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A stable fullerene-azide building block for the construction of a fullerene–porphyrin conjugate

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ABSTRACT

A stable C_{60} derivative bearing an azide functional group was prepared and used as a building block under the copper-mediated Huisgen 1,3-dipolar cycloaddition conditions for the preparation of a fullerene–porphyrin conjugate.

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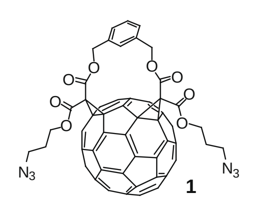
The synthetic appeal of click reactions relies upon their tolerance of water and oxygen, simple reaction conditions, and high yield.[1] The copper-mediated Huisgen 1,3-dipolar cycloaddition of organic azides and alkynes leading to 1,2,3-triazoles is without any doubt the most useful member of this family of reactions.[2] It quickly found applications in chemistry, biology, and materials science.[3] As part of this research, we have recently shown that this click reaction is an interesting tool for the functionalization of fullerene building blocks.[4] In general, the reactivity of C_{60} toward azides[5] is not significantly competing with the cycloaddition leading to the desired 1,2,3-triazole derivatives and good yields can be obtained when fullerene derivatives with reasonable solubility are used as starting materials.[4,6] Whereas fullerene alkyne building blocks are easy to produce, the preparation of fullerene azide derivatives is difficult due to their fast decomposition resulting from intermolecular cycloaddition reactions between the C_{60} and the azide groups.[4] We could however develop a fullerene bis-adduct (**1**) that was reasonably stable.[4] Indeed, upon preparation and purification, compound **1** must be used for the click reactions within the next couple of hours to obtain good yields. Therefore, the availability of this synthetic intermediate is quite limited and the preparation of a stable fullerene azide derivative remains a challenge. In this Letter, we report the synthesis of such a compound as well as its subsequent grafting onto a porphyrin core under the copper-mediated Huisgen 1,3-dipolar cycloaddition conditions. Indeed, porphyrins and fullerenes are interesting complementary building blocks for the preparation of artificial photosynthetic systems as photoinduced electron transfer is usually evidenced in fullerene–porphyrin conjugates.[7,8]



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In the design of C_{60} derivative **8** (Scheme 1), we have decided to take advantage of the encapsulation of the fullerene sphere in a cyclic addend surrounded by two 3,5-didodecylbenzyl ester moieties;[9] the azide function being attached onto the bridging subunit. In this way, steric hindrance should prevent the reaction of the azide group with the C_{60} core and, thus, provide a stable compound. The synthesis of building block **8** is depicted in Scheme 1. Alkylation of phenol **2**[9] with tosylate **3**[10] afforded **4** in a moderate yield (33%). Subsequent treatment of **4** with tetra-*n*-butylammonium fluoride (TBAF) gave diol **5** in 73% yield. The reaction of **5** with acid **6** and *N*,*N*′-dicyclohexylcarbodiimide (DCC) in the presence of 4-dimethylaminopyridine (DMAP) and 1-hydroxy-benzotriazole (HOBt) gave bis-malonate **7** in 65% yield. Fullerene derivative **8** was then prepared under the reaction conditions

