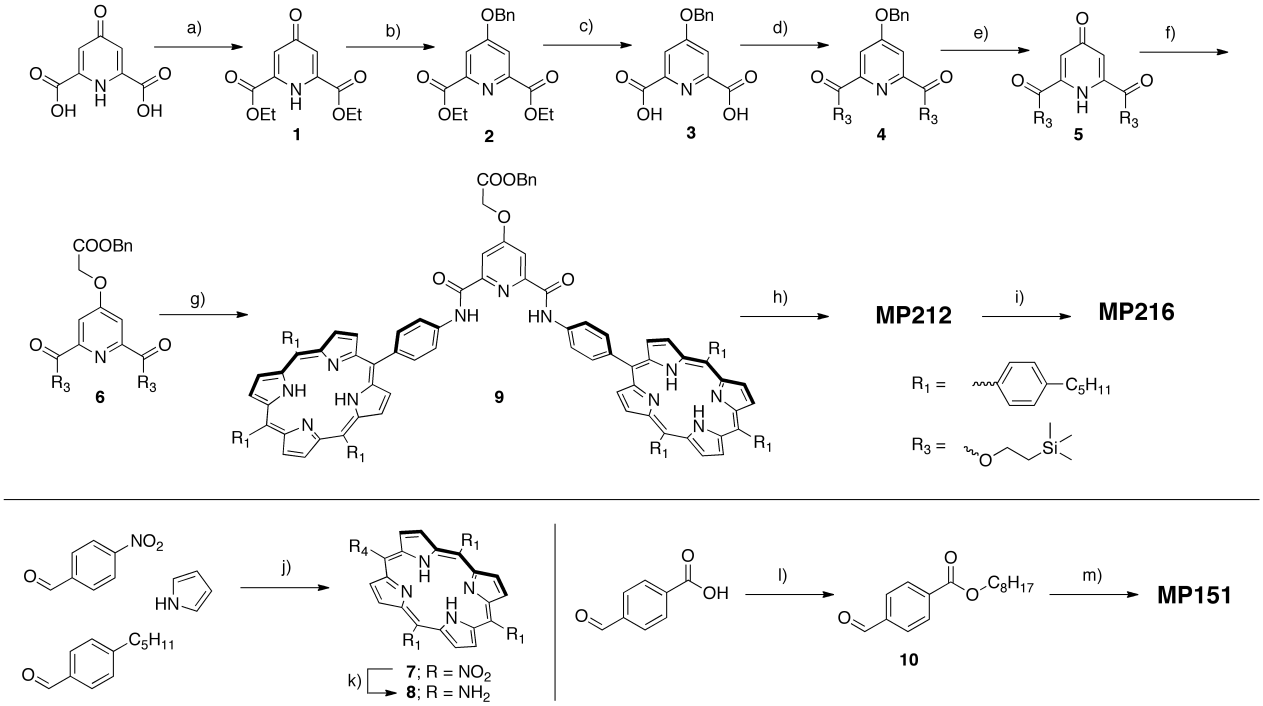
Detailed Synthetic Procedure:

General synthetic considerations: All reagents were purchased from either Sigma-Aldrich or Alfa Aesar and they were used as received without further purification unless otherwise stated. Common solvents were purchased from SdS and used without further purification. Dry solvents were purchased from Fluka with water content < 0.005%. *4-pentylbenzaldehyde* was synthesised according the procedure described previously by our group.[1]



