Facile Synthesis and Photophysical Properties of Sphere–Square Shape Amphiphiles Based on Porphyrin–[60]Fullerene Conjugates


Abstract: Molecules constructed from a combination of zero-dimensional ([60]fullerene (C60)) and two-dimensional (porphyrin (Por)) nanobuilding blocks represent an intriguing category of sphere–square “shape amphiphiles”. These sphere–square shape amphiphiles possess interesting optoelectronic properties. To efficiently synthesize a large variety of C60–Por shape amphiphiles, a facile route based on Steglich esterification was developed. The synthetic strategy enables the preparation of hydroxy-functionalized Por precursors (9–12) with high purity in a one-pot procedure. All of the C60–Por shape amphiphiles (1–5) can be readily synthesized in good yields through subsequent Steglich esterification with a highly soluble carboxylic acid derivative of methanofullerene (13). Photophysical studies indicated weak electronic coupling between the C60 and Por moieties and suggest an edge-to-face alignment for the moieties. The fluorescence of electronically excited Por portions of each amphiphile was efficiently quenched, which was indicative of electron transfer from 1Por to the C60 group(s). Increasing the number of C60 groups on the shape amphiphiles led to more pronounced quenching of the Por fluorescence, which indicated the potential for more effective generation of charge-separated species, C60–Por*, from the photoexcited C60–Por shape amphiphiles.

Keywords: fullerenes · photophysics · porphyrinoids · shape amphiphiles

Introduction

Driven by noncovalent interactions, self-assembling processes are recognized as one of the most important ways to build up complex supramolecular entities.[1–7] Based on self-assembly principles, various covalent functional supramolecular materials have been developed.[8–14] The synergy between geometric complementarity and noncovalent interactions is the determining factor in the formation of the final structure. Based on dimensionality and geometry, nanobuilding blocks can be generally divided into four categories: spheres (0D), cylinders (1D), discs (2D), and bulk complex structures (3D). Molecules consisting of geometrically distinct subunits are thus known as “shape amphiphiles”.[15–27] Because the covalent linkage changes not only the geometry, but also the symmetry of the molecules, the molecular shape is also an important factor in tuning the final self-assembled structures in addition to noncovalent interactions.

Porphyrin (Por) and [60]fullerene (C60) are representative 2D and 0D conjugated nanobuilding blocks (Scheme 1). Although the major noncovalent interactions are both π–π interactions, the shape and geometry define the favorable interaction orientations and the resulting supramolecular architectures. The 2D nanobuilding block, Por, prefers to form columnar phases through directional face-to-face π–π stacking,[28–29] whereas the 0D sphere, C60 favors the formation of a plastic crystal phase with a face-centered cubic unit cell, in which the π–π interaction is anisotropic.[30] Covalently bound Por and C60 breaks the centrosymmetry of the original nanobuilding blocks and gives a series of intriguing Por–C60 shape amphiphiles.[31–38] In terms of functionality, covalently bound Por and C60 forms an electron donor–acceptor dyad. Unique photophysical properties, such as ultrafast photocinduced charge separation, long-lived charge-separation state, ambipolar charge transport, and photovoltaic activities, demonstrated the potential of C60–Por shape amphiphiles in optoelectronic applications.[34,36,37,39–43]
Recently, we reported our efforts toward self-assembled, hierarchical “double cable” supramolecular structures in the bulk through the design and synthesis of Por–C₆₀ shape amphiphiles.[44–46] These shape amphiphiles first form hierarchical “double cable” columns and further organize into 3D orthorhombic or hexagonal columnar lattices.[45,46] An alternating arrangement of Por and C₆₀ in a triclinic lattice formed by trans-diC₆₀–Zn²⁺Por was also observed.[44] These studies demonstrated an abundance of supramolecular entities formed by C₆₀–Por shape amphiphiles and their potential use in optoelectronic applications. Because an efficient and precise synthesis is a prerequisite in the study of structure–property relationships, our attention focused on extending the previously reported two-step esterification strategy to the synthesis of a library of C₆₀–Por shape amphiphiles for a systematic study. The structures are thus constructed with a single Por core, as shown in Scheme 1. It is evident that, not only the chemical compositions (C₆₀/Por ratio per molecule), but also the molecular geometries, can be systematically varied. Intriguing optoelectronic and self-assembly behavior of these molecules is anticipated.

