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A tetraphenylmethane based dendritic tolan–anthracene dyad: synthesis and energy transfer properties†

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In order to synthesize a peripherally rigid dendritic donor–acceptor dyad for energy transfer studies, a tritolan dendron based on a tetraphenylmethane scaffold was prepared from New Fuchsin. The dendron showed a small degree of homoconjugation but a large hypochromic effect. Coupling of two such dendrons with an anthracene core led to a dendritic tolan–anthracene dyad whose steady state photophysical studies (UV, PL, PLE) showed vectorial transfer of excitation energy from the surface tolan units to the anthracene core.

Introduction

The photosynthetic unit of purple bacteria is a supramolecular assembly composed of a central reaction center surrounded by protein-embedded chlorophyll and carotenoid chromophores.[1] The latter act as the light harvesting antennae which transfer the excitation energy to the reaction center with almost unit efficiency.[2,3] Dendrimers are highly branched macromolecules composed of a central core from which numerous branches radiate outwards in an exponential manner.[4] As a result, higher generation dendrimers are globular in shape and possess high functional densities at their periphery. These features bear close resemblance to a natural photosynthetic unit, albeit in a covalent sense and have led to widespread activity in the design, synthesis and photophysical studies of bichromophoric (donor–acceptor) dendritic dyads.[5]

Dendrimers having flexible matrices can pose problems in energy transfer studies. Due to their conformational freedom, undesired interactions between the peripheral (donor) chromophores such as excimer formation and self-quenching can take place which may strongly interfere with the energy transfer process. In recent years, tetraphenylmethane (TPM) has emerged as a versatile building block for the construction of various functional architectures such as three dimensional metallostars,[6] amorphous molecular glasses,[7] supramolecular assemblies,[8] centrally tetrahedral multielectro- or multichromophoric modules,[9] molecular caltrops,[10] nanosized functional aromatic hydrocarbons,[11] *etc*. We have reported the synthesis of a number of TPM based architectures including ferrocene dendrimers, star shaped carbohydrate clusters and a new class of wheel and axle hydrocarbons.[12–15] TPM, which has a centrally tetrahedral geometry, promised to be an ideal scaffold for the construction of conformationally rigid multitopic dendritic wedges. Bichromophoric dendrimers derived from such wedges would have a rigid matrix and hence, would be better suited for energy transfer studies. In this article, we describe the synthesis and energy transfer properties of one such dendrimer in which TPM derived tolan (diphenylacetylene) wedges act as donors and an anthracene core as the acceptor. Recently, De Schryver *et al.*[16] have described the energy hopping photophysics of some TPM centered oligophenylenes substituted with peryleneimide chromophores which prompted us to disclose here our own results.

Results and discussion

The pairing of a tolan donor and an anthracene acceptor is based on the significant spectral overlap that exists between tolan fluorescence (λ_{max} ~360 nm) and the long wavelength absorption of anthracene (λ_{max} 380–390 nm) which concurs with the Forster's type ($S_1^D \longrightarrow S_1^A$) energy transfer mechanism. Moreover, anthracene derivatives are easy to functionalize, especially at the 9,10 positions and usually show strong fluorescence. Interestingly, the fluorescence transition in anthracene derivatives is polarized along the short axis *i.e.* the 9,10-direction. Hence, 9,10-disubstituted anthracene derivatives can be profitably used as a core in a dendritic donor–acceptor dyad.[17]