Scheme 1. Synthetic procedures for porphyrins **MP151**, **MP212** and **MP216**. Key: *a*) H_2SO_4, EtOH 16 h. 70 ºC (42%); *b*) benzyl bromide, K_2CO_3, 18-crown-6 ether, Acetone 16 h. 60 ºC (98%); *c*) NaOH 2M, THF/MeOH/H_2O (5:3:2) 16 h. 50 ºC. (46%); *d*) i) $SOCl_2$, 3 h. 80 ºC ii) trimethylsilylethanol, Et_3N, DMAP, CH_2Cl_2 16 h. 40 ºC (93%); *e*) Pd/C, H_2, EtOAc/EtOH (70:1) 16 h. r.t. (73 %); *f*) benzyl bromoacetate, K_2CO_3, 18-crown-6 ether, Acetone 16 h. 60 ºC (73%); *g*) i) TBAF 1M in THF 1 h. r.t., ii) $SOCl_2$, 3h. 75 ºC, iii) 8, Et_3N, DMAP, CH_2Cl_2 16 h. 40 ºC (54%); *h*) $Zn(OAc)_2{\cdot}2H_2O$, $CHCl_3$/MeOH (5:1) 1.5 h. r.t. (73%); *i*) Pd/C, H_2, EtOAc/ EtOH (60:1) 16 h. r.t (51%); *j*) i) $BF_3{\cdot}2Et_2O$, CH_2Cl_2 1 h. 40 ºC ii) DDQ, 1.5 h. r.t iii) Et_3N, 10 min, r.t (12%); *k*) i) $SnCl_2{\cdot}2H_2O$, HCl / dioxane (1:1) 2 h. 70 ºC, ii) NH_3 (95%); *l*) 1-octanol, DCC, DMAP, CH_2Cl_2 16 h. r.t. (91%); *m*) 4-pyridylcarbaldehyde, pyrrole, CH_3CH_2COOH 1 h. 110 ºC (3%).

Synthesis of diethyl 4-oxo-1,4-dihydropyridine-2,6-dicarboxylate (1): Chelidamic acid (1 g, 5.46 mmol) was added in a schlenk tube with 9.5 mL of EtOH. The mixture was stirred under N_2 at room temperature (r.t.) and then sulphuric acid (0.7 mL, 1.28 mmol) was added dropwise. The reaction was heated up to 70 ºC and stirred overnight under N_2. The reaction was quenched by the addition of 100 mL of satured $NaHCO_3$. The pH was adjusted to 4 by the addition of conc HCl and the aqueous layer was extracted with 100 mL of CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4 and the solvent removed. The crude was then purified by column chromatography (SiO_2, CH_2Cl_2 / EtOAc 6:1 up to 3:1) to afford a white solid as the final product (550 mg, 42% yield). ^{1}H-NMR (400 MHz, DMSO-d_6) δ_H: 7.57 (s, 2H); 4.35 (q, J = 7.1 Hz, 4H); 1.33 (t, J = 7.2 Hz, 6H). ^{13}C-NMR (100 MHz, DMSO-d_6) δ_C: 165.8; 164.2; 149.5; 115.1; 61.4; 14.1. MS-ESI (m/z): $[M+Na]^+$ calcd. for $C_{11}H_{13}NO_5Na$: 262.0691; found: 262.0698.

[1] A. Forneli, M. Planells, M. A. Sarmentero, E. Martinez-Ferrero, B. C. O'Regan, P. Ballester and E. Palomares, *J. Mater. Chem.*, 2008, **18**, 1652-1658.

Synthesis of diethyl 4-(benzyloxy)pyridine-2,6-dicarboxylate (2): **1** (1.66 g, 7 mmol), K_2CO_3 (1.91 g, 14 mmol) and 18-crown-6 ether (183 mg, 0.7 mmol) were added to a round bottom flask with 20 mL of acetone. The mixture was stirred under N_2 at room temperature (r.t.) and then benzyl bromide (1.5 mL, 12.6 mmol) was added via syringe. The reaction was heated up to 60 ºC and stirred overnight under N_2. The crude was filtered off and washed with acetone and the solvent was removed. The residue was then purified by column chromatography (SiO_2, CH_2Cl_2 up to CH_2Cl_2/2% Acetone) to afford a white solid as the final product (2.25 g, 98% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 7.86 (s, 2H); 7.43 (m, 5H); 5.22 (s, 2H); 4.47 (q, J = 7.1 Hz, 4H); 1.42 (t, J = 7.2 Hz, 6H). ^{13}C-NMR (100 MHz, CDCl3) δ_C: 166.8; 164.9; 150.4; 134.9; 129.0; 128.9; 127.9; 114.8; 70.9; 62.6; 14.4. MS-ESI (m/z): $[M+Na]^+$ calcd. for $C_{18}H_{19}NO_5Na$: 352.1161; found: 352.1146.

