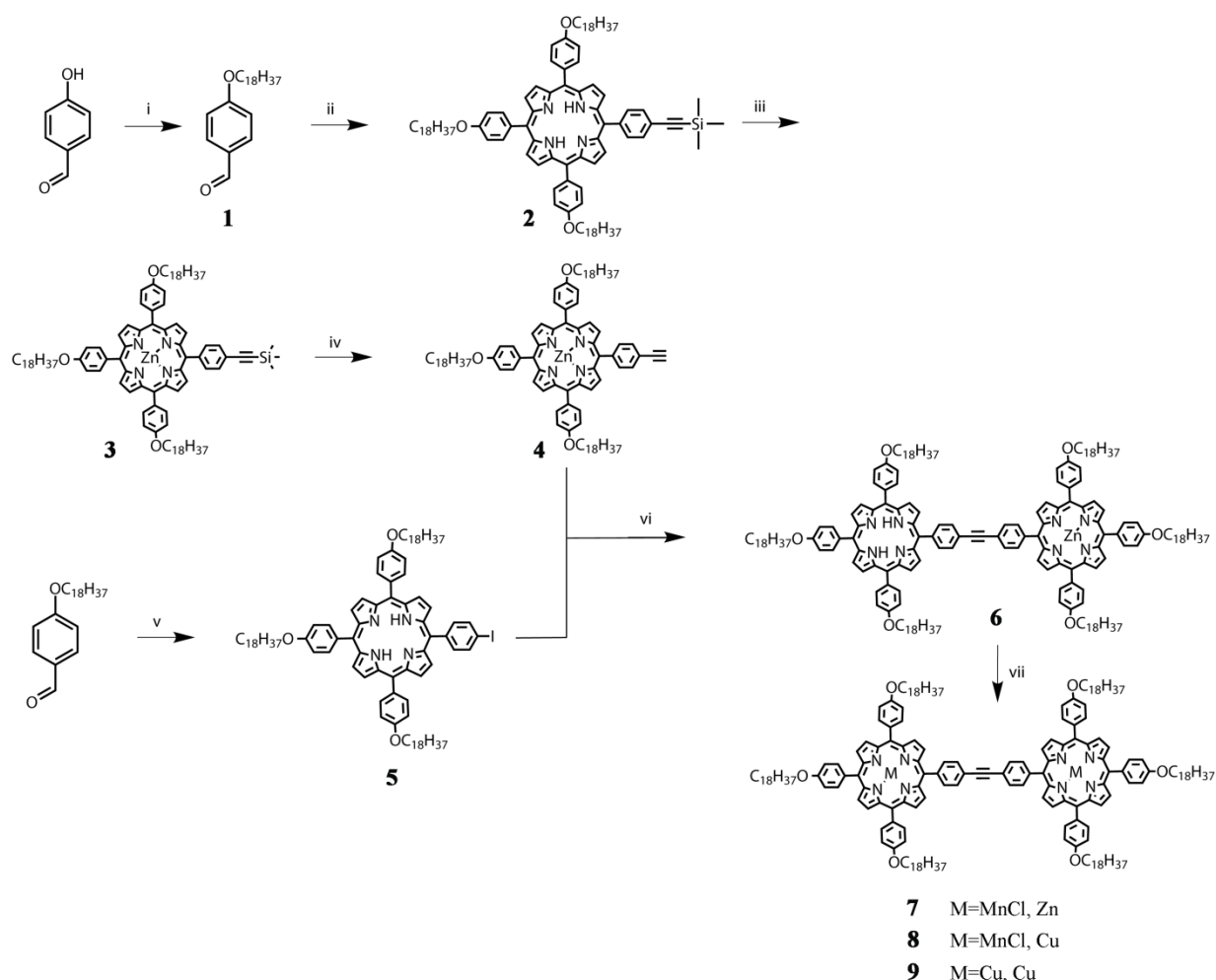
Figure 4 Top: three consecutive STM images ($V_b = -450$ mV, $I_s = 5$ pA, $\Delta t = 5$ min., scale bar 3.4 nm) of a bilayer of Cu-Mn porphyrin dimer **2** at the graphite/1-phenyloctane interface, showing a repositioning of the top layer with respect to the bottom layer, first to an H-type (A→B) and then to a J-type assembly (B→C). Red squares represent porphyrin dimers in the top layer, blue squares those in the bottom layer. The red arrows indicate the direction in which porphyrin dimers in the top layer (red squares) move along a lamellar arrays. Bottom: cross sections corresponding to the yellow dashed traces in the images.

