Supporting Information

A Novel Modular Approach to Triazole Functionalized Phthalocyanines Using Click Chemistry

Michal Juríček,[†] Paul H. J. Kouwer,[†] Juraj Rehák,[†] Joseph Sly,[‡] and Alan E. Rowan[†]*

[†] Institute for Molecules and Materials, Radboud University Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands

[‡] IBM Almaden Research Center, 650 Harry Road, San Jose, 95120 California, USA

a.rowan@science.ru.nl

Experimental Section

General. All chemicals and solvents were purchased from commercial sources and used without further purification unless stated otherwise. Solvents were distilled prior to use: THF (Na); CH_2Cl_2, 2-(dimethylamino)ethanol (DMAE), Et_3N, MeOH and pyridine (CaH_2). All cross-coupling and 'click' reactions were performed under an argon atmosphere using Schlenk techniques and deoxygenated solvents (freeze-pump-thaw in 3 cycles, <0.4 mbar). $ZnCl_2$ was dried by heating it to its melting temperature under vacuum (0.4 mbar). Silica gel (0.035-0.070 mm or 0.063-0.200 mm) was used for column chromatography and silica 60 F_{254} coated glass plates were used for thin layer chromatography (TLC). Chemical shifts are reported in ppm relative to the solvent residual peak (^1H and ^{13}C NMR, respectively): $CDCl_3$ (δ = 7.26 ppm, and 77.0 ppm), acetone-d_6 (δ = 2.05 ppm, and 29.8 ppm) and C_6D_6 (δ = 7.16 ppm, and 128.1 ppm). MALDI-TOF MS measurements of compounds **1a**, **1b** and **2** were performed using reflectron (**1a**, **1b**, **2**) or linear (**2**) mode and dithranol (20 mg/mL in THF) as a matrix. Accurate mass of **1b** (spotted using dithranol as a matrix) was determined using Proteo Mass^{TM} Peptide MALDI-MS Calibration Kit spotted on **1b** as a separate layer using α-cyano-4-hydroxycinamic acid (20 mg in 0.5 mL of MeCN and 0.5 mL of 0.1% TFA in H_2O) as a matrix. Gel permeation chromatography (GPC) was performed on size exclusion chromatographer (SEC) equipped with a guard column and a PL gel 5 μm mixed D column (*Polymer Laboratories*) with UV-Vis (700 nm) detection, using THF as an eluent at 1mL/min and t = 35 ºC. Polystyrene (PS) standards in the range of 580 to 377,400 g/mol were used to calibrate the SEC.

Dodecylazide. A mixture of dodecylbromide (10.0 g, 40.1 mmol), NaN_3 (2.90 g, 44.7 mmol) and MeOH (80 mL) was heated to reflux overnight before the solvent was evaporated. After addition of chloroform the white precipitate was filtered off. Evaporation of the solvent afforded the product as colorless oil in quantitative yield. IR (neat, cm^{-1}) 2094 (N_3). ^1H NMR (300 MHz, $CDCl_3$) δ 3.24 (t, J = 7.0 Hz, 2H, CH_2-N_3), 1.64–1.54 (m, 2H, C$H_2$$CH_2$-$N_3$), 1.38–1.27 (m, 18H, C$H_2$), 0.88 (t, J = 6.7 Hz, 3H, C*H*$_3$). ^{13}C NMR (75 MHz, CDCl$_3$) δ 51.5 (*C*H$_2$), 31.9 (*C*H$_2$), 29.6 (*C*H$_2$), 29.5 (*C*H$_2$), 29.46 (*C*H$_2$), 29.3 (*C*H$_2$), 29.1 (*C*H$_2$), 28.9 (*C*H$_2$), 26.7 (*C*H$_2$), 22.7 (*C*H$_2$), 14.0 (*C*H$_3$). IR and ^{1}H NMR are in accordance with previously reported results.[1]

1,2-Dibromo-4,5-diiodobenzene (4). A mixture of a fine-grounded I$_2$ (3.43 g, 13.5 mmol), NaIO$_3$ (1.34 g, 6.76 mmol) and 160 mL of 90% H$_2$SO$_4$ (v/v) was stirred at 40 °C for 1 h in the dark. The resulting dark solution was then cooled to 0 °C and 1,2-dibromobenzene (4.00 g, 16.9 mmol) was added in one portion. The solution was vigorously stirred at 0 °C for 4 h before it was poured on ice (400 g). White precipitate was filtered off and washed with an excess of water (1 L) before it was dissolved in chloroform (0.5 L), washed with 10% aq. NaHSO$_3$ and dried over Na$_2$SO$_4$. After filtration, the solvent was evaporated and the residue dried under vacuum to give 8.16 g of the crude product. Crystallization from chloroform/hexanes or chromatography over a short plug of silica (hexanes) afforded pure product in >90% yield as a white crystalline solid. Mp 165-166 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.05 (s, 2H, C$_{Ar}$-*H*). ^{1}H NMR (300 MHz, acetone-*d$_6$*) δ 8.22 (s, 2H, C$_{Ar}$-*H*). ^{13}C NMR (75 MHz, CDCl$_3$) δ 142.5 (*C*H), 125.3, 106.8. ^{13}C NMR (75 MHz, acetone-*d$_6$*) δ 143.4 (*C*H), 125.7, 108.2. EI-MS *m/z* (%) 490 (M$^+$ + 4, 50), 488 (M$^+$ + 2, 100), 486 (M$^+$, 55), 363 (13), 361 (23), 359 (13), 236 (9), 234 (18), 232 (10), 155 (14), 153 (14), 74 (66). HRMS (EI) *m/z* calcd for C$_6$H$_2$Br$_2$I$_2$ 485.6614, found 485.6614. Anal. Calcd for C$_6$H$_2$Br$_2$I$_2$: C, 14.78; H, 0.41. Found: C, 15.06; H, 0.52. ^{1}H NMR, ^{13}C NMR and EI-MS are in accordance with previously reported results.[2]