Synthesis of 4-(benzyloxy)pyridine-2,6-dicarboxylic acid (3): **2** (384 mg, 1.16 mmol) was added to a round bottom flask with a solvent mixture of THF (5 mL), MeOH (3 mL). 2 mL of NaOH 2M aqueous solution was then added and white precipitate was precipitated straightforward. The reaction was stirred at 50 ºC under N_2 overnight. Organic solvents were removed and HCl 2M was added until pH was 4. EtOAc was added to the aqueous layer and a white precipitate appeared at the interface, which was filtered off to afford a white solid as the final product (146 mg, 46% yield). It is worth to notice that the product was insoluble with the most common organic solvents. ^{1}H-NMR (400 MHz, DMSO-d_6) δ_H: 7.72 (s, 2H); 7.44 (m, 5H); 5.42 (s, 2H).

Synthesis of bis(2-(trimethylsilyl)ethyl) 4-(benzyloxy)pyridine-2,6-dicarboxylate (4): **3** (1.45 g, 5.3 mmol) was added in a schlenk tube with 9 mL of $SOCl_2$. The mixture was stirred under N_2 for 3 hours at 80 ºC. After that, the suspension of the starting material disappeared. $SOCl_2$ was then removed carefully under vacuum by using a pre-trap of liquid N_2. The crude was then dried under high vacuum for 2 hours. A previous mixture of trimethylsilylethanol (2.2 mL, 15.9 mmol), triethylamine (5.9 mL, 42,4 mmol) and 4-dimethylaminopyridine, DMAP (129 mg, 0.2 mmol) dissolved in 10 mL of CH_2Cl_2, were added to the schlenk tube. The reaction was stirred overnight at 40 ºC under N_2. The crude was dissolved in 100 mL of CH_2Cl_2 and washed with 100 mL of satured aqueous $NaHCO_3$ solution. The organic layer was dried over Na_2SO_4 and the solvent removed. The crude was then purified by column chromatography (SiO_2, CH_2Cl_2) to afford a white solid as the final product (2.06 g, 93% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 7.84 (s, 2H); 7.43 (m, 5H); 5.21 (s, 2H); 4.48 (m, 4H); 1.21 (m, 4H) 0.88 (s, 18H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ_C: 166.7; 165.1; 150.6; 135.0; 129.1; 129.0; 128.0; 114.6; 70.9; 64.9; 17.6; 1.3. MS-ESI (m/z): $[M+Na]^+$ calcd. for $C_{24}H_{35}NO_5NaSi_2$: 496.1952; found: 496.1946.

***Synthesis of bis(2-(trimethylsilyl)ethyl) 4-oxo-1,4-dihydropyridine-2,6-dicarboxylate (5)*: 4** (1.96 g, 4.7 mmol) and palladium on carbon (196 mg) were added to a round bottom flask and were dried under high vacuum for 1 hour. Then, 70 mL of EtOAc and 1 mL of EtOH were added and were also degassed by pump/freeze technique. The mixture was stirred overnight at r.t. under H_2 atmosphere. The crude was filtered off over celite and eluted with EtOAc. The solvent was removed and the residue was then purified by column chromatography (SiO_2, CH_2Cl_2/EtOAc 10:1 up to 10:2) to afford a white solid as the final product (1.31 g, 73% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 7.24 (s, 2H); 4.50 (m, 4H); 1.15 (m, 4H) 0.90 (s, 18H).

Synthesis of bis(2-(trimethylsilyl)ethyl) 4-(2-(benzyloxy)-2-oxoethoxy)pyridine-2,6-dicarboxylate (6): **5** (1.31 g, 3.4 mmol), K_2CO_3 (940 mg, 6.8 mmol) and 18-crown-6 ether (90 mg, 0.34 mmol) were added to a round bottom flask with 68 mL of acetone. The mixture was stirred under N_2 at room temperature (r.t.) and then benzyl bromoacetate (646 µL, 4.1 mmol) was added via syringe. The reaction was heated up to 60 ºC and stirred overnight under N_2. The crude was filtered off and washed with acetone and the solvent was removed. The residue was then purified by column chromatography (SiO_2, CH_2Cl_2) to afford colourless oil as the final product (1.31 g, 73% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 7.75 (s, 2H); 7.35 (m, 5H); 5.25 (s, 2H); 4.81 (s, 2H); 4.84 (m, 4H); 1.20 (m, 4H); 0.88 (s, 18H). ^{13}C-NMR

(100 MHz, $CDCl_3$) δ_C: 167.2; 165.9; 164.8; 150.8; 134.8; 129.0; 128.9; 128.8; 114.2; 67.8; 65.2; 64.9; 17.6; 1.2. MS-ESI (m/z): $[M+H]^+$ calcd. for $C_{26}H_{38}NO_7Si_2$: 532.2187; found: 532.2182.