The dendritic dyad used in this work was synthesized as shown in Scheme 1. Thus, starting from the cheap commercial dye New Fuchsin (**1**), a threefold diazotization ($NaNO_2$, dil. H_2SO_4, 0 °C) followed by Sandmeyer reaction (KI, H_2O, rt) produced the triiodoaryl carbinol **2** in 40% yield. A Friedel–Crafts type reaction of phenol with **2** under sulfuric acid catalysis at 80 °C then gave rise to the key TPM based AB_3 tecton **3** in 85% yield. The iodo-ends in **3** can be utilized to construct the tolan units *via* Sonogashira coupling whereas the phenolic end can be used for dendrimer assembly *via* reaction with an appropriate 9,10-disubstituted anthracene derivative. Accordingly, threefold Sonogashira reaction on **3** was carried out with phenylacetylene (cat. $PdCl_2(PPh_3)_2$, cat. CuI, Et_3N, DMF, rt) which led to the tritolan dendron **4** in 75% yield. The latter (2 equiv.) was then coupled to 9,10-bis(chloromethyl)-anthracene (**5**), under phase transfer catalysis (5% aq. NaOH, cat. Bu_4NBr, PhCl, 90 °C)[17d] to produce the desired dendritic dyad **6** (54%) after purification by preparative thin layer chromatography. The coupling reaction between **4** and **5** was best carried out under the PTC conditions described above since other methods (NaH–DMF or K_2CO_3–DMF) either led to incomplete reaction or produced a complex mixture of products. The dendrimer was found to be soluble in most organic solvents and was characterized by ^1H, ^{13}C NMR and MALDI-TOF mass spectra. The ^1H NMR spectrum of **6** showed a four proton singlet at 5.98 ppm due to the two methylene groups at the core and a four proton multiplet at 8.38 ppm due to the anthracene ring α-hydrogens. The anthracene ring β-hydrogens remained embedded along with other aromatic protons in a broad multiplet ranging from 6.97–7.72 ppm. The ^{13}C NMR spectrum showed the requisite number of carbons, the central sp^3 hybridized carbon of the TPM wedges appearing at 64.6 ppm. The MALDI-TOF mass spectrum of **6** showed a dominant $M + 1$ peak at m/z 1559.

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† Respectfully dedicated to Professor Goverdhan Mehta on the occasion of his 60th birthday.

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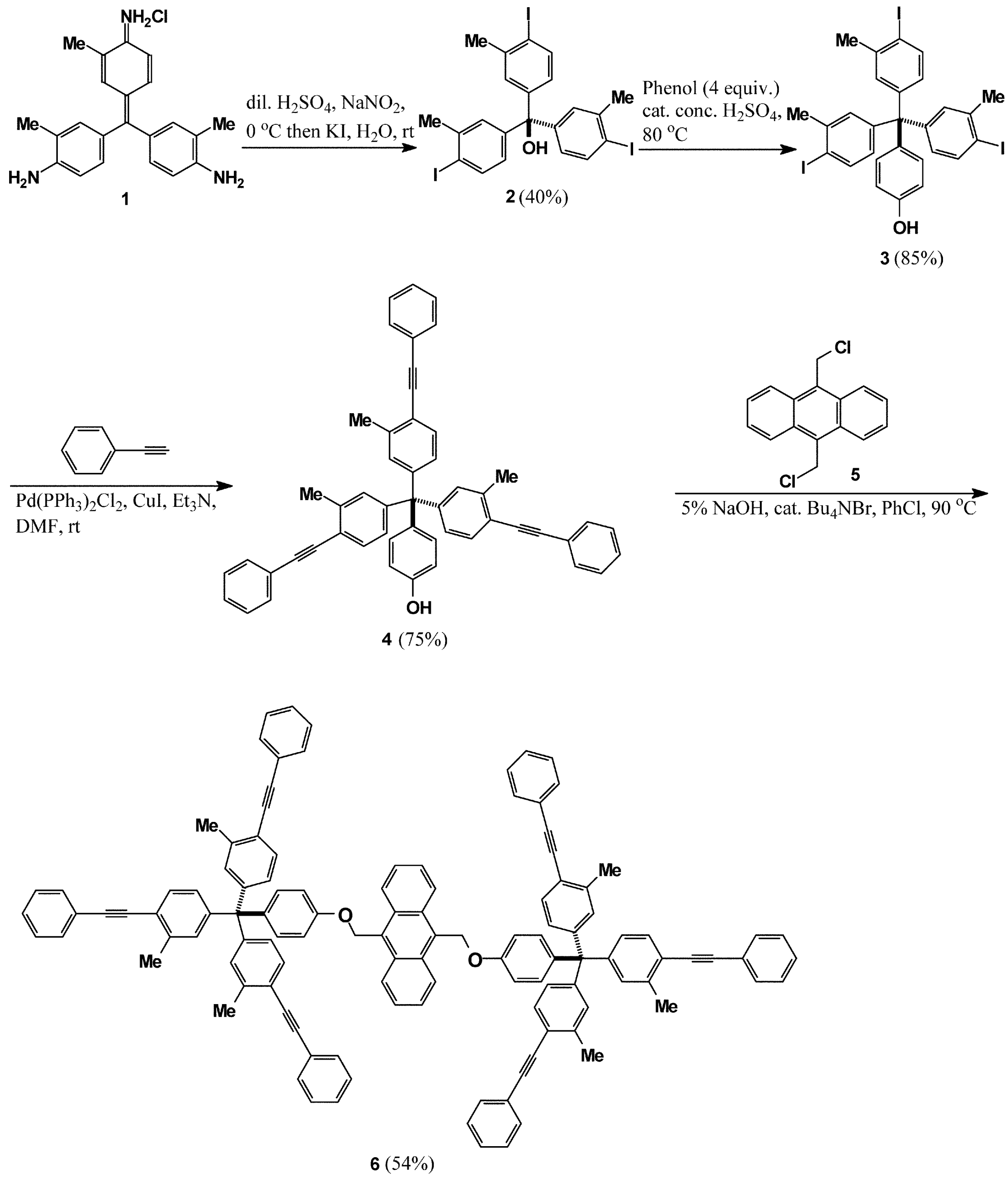