Procedure for cyanation of 4 using KCN. 4 (1.0 g, 2.05 mmol), KCN (0.27 g, 4.10 mmol), CuI (0.039 g, 0.205 mmol) and Pd(PPh$_3$)$_4$ (0.24 g, 0.205 mmol) were placed in a Schlenk tube equipped with a stirrer and the system was evacuated and filled with argon in 3 cycles. After THF (25 mL) was added with a syringe, the mixture was heated to reflux for 72 h under an argon atmosphere. The reaction was quenched using 10% aq. NH$_3$ and the crude products were extracted with chloroform. The combined organic layers were washed with 10% aq. NH$_4$Cl and dried over Na$_2$SO$_4$. After filtration, the solvent was evaporated and the residue was purified by chromatography over silica gel using hexane/dichloromethane 4/1 and 2/1 as eluents.

General procedure for cyanation of 4 using $Zn(CN)_2$. 4 (1,0 mmol), $Zn(CN)_2$ and $Pd(PPh_3)_4$ (0.10 mmol) were placed in a Schlenk tube equipped with a stirrer and the system was evacuated and filled with argon in 3 cycles. After DMF (20 mL, extra dry, <0.01% H_2O) and pyridine (1 mmol) were added with a syringe the mixture was heated under an argon atmosphere. The reaction was quenched using 10% aq. NH_3 and the crude products were extracted with chloroform. The combined organic layers were washed with 10% aq. NH_4Cl and dried over Na_2SO_4. After filtration, the solvent was evaporated and the residue was purified by chromatography over silica gel using hexane/dichloromethane 4/1 and 2/1 as eluents.

4,5-Dibromophthalonitrile (3b). White solid. IR (neat, cm^{-1}) 2234 (CN). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (s, 2H, C_{Ar}-*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.7 (*C*H), 131.5, 115.4, 113.6. EI-MS *m/z* (%) 288 (M^+ + 4, 60), 286 (M^+ + 2, 100), 284 (M^+, 64), 207 (15), 205 (17), 125 (19), 99 (10), 75 (17). HRMS (EI) *m/z* calcd for $C_8H_2N_2Br_2$ 283.8585, found 283.8597. Anal. Calcd for $C_8H_2N_2Br_2$: C, 33.61; H, 0.71; N, 9.80. Found: C, 33.69; H, 0.87; N, 9.73. IR, ^{1}H NMR and EI-MS are in accordance with previously reported results.[3]

4,5-Dibromo-2-iodobenzonitrile (5). White solid. IR (neat, cm^{-1}) 2225 (CN). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (s, 1H, C_{Ar}-*H*), 7.80 (s, 1H, C_{Ar}-*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5 (*C*H), 137.8 (*C*H), 131.3, 125.4, 121.0, 117.5, 96.3. EI-MS *m/z* (%) 389 (M^+ + 4, 50), 387 (M^+ + 2, 100), 385 (M^+, 52), 262 (11), 260 (23), 258 (12), 181 (13), 179 (13), 100 (27), 74 (6). HRMS (EI) *m/z* calcd for $C_7H_2NBr_2I$ 384.7599, found 384.7603. Side product **5** contained ca 5% of unknown impurities (^{1}H NMR) after several chromatographic separations and repeated crystallizations from MeOH and CH_2Cl_2/pentane, respectively.