4. Materials and methods

Unless stated otherwise, all solvents used for syntheses were used as received. All chemicals were purchased from either Sigma-Aldrich or VWR and used as received. Pyrrole was distilled prior to use. Chromatography was performed using Silicycle silica (40-63 μm) or Merck 60H for thin layer chromatography. Size exclusion chromatography was performed using BioRad BioBeads SX-1 with toluene as a mobile phase. ^1H NMR and ^{13}C NMR spectra were recorded on Varian Inova400 or Bruker Avance III 500 MHz instruments. Chemical shifts are reported in ppm downfield with respect to the internal standard TMS (0.00 ppm). UV-vis spectra were recorded on a Varian Cary 50 Conc. spectrophotometer at ambient conditions. Maldi-TOF spectra were measured on a Bruker Biflex III spectrometer in reflection or linear mode. The samples were prepared by mixing diluted solutions of the compounds in chloroform with equal amounts of matrix solution (dithranol: 20 mg/mL in chloroform). Electron Ionization Mass spectrometry was performed on a Jeol Accutof JMS-100GCv. STM experiments were carried out in constant current mode using the Nijmegen home-built low-current STM, using an Omicron Scala SPM controller. STM tips were mechanically cut from Pt/Ir wires (90:10) with a diameter of 0.5 mm. The HOPG used was ZYB NT-MDT, Zelenograd, Moscow. STM measurements were performed at the HOPG/liquid interface, with the tip immersed in a droplet of the solution.

5. Syntheses

The synthetic procedures are shown in Scheme 1.



Scheme 1 Synthesis of porphyrin dimers. Reaction conditions: i: $\text{C}_{18}\text{H}_{37}\text{Br}$, K_2CO_3 , DMF, 60°C , 15h. ii. Pyrrole, 4-((trimethylsilyl)ethynyl)benzaldehyde, DMF, 145°C , 5h. iii. $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, $\text{CHCl}_3/\text{MeOH}$, 70°C , 2h. iv. CsF , THF/EtOH, RT, 15 h. v. 4-iodobenzaldehyde, DMF, 145°C , 6 h. vi. Pd_2dba_3 , AsPh_3 , 35°C , 16 h. vii. $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, DMF, 140°C , 3h. Brine, RT, 15h. (**7**). 1. Conc. HCl, RT, 1h. 2. $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, $\text{CHCl}_3/\text{MeOH}$, 70°C , 2h. (**8**). 1. Conc. HCl, RT, 1h. 2. $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, $\text{CHCl}_3/\text{MeOH}$, 70°C , 15 h. (**9**)

Synthesis of 4-(octadecyloxy)benzaldehyde (1)

In a 1L roundbottom flask, 1-bromooctadecane (24.47 g, 73.4 mmol), potassium carbonate (27.7 g, 200 mmol) and 4-hydroxybenzaldehyde (8.15 g, 66.7 mmol) were dissolved in DMF (100 ml). The reaction mixture was stirred under argon at 60 °C for 15 hours. After cooling, the mixture was filtered and evaporated to dryness. The crude product was redissolved in CHCl_3 and this solution was washed twice with an aqueous 0.1 M HCl solution (150 mL) and with water (150 mL). The organic layer was collected and evaporated to dryness. The product was recrystallized from MeOH to yield a white solid in 78% (19.5 g, 52.1 mmol)

^1H NMR (400 MHz, CDCl_3) δ 9.88 (s, 1H, COH), 7.82 (d, J = 8.7 Hz, 2H, Ar-H), 6.99 (d, J = 8.7 Hz, 2H, Ar-H), 4.04 (t, J = 6.5 Hz, 2H, OCH_2), 1.87 – 1.75 (m, 2H, $\text{OC}_2\text{H}_4\text{CH}_2$), 1.53 – 1.41 (m, 2H), 1.26 (m, 28H, $\text{OC}_3\text{H}_6\text{C}_{14}\text{H}_{28}$), 0.88 (t, J = 6.7 Hz, 3H, CH_3).

^{13}C NMR (100 MHz, CDCl_3) δ 191.01, 164.48, 132.19, 129.96, 114.96, 68.66, 32.15, 29.92, 29.89, 29.80, 29.77, 29.59, 29.56, 29.28, 26.18, 22.92, 14.34.

EI: m/z M_{expected} : 374.6 g/mol. M_{found} : 374.3 g/mol.

Synthesis of 5-(((trimethylsilyl)ethynyl)phenyl)-10,15,20-(octadecyloxyphenyl)porphyrin (2)

In a 250 mL roundbottom flask, pyrrole (1.563 ml, 22.36 mmol), 4-(((trimethylsilyl)ethynyl)benzaldehyde (1.131 g, 5.59 mmol) and **1** (6.28 g, 16.77 mmol) were dissolved in propionic acid (30 ml) and heated to 145 °C for 5 hours, while stirring. The reaction mixture was allowed to cool to room temperature and then evaporated to dryness. The mixture was purified by column chromatography (eluent: CHCl_3), however a mixture was obtained of tetraoctadecyloxyphenylporphyrin (TTP), the desired product, disubstituted ((trimethylsilyl)ethynyl)phenyl porphyrin and trisubstituted ((trimethylsilyl)ethynyl)phenyl porphyrin. This was also confirmed by Maldi-TOF. Because no separation of these compounds could be achieved, the mixture was used in the next reaction in which a zinc ion is inserted in the core.

Maldi-TOF: m/z 1689: TTP + H^+ , 1518: product + H^+ , 1345, [bis-(((trimethylsilyl)ethynyl)-bis-(octadecyloxyphenyl)porphyrin] + H^+ , 1173 [tri-(((trimethylsilyl)ethynyl)phenyl-mono-(octadecyloxyphenyl)porphyrin] + H^+ .