Scheme 1

The absorption and photoluminescence (PL) spectra of the dendritic wedge **4** are shown in Fig. 1. The lowest energy absorption maximum at 314 nm is due to the tolan units and is red-shifted from that of diphenylacetylene by *ca.* 20 nm indicating small electronic interaction between the tolan units through the central sp^3-carbon. Bazan *et al.* were the first to report such homoconjugative effects in tetrastilbenylmethane derivatives[7b,c] which was later corroborated by Müller *et al.*[9b] as well as by us[12c] for analogous tetrachromophoric TPM derivatives. Interestingly, the molar extinction coefficient of the 314 nm peak (ε_{max} 3.3 × 10^4 dm^3 mol^{-1} cm^{-1}) is significantly less than three times the value of diphenylacetylene (ε_{max} 1.7 × 10^4 dm^3 mol^{-1} cm^{-1}) indicating excitonic coupling between the three tolan arms in **4**. Such a pronounced hypochromic effect is perhaps due to the rigid tetrahedral arrangement in **4** which leads to a high degeneracy of the molecular orbitals.[9d,18,19] The dendron **4** produced a strong fluorescence with a maximum at 365 nm (λ_{exc} 314 nm) which is also red-shifted from tolan fluorescence by *ca.* 20 nm.

The UV/Vis absorption spectrum of the dendrimer **6** is shown in Fig. 2. The peaks at 294 and 313 nm (ε_{max} 6.0 × 10^4 dm^3 mol^{-1} cm^{-1}) are due to the tolan units at the periphery (*cf.* Fig. 1). The molar absorptivity of the 313 nm peak is nearly twice that of the 314 nm peak of **4** since two dendron moieties are present in the dendrimer. Weak absorptions were also found at 354 (logε 3.42), 374 (logε 3.62) and 394 nm (logε 3.61) which after comparison with the model core 9,10-bis(phenoxymethyl)anthracene (PMA) [λ_{max} (nm): 230 (logε 3.86), 246 (logε 3.87), 354 (logε 3.44), 374 (logε 3.62) and 394 (logε 3.62)] were assigned to the anthracene unit. The absorption spectrum of **6** is thus a superimposition of peaks arising out of the surface tolan units and the anthracene core. This was as expected since the two types of chromophores in **6** are connected by a non-conjugated linker.

The PL spectrum of the dendrimer is shown in Fig. 3. Excitation at 315 nm, where only the tolan moieties have strong absorption, produced a broad peak at 367 nm and a structured emission pattern beyond 400 nm. The former corresponds to emission from the tolan moieties (*cf.* Fig. 1) whereas the latter is due to emission from the anthracene ring [fluorescence data for PMA (λ_{exc} 260 nm): 402 nm, 423 nm (λ_{max}) and 450 nm] clearly indicating energy transfer from the surface tolan units to the dendrimer core. In a control experiment, a solution containing equimolar mixture of **4** and the model core PMA in CH_2Cl_2 was irradiated at 313 nm which produced an emission spectrum (λ_{max} 365 nm) which was fully superimposable on the PL

