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Postfunctionalization of Helical Polyisocyanopeptides with Phthalocyanine Chromophores by "Click Chemistry"

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In memory of Rafael Suau

Rigid rod polyisocyanopeptides bearing phthalocyanines as pendant groups have been synthesised through CuAAC of polyisocyanopeptides containing acetylene groups with zinc(II) phthalocyanine azide. As confirmed by UV/Vis, fluorescence, and circular dichroism spectroscopies, the phthalocyanines are arranged in a helical fashion along the polymer backbone, forming the longest reported well-defined phthalocyanine assembly described to date.

Introduction

The development of well-defined arrays of chromophoric molecules inspired by the naturally occurring photosynthetic machinery has attracted great interest in recent years owing to their potential application in the fields of molecular photonics.[1] The naturally occurring photosynthetic light-harvesting antenna complexes exhibit a precise organization and orientation of the chromophores, thus ensuring an efficient absorption and transportation of light and its subsequent conversion into chemical energy.[2]

The self-organization of programmed chromophores by non-covalent interactions such as hydrogen bonding, π–π stacking, and metal–ligand coordination has been used as a tool for the construction of well-defined chromophoric architectures with interesting photophysical and (opto)electronic properties as a result of excitonic interactions between the chromophores.[3] Certain applications, however, require more robust assemblies that cannot be obtained by non-covalent synthesis, that is applications in which a full control of the final structure is needed, which until now can only be afforded by covalent synthesis.[4]

Nolte, Rowan, and co-workers have developed a covalent strategy to prepare long and well-ordered arrays of chromophore molecules by grafting them onto a rigid and well-defined helical polyisocyanide backbone.[5] Polyisocyanides are stable helical polymers that do not unfold if bulky side chains are present.[6] The polyisocyanide helical structure can also be stabilized and rigidified if chiral amino acid or peptide residues are attached close to the polymeric backbone to promote the formation of hydrogen bonding interactions between the side chains of the resulting polymer.[7]

Polyisocyanopeptides exhibit a 15_4-helical conformation with an average spacing between the side chains n and $(n+4)$ of 4.6 Å.[8] In addition, the chiral centers of the amino acid or peptide units control the handedness (left or right) of the helix.[9] By making use of the well-defined nature of polyisocyanides, long arrays of porphyrin[10] and perylenediimide[11] dyes have been constructed which exhibit excellent exciton and charges migration properties along the stacked chromophores.[12]

Phthalocyanines (Pcs) are well-known chromophoric compounds characterized by their intense absorption in the red/IR region (Q-band).[13] The aggregation properties of Pcs, mainly realized by π–π stacking interactions between the flat aromatic macrocycles, favor their self-organization into one-dimensional columnar aggregates,[14] which exhibit high charge mobilities.[15] However, as in the case of other chromophoric molecules, there is a persistent need of controlling the Pc organization into well-defined, robust systems to integrate these dye molecules into materials in which energy transfer between the units would be possible over large distances.

Several strategies for the incorporation of phthalocyanines into polymers have been described.[16] Poly(phthalocyaninate siloxane)s[17] and the so-called "Shish-kebab polymers"[18] are examples of polymers in which the main backbone consists of a cofacial arrangement of the Pc molecules, leading to materials with electrical conductivity owing to the overlap of the π orbitals. Furthermore, ordered stacked phthalocyanine polymers based on long-chain octa-substituted phthalocyanines bearing terminal olefin groups have also been prepared by a photostimulated [2+2] cycloaddition reaction[19] or a metathe-

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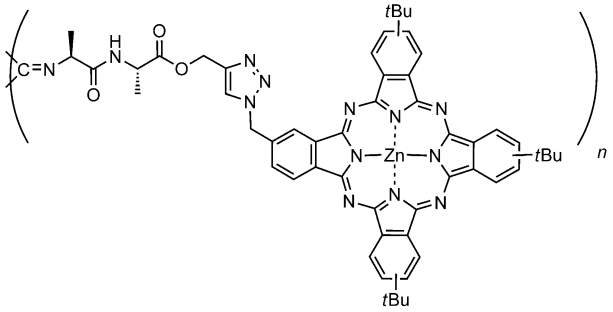
sis.[20] Other approaches consist of incorporating phthalocyanines as pending groups linked to the main backbone. For example, [60]fullerene–phthalocyanine-based copolymers have been prepared by metathesis copolymerization of fullerene– and phthalocyanine–norbornene monomers for application in organic solar cells.[21] The possible contact between the electron-donor phthalocyanine and the electron-acceptor fullerene accounts for an efficient photoinduced charge separation. Other examples of polymers incorporating phthalocyanines as pendant groups for photovoltaic applications make use of modified poly-3-hexylthiophene (P3HT) and poly(2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene) (MDMO-PPV).[22]