Synthesis of Zn(II)-[5-(((trimethylsilyl)ethynyl)phenyl)-10,15,20-(octadecyloxyphenyl)porphyrin] (3)

The mixture obtained in the previous reaction (8.48 g) was dissolved in CHCl_3 (100 ml) and methanol (50 ml) while stirring. Zinc(II) acetate dihydrate (12.28 g, 55.9 mmol) was added, and the mixture was stirred under argon at 70 °C for 2 hours. The mixture was allowed to cool to room temperature and was washed with a saturated aqueous NaHCO_3 solution (150 mL) and with water (100 mL). The organic phase was dried over MgSO_4 and evaporated to dryness. The product was purified by column chromatography (eluent: CHCl_3), however compound **3** proved also to be unseparable from the TTP. NMR confirmed that the Zn ion had been inserted, since no NH protons could be observed. The mixture of **3** and TTP was used further in the next reaction.

Synthesis of Zn(II)-[5-(ethynylphenyl)-10,15,20-(octadecyloxyphenyl)porphyrin] (4)

The mixture obtained in the previous reaction (2.85 g) was dissolved in THF (350 ml) and ethanol (75 mL) and the solution was stirred under argon. Cesium fluoride (5.48 g, 36.1 mmol) was dissolved in 100 mL of ethanol. This solution was added to the mixture and the mixture was stirred for 15 hours. The reaction was monitored by TLC (eluent: DCM/heptane 5/4), and after 15 hours it was concluded that the reaction was finished.

The solution was evaporated to dryness, the residue was redissolved in 100 mL CHCl_3 , and this solution was washed with water. The organic phase was evaporated to dryness and the product was purified using column chromatography (eluent: DCM/heptane 5:4, v/v). This resulted in a mixture of the desired product with TTP after evaporation of the solvent as a purple solid. The mixture could not be separated, but the presence of the desired product was confirmed by Maldi-TOF. Since the TTP does not interfere with the synthesis of the porphyrin dimer **6**, the mixture was used in the synthesis of **6**.

Maldi-TOF: m/z 1784: [2 Zn-TPP + Na^+ + K^+] $^{2+}$, 1752: Zn-TPP – H^+ , 1540: [2 product + Na^+ + K^+] $^{2+}$, 1506: product – H^+ , 1409: [product – $\text{C}_{18}\text{H}_{37}$ + 2 Na^+ + K^+], 1262 [2 product – 2 $\text{C}_{18}\text{H}_{37}$ + Na^+] $^{2+}$, 1163: unknown

Synthesis of [5-(iodophenyl)-10,15,20-(octadecyloxyphenyl)porphyrin] (5)

In a 250 mL roundbottom flask, 4-iodobenzaldehyde (0.70 g, 3.02 mmol), 4-(octadecyloxy)benzaldehyde (3.39 g, 9.05 mmol) and pyrrole (0.837 ml, 12.07 mmol) were added to propionic acid (100 ml). The solution was stirred under argon at 145 °C for 6 hours. After cooling, the propionic acid was evaporated. The residue was redissolved in a minimal amount of CHCl_3 (30 mL) and this solution was precipitated in MeOH (300 mL). The black precipitate was filtered off and washed with MeOH. The residue was purified using column chromatography (eluent: toluene/ heptane 1:1, v/v), which resulted in four purple fractions of which the fourth one is the product, which was isolated as a purple solid. The product was recrystallized from CHCl_3 /MeOH to yield a purple solid in 5% yield (245 mg, 0.16 mmol).

^1H NMR (500 MHz, CDCl_3) δ 8.96 – 8.84 (m, 6H, β -pyrrolic-H), 8.79 (d, J = 4.7 Hz, 2H, β -pyrrolic-H), 8.14 – 8.04 (m, 8H, Ar-H), 7.96 – 7.91 (m, 2H, Ar-H), 7.29 – 7.23 (m, 6H, Ar-H), 4.23 (t, J = 6.5 Hz, 6H, OCH_2), 1.97 (qn, J = 7.5 Hz, 6H, OCH_2CH_2), 1.62 (qn, J = 7.5 Hz, 6H, OCH_2CH_3), 1.53 – 1.19 (m, 84H, $\text{OC}_2\text{H}_4\text{C}_{14}\text{H}_{28}\text{CH}_2\text{CH}_3$), 0.87 (t, J = 6.9 Hz, 9H, CH_3), -2.77 (s, 2H, NH).

^{13}C NMR (125 MHz, CDCl_3) δ 159.02, 141.94, 136.20, 135.82, 135.60, 134.27, 120.36, 120.10, 118.03, 94.02, 76.77, 68.36, 31.95, 29.76, 29.71, 29.71, 29.69, 29.58, 29.55, 29.39, 26.28, 22.72, 14.15.