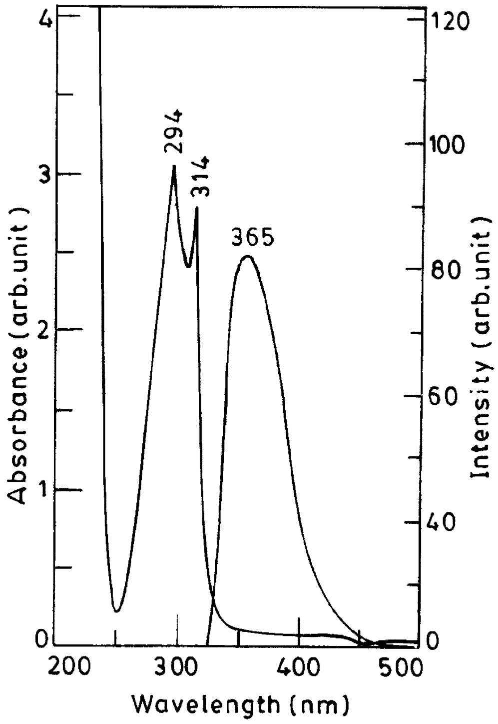

Fig. 1 Absorption and emission spectra of **4** in CH_2Cl_2.

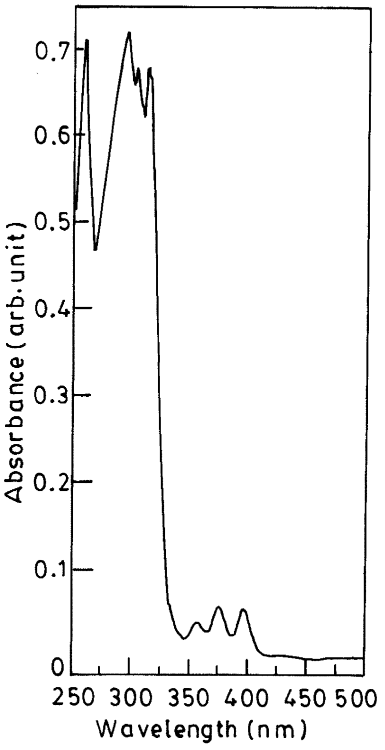

Fig. 2 Absorption spectrum of **6** in CH_2Cl_2.

spectrum of **4** showing that the energy transfer in **6** is purely an intramolecular process. The fluorescence intensity of **6** at 420 nm is nearly 500 times that of the emission peak produced by direct core excitation, again pointing to light harvesting by the tolan periphery and subsequent energy transfer to the anthracene core. Further proof of energy transfer in **6** comes from its photoluminescence excitation (PLE) spectrum monitored at 421 nm (Fig. 4) which is very similar to the absorption spectrum of **6** indicating effective coupling between the tolan and anthracene units. Notably, the emission spectrum of **6** was devoid of much red-tailing, a phenomenon previously observed by us for a first generation *m*-distyrylbenzeneanthracene dendrimer,[17e]

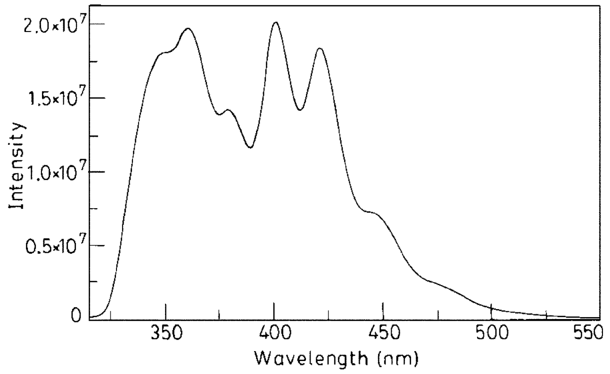

Fig. 3 Emission spectrum of **6** (λ_{exc} 315 nm) in CH_2Cl_2.