The copper(I)-catalyzed 1,3-dipolar cycloaddition of alkynes and azides (CuAAC) to give substituted 1,2,3-triazoles has emerged as a powerful tool to link molecules together.[23] In materials science, this reaction has proven to be a successful synthetic tool for the quantitative functionalization of single-wall carbon nanotubes (SWNTs),[24] polymers, and surfaces.[25] By using the CuAAC approach, the research groups of Nolte and Rowan have overcome the classical difficulties encountered in the synthesis of polyisocyanides with pendant chromophoric moieties, that is in fact the synthesis of the chromophore-containing isocyanide monomer is tedious and considerable problems are often encountered in the dehydration step of the formamide into the isocyanide. The CuAAC approach makes use of terminal alkyne-containing[26a,b] or terminal azide-containing[26c] polyisocyanopeptides, which can be used as a modular scaffold to which a variety of derivatized azides or acetylenes can be attached.

Despite the interest in the field of molecular electronics to organize phthalocyanines with the help of a rigid macromolecular skeleton, polyisocyanides bearing phthalocyanine units as side groups have never been reported. Herein, we describe the synthesis and characterization of the polyisocyanide L,L-PIAA-PEZnPc **1** (Scheme 1) prepared by postfunctionalization by CuAAC between the rigid rod alkynyl-terminated polyisocyanide L,L-PIAAPE **2** and $ZnPcN_3$ **3**, which contains three solubilizing *tert*-butyl groups and one azide functional group.

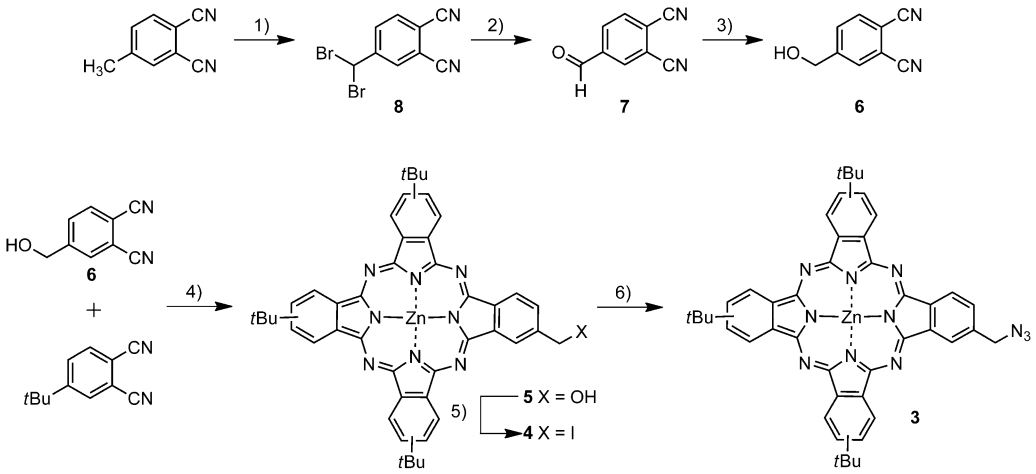


Scheme 1. Molecular structure of L,L-PIAAPEZnPc **1**.

Results and Discussion

When planning the synthesis of a new unsymmetrically substituted Pc derivative, the choice of the peripheral substituents can be crucial to successfully carry out the final isolation of the desired compound from the statistical mixture of Pcs formed by cross-condensation of two differently substituted phthalonitrile precursors. The separation of the mixture of Pcs by column chromatography can be facilitated by using peripheral substituents of rather different polarity and/or bulky groups that reduce the strong tendency of Pcs towards aggregation. Our research group has reported an efficient synthesis (38% yield) of the hydroxymethyl-substituted Pc derivative **5**,[27] which is carried out by statistical cross-condensation of a 3:1 mixture of *tert*-butylphthalonitrile and 4-hydroxyphthalonitrile (**6**; Scheme 2).