Maldi-TOF: m/z 1546: M^+ , 1420: (product – I + 2 H) $^+$

UV-Vis ($c = 2.07 \times 10^{-6}$ M in CHCl_3): 422 ($\epsilon = 5.68$), 454 ($\epsilon = 4.88$), 519 ($\epsilon = 4.65$), 555 ($\epsilon = 4.59$), 595 ($\epsilon = 4.51$), 651 ($\epsilon = 4.54$), 678 ($\epsilon = 4.52$)

Synthesis of Zn-H2-porphyrin dimer (6)

The mixture obtained in the synthesis of **4** (190.4 mg, 0.126 mmol) was placed in a 250 mL Schlenck flask to which **5** (195.3 mg, 0.126 mmol), triphenylarsine (46.5 mg, 1.52×10^{-4} mol) and tris(dibenzylideneacetone)dipalladium(0) (4.4 mg, 4.8 μmol) were added and dissolved in distilled toluene (100 ml) and closed off with a septum. The flask was freeze-pump-thawed three times. Distilled triethylamine (20 ml) was purged with argon for 5 minutes and added by syringe to the porphyrin solution, which was under an argon atmosphere. The reaction mixture was heated to 35 $^\circ\text{C}$ and stirred for 16 hours. The reaction was evaporated to dryness and the product was purified by column chromatography. When using CHCl_3 /heptane (5/4), AsPh_3 came off quickly followed by the first purple band. When this band had eluted, the eluent was changed to CHCl_3 /heptane (3/1), which yielded a second purple band, further washing of the column with chloroform or mixtures of chloroform with MeOH did not yield any further bands.

The second band was taken and purified SEC (eluent: toluene), which yielded one band. The solvent was evaporated to yield a purple/pink solid in 30% (0.11 g, 39 μmol)

^1H NMR (500 MHz, CDCl_3) δ 9.12 – 8.81 (m, 16H, β -pyrrolic), 8.36 – 8.27 (m, 4H, Ar-H), 8.20 – 8.04 (m, 15H, Ar-H), 7.35 – 7.26 (m, 12H, Ar-H), 4.33 – 4.14 (m, 12H, OCH_2), 2.10 – 1.89 (m, 12H, $\text{OC}_2\text{H}_4\text{CH}_2$), 1.76 – 1.57 (m, 12H, OCH_2CH_2), 1.57 – 1.16 (m, 168H, $\text{OC}_3\text{H}_6(\text{C}_{14}\text{H}_{28})$), 0.87 (dt, J = 6.7, 3.6 Hz, 18H, CH_3), -2.71 (s, 2H, NH).

^{13}C NMR (125 MHz, CDCl_3) δ 159.03, 158.88, 150.70, 150.59, 150.57, 149.85, 143.30, 135.63, 135.43, 134.96, 134.74, 134.60, 134.39, 134.35, 132.27, 132.08, 132.01, 130.10, 129.99, 121.28, 121.10, 120.31, 120.10, 118.85, 112.77, 112.74, 112.64, 112.61, 68.37, 31.95, 29.76, 29.72, 29.69, 29.59, 29.56, 29.39, 26.29, 22.71, 14.14.

Maldi-TOF: m/z 2926: M^+

UV-Vis ($c = 1.67 \times 10^{-6}$ M in CHCl_3): λ/nm ($\log(\epsilon/\text{M}\cdot\text{cm}^{-1})$) 426 (5.76), 458 (4.75), 520 (4.16), 553 (4.37), 592 (3.95), 651 (3.76), 691 (2.86).

Synthesis of MnCl-Zn-porphyrin dimer (7)

In a 100 mL roundbottom flask, compound **6** (20 mg, 6.84 μmol) was dissolved in DMF (10 mL). Manganese(II) acetate tetrahydrate (10.3 mg, 0.042 mmol) was added and the mixture was heated to reflux while stirring under an argon atmosphere. After 1 hour, the mixture was cooled to room temperature and the solvent was evaporated. The green/purple solid was redissolved in CHCl_3 (30 mL) and stirred as a two phase system with a saturated brine solution for 2 days. The organic phase was separated and the solvent was evaporated. The product was purified by column chromatography (eluent: 1-3% MeOH in CHCl_3 v/v) resulting in 3 bands, of which the second band proved to be the product. The solvent was evaporated yielding a red/green solid in 78%. (16.1 mg, 6.84 μmol).

Maldi-TOF: m/z 2978: $[\text{M} - \text{Cl}]^+$

UV-vis ($c = 3.6 \times 10^{-6}$ M in CHCl_3): λ/nm ($\log(\epsilon/\text{M}^{-1}\text{cm}^{-1})$) 425 (4.71), 481 (4.06), 550 (3.44), 589 (3.22), 625 (3.15).

Synthesis of MnCl-Cu-porphyrin dimer (8)

In a test tube, Zn-Mn-TPP-acetylene-dimer **7** (10.55 mg, 3.5 μmol) was dissolved in CHCl_3 (3 mL) and stirred. To this 4 drops of concentrated HCl were added and the reaction was monitored by Maldi-TOF. After 10 minutes no more Zn-porphyrin was present and the reaction was washed with a saturated bicarbonate solution. Dried over MgSO_4 , filtered and evaporated to dryness. To solid was placed in a 25 mL RB flask together with copper (II) acetate monohydrate (15 mg, 83 μmol) and dissolved in chloroform (10 mL) and MeOH (3 mL). The mixture was refluxed for 2 hours and hereafter washed with water (10 mL), dried over MgSO_4 , filtered and evaporated to dryness. The compound was purified by column chromatography (eluent: CHCl_3 + 2% MeOH) to yield a red/brown solid in 95% yield (10 mg, 3.3 μmol)