The synthesis of Por–C₆₀ conjugates mainly involves two approaches: 1) condensation of a C₆₀-containing component to form the Por core,[47–49] and 2) attaching C₆₀ to a preformed functionalized Por.[50] The preparation of Pors through the condensation of aldehyde and pyrrole is known to give a mixture of compounds that are usually difficult to separate.[51,52] The synthesis of Por–C₆₀ by using the first method is thus costly. The post-functionalization method circumvents the difficulties associated with Por synthesis and has become prevalent. However, this approach is also limited by the low solubility of both Por and C₆₀ and the functional group tolerance of the coupling reaction when considering the multitude of functional groups in the system. Recently, click chemistry has been applied to the synthesis of such a construct with a triazole linkage.[53–57] Our approach uses a two-step esterification process and introduces 3,4,5-trisdodecyloxy benzoate and 3,5-bis(dodecyloxy)benzyl groups with long alkyl groups to make both components highly soluble, thereby facilitating the synthesis and purification of the final molecule.

Scheme 1. Molecular structures of C₆₀, the Por nanobuilding blocks, and the C₆₀–Por shape amphiphiles.
First, sequential esterification strategies were used to effectively generate a library of C_{60}-Por shape amphiphiles. First, 5,10,15,20-tetra(p-hydroxyphenyl)porphyrin (6) was chosen as the core unit and Steglich esterification was used to sequentially connect the peripheral substituents, which were 3,4,5-trisdecyloxybenzoic acid (7) and a carboxylic acid derivative of methanofullerene (13).[58] By taking advantage of the large polarity difference between the hydroxy group and the ester group, all of the specifically hydroxyfunctionalized porphyrins (OH-Pors in Scheme 2) can be prepared effectively and separated easily in a one-pot reaction. The C_{60}-Por shape amphiphiles were then synthesized by treating the OH-Pors with 13 through a second Steglich esterification. This synthetic procedure has the following advantages: First, control of the number of functional groups per Por is achieved at an early stage of the synthesis. As shown in Scheme 3, monoOH-Por (9), 5,10-diOH-Por (10), 5,10-diOH-Por (11), and 5,10,15-triOH-Por (12) were separated and obtained during the first step of the synthesis. Second, the carboxylic acid derivative of methanofullerene, which is more time-consuming and costly to prepare, is only used in the last step of the synthesis. Third, the mild reaction conditions of Steglich esterification prevent potential decomposition in the reaction to the conjugated molecules.

Results and Discussion

Synthesis and Characterization of the OH-Por Precursors

The synthesis of the OH-Pors is outlined in Scheme 3. The molecules were prepared by treating 5,10,15,20-tetra(p-hydroxyphenyl)porphyrin with 2.2 equivalents of 3,4,5-trisdecyloxybenzoic acid. Mixtures of the reference molecule (8) and compounds 9, 10, 11, and 12 were obtained through this procedure; these were readily separated by flash column chromatography on silica gel as a result of the large polarity differences in 8-12, thus resulting from the different number and positions of the −OH groups (polarity: 8<9<10<11<12). The yields of these reactions were 13 (8), 13 (9), 13 (10), 19 (11), and 20% (12), with a total yield of all products of about 78% after purification. The molecular structures of 8,[59] 9, 10, 11, and 12 were characterized by H and 13C NMR spectroscopy and MALDI-TOF mass spectrometry. MALDI-TOF mass spectra clearly confirmed the structures of 9, diOH-Por, and triOH-Por. The parent-ion peaks observed at m/z 2648.02, 1991.39, 1991.41, and 1334.43 in Figure S1 in the Supporting Information correspond to the molecular ions [M^+] of 9, 10, 11, and 12, respectively, and agree well with the calculated molecular weights of the corresponding molecules. Although the 5,15- and 5,10-isomers of the diOH-substituted compound cannot be distinguished from their MALDI-TOF mass spectra, their molecular symmetry is distinctly different and NMR spectroscopy experiments can readily distinguish between the two isomers. As shown in Figure 1, the molecular structure of 10 includes two twofold rotational axes, whereas 11 only has one. The difference in molecular symmetry leads to different chemical environments for the β protons on the pyrrole rings and different chemical shifts and splitting patterns in the 1H NMR spectra. As a result, only one signal was observed at δ = 8.91 ppm for the β protons of 10, but three signals were observed at δ = 8.96, 8.90, and 8.82 ppm for the β protons of 11 (Figure 1). Thus, from a combination of molecular characterization techniques, the molecular identities of 9–12 were established unambiguously.