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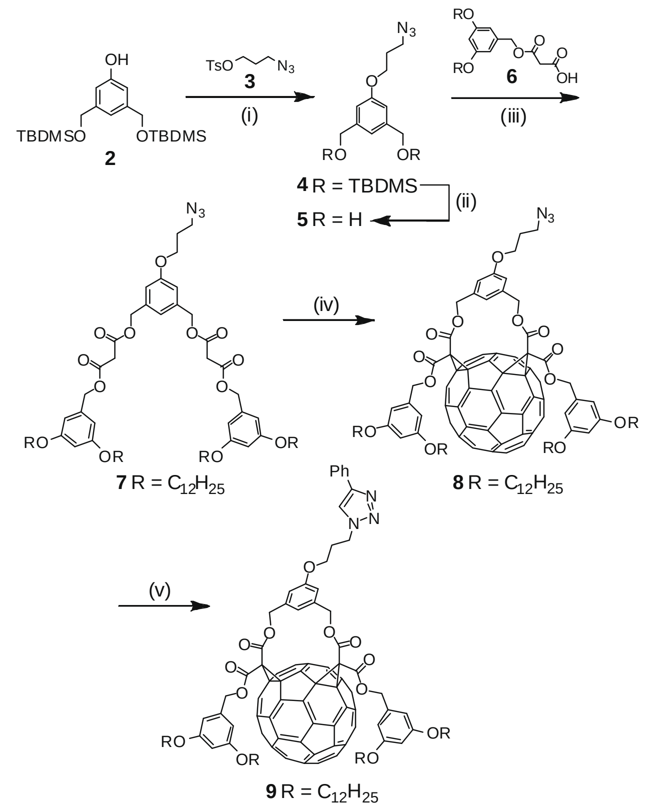
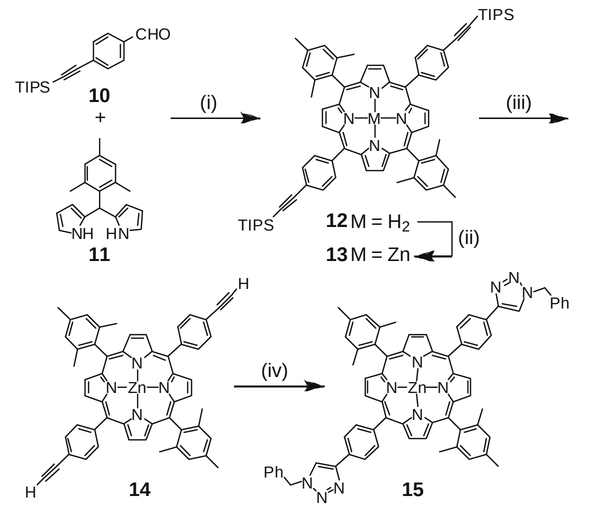


Scheme 1. Reagents and conditions: (i) K_2CO_3, LiBr, DMF, 80 °C, 96 h (33%); (ii) TBAF, THF, 0 °C, 3 h (73%); (iii) DCC, DMAP, HOBt, CH_2Cl_2, 0 °C to rt, 72 h (65%); (iv) C_{60}, DBU, I_2, PhMe, rt, 12 h (56%); (v) phenylacetylene, $CuSO_4{\cdot}5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, rt, 16 h (73%).

developed by Diederich and co-workers,[11] which led to macrocyclic bis-adducts of C_{60} by a regioselective cyclization reaction at the carbon sphere with bis-malonate derivatives in a double Bingel[12] cyclopropanation. Reaction of **7** with C_{60}, I_2, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene at room temperature afforded the desired cyclization product **8** in 56% yield. The relative position of the two cyclopropane rings in **8** on the C_{60} core was determined based on the molecular symmetry (C_s) deduced from the ^1H and ^{13}C NMR spectra.[13] It is also well established that the 1,3-phenylenebis(methylene)-tethered bis-malonates produce regioselectively the C_s symmetrical cis-2 addition pattern at C_{60}.[14] Importantly, fullerene azide derivative **8** was found to be a stable compound under normal laboratory conditions. A sample was stored in the refrigerator for several months without any detectable decomposition. The reaction conditions for the 1,3-dipolar cycloaddition of compound **8** with terminal alkynes were first adjusted with phenylacetylene (Scheme 1). Under optimized conditions, a mixture of **8** (1 equiv), phenylacetylene (2 equiv), $CuSO_4{\cdot}5H_2O$ (0.1 equiv), and sodium ascorbate (0.3 equiv) in CH_2Cl_2/H_2O was vigorously stirred at room temperature for 12 h. After work-up and purification, compound **9** was thus obtained in 73% yield. The structure of compound **9** was confirmed by its ^1H and ^{13}C NMR spectra as well as by mass spectrometry.[15] Inspection of the ^1H NMR spectrum clearly indicates the disappearance of the CH_2-azide signal at δ 3.55 ppm. Importantly, the ^1H NMR spectrum of **9** shows the typical singlet of the 1,2,3-triazole unit at δ 7.80 ppm as well as the signal corresponding to the CH_2-triazole protons at δ 4.65 ppm.