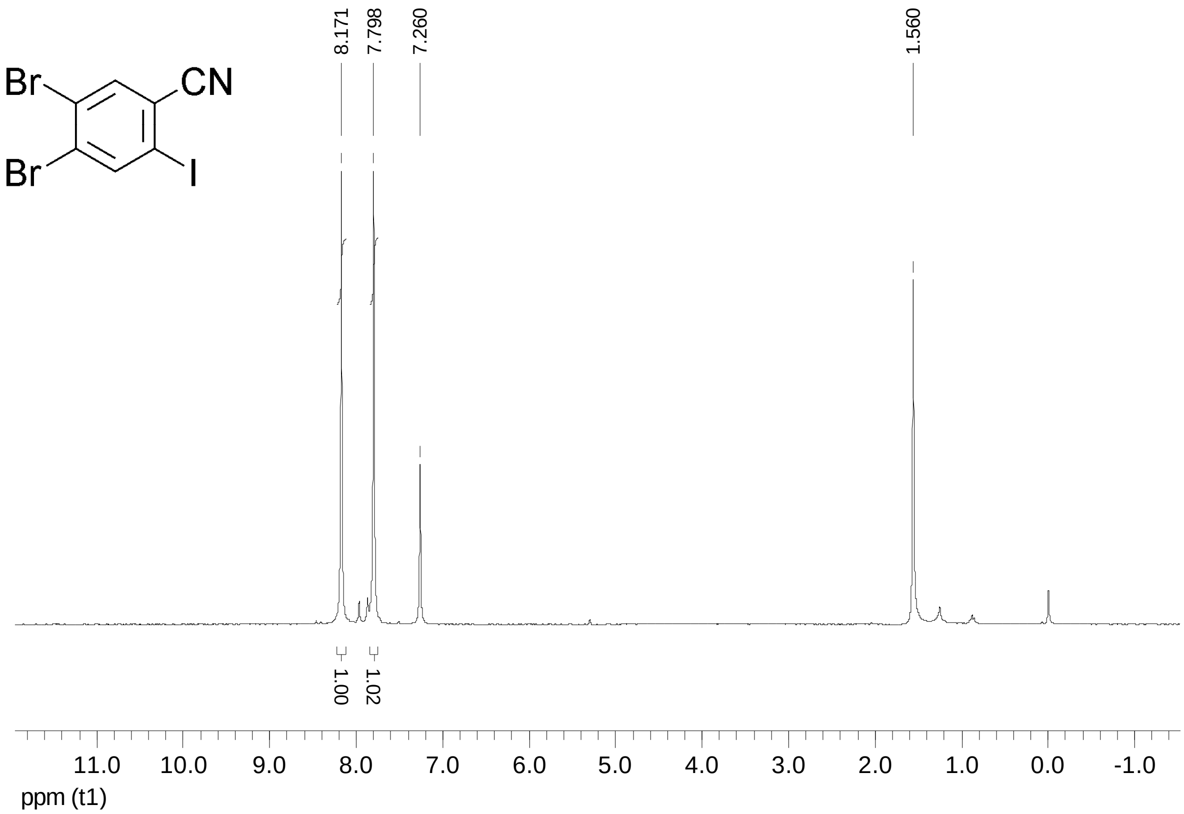
4,5-Bis(*tert*-butyldimethylsilylethynyl)phthalonitrile (6). 3b (0.56 g, 1.96 mmol), *tert*-butyldimethylsilylacetylene (0.73 g, 5.20 mmol), CuI (0.15 g, 0.785 mmol) and $Pd(PPh_3)_4$ (0.23 g, 0.196 mmol) were placed in a Schlenk tube equipped with a stirrer and the system was evacuated and filled with argon in 3 cycles. After Et_3N (25 mL) was added with a syringe the mixture was heated to 60 °C for 36 h under an argon atmosphere. The reaction was quenched using 10% aq. NH_3 and the crude product was extracted with chloroform. The combined organic layers were washed with 10% aq. NH_4Cl and dried over Na_2SO_4. After filtration, the solvent was evaporated and the residue was purified by chromatography over silica gel using hexane/CH_2Cl_2 2/1 as eluent to afford 0.69 g (87% yield) of the product as an off-white solid. IR (neat, cm^{-1}) 2232 (CN), and 2159 (C≡C). ^1H NMR (300 MHz, $CDCl_3$) δ 7.83 (s, 2H, C_{Ar}-*H*), 1.00 (s, 18H, C-C*H*$_3$), 0.21 (s, 12H, Si-C*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.3 (*C*H), 130.5, 114.4, 114.2, 105.8, 100.4, 26.1 (*C*H$_3$), 16.7, –4.90 (*C*H$_3$). EI-MS *m/z* (%) 404 (M^+, 10), 347 (92), 291 (20), 73 (100). HRMS (EI) *m/z* calcd for $C_{24}H_{32}N_2Si_2$ 404.2104, found 404.2097. Anal. Calcd for $C_{24}H_{32}N_2Si_2$: C, 71.23; H, 7.97; N, 6.92. Found: C, 71.22; H, 7.99; N, 6.66. IR, ^1H NMR, ^{13}C NMR and EI-MS are in accordance with previously reported results.[3]

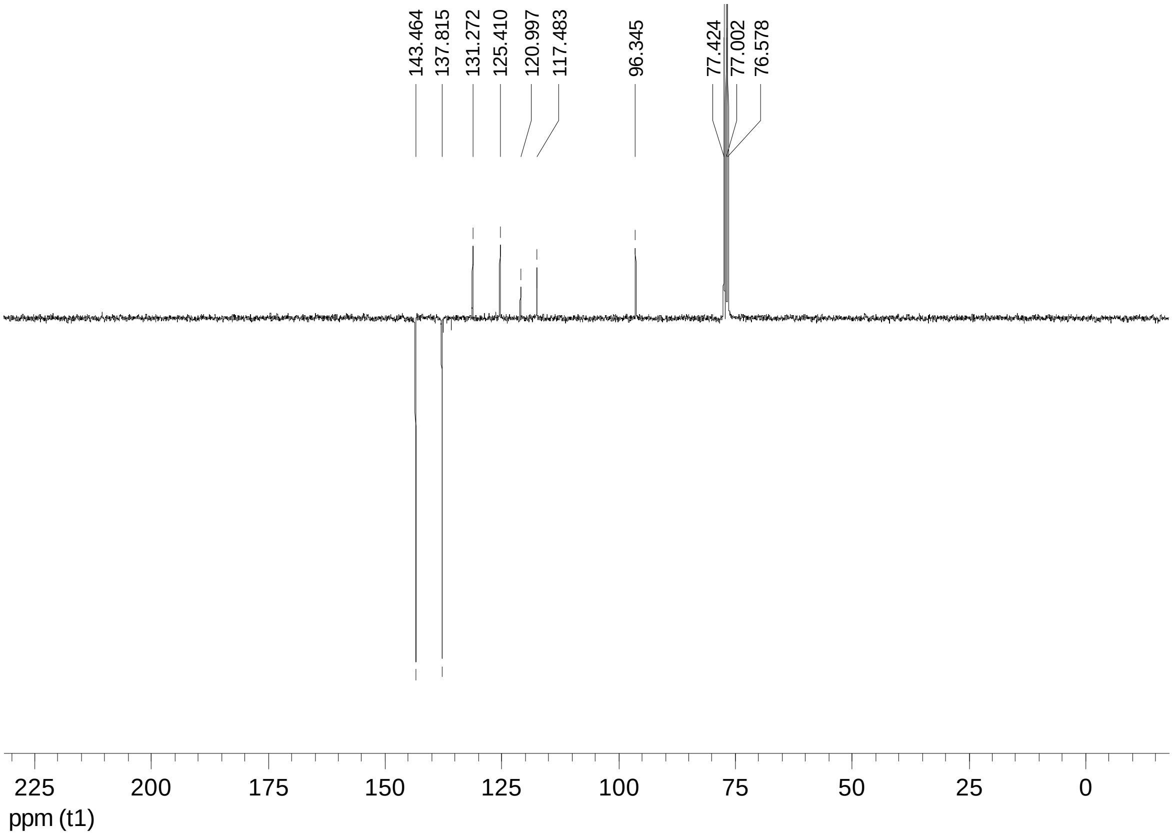
2,3,9,10,16,17,23,24-Octakis(*tert*-butyldimethylsilylethynyl)phthalocyanato zinc(II) (1b). A mixture of **6** (525 mg, 1.30 mmol), $ZnCl_2$ (44.2 mg, 0.325 mmol) and DMAE (4 mL) was heated to 140 °C overnight. The solvent was evaporated and the residue was dried under vacuum. Column chromatography over silica ($CHCl_3$ followed by $CHCl_3$/EtOH 99/1) and crystallization from CH_2Cl_2/MeOH afforded 355 mg (65% yield) of the product as a dark green solid. IR (neat, cm^{-1}) 2150 (C≡C). UV-Vis (THF) 712, 680, 640, and 375 nm. ^1H NMR (300 MHz, $CDCl_3$) δ 9.51 (s, 8H, C_{Ar}-*H*), 1.20 (s, 72H, C-C*H*$_3$), 0.40 (s, 48H, Si-C*H*$_3$). ^1H NMR (300 MHz, C_6D_6) δ 9.83 (s, 8H, C_{Ar}-*H*), 1.29 (s, 72H, C-C*H*$_3$), 0.50 (s, 48H, Si-C*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6, 137.0, 127.7 (*C*H), 126.7, 104.8, 99.2, 26.5 (*C*H$_3$), 17.0, –4.34 (*C*H$_3$). ^{13}C NMR (75 MHz, C_6D_6) δ 153.7, 137.7, 128.5 (*C*H), 127.3, 105.9, 99.6, 26.8 (*C*H$_3$), 17.3, –3.97 (*C*H$_3$). HRMS (MALDI-TOF) *m/z* calcd for $C_{96}H_{128}N_8Si_8Zn + H^+$ 1681.77, found 1681.81. GPC (THF): $t_R = 8.55$ min, $M_n = 1927$ g/mol, $M_w/M_n = 1.06$. IR, UV-Vis and ^1H NMR are in accordance with previously reported results.[3]