Maldi-TOF: 2977: $[M - Cl]^-$

UV-vis: Soret band ($c=6.5 \cdot 10^{-7}$ M in $CHCl_3$): λ/nm ($\log(\epsilon/M^{-1}cm^{-1})$) 421 (6.15). Q-bands ($c=1.3 \cdot 10^{-6}$ M in $CHCl_3$): λ/nm ($\log(\epsilon/M^{-1}cm^{-1})$) 481(5.52), 542(4.89), 583 (4.60), 625 (4.61)

Synthesis of Cu-Cu-porphyrin dimer (9)

In a test tube Zn-H₂-TPP-acetylene-dimer **7** (5.12 mg, 1.75 μ mol) was dissolved in $CHCl_3$ (3 mL) and this solution was stirred. To this solution 4 drops of concentrated HCl were added and the course of the reaction was monitored by Maldi-TOF. After 10 minutes no more Zn-porphyrin was present and the solution was washed with a saturated aqueous $NaHCO_3$ solution. Dried over $MgSO_4$, filtered and evaporated to dryness. The residue was transferred in a 100 mL roundbottom flask and dissolved in $CHCl_3$ (20 ml) and MeOH (5 ml). To this stirring mixture copper (II) acetate monohydrate (3.13 mg, 0.016 mmol) was added and the mixture was refluxed for 15 hours. After cooling, the solution was washed with water (10 mL), dried over $MgSO_4$ and evaporated to dryness. The product was further purified by column chromatography (eluent: $CHCl_3$) to give a red product in quantitative yield (5.2 mg, 1.8 μ mol).

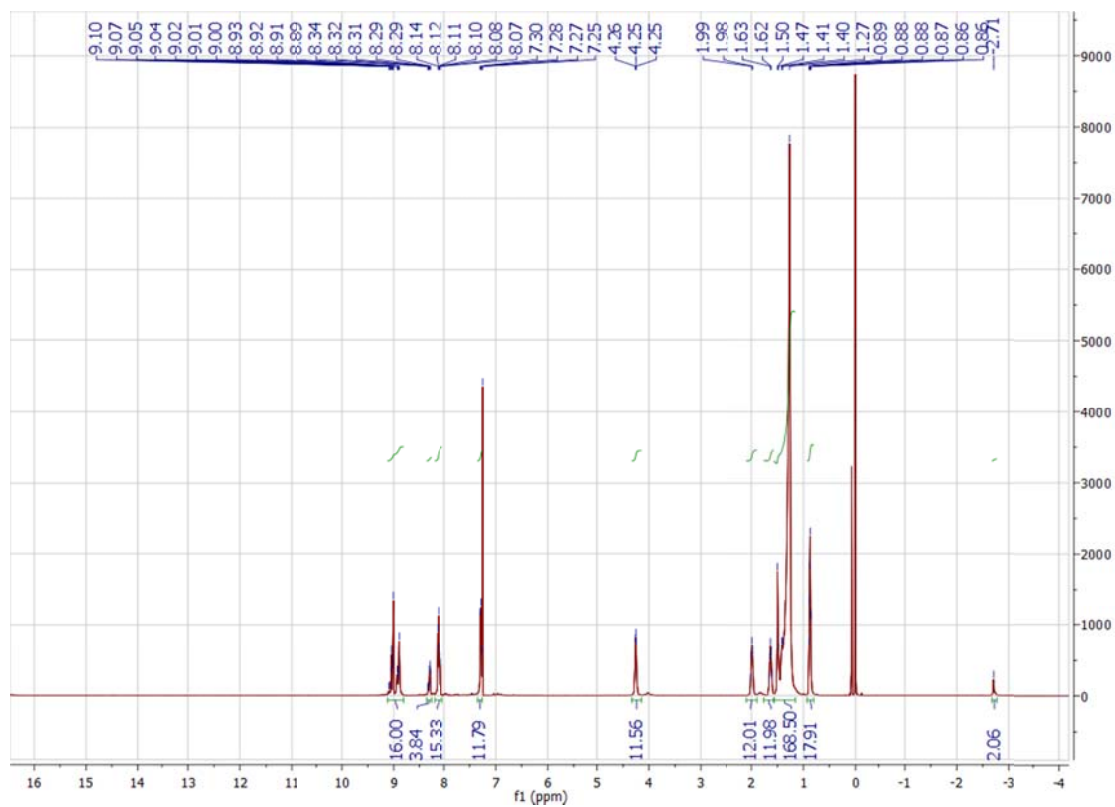
Maldi-TOF: m/z 2986: $[M + H]^+$

UV vis ($c=7.0 \cdot 10^{-6}$ M in $CHCl_3$): λ/nm ($\log(\epsilon/M^{-1}cm^{-1})$) 398(3.90), 423(5.09), 542(3.78)