Synthesis of 5-(4-nitrophenyl)-10,15,20-(4-pentylphenyl)porphyrin (7): freshly distilled pyrrole (1.15 mL, 16.5 mmol), 4-nitrobenzaldehyde (1 g, 6.6 mmol) and 4-pentylbenzaldehyde (1.7 g, 10 mmol) were added to a round bottom flask with 600 mL of CH_2Cl_2 and 5 mL of EtOH. The mixture was stirred under N_2 in the dark and degassed for 10 minutes. Then, $BF_3{\cdot}2Et_2O$ (836 µL, 6.6 mmol) was added and the reaction was stirred for 1 hour at 40 ºC. The reaction changed the colour to black. After that, 2,3-dichloro-5,6-dicyanobenzoquinone (3.7 g, 16.5 mmol) was added and the reaction was stirred for another 1.5 hours. Finally, triethylamine (7.4 mL, 52.8 mmol) was added in order to quench the reaction. The crude was then purified by column chromatography (SiO_2, CH_2Cl_2/Hexane 3:2 up gradually to pure CH_2Cl_2) to afford a purple solid as the final product (425 mg, 12% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 8.91 (d, *J* = 4.8 Hz, 2H); 8.87 (s, 4H); 8.72 (d, *J* = 5.2 Hz, 2H); 8.63 (d, *J* = 8.0 Hz, 2H); 8.40 (d, *J* = 8.3 Hz, 2H); 8.11 (d, *J* = 7.6 Hz, 6H); 7.56 (d, *J* = 7.6 Hz, 6H); 2.95 (t, *J* = 7.7 Hz, 6H); 1.92 (m, 6H); 1.51 (m, 12H); 1.02 (t, *J* = 7.0 Hz, 9H); -2.77 (s, 2H). MS-ESI (m/z): $[M+H]^+$ calcd. for $C_{59}H_{60}N_5O_2$: 870.4747; found: 870.4755.

Synthesis of 5-(4-aminophenyl)-10,15,20-(4-pentylphenyl)porphyrin (8): **7** (425 mg, 0.49 mmol) was added to a preheated mixture at 70 ºC of 50 mL of conc. HCl and 50 mL of dioxane. $SnCl_2{\cdot}2H_2O$ (1.3 g, 5.88 mmol) was added and the reaction was stirred at 70 ºC for 2 hours under N_2. The heater was shutted down and with the reaction still hot, 100 mL of NH_3 was added dropwise in order to quench the reaction. The crude was extracted with 100 mL of EtOAc. The organic layer was washed with brine, dried over Na_2SO_4 and the solvent removed. The crude was then purified by column chromatography (SiO_2, CH_2Cl_2/Hexane 2:1 up to 4:1) to afford a purple solid as the final product (390 mg, 95% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 8.92 (d, *J* = 4.8 Hz, 2H); 8.8 (m, 6H); 8.11 (d, *J* = 7.9 Hz, 6H); 8.00 (d, *J* = 8.1 Hz, 2H); 7.55 (d, *J* = 7.6 Hz, 6H); 7.07 (d, *J* = 8.3 Hz, 2H); 4.03 (br s, 2H); 2.95 (t, *J* = 7.9 Hz, 6H); 1.93 (m, 6H); 1.53 (m, 12H); 1.03 (t, *J* = 6.9 Hz, 9H); -2.73 (s, 2H). MS-ESI (m/z): $[M+H]^+$ calcd. for $C_{59}H_{62}N_5$: 840.5005; found: 840.4973.