2,3,9,10,16,17,23,24-Octakis(ethynyl)phthalocyanato zinc(II) (1a). Mixture of **1b** (170 mg, 0.101 mmol), TBAF (1 M, 5 mL), water (10 drops) and THF (100 mL) was stirred for 42 h under an argon atmosphere. After the volume was reduced to ca 30 mL, several precipitations in MeOH afforded the product as dark green solid in quantitative yield. IR (neat, cm^{-1}) 3272 (CC-H), and 2103 (C≡C). UV-Vis (THF) 699, 667, 629, and 368 nm. MALDI-TOF MS *m/z* calcd for $C_{48}H_{16}N_8Zn$ 768.079, found 767.585. IR and UV-Vis are in accordance with previously reported results.[3]

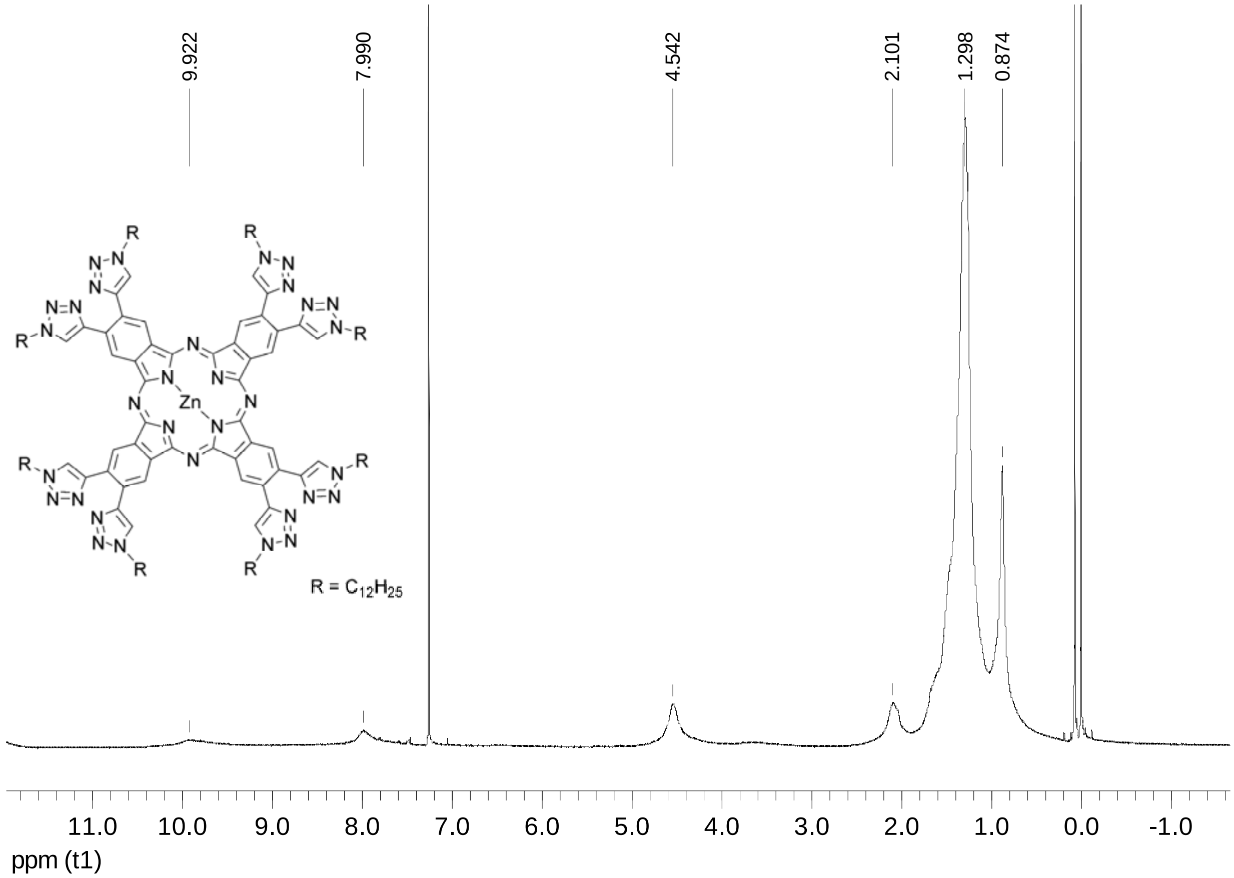
2,3,9,10,16,17,23,24-Octakis(1-dodecyl-1*H*-1,2,3-triazole-4-yl)phthalocyanato zinc(II) (2). **1b** (17.3 mg, 0.0103 mmol), dodecylazide (138 mg, 0.658 mmol) and CuI (62 mg, 0.329 mmol) were placed in a Schlenk tube equipped with a stirrer and the system was evacuated and filled with argon in 3 cycles. Then THF (10 mL) and 1,1,4,7,7-pentamethyldiethylenetriamine (114 mg, 0.658 mmol) were added with a syringe and the mixture was stirred until all CuI dissolved (10 min). TBAF (1 M, 0.66 mL) was added dropwise (the first portion of 0.11 mL over 1 h and the second portion of 0.55 mL over 1.5 h) and the reaction mixture was stirred for 24 h under an argon atmosphere before it was quenched with 10% aq. NH_3. The crude product was extracted with CH_2Cl_2 and the combined organic layers were washed with 10% aq. NH_4Cl and dried over Na_2SO_4. After filtration, the solvent was evaporated and the desired product was obtained after 5 precipitations from CH_2Cl_2 in MeOH as a dark green solid in >90% yield. IR (neat, cm^{-1}) 2956, 2922, 2851, 1258, 1094, 1017, and 798. UV-Vis (THF) 698, 665, 629, and 370 nm. ^{1}H NMR (500 MHz, $CDCl_3$ + TFA) δ 9.98 (br, 8H, C_{Ar}-*H*), 8.74 (br, 8H, C_{Ar}-*H*), 4.72 (br, 16H, C*H*$_2$), 2.16 (br, 16H, C*H*$_2$), 1.45–1.30 (br, 144H, C*H*$_2$), 0.88 (br, 24H, C*H*$_3$). MALDI-TOF MS *m/z* calcd for $C_{144}H_{216}N_{32}Zn + H^+$ 2458.72, found 2458.96. GPC (THF): t_R = 8.42 min, M_n = 2566 g/mol, M_w/M_n = 1.12. NMR analysis indicates that **2** contains a small fraction of silicon-based grease that could not be removed by the precipitation procedure.