Synthesis of the C_{60}-Por Shape Amphiphiles

As outlined in Scheme 4, the shape amphiphiles, monoC_{60}Por (1), trans-diC_{60}Por (2), cis-diC_{60}Por (3), triC_{60}Por (4), and tetraC_{60}Por (5) were prepared by treating 9, 10, 11, 12, and 6 separately with 13 through a second Steglich esterification.
The yields of each shape amphiphile after purification were 71 (1), 63 (2), 83 (3), 73 (4), and 53% (5). Comparisons of the \(^1\)H NMR spectra of 9 and 1 are given in Figure 2a and b. After the esterification reaction, the protons on the \(\rho\)-hydroxyphenyl group of 9 (\(\delta = 8.09\) and 7.21 ppm) shifted downfield to \(\delta = 8.26\) and 7.60 ppm owing to the resonance effect of the electron-withdrawing carbonyl group, and the signals of the protons on the attached \(\text{C}_{60}\) arm appeared at \(\delta = 4.15-4.19\) ppm. Comparing the integration of this signal to those protons belonging to the \(\text{C}_{60}\) units, it is clear that, as the number of \(\text{C}_{60}\) units per molecule increases, the integration of this signal decreases, whereas those signals belonging to the \(\text{C}_{60}\) arms show increased integration. In addition, differ-
ent molecular symmetries of 2 and 3 affect the signals of the β protons on the pyrrole rings of the Por core. In the region between δ = 8.8 and 9.0 ppm, the β protons of the more symmetrical compound, 2, has two doublet signals, whereas less symmetrical 3 has two groups of multiple signals. The MALDI-TOF mass spectra (Figures S3–S6 in the Supporting Information) have m/z values that closely match the molecular ions [M⁺] of each C₆₀–Por shape amphiphile. These combined results confirmed the success in obtaining the C₆₀–Por shape amphiphiles.

**Photophysical Properties of the C₆₀–Por Shape Amphiphiles**

The ground-state absorption spectra of the C₆₀–Por amphiphiles (1–5) and reference molecules 8 and 13 were examined in THF (Figure 3). Comparison of reference compounds 8 and 13 with 1–5 indicate little, if any, ground-state electronic coupling occurs between the two chromophores. The absorption spectra of 1–5 are similar to one another and are characterized by absorptions in the Q-band region at 515, 550, 590 and 646 nm, and in the more intense Soret band region at 419 nm. The two higher energy bands at λ_max = 258 and 326 nm result from the C₆₀ groups and the intensity of these bands scales linearly with the number of C₆₀ groups in each dyad.

Electronic coupling between the Por and C₆₀ moieties in covalently bound C₆₀–Por derivatives typically leads to a bathochromic shift of the Soret and Q bands of the Por moiety.[42,60] The degree of the bathochromic shift depends on the relative spatial orientation of the C₆₀ and Por moieties. Guldi et al. showed that C₆₀–Por dyads aligned in face-to-face orientations underwent bathochromic shifts to a greater extent than edge-to-face aligned C₆₀–Por dyads, most likely because of stronger Por-to-C₆₀ electronic coupling present in the face-to-face aligned dyad.[42] In the case of 1–5, bathochromic shifts were not observed in either the Soret or Q-band absorptions, relative to 8. Thus, electronic coupling between Por and C₆₀ in 1–5 is weak and the relative position of Por and C₆₀ in 1–5 is likely to be close to an edge-to-face alignment. Considering the fact that the C₆₀ moieties in 1–5 are connected to the Por core at only one point (instead of two points in the study by Guldi et al.),[42] the C₆₀ groups in 1–5 are likely to be oriented away from the Por core; this accounts for the small Por-to-C₆₀ electronic coupling and lack of a bathochromic shift in the absorption bands.