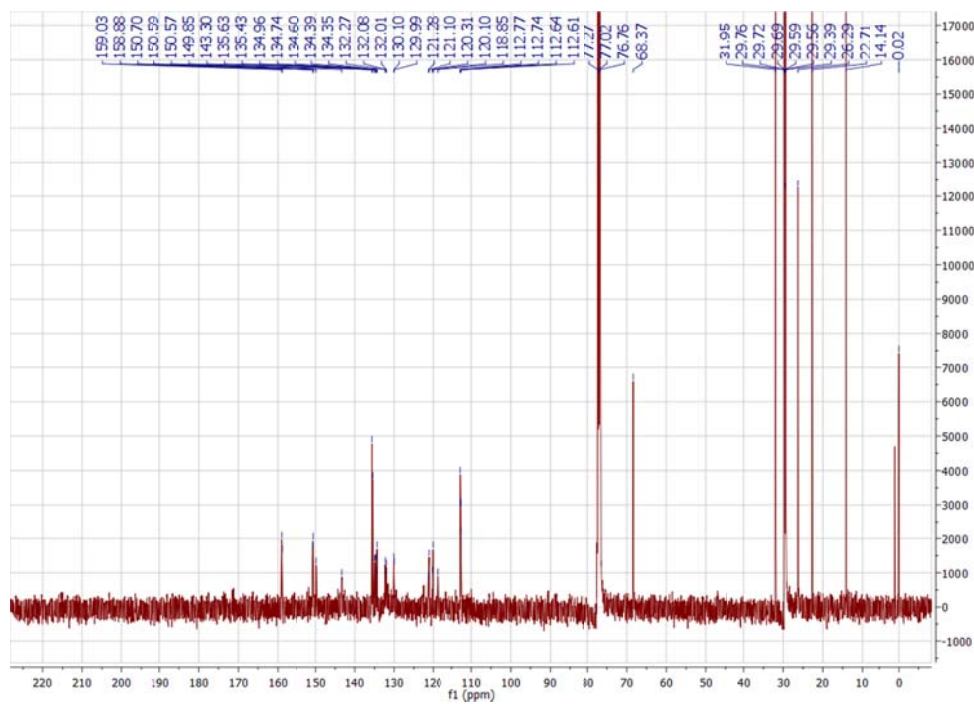
6. Spectral data

NMR

^1H NMR spectrum of Zn-H₂-porphyrin dimer **6** in CDCl₃

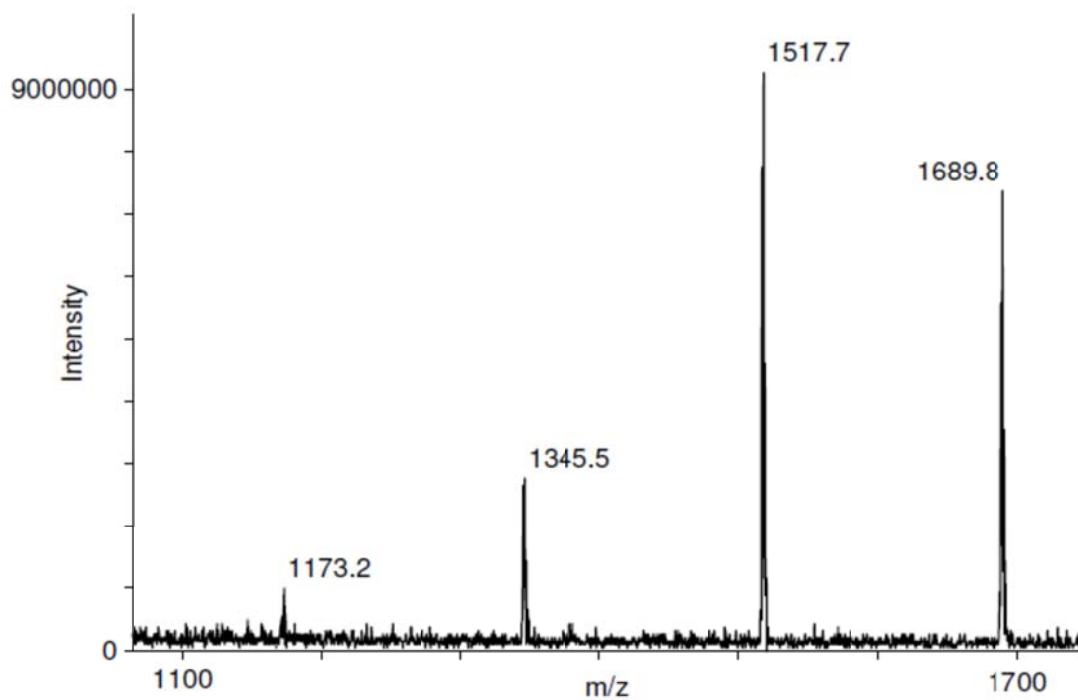


^{13}C NMR spectrum of Zn-H₂-porphyrin dimer **6** in CDCl₃

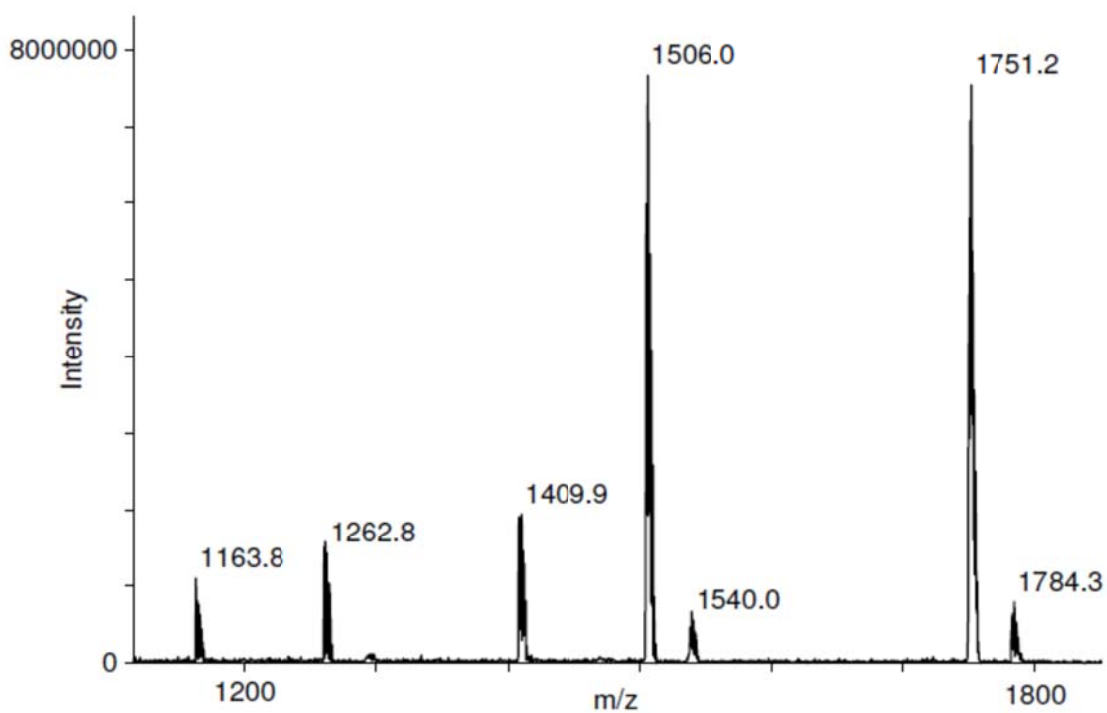


Mass spectrometry