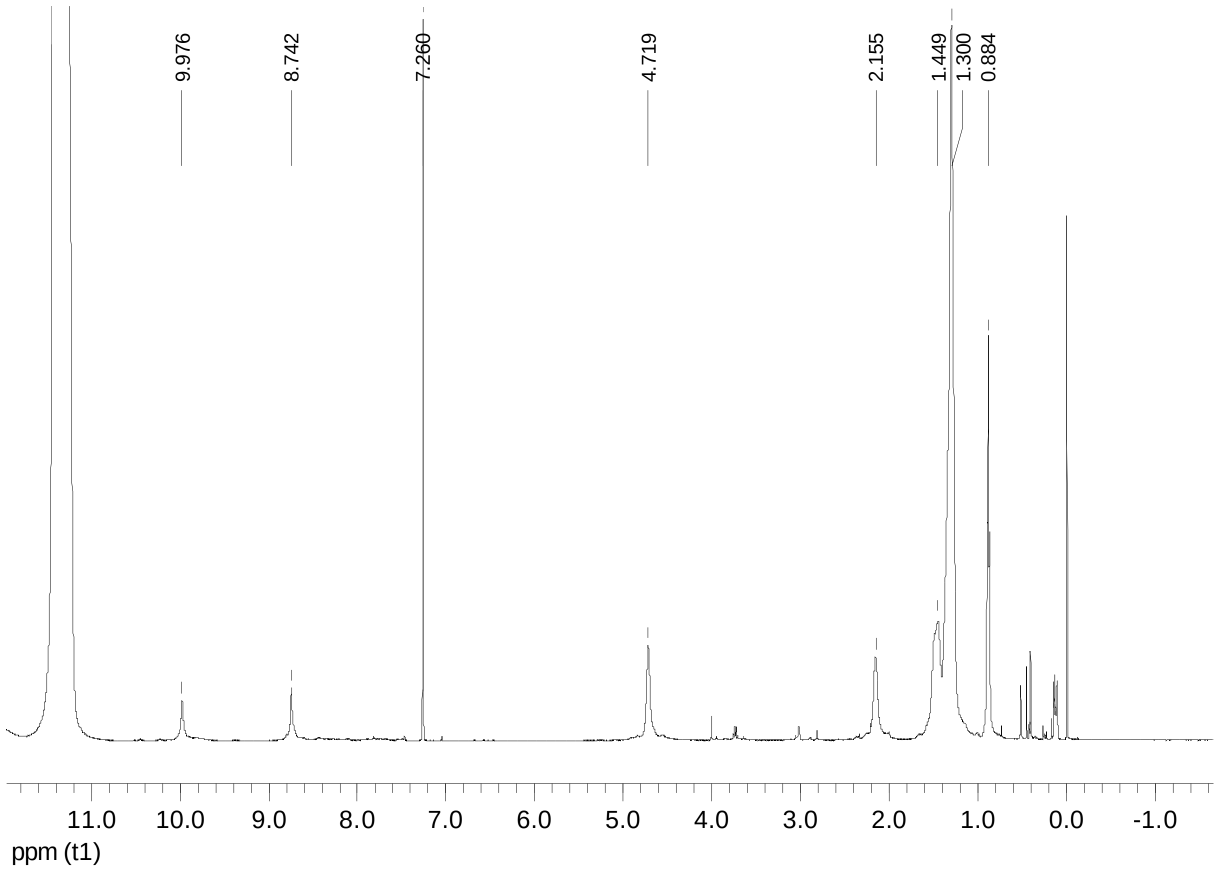
^1H and ^{13}C NMR spectra of compound 5 in $CDCl_3$ (300 MHz)