Having developed a stable fullerene azide building block allowing its further transformation under the copper-mediated Huisgen 1,3-dipolar cycloaddition conditions, we have decided to use it for



Scheme 2. Reagents and conditions: (i) $BF_3{\cdot}Et_2O$, $CHCl_3$, rt, 16 h, then *p*-chloranil, Δ, 2 h (23%); (ii) $Zn(OAc)_2$, $MeOH/CHCl_3$, Δ, 2 h (95%); (iii) TBAF, THF, 0 °C, 2 h (94%); (iv) benzyl azide, $CuSO_4{\cdot}5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, rt, 12 h (63%).

the preparation of a porphyrin-fullerene conjugate. For this purpose, we have developed a porphyrin building block bearing two terminal alkyne units. The synthesis of this compound is depicted in Scheme 2.

Compounds **10**[16] and **11**[17] were prepared according to previously reported methods. The condensation of **10** and **11** was performed in $CHCl_3$ (commercial $CHCl_3$ containing 0.75% ethanol as stabilizer) in the presence of $BF_3{\cdot}Et_2O$.[17] After 16 h, *p*-chloranil (tetrachlorobenzoquinone) was added to irreversibly convert the porphyrinogen to the porphyrin. The desired tetraphenylporphyrin **12** was subsequently isolated in 23% yield. Metalation of porphyrin **12** with $Zn(OAc)_2$ afforded **13** in 95% yield which after treatment with TBAF gave terminal alkyne **14** as a crystalline purple solid. Crystals suitable for X-ray crystal-structure analysis were obtained by slow diffusion of hexane into a $CHCl_3$ solution of **14** (Fig. 1).[18]

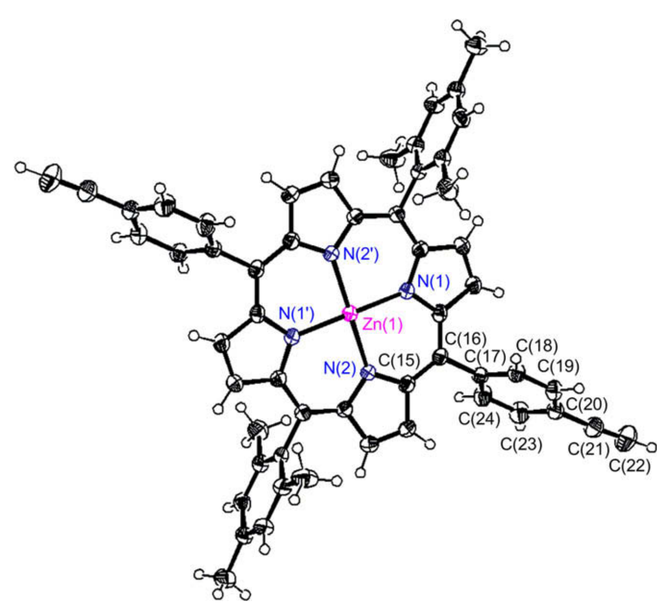


Figure 1. ORTEP plot of the structure of **14**. Thermal ellipsoids are drawn at the 50% probability level. The prime (′) characters in the atom labels indicate that these atoms are at equivalent position. Selected bond lengths and bond angles: Zn(1)–N(1): 2.030(2) Å; Zn(1)–N(2): 2.034(2) Å; C(21)–C(22): 1.170(4) Å; N(1)–Zn(1)–N(2): 90.55(8)°; N(1)–Zn(1)–N(2′): 89.45(8)°; C(20)–C(21)–C(22): 175.8(3)°.