The generation of charge carriers is a critical step in the photon-to-electron conversion process in photovoltaic cells.[61] Previous studies have demonstrated the potential of C₆₀–Por dyads in photovoltaic applications,[36,37,45,46] in which the generation of long-lived charge carriers makes these materials an attractive component in bulk-heterojunction photovoltaics. Great interest lies in how the variation in the C₆₀/Por ratio affects the photophysical behavior of C₆₀–Por shape amphiphiles. Because quenching of the Por fluorescence (FL) in Por-containing donor–acceptor dyads is a good qualitative indicator of electron transfer, and therefore, of the generation of charge carriers,[39–41,43,62] we decided to examine the FL spectra of 1–5 (Figure 4). The FL spectrum of 8 is typical of tetraarylporphyrins, and has emission bands at λ_max = 653 and 721 nm (Figure 4a). The FL spectra of 1–5 displayed emission bands at the same energies, but with intensities significantly reduced relative to 8. The FL quantum yields (Φ FL) of each compound were deter-
Table 1. Summary of time-resolved FL data for 8 and the shape amphiphiles 1–5 in THF[a]

<table>
<thead>
<tr>
<th>Compounds</th>
<th>τ1 [ns]</th>
<th>Fluorescence lifetime</th>
<th>τ2 [ns]</th>
<th>τ3 [ns]</th>
<th>τ4 [ns]</th>
<th>k_{ET1} [s⁻¹]</th>
<th>k_{ET2} [s⁻¹]</th>
<th>k_{ET(avg)} [s⁻¹]</th>
</tr>
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<tbody>
<tr>
<td>8</td>
<td>10.1 (100 %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2.16 (71 %)</td>
<td>0.499 (29 %)</td>
<td>2.02</td>
<td>0.36 x 10⁸</td>
<td>1.91 x 10⁸</td>
<td>0.40 x 10⁸</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.16 (65 %)</td>
<td>0.331 (37 %)</td>
<td>1.04</td>
<td>0.76 x 10⁸</td>
<td>2.92 x 10⁸</td>
<td>0.86 x 10⁸</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.29 (59 %)</td>
<td>0.427 (41 %)</td>
<td>1.13</td>
<td>0.68 x 10⁸</td>
<td>2.24 x 10⁸</td>
<td>0.79 x 10⁸</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.769 (61 %)</td>
<td>0.273 (39 %)</td>
<td>0.68</td>
<td>1.20 x 10⁸</td>
<td>3.56 x 10⁸</td>
<td>1.38 x 10⁸</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.25 (4.8 %)</td>
<td>0.511 (43 %)</td>
<td>0.109</td>
<td>1.86 x 10⁸</td>
<td>9.08 x 10⁸</td>
<td>1.63 x 10⁸</td>
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</tr>
</tbody>
</table>

[a] An excitation wavelength of λ_{ex}=560 nm and an emission wavelength of λ_{em}=651 nm were used. [b] The average lifetimes were calculated by using the formula τ_{avg}=ατ₁+βτ₂+γτ₃, in which α represents the percentage of each decay component.

An effective two-step sequential esterification strategy was developed for the preparation of a series of C₆₀-Pors shape amphiphiles. The hydroxy-functionalized Por precursors (9–12) were prepared with high purity in a one-pot procedure and all of the C₆₀-Por shape amphiphiles (1–5) were readily synthesized in good yields in the subsequent Steglich esterification reaction with 13. Photophysical studies showed that the UV/Vis absorption spectra of the C₆₀-Por shape amphiphiles obeyed the simple addition of the absorption of the C₆₀ nanoparticles and the Por core. These results implied weak electronic coupling between the C₆₀ and Por moieties and suggested that the relative orientation of the two moieties was close to the edge-to-face alignment. Compared with reference molecule 8, the FL of the Por core in the C₆₀-Por shape amphiphiles was significantly quenched owing to the presence of the covalently bonded C₆₀ units. The FL quenching became even more pronounced as the number of C₆₀ units per molecule increased from one to four. TCSPC experiments also showed a decrease in τ and an increase in k_{ET} of the Por core with the addition of each C₆₀ group. Photophysical studies suggested the potential for the effective generation of charge-separated species, C₆₀-Por⁺, from the photoexcited C₆₀-Por shape amphiphiles. Further investigations are ongoing with regard to phase behavior, phase structures, and the potential use of the C₆₀-Por shape amphiphiles as light harvesters and charge-carrier generators in optoelectronic applications.