^{1}H NMR spectra of compound 2 in $CDCl_3$ and $CDCl_3$ + TFA (500 MHz)





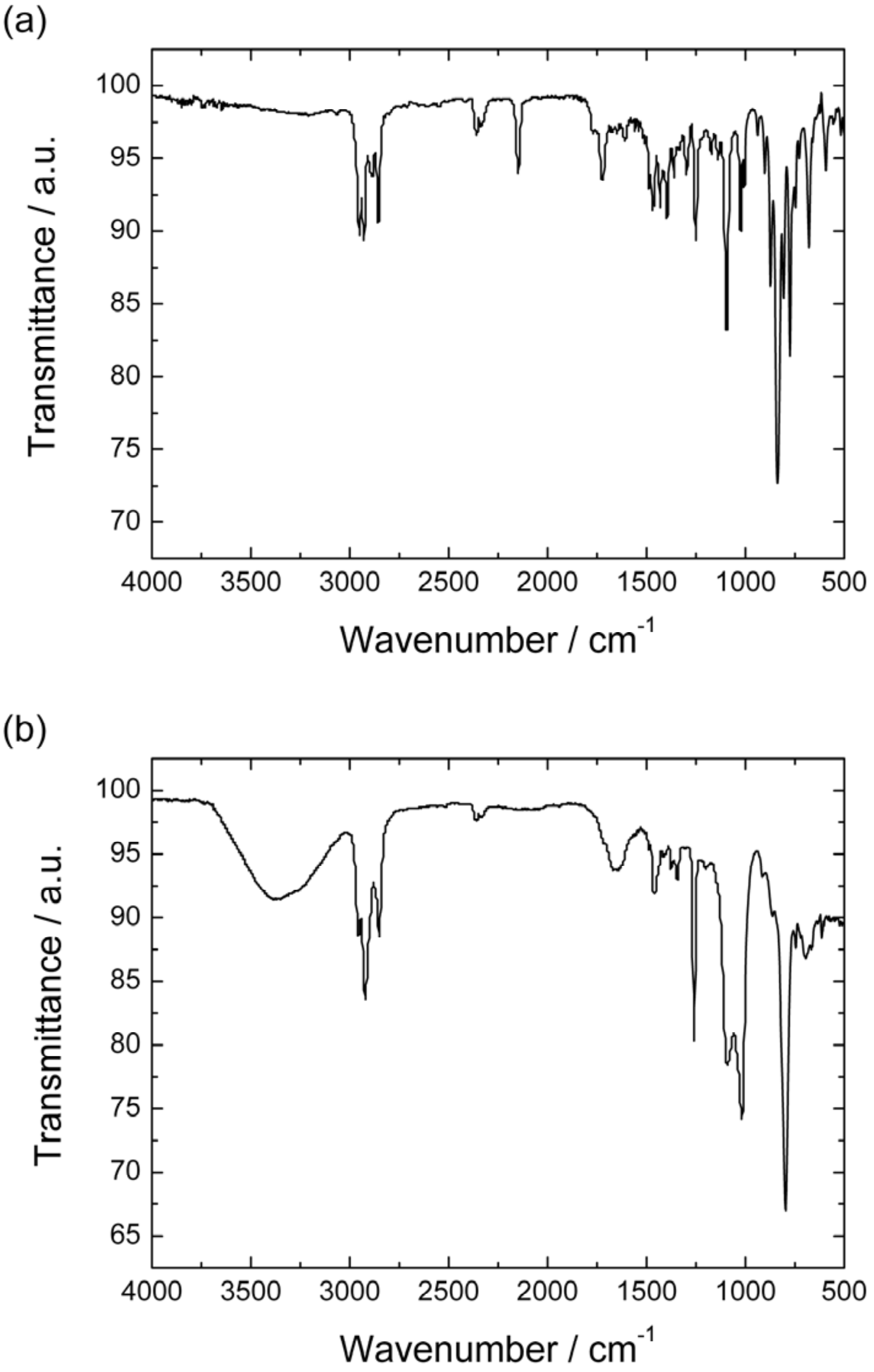


Figure S1. IR spectra of compounds **1b** (a) and **2** (b) showing complete disappearance of acetylene (C≡C) stretch at 2150 cm^{-1} in **2**.