Synthesis of free base bisporphyrin 9: **6** (98 mg, 0.185 mmol) was added to a schlenk tube with 3.7 mL of CH_2Cl_2. The mixture was stirred at r.t. under N_2 for 5 minutes and then tetrabutylamonium fluoride 1M solution in THF (460 µL, 0.46 mmol) was added. The reaction was stirred for 1 hour and then the solvent was removed. $SOCl_2$ (670 µL, 9.25 mmol) and the mixture was heated up to 75 ºC and stirred for 3 hours under N_2. After that, $SOCl_2$ was removed carefully under vacuum by using a pre-trap of liquid N_2. The crude was then dried under high vacuum for 2 hours. A previous mixture of **8** (390 mg, 0.46 mmol), triethylamine (206 µL, 1.48 mmol) and DMAP (4.5 mg, 0.037 mmol) dissolved in 4 mL of dry CH_2Cl_2, were added to the schlenk tube. The reaction was stirred overnight at 40 ºC under N_2. The crude was dissolved in 30 mL of CH_2Cl_2 and washed with 50 mL of satured aqueous $NaHCO_3$ solution. The organic layer was dried over Na_2SO_4 and the solvent removed. The crude was then purified by column chromatography (SiO_2, CH_2Cl_2/Hexane 4:1 up to pure CH_2Cl_2) to afford a purple solid as the final product (197 mg, 54% yield). ^{1}H-NMR (400 MHz, $CDCl_3$ + 5% TFA) δ_H: 10.41 (s, 2H); 8.77 (m, 22H); 8.47 (m, 16H); 8.32 (s, 2H); 7.85 (m, 12H); 7.42 (m, 5H); 5.42 (s, 2H); 5.19 (s, 2H); 3.02 (m, 12H); 1.94 (m, 12H); 1.55 (m, 24H); 1.01 (m, 18H); -7.2 (6H). MS-MALDI (m/z): $[M]^+$ calcd for $C_{134}H_{131}N_{11}O_5$: 1974.0329; found: 1974.0221.

Synthesis of zinc bisporphyrin MP212: **9** (93 mg, 0.047 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (165 mg, 0.75 mmol) were added in a round bottom flask with a mixture of 15 mL of $CHCl_3$ and 3 mL of MeOH. The reaction was stirred under N_2 in the dark for 1.5 hours. The solvent was removed and the crude was then purified by column chromatography (SiO_2, CH_2Cl_2 up to CH_2Cl_2/EtOAc 2%) to afford a purple solid as the final product (73 mg, 73% yield). ^{1}H-NMR (400 MHz, $CDCl_3$ + 5% pyridine-d_5) δ_H: 10.27 (s, 2H); 8.86 (s, 8H); 8.83 (s, 8H); 8.21 (d, *J* = 8.4 Hz, 4H); 8.19 (s, 2H); 8.10 (d, *J* = 8.4 Hz, 4H); 8.04 (d, *J* = 7.6 Hz, 12H); 7.46 (d, *J* = 8.0 Hz, 12H); 7.39 (m, 5H); 5.24 (s, 2H); 4.99 (s, 2H); 2.88 (m, 12H); 1.84

(s, 12H); 1.46 (m, 24H); 0.96 (m, 18H). MS-MALDI (m/z): $[M]^+$ calcd for $C_{134}H_{127}N_{11}O_5Zn_2$: 2097.8599; found: 2097.8660. Anal. Calcd for $C_{134}H_{127}N_{11}O_5Zn_2$: C, 76.56; H, 6.09; N, 7.33; Found: C, 75.63; H, 6.02; N, 6.86.

Synthesis of zinc bisporphyrin MP216: **MP212** (165 mg, 0.082 mmol) and palladium on carbon (25 mg) were added to a round bottom flask and were dried under high vacuum for 1 hour. Then, 20 mL of EtOAc and 0.4 mL of EtOH were added and were also degassed by pump/freeze technique. The mixture was stirred overnight at r.t. under H_2 atmosphere. The crude was filtered off over celite and eluted with EtOAc/MeOH 5%. The solvent was removed and the residue was then purified by column chromatography (SiO_2, CH_2Cl_2 up gradually to CH_2Cl_2/MeOH 10%) to afford a purple solid as the final product (84 mg, 51% yield). ^{1}H-NMR (400 MHz, DMSO-d_6) δ_H: 11.51 (s, 2H); 8.87 (d, J = 4.5 Hz, 4H); 8.78 (d, J = 4.8 Hz, 4H); 8.76 (m, 8H); 8.41 (d, J = 8.1 Hz, 4H); 8.26 (d, J = 8.5 Hz, 4H); 8.06 (d, J = 7.6 Hz, 12 H); 7.93 (s, 2H); 7.58 (m, 12H); 4.58 (br s, 2H); 2.91 (m, 12H); 1.97 (m, 12H); 1.48 (m, 24 H); 0.99 (m, 18H). MS-MALDI (m/z): $[M]^+$ calcd. for $C_{127}H_{121}N_{11}O_5Zn_2$: 2007.8135; found: 2007.8267. Anal. Calcd for $C_{127}H_{121}N_{11}O_5Zn_2 \cdot 5H_2O$: C, 72.56; H, 6.28; N, 7.33; Found: C, 72.63; H, 5.95; N, 7.11.