The synthesis of 4-hydroxyphthalonitrile (**6**)[28] was carried out by reduction of the corresponding formyl derivative **7** by $NaBH_4$ in 85% yield after purification by column chromatography. Although the synthesis of the 4-formylphthalonitrile (**7**) was first carried out from oxidative cleavage of 4-vinylphthalonitrile by ozonolysis,[29] a simpler synthetic route has been developed by starting from the commercially available 4-methyl-

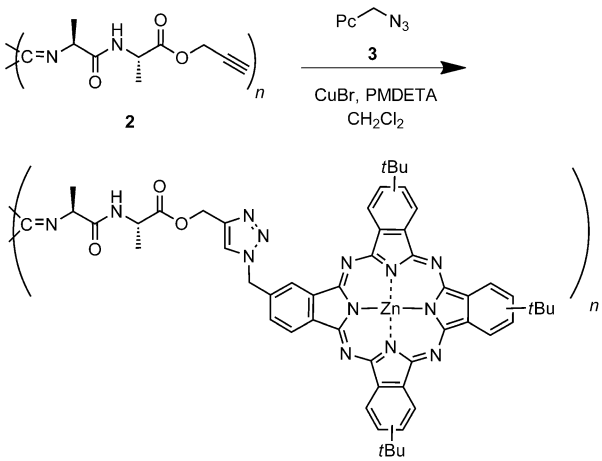


Scheme 2. Synthesis of phthalocyanine $ZnPcN_3$ **3**. 1) NBS, AIBN, CCl_4, reflux; 2) aqueous Me_2NH, 60 °C; 3) $NaBH_4$, EtOH; 4) $Zn(OAc)_2$, DMAE, 140 °C; 5) PPh_3, I_2, CH_2Cl_2; 6) NaN_3, THF/H_2O (10:1 v/v), reflux. AIBN = azobisisobutyronitrile, DMAE = *N*,*N*-dimethylaminoethanol, THF = tetrahydrofuran.

phthalonitrile, which was subjected to benzylic bromination using *N*-bromosuccinimide (NBS) to yield 4-dibromophthalonitrile (**8**). According to Bankston,[30] compound **8** was further transformed into the corresponding 4-formylphthalonitrile (**7**) in 80% yield by reaction with aqueous dimethylamine (40%) for 1 hour at 60 °C.

Classic routes for preparing organic azides imply a two-step transformation of the corresponding alcohol into a sulfonate or halide derivative and subsequent displacement of the leaving group by the azide ion.[31] Thus, hydroxymethyl derivative ZnPcOH **5** was reacted with triphenylphospine and resublimed iodine at room temperature, and afforded iodide compound ZnPcI **4** in 80% yield. Then, ZnPcI **4** was converted into the azide derivative **3** by heating a solution of **4** in a THF/H_2O mixture in the presence of sodium azide (Scheme 2). The azido compound $ZnPcN_3$ **3** was characterized by ^1H and ^{13}C NMR, FT-IR, UV/Vis, and fluorescence spectroscopies as well as by mass spectrometry. The characteristic intense band of the azide stretch at $\nu = 2100\ cm^{-1}$ in the IR spectrum confirmed the presence of the azide functionality in **3** (see the Supporting Information).

The introduction of the Pcs side groups onto the polyisocyanide scaffold of L,L-PIAAPE **2**, which was synthesized according to published procedures,[26] was accomplished by CuAAC using 1.6 equivalents of $ZnPcN_3$ **3** (with respect to the number of acetylene units in the polymer), copper bromide (0.17 equiv) as catalyst, and an excess of *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) as ligand at room temperature (Scheme 3). After 12 hours of reaction, the polymer was



Scheme 3. Synthesis of polyisocyanopeptide **1**.

washed several times with diethyl ether to remove any starting azide and further purified by size-exclusion chromatography.