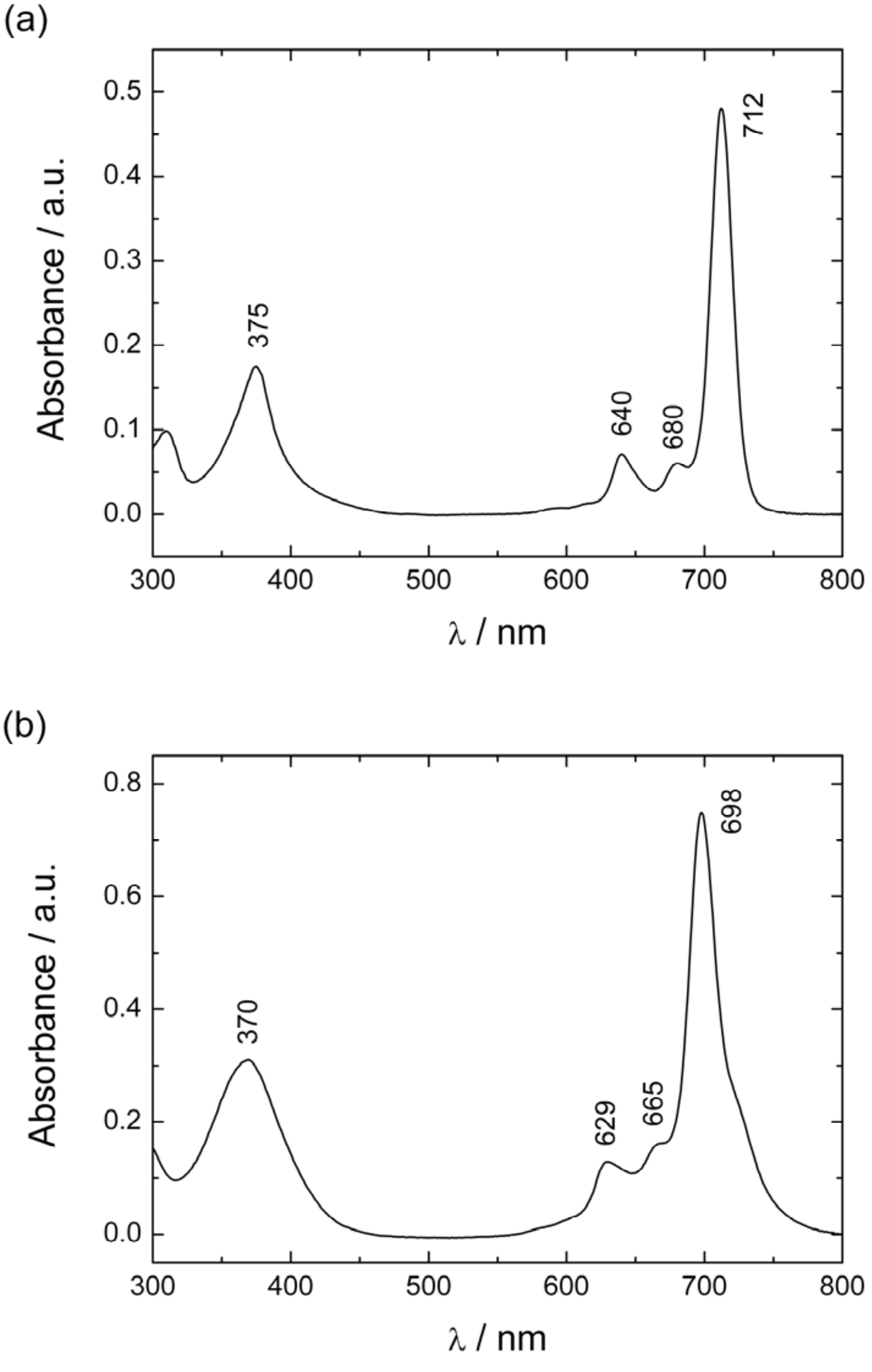


Figure S2. UV-Vis spectra of compounds **1b** (a) and **2** (b) in THF.