Synthesis of octyl 4-formylbenzoate (10): 4-formylbenzoic acid (2.3 g, 15.8 mmol) and 1-octanol were added in a round bottom flask with 60 mL of CH_2Cl_2. The mixture was cooled at 0 ºC and was stirred for 10 minutes. Then, a previous solution of *N*,*N*'-dicyclohexylcarbodiimide, DCC (3.6 g, 17.4 mmol) and DMAP (2.1 g, 17.4 mmol) in 20 mL of CH_2Cl_2 was added. The reaction was stirred 10 minutes at 0 ºC and after that overnight at r.t. The reaction was then filtered off and the solvent removed. The crude was dissolved in 100 mL of Et_2O and washed with 100 mL satured $NaHCO_3$ aqueous solution. The organic layer was dried over Na_2SO_4 and solvent removed. The residue was then purified by column chromatography (SiO_2, CH_2Cl_2) to afford colourless oil as the final product (3.7 g, 91% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 10.10 (s, 1H); 8.20 (d, J = 8.2 Hz, 2H); 7.95 (d, J = 8.2 Hz, 2H); 4.36 (t, J = 6.7 Hz, 2H); 1.78 (m, 2H); 1.47 (m, 2H); 1.29 (m, 8H); 0.88 (t, J = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ_C: 191.8; 165.8; 139.2; 135.7; 130.4; 129.7; 66.0; 31.9; 29.4; 29.3; 28.8; 26.2; 22.8; 14.3.

Synthesis of 5,10-(4-pyridyl)-15,20-(4-carboxyoctylphenyl)porphyrin (MP151): **10** (3.7 g, 14.3 mmol) and 4-pyridylcarbaldehyde (1.3 mL, 14.3 mmol) were added to a round bottom flask with 100 mL of propanoic acid. The mixture was stirred 10 minutes under N_2 and then was heated up to 110 ºC. When the mixture reached that temperature, freshly distilled pyrrole (2 mL, 28 mmol) was added slowly. The colour of the reaction changed to black and was stirred for 1 hour at 110 ºC. The reaction was cooled down to r.t. and propanoic acid was removed carefully under vacuum. The crude was then purified by column chromatography (CH_2Cl_2 - CH_2Cl_2/pyridine 1% up gradually to CH_2Cl_2/THF 8%/ pyridine 1%). The desired product was on the 4th red fluorescent spot.[2] Several columns on SiO_2 and size exclusion chromatography (Bio-Beads S-X1 in CH_2Cl_2) were required in order to obtain the final product as purple solid (208 mg, 3.1% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 9.06 (d, J = 5.9 Hz, 4H); 8.85 (m, 8H); 8.46 (d, J = 8.2 Hz, 4H); 8.29 (d, J = 8.2 Hz, 4H); 8.16 (d, J = 5.9 Hz, 4H); 4.52 (t, J = 6.7 Hz, 4H); 1.92 (m, 4H); 1.52 (m, 4H); 1.33 (m, 16H); 0.91 (t, J = 7.0 Hz, 6H). MS-ESI (m/z): $[M+H]^+$ calcd. for $C_{60}H_{61}N_6O_4$: 929.4754; found: 929.4760. Anal. Calcd for $C_{60}H_{60}N_6O_4$: C, 77.56; H, 6.51; N, 9.04; Found: C, 77.66; H, 6.43; N, 8.83.

Characterization techniques: ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometer. The deuterated solvents used are indicated; chemical shifts, δ, are given in ppm, referenced to the solvent residual signal (^{1}H, ^{13}C). Coupling constants, J, are given in Hz. MS spectra were recorded on Waters LCT Premier, using electrospray ionization (ESI) and matrix-assisted laser desorption/ionization (MALDI) modes depending on the sample. Elemental analyses were carried out by elemental analysis services from Santiago de Compostela University using a LECO 932 CHNS elemental analyzer.