Polymer L,L-PIAAPEZnPc **1** was characterized by ^1H NMR, UV/Vis, FT-IR, and fluorescence spectroscopies as well as by atomic force microscopy (AFM). The ^1H NMR spectrum of **1** in $CDCl_3$ led to poorly resolved resonance signals, indicating aggregation of the phthalocyanines. The FT-IR measurements allowed us to determine the scope of the CuAAC reaction (see the Supporting Information). The absence of any residual stretching frequency corresponding to the acetylene moieties gave us an indication that polyisocyanopeptide **2** underwent almost complete grafting by the azide derivative $ZnPcN_3$ **3**. In addition, the characteristic band of the azide stretch was no longer present, thus indicating that the removal of excess azide was successful during the purification process. Figure 1a shows the

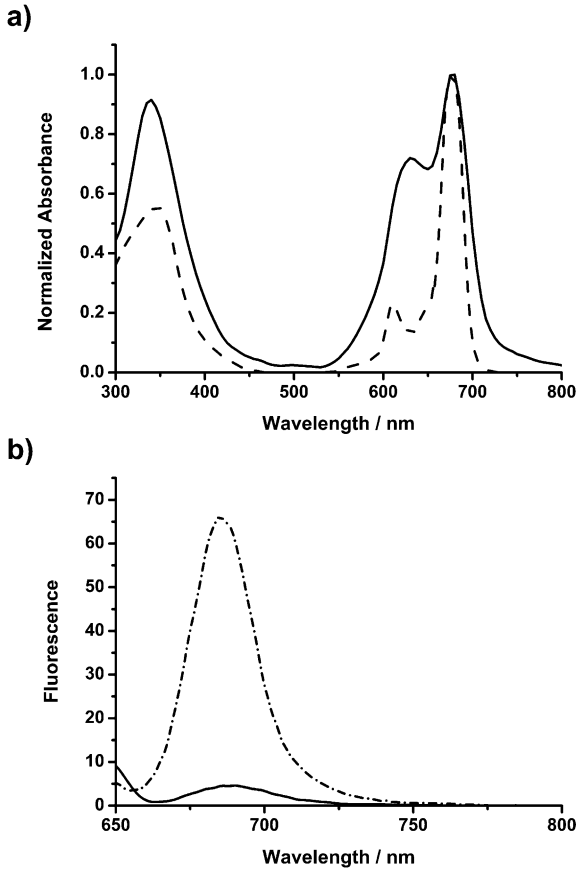


Figure 1. a) UV/Vis spectra of $ZnPcN_3$ **3** (dotted line) and polymer L,L-PIAAPEZnPc **1** (solid line) in $CHCl_3$. b) Emission spectra of $ZnPcN_3$ **3** (dotted line) and polymer L,L-PIAAPEZnPc **1** (solid line) in $CHCl_3$.

UV/Vis spectra of azide **3** and polymer **1** in $CHCl_3$. The broad and blue-shifted absorption centered at about 630 nm indicates the presence of exciton-coupled stacks of phthalocyanines forming H-type aggregates along the polymeric backbone. In addition, the fluorescence of polymer L,L-PIAAPEZnPc **1** is significantly quenched in comparison to that of the compound $ZnPcN_3$ **3** (Figure 1b), which confirms the presence of excited-state–chromophoric interactions between neighboring phthalocyanine compounds.

The circular dichroism (CD) spectrum of polymer **1** in $CHCl_3$ is shown in Figure 2. The positive Cotton effect at $\lambda = 310$ nm can be assigned to the n–π* transition of the helically arranged imine groups present in the polymer backbone, indicating that the right-handed (*P*) helix of the polymer scaffold[26] is not affected by the click reaction. The positive Cotton effects found at $\lambda = 350$ and 690 nm are assigned, respectively, to the Soret- and Q-bands of the phthalocyanine moieties, thus showing

