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Synthesis and characterization of well-defined fully conjugated hyperbranched oligomers of β,β-dibromo-4-ethynylstyrene

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Well-defined dendritic oligomers of poly(β,β-dibromo-4-ethynylstyrene) of the first and second generation have been synthesized by a stepwise synthesis, and characterized. It was found from n.m.r. analysis and by theoretical calculations that free rotation around formal single bonds is hampered by conjugation. All oligomers were found to be blue emitters with their emission maxima correlating with the number of repeating units. All dendrimers except dendrimer **12** (β,β-bis[β′,β′-di(β″,β″-dibromostyryl-4″-ethynyl)styryl-4′-ethynyl]-4-ethynylstyrene) showed two maxima in the excitation spectra. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: dendrimers; Heck reaction; acetylenes)

INTRODUCTION

There is growing interest in macromolecules having architectures where the ratio of the branches to the monomer unit approaches unity due to the excellent solubility and high concentration of the end group, even for high polymers. The synthesis of these macromolecules can be conveniently divided into two separate groups. The first is the synthesis of perfect dendritic macromolecules by stepwise synthetic approaches[1–3]. Their properties are easy to control but they are obtained only in limited quantities and after much effort. The second is the direct polymerization of AB_n[4,5] monomers, resulting in hyperbranched polymers. Hyperbranched polymers generally have less perfect branching, show polydispersity, and their properties are not so easily tailored; however, they are readily available by simply polymerization.

The present authors are interested in the development of polymers with new chemical structures for application in photoluminescence, electroluminescence and non-linear optics, and have previously reported the synthesis and polymerization of a monomer of the AB_2 type, β,β-dibromo-4-ethynylstyrene, by the Heck reaction, to produce a conjugated hyperbranched polymer[6]. This polymer was partially soluble in hot chlorinated solvents, was shown to have an M_w of 70000 by g.p.c. and exhibited intense photoemission at 500 nm. Theoretical calculations and model compound synthesis indicated an effective conjugation length in the polymer not exceeding the length of a repeating unit due to steric hindrance. The goal of this paper is to synthesize well-defined oligomers of poly(β,β-dibromo-4-ethynylstyrene), and to establish the relationship between their structure and properties.

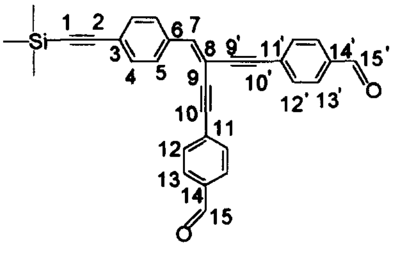
EXPERIMENTAL

Materials

β,β-Dibromo-4-(trimethylsilyl)styrene (**1**), 4-trimethylsilylethynylbenzaldehyde (**2**) and 4-ethynylbenzaldehyde (**3**) were prepared according to the literature[7,8]. Other reagents were used as received (Aldrich).

β,β-Di(4′-formylphenylethynl)-4-(trimethylsilyl)styrene (**4**)

Compound **1** (5.30 g; 14.8 mmol), 4-ethynlbenzaldehyde (3.84 g; 29.5 mmol), triphenylphosphine (TPP; 0.2 g), CuI (0.03 g) and $Pd(TPP)_2Cl_2$ (0.04 g) were refluxed under nitrogen in a mixture of triethylamine (100 ml) and pyridine (100 ml) for 3 h. The solvent was then removed under reduced pressure. The residue was purified by chromatography on SiO_2 employing a mixture of benzene–hexane (volume ratio, 1/3). The yield was 53%, and the compound characteristics were m.p., 168–170°C; i.r. (cm^{-1}): 2960 (CH aliph), 2840 (CH, aldehyde), 2200 (C≡C), 2154 (Si–C≡C), 1693 (C=O, aldehyde); ^1H n.m.r. ($CDCl_3$): 10.05, 10.03 (two s, 2H, H^{15}, $H^{15\prime}$), 7.88 (d, 2H, J 8.4 Hz, H^5), 7.83 (d, 4H, J 8.1 Hz, H^{13}, $H^{13\prime}$), 7.66 (d, 4H, J 8.1 Hz, H^{12}, $H^{12\prime}$), 7.49 (d, 2H, J 8.4 Hz, H^4), 7.22 (s, 1H, H^7), 0.24 (s, 9H, $Si(Me)_3$); ^{13}C n.m.r.: 191.34, 191.28 (C^{15}, $C^{15\prime}$), 144.58 (C^7), 136.09, 135.48, 135.27, 133.21 (C^6, C^{11}, $C^{11\prime}$, C^{14}, $C^{14\prime}$), 133.30, 132.15, 129.75, 129.66, 129.10 (C^4, C^5, C^{12}, $C^{12\prime}$, C^{13}, $C^{13\prime}$), 124.65 (C^3), 104.78 (C^2), 103.17 (C^8) 94.35 (C^1), 97.15, 92.52, 90.13, 88.42 (C^9, $C^{9\prime}$, C^{10}, $C^{10\prime}$).