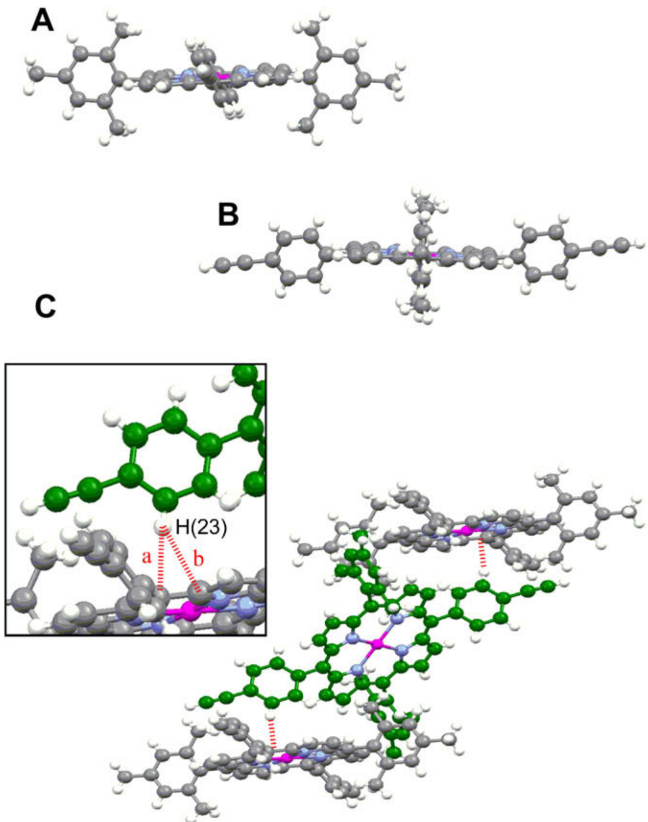
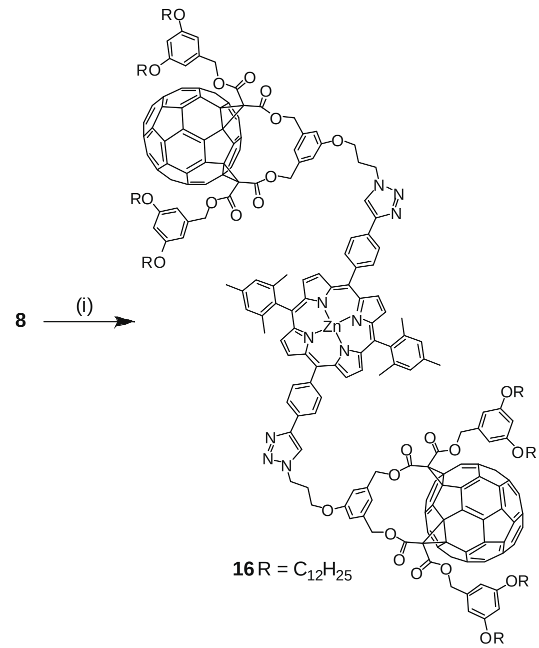


Figure 2. (A) and (B): views of the structure of **14** highlighting the dihedral angles between the central porphyrin ring and the phenyl substituents; (C) stacking within the **14** lattice showing the intermolecular CH–π interactions of the *para*-disubstituted phenyl rings with the neighboring porphyrin moieties; (a) 2.815(3) Å [H(23)–C(16)]; (b) 2.807(3) Å [H(23)–C(15)] (see Fig. 1 for the numbering).

As shown in Figures 1 and 2, the aromatic porphyrin ring is nearly perfectly planar. It can also be noted that the central Zn atom lies on an inversion center. Whereas the two mesityl units are almost perpendicular to the porphyrin core, a dihedral angle of ca. 63° is observed for the two other phenyl substituents with respect to the porphyrin plane. The peculiar orientation of these aromatic subunits can be explained by close inspection of the packing. Indeed, this orientation allows the establishment of intermolecular CH–π interactions between the *para*-disubstituted phenyl rings and the neighboring aromatic porphyrin rings (Fig. 2C). The packing forces resulting from these interactions also explain why the angle Zn(1)–C(16)–C(17) deviates from 180°. The observed angle is effectively 173.7°. Furthermore, attractive interactions of the acetylenic protons with the mesityl units of other neighboring molecules (not shown) explain the slight distortion of the terminal alkyne group with a value of 175.8(3)° for the C(20)–C(21)–C(22) angle.