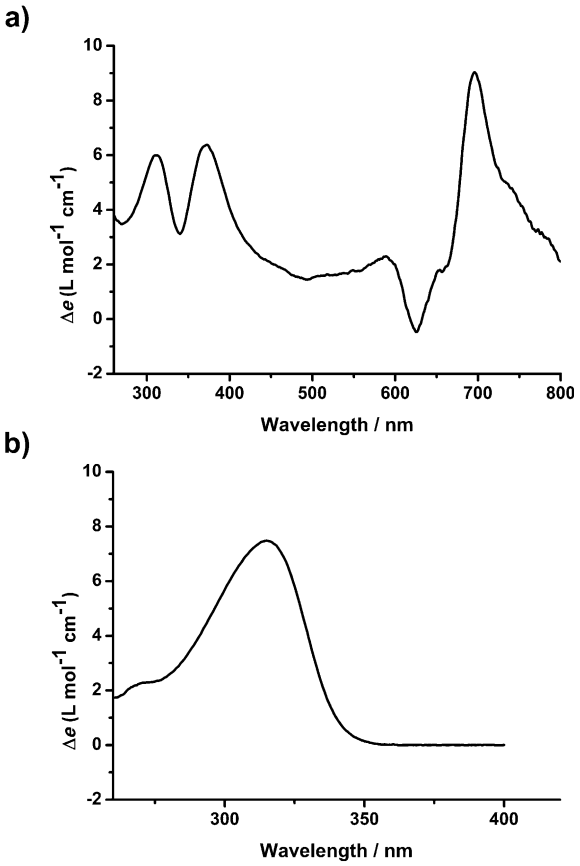


Figure 2. a) CD spectrum of polymer L,L-PIAAPEZnPc **1** in $CHCl_3$ indicating that the Pcs are in a chiral environment. b) CD spectrum of polymer **2** in $CHCl_3$.

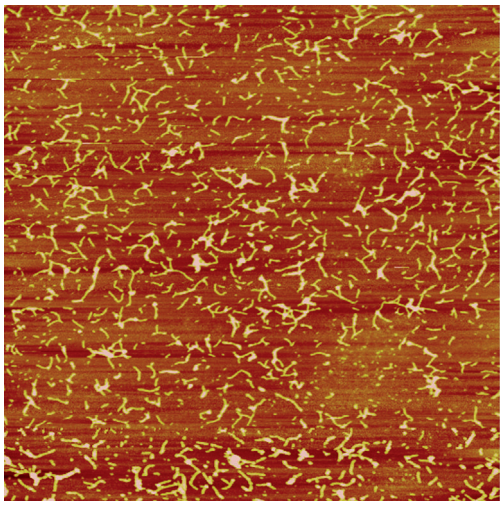


Figure 3. AFM image of polymer L,L-PIAAPEZnPc **1** (1 mg L^{-1} in $CHCl_3$ spin coated on mica).

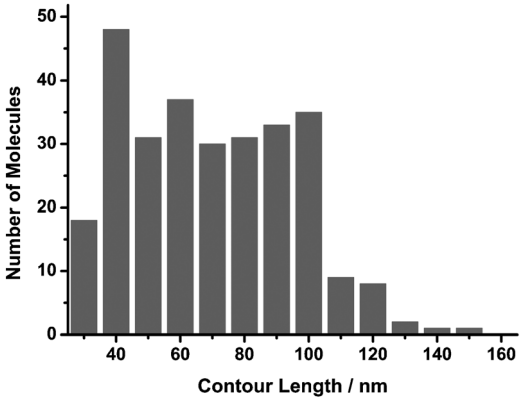


Figure 4. Histogram of the length distribution of polymer L,L-PIAAPEZnPc **1**, as calculated from the AFM images of **1**.

that these dyes are in a chiral environment created by the inner core of the helix. This result is in sharp contrast to previous results on dye-functionalized polyisocyanopeptides synthesized using CuAAC. When a perylene azide was clicked to the polymer scaffold **2**, no signals were observed in the perylene-diimide region (i.e., $\lambda = 450$–650 nm).[26b] The observed differences might be attributed to a small change of the helical pitch induced by the bulky phthalocyanine. However, (empirically) this would be accompanied by a change in the Cotton effect at $\lambda = 310$ nm, as observed for polymers to which dodecylazide or 1-azido-11-methoxy-3,6,9-trioxaundecane were clicked.[26] Therefore, the presence of the additional CD signals, besides the signals corresponding to the n–π* transition of the polyimine, might be attributed to the properties of the azido compounds that are clicked to the polyisocyanide.

Polymer L,L-PIAAPEZnPc **1** could be visualized by atomic force microscopy (AFM) after spin-coating dilute solutions (ca. 1 mg L^{-1}) of **1** in $CHCl_3$ on mica samples. As seen in Figure 3, individual polymer strands of **1** are visible, highlighting the rodlike character of the well-folded polyisocyanopeptides. As in previous examples, the molecular weight and polydispersity of these materials could not be determined by MALDI-MS or GPC techniques owing to the rod-like nature of the polymers.[9] However, it has been reported that by measuring the contours of rigid polymers in AFM images the molecular weight and polydispersity parameters can be reliably calculated.[32,33] Hence, the analysis of AFM images such as the one shown in Figure 3, summarized in the histogram depicted in Figure 4, allowed us to determine the weight-average (*Lw*) and number-average (*Ln*) apparent lengths as well as the length polydispersity (PD) by using the Equations (1)–(3):