Conclusion
Experimental Section

Instrumentation

All 1H and 13C NMR spectra were obtained with a Varian Gemini 300 spectrometer at 300 and 75 MHz, respectively. The 1H NMR spectra were referenced to the residual proton impurities in the CDC13 at δ = 7.27 ppm. The 13C NMR spectra were referenced to 1CDCl3 at δ = 77.00 ppm. MALDI-TOF measurements were carried out on a Bruker Ultraflex III TOF instrument (Bruker Daltonics, Inc., Billerica, MA) equipped with a Nd:YAG laser emitting at a wavelength of 355 nm. All spectra were measured in the positive reflector mode. The instrument used in this work was prepared according to procedures reported in the literature.[29,56] The synthesis of trans-DiC60ZnIIPor,[44] was reported in our previous work. The samples were kept in vacuum before characteriza-

Compound 10

Eluted with hexane/EA = 3:1 (v/v); yield: 308 mg, 13%; 1H NMR (300 MHz, CDCl3): δ = 8.91 (s, 9H), 8.28 (d, J = 8.4 Hz, 4H), 8.07 (d, J = 8.4 Hz, 4H), 7.62 (d, J = 8.4 Hz, 4H), 7.40–7.35 (m, 6H), 7.16–7.11 (m, 6H). All 1H and 13C NMR spectra were obtained with a Varian Gemini 300 spectrometer at 300 and 75 MHz, respectively. The 1H NMR spectra were referenced to the residual proton impurities in the CDC13 at δ = 7.27 ppm. The 13C NMR spectra were referenced to 1CDCl3 at δ = 77.00 ppm. MALDI-TOF measurements were carried out on a Bruker Ultraflex III TOF instrument (Bruker Daltonics, Inc., Billerica, MA) equipped with a Nd:YAG laser emitting at a wavelength of 355 nm. All spectra were measured in the positive reflector mode. The instrument used in this work was prepared according to procedures reported in the literature.[29,56] The synthesis of trans-DiC60ZnIIPor,[44] was reported in our previous work. The samples were kept in vacuum before characteriza-

Compound 11

Eluted with hexane/EA = 3:1 (v/v); yield: 455 mg, 19%; 1H NMR (300 MHz, CDCl3): δ = 8.96 (s, 2H), 8.90 (s, 4H), 8.82 (d, J = 8.4 Hz, 2H), 8.28 (d, J = 8.4 Hz, 4H), 8.06–8.02 (m, 6H), 7.63–7.60 (m, 4H), 7.18–7.11 (m, 6H), 4.18–4.11 (m, 1H), 1.94–1.84 (m, 6H), 1.56 (bs, 6H), 1.43–1.30 (m, 48H), 0.93–0.88 ppm (m, 9H); 13C NMR (75 MHz, CDCl3): δ = 165.7, 155.8, 153.3, 151.1, 143.3, 140.0, 135.9, 135.6, 134.9, 124.1, 120.3, 119.0, 113.9, 108.9, 74.0, 69.4, 32.2, 31.2, 30.0, 29.9, 29.8, 29.6, 26.4, 23.2, 22.9, 14.4 ppm; HRMS (MALDI-TOF): m/z calcd for C198H148N4O12 [M+]: 2647.95; found: 2647.98.