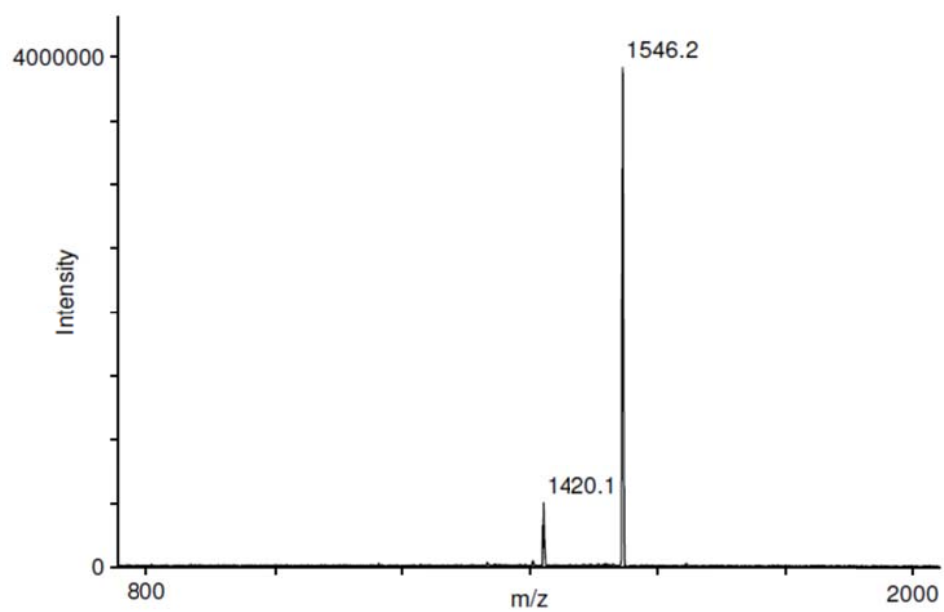
Maldi-TOF spectrum of 5-(((trimethylsilyl)ethynyl)phenyl)-10,15,20-(octadecyloxyphenyl)porphyrin (**2**)



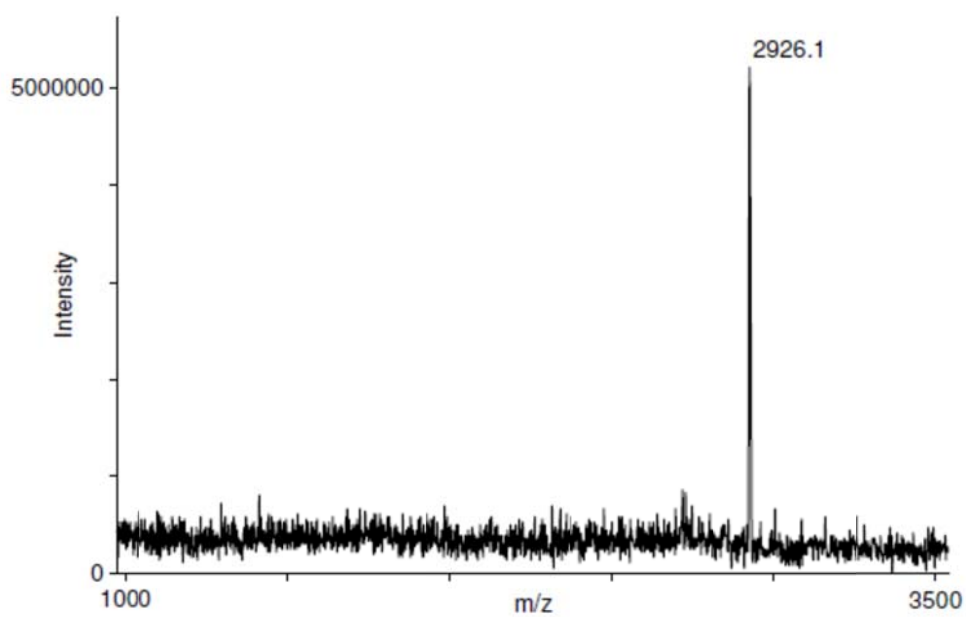
Maldi-TOF spectrum of Zn(II)-[5-(ethynylphenyl)-10,15,20-(octadecyloxyphenyl)porphyrin] (**4**)