$$L_w = \frac{\sum_i N_i \cdot L_i^2}{\sum_i N_i \cdot L_i} \quad (1)$$

$$L_n = \frac{\sum_i N_i \cdot L_i}{\sum_i N_i} \quad (2)$$

$$PD = \frac{L_w}{L_n} \quad (3)$$

The former two values amounted to $L_w \approx 79$ nm and $L_n \approx 68$ nm, respectively, giving a PD ≈ 1.15. Assuming a helical pitch of 0.46 nm (i.e., every monomer segment adds 1.15 Å to the polymer chain) as measured by powder X-ray diffraction of poly(L-isocyanoalanyl-L-alanine methyl ester),[8] these values

amount to a degree of polymerization of approximately 750, a M_w of 694 kg mol^{-1}, and a M_n of 598 kg mol^{-1}. To our knowledge, this is the longest well-defined phthalocyanine assembly described so far. Identical results were obtained using the starting material polyisocyanide L,L-PIAAPE **2**, further confirming that "postfunctionalization" does not affect the rod-like starting polymer.[26a]

Conclusion

The preparation and characterization of a polyisocyanide bearing phthalocyanines as pendant groups has been achieved through CuAAC of polyisocyanopeptides containing acetylene groups with zinc(II) phthalocyanine azide, forming the longest reported well-defined phthalocyanine assembly described to date.

The polymer has a rigid chiral core to which the phthalocyanine dyes have been attached in a helical arrangement as confirmed by UV/Vis, fluorescence, and CD spectroscopies. It was found that in the postfunctionalized polymer, electronic interactions between the phthalocyanine units take place, as shown by UV/Vis and fluorescence spectroscopies.

Experimental Section

All click reactions were performed under Schlenk conditions using distilled solvents. Sodium azide and PMDETA were purchased from ACROS chemicals. Copper bromide was purchased from Sigma Aldrich. All purchased chemicals were used as received. Polymer L,L-PIAAPE **2** was prepared by literature procedures.[26] Column chromatography was performed using silica gel (40–60 μm) purchased from Merck. The TLC analyses were carried out using glass coated with silica 60 F_{254} obtained from Merck. Size-exclusion chromatography was performed by using a column packed with Bio Bead S-X1 using $CHCl_3$ as eluent. The ^{1}H NMR spectra were recorded, at 20 °C, on a Bruker AC-300 spectrometer operating at 300 MHz. The ^{13}C NMR spectra were recorded on a Bruker AC-300 spectrometer operating at 75 MHz. The FT-IR spectra were recorded on a Thermo-Mattson IR300 spectrometer equipped with a Harrick ATR unit; compounds were measured as solids. Mass spectrometry measurements were performed on a VG 7070E instrument (EI/CI). The CD spectra were recorded on a Jasco 810 instrument equipped with a Peltier temperature control unit and were measured at 20 °C. The AFM experiments were performed by using a Nanoscope IV instrument from Digital Instruments. Solutions of the samples were spin coated onto freshly cleaved Muscovite mica. All images were recorded with the AFM operating in tapping mode in air at room temperature with a resolution of 512×512 pixels using moderate scan rates (1–2 lines s^{-1}). Commercial tapping-mode tips (NT-MDT) were used with a typical resonance frequency around 300 kHz. The UV/Vis absorption spectra were obtained with a Varian 4000 UV/Vis spectrophotometer or a Varian Cary 50 spectrometer and fluorescence spectra on a PerkinElmer Luminescence spectrometer LS50B. The MALDI-TOF spectra were measured on a Bruker Biflex III spectrometer using dithranol as the matrix.