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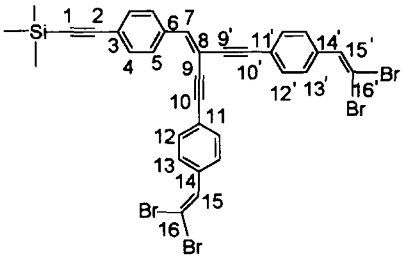
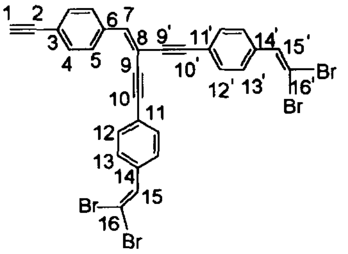
*β,β-Bis(β′,β′-dibromostyryl-4′-ethynyl)-4-(trimethylsiyl)ethynylstyrene (**5**)*

To a solution of CBr_4 (7.63 g; 23 mmol) in anhydrous CH_2Cl_2 (100 ml) TPP (12.078 g; 46 mmol) was added dropwise under nitrogen. Compound **3** (3.5 g; 7.7 mmol) dissolved in CH_2Cl_2 (20 ml) was added to the solution during 15 min. and the reaction was stirred for 5 h. The solvent was then evaporated at room temperature and the residue was purified by chromatography on SiO_2 employing a mixture of benzene–hexane (volume ratio, 1/3). The yield was 69%. The compound characteristics were m.p., 60–62°C;. i.r. (cm^{-1}): 2960 (CH aliph), 2200 (C≡C), 2150 (Si-C≡C); ^{1}H n.m.r. ($CDCl_3$): 7.87 (d, 2H, *J* 7.8 Hz, H^5), 7.60–7.50 (m, 10H, arom), 7.48, 7.47 (two s, 2H, H^{15}, $H^{15'}$), 7.15 (s, 1H, H^7), 0.21 (s, 9H, Si(Me)$_3$); ^{13}C n.m.r.: 142.77 (C^7), 136.15, 136.08 (C^{15}, $C^{15'}$), 135.65, 135.58, 135.27 (C^6, C^{14}, $C^{14'}$), 131.96, 131.68, 128.80, 128.47, 128.35, 127.37 (C^4, C^5, C^{12}, $C^{12'}$, C^{13}, $C^{13'}$), 123.89 (C^3), 122.92, 122.70 (C^{11}, $C^{11'}$), 104.87 (C^2), 103.79 (C^8), 94.98 (C^1), 90.87, 90.56 (C^{16}, $C^{16'}$) 96.51, 90.27, 88.79, 87.98 (C^9, $C^{9'}$, C^{10}, $C^{10'}$); elemental analysis: ($C_{33}H_{24}SiBr_4$) calc. 41.6% Br, found 42.0% Br.



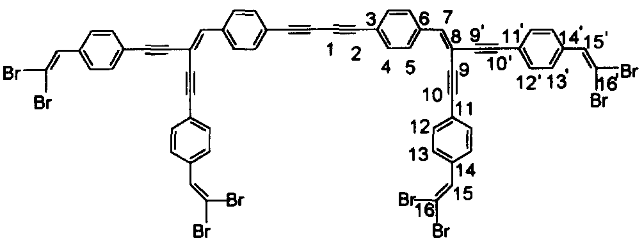
*β,β-Bis(β′,β′-dibromostyryl-4′-ethynyl)-4-ethynylstyrene (**6**)*