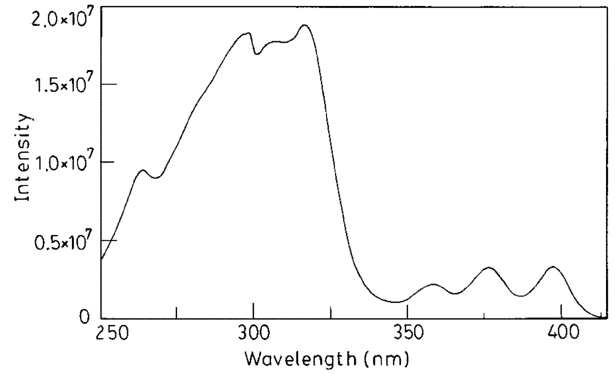

Fig. 4 Photoluminescence excitation spectrum of **6** (monitored at 420 nm) in CH_2Cl_2.

suggesting that the highly branched nature of the dendrons in **6** probably discourages aggregate formation. However, the energy transfer in **6** is less than quantitative. This may be due to the presence of only six energy collection sites at the dendrimer periphery. More importantly, in a Förster's type energy transfer process, the rate constant (k_{ET}) is directly proportional to the overlap integral (J) and inversely proportional to the sixth power of the interchromophoric distance (R). In an anthracene cored dendrimer such as **6**, the molar extinction coefficient at the acceptor wavelength (*ca.* 360–390 nm) is small which lowers the J value and hence, the k_{ET}. In addition, the interchromophoric distance in **6** is also large (9 atom length) which further lowers the rate of the energy transfer process. Consequently, non-radiative dissipation of excitation energy effectively competes with energy transduction in **6**. We are currently investigating other strongly absorbing chromophores as the core component to improve the energy transfer efficiency.

Experimental

All melting points are uncorrected. IR spectra were taken on a Perkin–Elmer 297 spectrometer as KBr pellets. The UV/Vis absorption spectra were recorded on a Shimadzu UV 240 spectrophotometer. Fluorescence spectra were recorded on a Spex Fluorolog spectrofluorimeter. The optical density of the solution for fluorescence measurement was less than 0.2 at the excitation wavelength. NMR spectra were recorded on a Bruker Avance 300 instrument. Operating frequencies were 300 MHz (^1H) and 75 MHz (^{13}C). Chemical shifts are expressed in the δ scale, ppm downfield from tetramethylsilane internal standard. Coupling constants, J, are given in Hertz. Light petroleum refers to the fraction boiling at 60–80 °C range. Column chromatography was carried out over silica gel (60–120, Tara Chemicals). New Fuchsin (**1**) was purchased from Loba Chemie.

Tris(4-iodo-3-methylphenyl)methanol 2

A solution of $NaNO_2$ (0.62 g, 9.0 mmol) in water (2 cm^3) was added dropwise to a stirred solution of New Fuchsin (**1**, 1.0 g, 2.73 mmol) in concentrated H_2SO_4 (1.7 cm^3) and water (5 cm^3) kept at 0 °C. After the addition was complete, the solution was stirred at 0 °C for 15 min and then treated dropwise with a solution of KI (5.0 g, 30 mmol) in water (5 cm^3). The mixture was stirred at room temperature for 5 h and then heated at 80 °C for 30 min. It was cooled, the precipitate filtered and washed thoroughly with water. The residue was purified by column chromatography over silica gel (5% EtOAc in light petroleum) to give **2** (0.74 g, 40%) as a white solid; mp 98–99 °C (from MeOH); (Anal. Calcd for $C_{22}H_{19}I_3O$: C, 38.86; H, 2.79. Found: C, 38.54; H, 3.11); ν_{max} (KBr/cm^{-1}) 3560, 1450, 1365 and 1185; δ_H (300 MHz, $CDCl_3$) 2.40 (9 H, s), 6.72 (3 H, dd, *J* 8.4 and 2.1), 7.18 (3 H, d, *J* 2.1) and 7.74 (3 H, d, *J* 8.4); δ_C (75 MHz, $CDCl_3$) 28.2, 81.0, 100.3, 126.9, 128.9, 138.5, 141.2 and 146.2.