4-Formylphthalonitrile (7): A mixture of 4-methylphthalonitrile (5 g, 34.5 mmol), NBS (31 g, 138 mmol) and AIBN (1 g, 6 mmol) in CCl_4 (400 mL) was refluxed for 24 h. After cooling down to room temperature, the liquid was filtered through a plug of silica gel using CH_2Cl_2 as eluent to remove the succinimide. Subsequently, the organic solvent was evaporated and the resulting crude reaction mixture was dissolved in 40% aqueous dimethylamine (100 mL) and heated to 60 °C under argon for 1 h. The brown solution was cooled to room temperature and poured into CH_2Cl_2 (100 mL). The layers were separated and the organic layer was washed consecutively with brine (2×50 mL), aqueous HCl (1 N) (2×50 mL) and water. The organic layer was dried over anhydrous Na_2SO_4 and purified by column chromatography using CH_2Cl_2 as eluent to give 4-formylphthalonitrile (7) (2.4 g, 45%). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 10.12 (s, 1H, CHO), 8.31 (d, J(H,H) = 2 Hz, 1H), 8.23 (dd, J(H,H) = 8 Hz, 2 Hz, 1H), 8.03 ppm (d, J(H,H) = 8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): δ = 188.21 (CHO), 138.82, 134.50, 133.73, 133.21, 120.26, 117.25, 114.51 (CN), 114.31 ppm (CN); FTIR (KBr): ν = 3106, 3071, 3047, 2878, 2233 (CN), 1709, (C=O), 1567, 1381, 1149, 1096, 850, 752 cm^{-1}; MS (EI): m/z (%): 156 (61) [M^+].

4-Hydroxymethylphthalonitrile (6): 4-Formylphthalonitrile (1.7 g, 10.8 mmol) was dissolved in EtOH (100 mL) and the mixture was cooled to 0 °C. Then, $NaBH_4$ (104 mg, 27.5 mmol) was added portionwise. The reaction mixture was stirred for 2 h at RT, and then water was added dropwise to neutralize the excess $NaBH_4$. The solvent was evaporated under vacuum, and then the crude reaction mixture was dissolved in EtOAc (100 mL), and further washed with water (2×100 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and the solvent was removed under vacuum. The product was purified by column chromatography on silica gel using CH_2Cl_2/EtOAc (5:1) to afford the 4-hydroxymethylphthalonitrile (**6**; 1.4 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 7.9 (m, 2H), 7.81 (d, J(H,H) = 6 Hz, 1H), 4.73 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): δ = 150.48, 134.86, 132.36, 132.27, 116.78, 116.67, 114.88 (CN), 63.38 ppm (CH_2-O); FT-IR (KBr): ν = 3356, 3106, 3071, 3047, 2230 (C≡N), 1567, 1381, 1163,1097, 852, 749 cm^{-1}; MS (EI): m/z (%): 158 (16) [M^+].

2(3),9(10),16(17)-Tri-*tert*-butyl-23-(iodomethyl)phthalocyaninato zinc(II) (4): A solution of PPh_3 (175 mg, 0.66 mmol) and resublimed iodine (178 mg, 0.67 mmol) in CH_2Cl_2 (5 mL) was stirred at RT for 5 min. Subsequently, a solution of ZnPcOH **5** (100 mg, 0.13 mmol) in CH_2Cl_2 (10 mL) was added and the mixture was further stirred for 3 h at RT. Then, it was diluted with diethyl ether (50 mL) and successively washed with aqueous 5% $NaHCO_3$ (2×25 mL) and brine (2×25 mL), dried over anhydrous $MgSO_4$, and evaporated to give a crude product which was purified by column chromatography on silica gel using a mixture of hexanes/THF (4:1) to afford the corresponding ZnPcI **4** (92 mg, 80%). ^{1}H NMR (300 MHz, [D$_8$]THF, 20 °C): δ = 9.0 (m, 8H), 8.3 (m, 3H), 7.8 (m, 1H), 5.1 (m, 2H), 1.8 ppm (m, 27H). ^{13}C NMR (75 MHz, [D$_8$]THF, 20 °C): δ = 149.26, 138.51, 138.45, 138.27, 137.16, 137.04, 136.90, 136.73, 135.18, 134.76, 134.68, 134.35, 127.51, 127.22, 125.04, 124.92, 124.79, 120.47, 120.21, 117.03, 116.78, 33.75 (C(CH_3)), 29.68 ppm (C(CH_3)). UV/Vis (THF): λ_{max} (ε) = 341 (80000), 642 (sh), 700 nm (148000 mol^{-1} m^3 cm^{-1}); FT-IR (KBr): ν = 3443, 3075, 2956, 2901, 2858, 1613, 1502, 1482, 1462, 1427, 1392, 1363, 1317, 1281, 1258, 1112, 1089, 1008, 893, 828, 749, 702, 674 cm^{-1}; EM (MALDI-TOF, dithranol): m/z: 757–761 [M−I]$^+$.