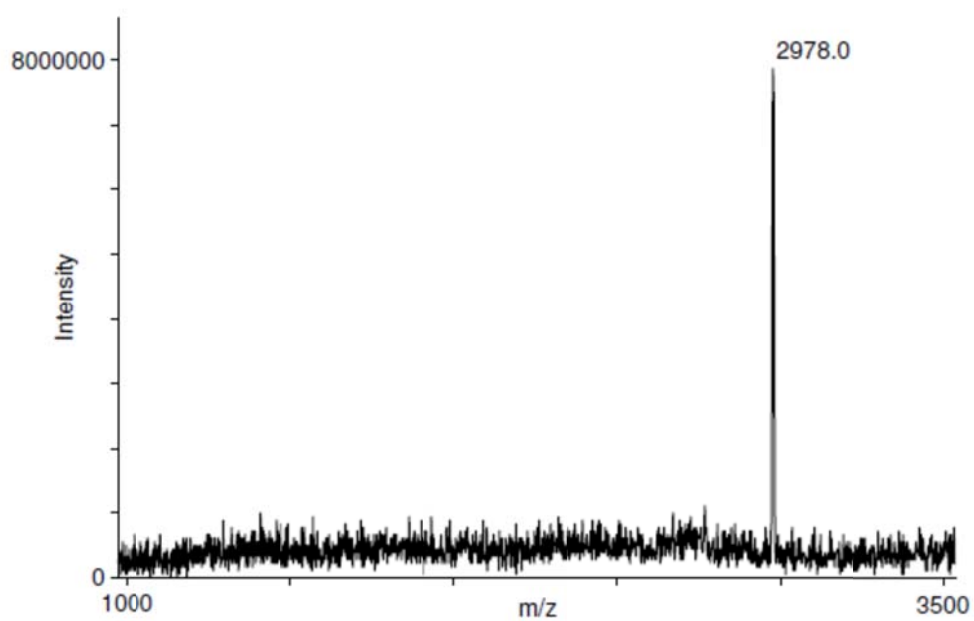
Maldi-TOF spectrum of 5-iodophenyl-10,15,20-octadecyloxyphenyl porphyrin (**5**)



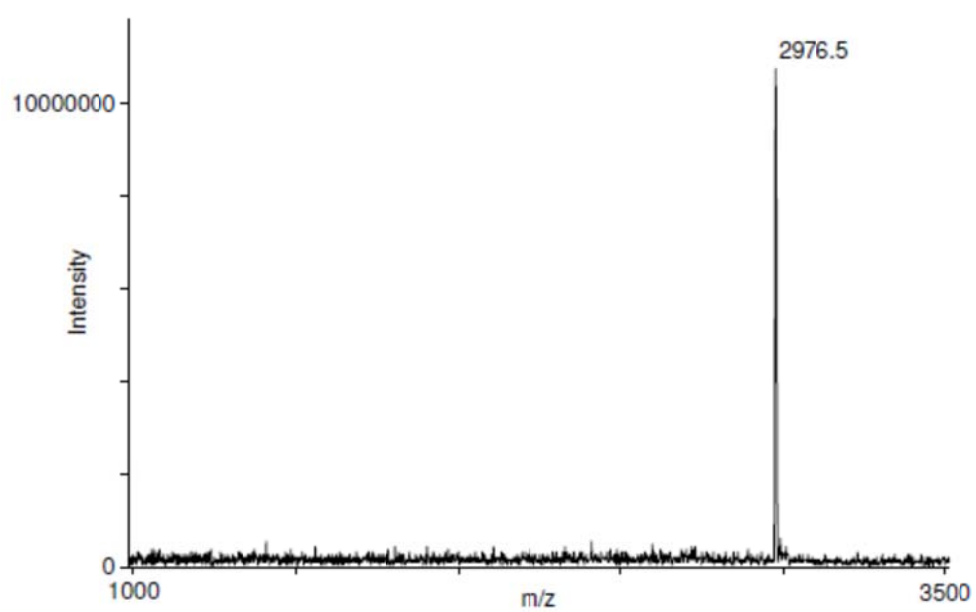
Maldi-TOF spectrum of Zn-H₂-porphyrin dimer (**6**)



Maldi-TOF spectum of MnCl-Zn-porphyrin dimer (7)



Maldi-TOF spectrum of MnCl-Cu-porphyrin dimer (8)



Maldi-TOF spectrum of Cu-Cu-porphyrin dimer (9)