To a solution of compound **4** (0.5 g; 0.650 mmol) powdered K_2CO_3 (0.1 g) was added and the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was then poured into dilute hydrocholoric acid and the precipitate formed was filtered off, rinsed with water and dried under vacuum at room temperature. The yield was 99%. The compound characteristics were m.p., 95–97°C; i.r. (cm^{-1}): 3290 (≡C–H), 2200 (C≡C), 2100 (C≡CH); ^{1}H n.m.r. ($CDCl_3$): 7.87 (d, 2H, *J* 8.4 Hz, H^5), 7.60–7.50 (m, 10H, arom), 7.50, 7.49 (two s, 2H, H^{15}, $H^{15'}$), 7.15 (s, 1H, H^7), 3.17 (s, 1H, H^1); ^{13}C n.m.r.: 142.56 (C^7), 136.24, 136.16 (C^{15}, $C^{15'}$), 136.00, 135.81, 135.43 (C^6, C^{14}, $C^{14'}$), 132.19, 131.75, 128.90, 128.52, 128.41, 127.44 (C^4, C^5, C^{12}, $C^{12'}$, C^{13}, $C^{13'}$), 126.77 (C^3), 122.93 (C^{11}, $C^{11'}$), 104.25 (C^8), 95.10, 90.96, 90.64, 90.27, 88.92, 87.96 (C^9, $C^{9'}$, C^{10}, $C^{10'}$, C^{16}, $C^{16'}$), 83.56 (C^2), 78.99 (C^1); elemental analysis: ($C_{30}H_{16}Br_4$) calc. 45.9% Br, found 44.8% Br.



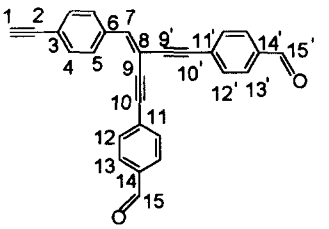
*Bis[β,β-di(β′,β′-dibromostyryl-4′-ethynyl)-4-styryl]butadiyne (**7**)*

Oxygen was bubbled for 4 h through a solution containing compound **5** (0.252 g; 0.362 mol), CuCl (0.01 g) and N,N,N′,N′-tetramethylethylenediamine in a mixture of 2-propanol and acetone (1/1 by volume). The reaction mixture was poured into water, the precipitate formed was filtered off and was crystallized from toluene. The yield was 10%. The compound characteristics were m.p., 143–145°C; ^{1}H n.m.r. ($CDCl_3$): 7.90 (d, 4H, *J* 8.0 Hz, H^5), 7.60–7.50 (m, 20 H arom), 7.49, 7.48 (two s, 4H, H^{15}, $H^{15'}$), 7.15 (s, 2H, H^7); ^{13}C n.m.r.: 142.32 (C^7), 136.19, (C^{15}, $C^{15'}$), 136.47 (C^6), 135.45 (C^{14}, $C^{14'}$), 136.10, 132.56, 131.71, 128.99, 128.53, 128.41 (C^4, C^5, C^{12}, $C^{12'}$, C^{13}, $C^{13'}$), 122.91, 122.67 (C^{11}, $C^{11'}$), 122.37 (C^3), 104.56 (C^8), 95.40, 91.00, 90.67, 90.26, 89.21, 87.94 (C^9, $C^{9'}$, C^{10}, $C^{10'}$, C^{16}, $C^{16'}$), 82.67 (C^2), 76.00 (C^1); elemental analysis: ($C_{60}H_{30}Br_8$) calc. 46.0% Br, found 44.3% Br.