[2] T. Gianferrara, D. Giust, I. Bratsos and E. Alessio, *Tetrahedron*, 2007, **63**, 5006-5013.

Supporting Information Figures:

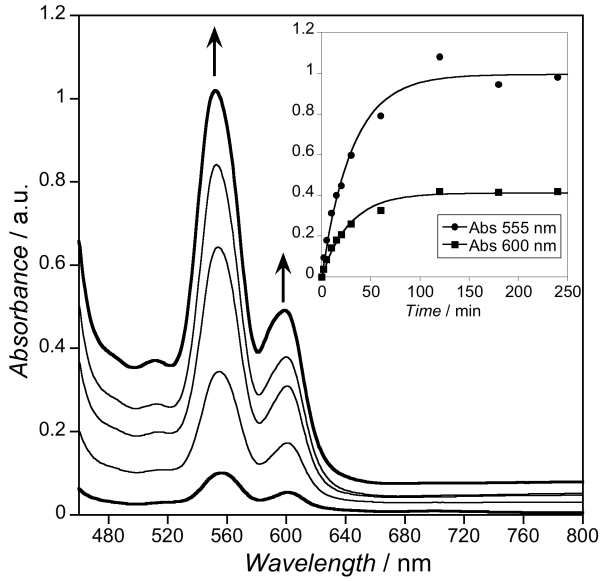


Figure S1. Selected absorption spectra for 4 μm mesoporous TiO_2 films after the immersion into **MP216** $CHCl_3$ solution. Corresponding immersion time: 2, 10, 30, 60 and 180 minutes. The insets shows the kinetics fitted to Lagergren equation.

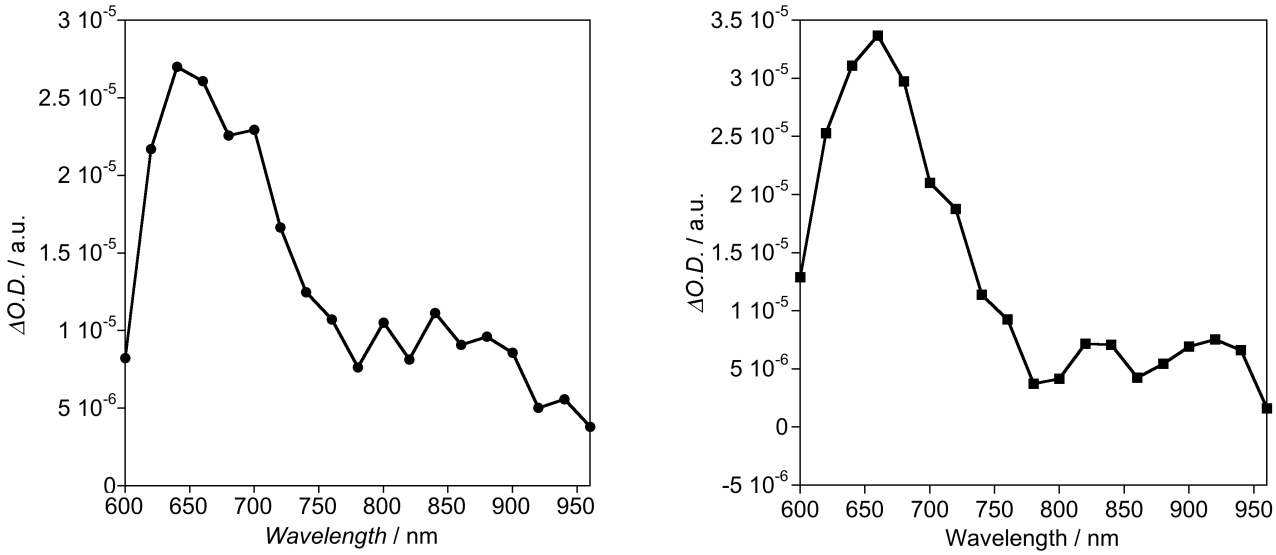


Figure S2. L-TAS spectra for **MP216**/TiO_2 (left) and **MP216**+**BP**/TiO_2 (right) after laser excitation at 580 nm. Acquisition time was fixed at 100 μs.