Tris(4′-iodo-3′-methylphenyl)-4-methylphenol 3

A mixture of **2** (1.0 g, 1.47 mmol), phenol (0.41 g, 4.41 mmol) and concentrated H_2SO_4 (2 drops) was heated at 80 °C for 4 h. After being cooled to room temperature, the mixture was treated with aqueous 10% NaOH solution (10 cm^3) and the precipitated solid filtered and washed thoroughly with water. The residue was purified by column chromatography over silica gel (10% EtOAc in light petroleum) to give **3** (0.95 g, 85%) as a white solid; mp 206–207 °C (from MeOH); (Anal. Calcd for $C_{28}H_{23}I_3O$: C, 44.48; H, 3.04. Found: C, 44.56; H, 3.18); ν_{max} (KBr/cm^{-1}) 3400, 1605, 1500, 1460, 1370 and 1170; δ_H (300 MHz, $CDCl_3$) 2.33 (9 H, s), 6.65 (3 H, dd, *J* 8.4 and 2.1), 6.70 (2 H, d, *J* 6.6), 6.99 (2 H, d, *J* 6.6), 7.02 (3 H, d, *J* 2.1) and 7.65 (3 H, d, *J* 8.4); δ_C (75 MHz, $CDCl_3$) 28.2, 63.3, 98.7, 114.5, 130.1, 131.9, 138.0, 140.5, 146.5 and 153.6

Tris(4′-phenylethynyl-3′-methylphenyl)-4-methylphenol 4

$Pd(PPh_3)_2Cl_2$ (0.015 g, 0.02 mmol) was added to a degassed solution of **3** (0.10 g, 0.13 mmol), phenylacetylene (0.08 g, 0.79 mmol) and CuI (4 mg, 0.02 mmol) in a mixture of DMF (3 cm^3) and Et_3N (2 cm^3). The reaction mixture was stirred at room temperature for 16 h. It was then concentrated under reduced pressure, diluted with water and extracted with CH_2Cl_2. Removal of solvent followed by column chromatography over silica gel (10% EtOAc in light petroleum) gave **4** (0.067 g, 75%) as a pale yellow solid; mp 126–127 °C (from $CHCl_3$–MeOH); (Anal. Calcd for $C_{52}H_{38}O$: C, 92.03; H, 5.60. Found: C, 92.26; H, 5.28); ν_{max} (KBr/cm^{-1}) 3410, 1600, 1520, 1465, 1360 and 1170; δ_H ($CDCl_3$, 300 MHz) 2.43 (9 H, s), 6.73 (2 H, d, *J* 8.6), 6.90–7.16 (8 H, m), 7.29–7.48 (12 H, m) and 7.49–7.62 (6 H, m); δ_C (75 MHz, $CDCl_3$) 21.0, 64.5, 88.5, 93.8, 114.5, 121.2, 123.9, 125.6, 128.3, 128.7, 128.9, 130.1, 131.9, 132.2, 138.0, 139.5, 147.0 and 156.5

Dendrimer 6

An aqueous 5% KOH solution (2 cm^3) was added to a mixture of **4** (0.075 g, 0.11 mmol), **5** (0.015 g, 0.05 mmol) and Bu_4NBr (3 mg) in chlorobenzene (6 cm^3) and heated under vigorous stirring at 90 °C for 5 h. After being cooled to room temperature, it was neutralized with dilute HCl and diluted with CH_2Cl_2 (10 cm^3). The organic layer was separated, washed with water and dried. All volatiles were then removed under reduced pressure and the residue triturated with light petroleum to give an off white solid. The latter was purified by preparative thin layer chromatography over silica gel (5% EtOAc in light petroleum) to give **6** (0.046 g, 54%); mp > 220 °C; ν_{max} (KBr/cm^{-1}) 1610, 1510, 1460, 1360, 1175 and 1150; δ_H ($CDCl_3$, 300 MHz) 2.46 (18 H, s), 5.98 (4 H, s), 6.82–7.70 (60 H, m) and 8.38 (4 H, m); δ_C ($CDCl_3$, 75 MHz) 21.5, 63.2, 64.6, 88.6, 93.8, 114.3, 121.1, 123.9, 125.2, 126.6, 128.5, 128.7, 128.9, 129.5, 131.2, 131.4, 131.9, 132.2, 132.6, 139.1, 139.8, 147.2 and 157.7; *m*/*z* (MALDI-TOF) 1559 (*M* + 1).

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