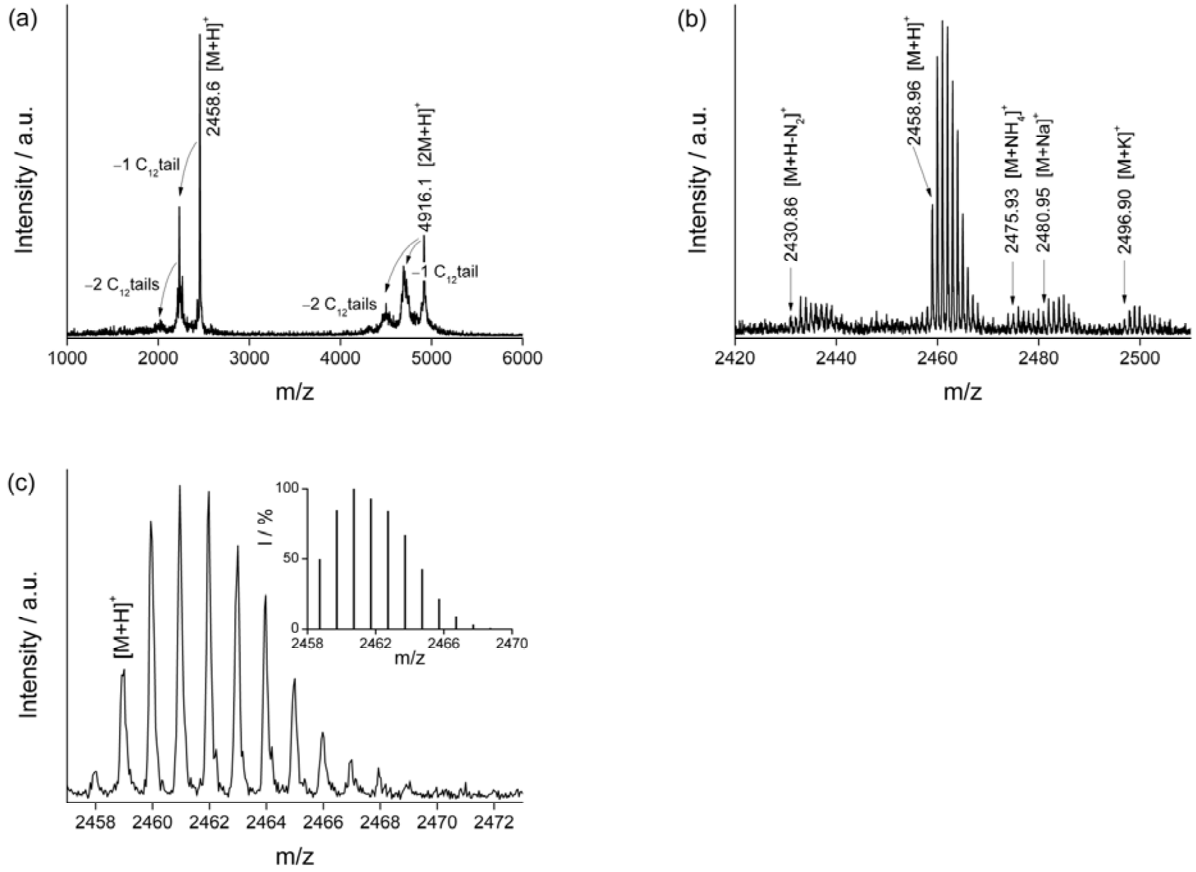


Figure S3. MALDI-TOF spectra of **2**: (a) Linear mode with molecular $[M+H]^+$ peak at 2458.6 (with the corresponding NH_4^+, Na^+ and K^+ peaks. Major fragments are –28 (–N_2 from triazole), –197 (–$C_{12}H_{25}$–N_2, small) and –225 (–$C_{12}H_{25}$–2xN_2 with the corresponding NH_4^+, Na^+ and K^+ peaks). In the dimers (clearly visible) and higher oligomers (not shown), a similar fragmentation patterns is visible. (b) Reflectron mode: Molecular peak with H^+, NH_4^+, Na^+, K^+ and first fragment (M–28). (c) Reflectron mode: Isotopic distribution of the molecular peak and in the inset the calculated distribution. Reflectron mode: M+H = 2458.96 g/mol, calculated 2458.72 g/mol.

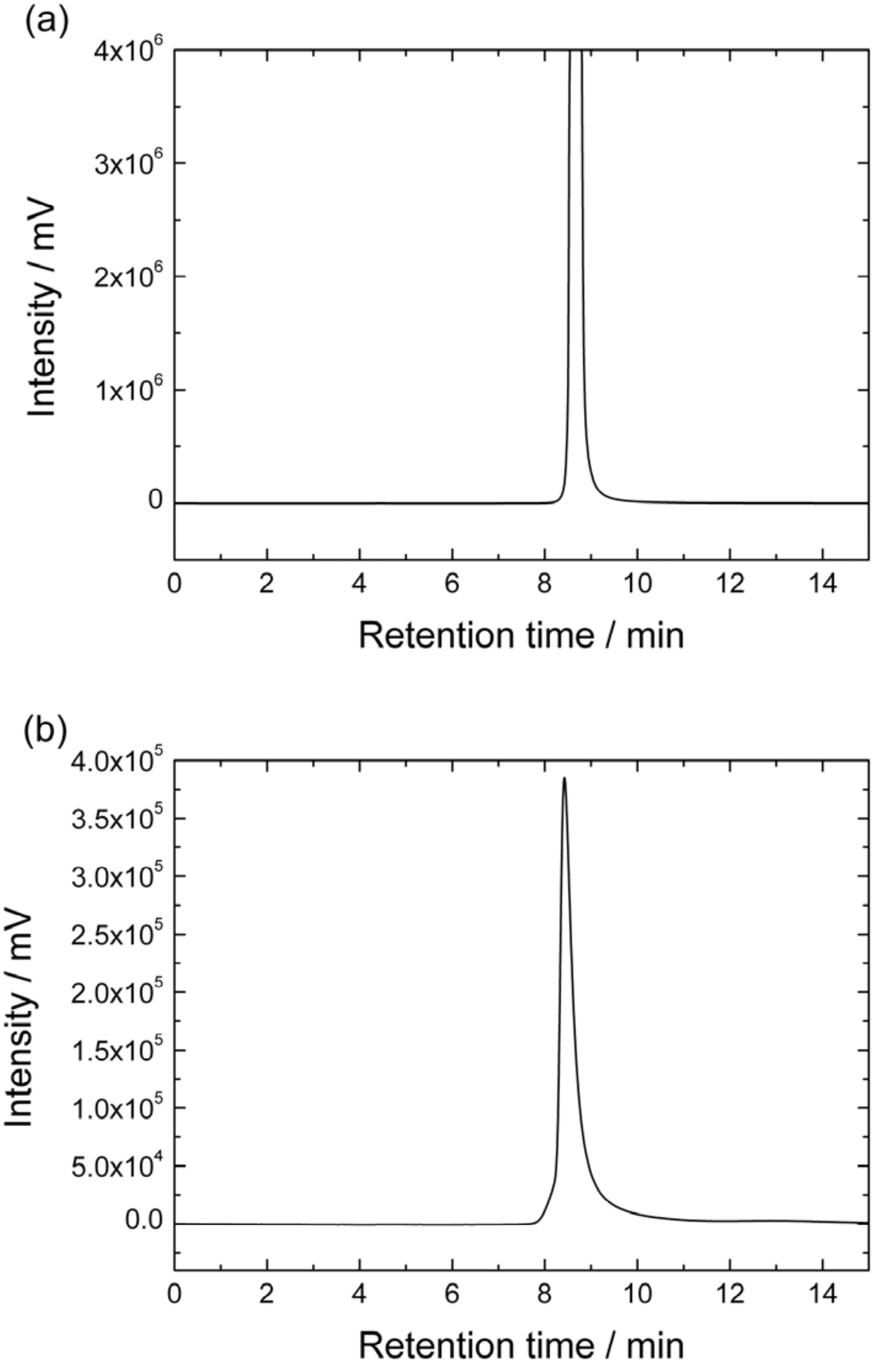


Figure S4. GPC chromatograms with UV-Vis (700 nm) detection of compounds **1b** (a) and **2** (b) using THF as an eluent and PS standards. IR is conclusive that full substitution occurs. The broadening on GPC of **2** is due to aggregation, not product distribution.

References

(1) Ito, M.; Koyakumaru, K.; Ohta, T.; Takaya, H. *Synthesis* **1995**, 376–378.

(2) Miljanić, O. Š.; Vollhardt, K. P. C.; Whitener, G. D. *Synlett* **2003**, 29–34.

(3) Leznoff, C. C.; Li, Z.; Isago, H.; d'Asciano, A. M.; Terekhov, D. S. *J. Porphyrins Phthalocyanines* **1999**, *3*, 406–416.