The reaction conditions used for the preparation of **9** from phenylacetylene and **8** were then applied to porphyrin **14** and benzyl azide. The clicked derivative **15** was thus obtained in 63% yield (Scheme 2). Similarly, treatment of **14** with fullerene azide **8** in the presence of $CuSO_4 \cdot 5H_2O$ and sodium ascorbate gave the targeted fullerene–porphyrin conjugate **16** in 64% yield (Scheme 3). The ^1H and ^{13}C NMR spectra of **16** are in perfect agreement with proposed formulation.[19] IR data also revealed that no terminal alkyne (3294 cm^{-1}) or azide (2092 cm^{-1}) residues remain in the final product. The MALDI-TOF mass spectrum confirmed the structure of **16** with a very intense signal at 4898.5 corresponding to the expected molecular ion peak ($[MH]^+$, calcd for $C_{332}H_{287}N_{10}O_{26}Zn$: 4898.36).



Scheme 3. Reagents and conditions: (i) **14**, $CuSO_4 \cdot 5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, rt, 1 h (64%).

The absorption spectrum of **16** recorded in CH_2Cl_2 shows the characteristic Zn(II)-porphyrin absorptions.[17] The Soret band (423 nm) and the two Q bands (551 and 585 nm) are clearly visible. Furthermore, the characteristic fullerene cis-2 bis-adduct absorption profile[13] is also distinguishable in the UV region and the absorption coefficients are consistent with a 2:1 fullerene to porphyrin ratio. Finally, preliminary luminescence measurements reveal no emission from the porphyrin moiety in **16** indicating a strong quenching of its fluorescence by the fullerene subunits and thus, the occurrence of intramolecular photo-induced processes. Detailed photophysical studies are currently under investigation and will be reported in due time.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.02.185.