2(3),9(10),16(17)-Tri-*tert*-butyl-23-(azidomethyl)phthalocyaninato zinc(II) (3): A solution of ZnPcI **4** (61 mg, 0.068 mmol) and NaN_3 (45 mg, 0.68 mmol) in a 10/1 mixture of THF/H_2O (11 mL) was heated at reflux until full conversion of starting material (as determined by MALDI-TOF analysis; ca. 5 h). The mixture was diluted with EtOAc (100 mL) and successively washed with water (2× 100 mL) and brine (2×100 mL). The organic layer was dried over

anhydrous Na_2SO_4, filtered and the solvent was evaporated under vacuum. The crude product was purified by column chromatography on silica gel eluting with hexanes/THF (4:1) to afford the corresponding $ZnPcN_3$ **3** (49 mg, 90%). ^{1}H NMR (300 MHz, [D_8]THF, 20 °C): δ = 9.0 (m, 8H), 8.3 (m, 3H), 7.8 (m, 1H), 4.9 (m, 2H), 1.8 ppm (m, 27H); ^{13}C NMR (75 MHz, [D_8]THF, 20 °C): δ = 153.44, 153.30, 152.32, 152.25, 152.14, 151.14 151.06, 150.99, 138.68, 138.53, 138.42, 137.76, 137.23, 136.79, 136.17, 135.84, 128.09, 126.51, 126.41, 121.87, 121.67, 121.07, 118.55, 118.50, 118.28, 54.70 (CH_2-N_3). 35.23 (C(CH_3)), 31.11 ppm (C(CH_3)). UV/Vis (THF): λ_{max} (ε) = 341 (85000), 643 (sh), 700 nm (163000 $mol^{-1}\,m^3\,cm^{-1}$); FT-IR (KBr): ν = 3374, 3075, 2956, 2902, 2866, 2100 (N3), 1613, 1487, 1431, 1393, 1363, 1330, 1282, 1256, 1149, 1085, 1047, 831, 753, 693, 674 cm^{-1}; EM (MALDI-TOF, dithranol): *m/z*: 799–804 $[M]^+$.

Polyisocyanide L,L-**PIAAPEZnPc 1**: $ZnPcN_3$ **3** (50 mg, 0.062 mmol) was added to a suspension of polymer L,L-PIAAPE **2** (8 mg, 0.038 mmol) in freshly distilled CH_2Cl_2 (5 mL) under argon. The solution was repeatedly degassed by freeze, pump, and thaw cycles (3 times). Then PMDETA (1 mL, 4.1 mmol, 47 equiv) and CuBr (25 mg, 0.17 mmol) were added, and the solution was stirred for 18 h at RT. The precipitated copper salts were removed from the solution by the repeated addition of a saturated aqueous solution of EDTA and removal of the water layer from the top. The organic layer was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed to give a residue which was subjected to size-exclusion chromatography to remove any starting azides to afford the desired polymer L,L-PIAAPEZnPc **1** (30 mg). FT-IR (ATR): ν = 3263 (NH), 2129 (C≡C), 1746 (C=O ester), 1656 (amide I), 1525 cm^{-1} (amide II); UV/Vis ($CHCl_3$): λ_{max} = 350, 630, 680 nm. For further characterization see text.

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Keywords: click chemistry · helical structures · phthalocyanines · polyisocyanopeptides · polymers

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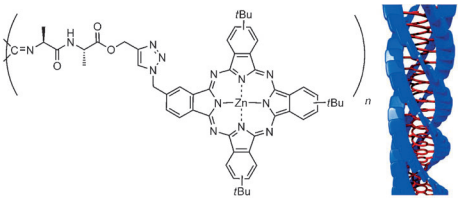
VIP **Postfunctionalization of Helical Polyisocyanopeptides with Phthalocyanine Chromophores by "Click Chemistry"**



Rigid rod polyisocyanopeptides bearing phthalocyanines as pendant groups, arranged in a helical fashion along the polymer backbone, have been prepared by "click chemistry" reaction of polyisocyanopeptides containing acetylene side-arms with zinc(II) phthalocyanine azide, resulting in the longest well-defined phthalocyanine assembly reported to date (see scheme).