Compound 12

Eluted with hexane/EA = 2:1 (v/v); yield: 315 mg, 20%; 1H NMR (300 MHz, CDCl3): δ = 8.90 (s, 4H), 8.68 (s, 4H), 8.28 (d, J = 8.4 Hz, 2H), 8.06–8.02 (m, 6H), 7.63–7.60 (m, 4H), 7.18–7.11 (m, 6H), 4.18–4.11 (m, 1H), 1.94–1.84 (m, 6H), 1.56 (bs, 6H), 1.43–1.30 (m, 48H), 0.93–0.88 ppm (m, 9H); 13C NMR (75 MHz, CDCl3): δ = 165.6, 155.4, 153.1, 150.9, 143.3, 139.9, 135.6, 135.4, 134.5, 123.9, 120.1, 119.0, 118.7, 113.6, 108.9, 73.8, 69.5, 32.0, 31.9, 30.4, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.4, 26.2, 26.1, 22.7, 14.1, 14.1 ppm; HRMS (MALDI-TOF): m/z calcd for C198H148N4O12 [M+]: 1991.38; found: 1991.39.

Compound 13

Eluted with hexane/EA = 2:1 (v/v); yield: 422 mg, 13%; 1H NMR (300 MHz, CDCl3): δ = 8.96 (s, 4H), 8.93 (s, 4H), 8.30 (d, J = 8.4 Hz, 6H), 8.09 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.4 Hz, 6H), 7.62 (s, 6H), 7.21 (d, J = 8.4 Hz, 2H), 4.20–4.13 (m, 1H), 1.97–1.82 (m, 1H), 1.58 (bs, 1H), 1.31 (bs, 1H). 13C NMR (75 MHz, CDCl3): δ = 165.5, 155.8, 153.8, 153.3, 152.2, 143.9, 139.9, 136.0, 135.6, 134.7, 124.2, 120.5, 119.4, 119.2, 114.9, 114.0, 109.0, 73.9, 69.6, 32.2, 32.1, 30.6, 30.0, 30.0, 29.9, 29.8, 29.7, 29.6, 26.4, 26.3, 22.9, 14.4 ppm; HRMS (MALDI-TOF): m/z calcd for C232H204N6O16 [M+]: 3968.35; found: 3968.29.
Compound 2

Compound 13 (86 mg, 6.4 × 10⁻² mmol), 18 (58 mg, 2.9 × 10⁻² mmol), and DPTS (18 mg, 6.1 × 10⁻³ mmol) were dissolved in CH₂Cl₂ (10 mL) and cooled to 0°C. DIPC (9.6 mg, 7.7 × 10⁻² mmol) was slowly added into the solution by using a microsyringe. The solution was stirred at room temperature for 1 day. The solvent was then removed in vacuo. The residue was dissolved in CH₂Cl₂ and subjected to column chromatography (SiO₂, CH₂Cl₂/THF = 20:1 (v/v)) to allow isolation of 2. The obtained dark brown fraction was then concentrated. The product was dissolved in CH₂Cl₂ and precipitated in acetone as a black solid (91 mg, 63%).

1H NMR (300 MHz, CDCl₃): δ = 8.93 (d, J = 4.5 Hz, 4H), 8.85 (d, J = 4.5 Hz, 4H), 8.29–8.23 (m, 8H), 7.66–7.58 (m, 12H), 6.68 (d, J = 1.8 Hz, 4H), 6.45 (brs 2H), 5.54 (s, 4H), 5.36 (s, 4H), 4.18–4.12 (12H, m), 3.99 (t, J = 6.3 Hz, 8H), 1.93–1.71 (m, 20H), 1.58 (brs, 12H), 1.30–1.21 (m, 60H), 0.91–0.83 (m, 30H), −2.82 ppm (2H, s).

13C NMR (75 MHz, CDCl₃): δ = 165.5, 165.4, 163.4, 163.2, 160.7, 153.3, 151.3, 150.1, 145.3, 145.1, 145.0, 144.8, 144.7, 144.6, 143.9, 143.3, 143.1, 143.0, 143.0, 142.4, 142.0, 141.9, 140.9, 140.9, 139.7, 138.9, 136.8, 135.7, 123.4, 120.4, 119.9, 119.7, 110.9, 108.9, 107.5, 101.9, 73.9, 73.5, 69.5, 68.4, 63.1, 32.2, 32.1, 30.6, 30.0, 29.9, 29.8, 29.7, 29.6, 29.5, 26.4, 26.3, 22.9, 22.9, 14.4 ppm; HRMS (MALDI-TOF): m/z calcd for C₃₂H₂₉₄N₄O₂₆ [M⁺]: 5960.84; found: 5960.93.

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