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14. *Compound* **8**. IR (neat): 2096 ($-N_3$), 1748 (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz): 0.89 (t, *J* = 7 Hz, 12H), 1.20–1.45 (m, 72H), 1.72 (m, 8H), 2.08 (m, 2H), 3.55 (t, *J* = 6 Hz, 2H), 3.85 (t, *J* = 7 Hz, 8H), 4.09 (t, *J* = 6 Hz, 2H), 5.04 (d, *J* = 12 Hz, 2H), 5.29 (AB, *J* = 12 Hz, 4H), 5.75 (d, *J* = 12 Hz, 2H), 6.36 (t, *J* = 2 Hz, 2H), 6.47 (d, *J* = 2 Hz, 4H), 6.78 (s, 2H), 7.11 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): 14.3, 22.8, 26.3, 28.9, 29.4, 29.5, 29.6, 29.8, 29.85, 29.9, 31.1, 31.6, 32.1, 48.3, 49.2, 64.8, 67.0, 67.4, 68.3, 68.8, 70.7, 101.8, 107.3, 112.6, 115.6, 134.6, 135.9, 136.3, 136.7, 138.0, 138.4, 140.2, 141.2, 141.3, 142.5, 142.9, 143.3, 143.7, 143.9, 144.1, 144.3, 144.5, 144.7, 145.1, 145.2, 145.3, 145.5, 145.7, 145.9, 146.2, 147.5, 147.6, 148.8, 158.9, 160.6, 162.7; MALDI-TOF-MS: 2043 ([MH]$^+$, calcd for $C_{139}H_{124}N_3O_{13}$: 2042.91).
15. *Compound* **9**. IR (neat): 1748 (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz): 0.89 (t, *J* = 7 Hz, 12H), 1.20–1.45 (m, 72H), 1.72 (m, 8H), 2.48 (m, 2H), 3.85 (t, *J* = 7 Hz, 8H), 4.06 (t, *J* = 6 Hz, 2H), 4.65 (t, *J* = 6 Hz, 2H), 5.04 (d, *J* = 12 Hz, 2H), 5.29 (AB, *J* = 12 Hz, 4H), 5.72 (d, *J* = 12 Hz, 2H), 6.36 (t, *J* = 2 Hz, 2H), 6.47 (d, *J* = 2 Hz, 4H), 6.76 (m, 2H), 7.13 (m, 1H), 7.33 (m, 1H), 7.43 (m, 2H), 7.80 (s, 1H), 7.83 (d, *J* = 8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): 14.3, 22.8, 26.2, 29.4, 29.5, 29.6, 29.7, 29.75, 29.8, 30.1, 32.0, 47.3, 49.2, 64.4, 66.9, 67.3, 68.2, 68.8, 70.7, 101.8, 107.3, 112.5, 115.7, 120.2, 125.8, 128.3, 128.9, 130.6, 134.5, 135.9, 136.2, 136.6, 137.9, 138.5, 140.1, 141.2, 141.3, 142.4, 142.8, 143.3, 143.7, 143.8, 144.1, 144.2, 144.4, 144.7, 145.1, 145.2, 145.3, 145.4, 145.7, 145.8, 146.2, 147.4, 147.5, 147.6, 147.9, 148.7, 158.6, 160.5, 162.7; Anal. Calcd for $C_{147}H_{129}N_3O_{13}\cdot H_2O$: C, 81.60; H, 6.10; N, 1.94. Found: C, 81.53; H, 6.11; N, 1.91. MALDI-TOF-MS: 2146 ([M]$^+$, calcd for $C_{147}H_{139}N_3O_{13}$: 2145.65).
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18. $C_{54}H_{40}N_4Zn$ (M = 810.27 g mol^{-1}), monoclinic; space group $P2_1/c$; a = 13.3374(6) Å; b = 12.1528(9) Å; c = 12.9668(9) Å; α = 90.00°; β = 103.104(4)°; γ = 90.00°; Z = 2; μ (Mo Kα) = 1.136 mm^{-1}; $F(000)$ = 844; a total of 13,564 reflections collected; 1.57° < θ < 27.46°, 4660 independent reflections with 3499 having $I > 2\sigma(I)$; 271 parameters; Final results: $R_1(F^2)$ = 0.0452; w$R_2(F^2)$ = 0.1311, Goof = 1.087. Full data collection parameters and structural data are available as CIF file (Cambridge Crystallographic Data Centre deposition number CCDC 717039).
19. Compound **16**. IR (neat): 1749 (C=O); UV–vis (CH_2Cl_2): 258 (341400), 423 (486900), 551 (27900), 585 (14800); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.88 (t, *J* = 7 Hz, 24H), 1.20–1.45 (m, 144H), 1.71 (m, 16H), 1.81 (s, 12 H), 2.60 (m, 10H), 3.82 (t, *J* = 7 Hz, 16H), 4.12 (m, 4H), 4.80 (m, 4H), 5.11 (d, *J* = 12 Hz, 4H), 5.26 (AB, *J* = 12 Hz, 8H), 5.73 (d, *J* = 12 Hz, 4H), 6.33 (m, 4H), 6.44 (d, *J* = 2 Hz, 8H), 6.84 (m, 4H), 7.14 (m, 2H), 7.23 (s, 4H), 8.00 (s, 2H), 8.14 (d, *J* = 8 Hz, 4H), 8.28 (d, *J* = 8 Hz, 4H), 8.75 (d, *J* = 5 Hz, 4H), 8.90 (d, *J* = 5 Hz, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.0, 21.3, 21.8, 22.85, 26.2, 29.4, 29.5, 29.6, 29.7, 29.8, 29.9, 32.1, 49.37, 64.5, 66.9, 67.2, 68.3, 68.8, 70.7, 101.6, 107.1, 112.1, 115.1, 119.4, 120.0, 121.0, 123.9, 127.7, 129.9, 130.7, 132.2, 134.6, 135.1, 135.7, 135.9, 137.5, 135.6, 138.7, 139.1, 139.2, 139.8, 140.9, 141.6, 142.7, 142.8, 142.9, 143.1, 143.2, 143.9, 144.0, 144.1, 144.2, 144.6, 144.7, 144.8, 144.9, 145.1, 145.3, 145.4, 145.8, 147.1, 147.2, 147.3, 147.6, 148.5, 149.8, 149.9, 158.9, 160.5, 162.5, 162.6; Anal. Calcd for $C_{332}H_{286}N_{10}O_{26}Zn\cdot 2H_2O$: C, 80.83; H, 5.92; N, 2.84. Found: C, 80.99; H, 6.22; N, 2.79. MALDI-TOF-MS: 4898.5 ([MH]$^+$, calcd for $C_{332}H_{287}N_{10}O_{26}Zn$: 4898.36).