*β,β-Di(4′-formylphenylethynyl)-4-ethynylstyrene (**8**)*

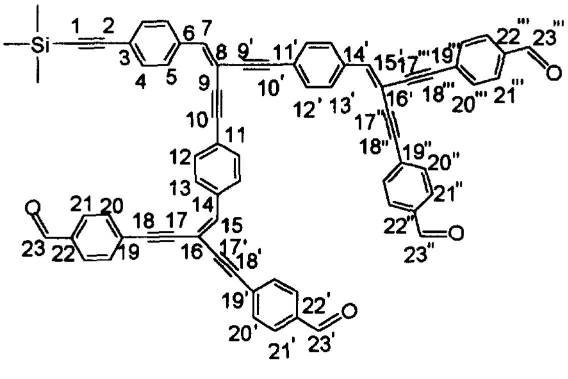
A solution of compound **3** (5.0 g; 11 mmol) and K_2CO_3 (0.3 g) in a mixture of methanol (200 ml) and benzene (200 ml) was stirred for 2 h at room temperature. The reaction mixture was then acidified with 1 ml of concentrated HCl, the solvent was evaporated under reduced pressure, and the residue was chromatographed on SiO_2 emploing benzene as eluent. The yield was 87%. Compound characteristics were m.p., 155–157°C; i.r. (cm^{-1}): 3250 (≡C–H), 2820 (CH, aldehyde), 2200 (C≡CH), 2120 (C≡CH), 1693 (C=O, aldehyde); ^{1}H n.m.r. ($CDCl_3$): 10.04, 10.03 (two s, 2H, H^{15}, $H^{15'}$), 7.90 (d, 2H, *J* 8.4 Hz, H^5); 7.88, 7.87 (two d, 4H, *J* 8.4 Hz, 7.8 Hz, H^{13}, $H^{13'}$), 7.690, 7.685 (two d, 4H, *J* 8.4 Hz, 7.8 Hz, H^{12}, $H^{12'}$), 7.54 (d, 2H, *J* 8.4 Hz, H^4), 7.24 (s, 1H, H^7), 3.20 (s, 1H, H^1); ^{13}C n.m.r.: 191.22 (C^{15}, $C^{15'}$), 144.29 (C^7), 136.0, 135.86, 135.60, 133.10 (C^6, C^{11}, $C^{11'}$, C^{14}, $C^{14'}$) 132.28, 129.69, 129.60, 129.1 (C^4, C^5, C^{12}, $C^{12'}$, C^{13}, $C^{13'}$), 123.54 (C^3), 103.46 (C^8), 97.20, 92.50, 90.10, 88.40 (C^9, $C^{9'}$, C^{10}, $C^{10'}$), 83.36 (C^2), 79.37 (C^1).



*β,β-Bis[β′,β′-di(4″-formylphenylethynyl)styryl-4′-ethynyl]-4-(trimethylsiyl)ethynylstyrene (**9**)*

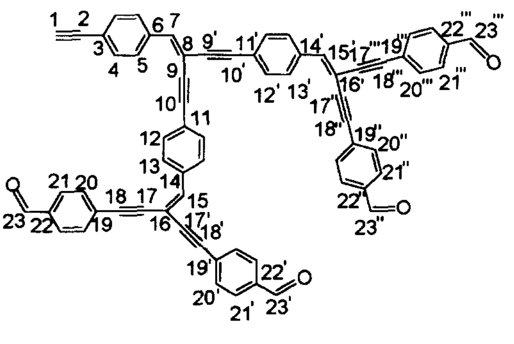
A solution of compound **7** (3.5 g; 9.1 mmol), compound **1** (1.63 g; 4.55 mmol), TPP (0.034 g), CuI (0.014 g) and Pd(TPP)$_2$Cl$_2$ in a mixture of triethylamine (200 ml) and pyridine (200 ml) was refluxed under nitrogen for 3 h. The solvent was removed under reduced pressure, and the residue was washed with water and was purified by column chromatography on SiO_2 employing a mixture of hexane and benzene (1/4 by volume). The yield was 14%. Compound characteristics were m.p., 130–132°C; i.r. (cm^{-1}): 2960 (CH aliph), 2840 (CH, aldehyde), 2200 (C≡C), 2154 (Si–C≡C), 1700 (C=O, aldehyde); ^{1}H n.m.r. ($CDCl_3$): 10.05–10.03

(m, 4H, H^{23}, $H^{23'}$, $H^{23''}$, $H^{23'''}$), 7.91 (d, 6H, *J* 8.4 Hz, H^5, H^{13}, $H^{13'}$), 7.88 (d, 8H, *J* 8.4 Hz, H^{21}, $H^{21'}$, $H^{21''}$, $H^{21'''}$), 7.68 (d, 8H, *J* 9.9 Hz, H^{20}, $H^{20'}$, $H^{20''}$, $H^{20'''}$), 7.57 (d, 2H, *J* 8.4 Hz, H^4), 7.47–7.40 (m, 4H, H^{12}, $H^{12'}$), 7.26–7.24 (m, 3H, H^7, H^{15}, $H^{15'}$), 0.24 (s, 9H, $Si(Me)_3$); ^{13}C n.m.r.: 191.45, 191.39, 191.26 (C^{23}, $C^{23'}$, $C^{23''}$, $C^{23'''}$), 144.18 (C^7, C^{15}, $C^{15'}$), 136.41, 136.08, 135.90, 128.94, 128.59, 127.69, 124.32, 123.1, 121.67 (C^3, C^6, C^{11}, $C^{11'}$, C^{14}, $C^{14'}$, C^{19}, $C^{19'}$, $C^{19''}$, $C^{19'''}$, C^{22}, $C^{22'}$, $C^{22''}$, $C^{22'''}$), 133.25, 132.76, 132.39, 132.12, 129.85, 129.73, 129.29 (C^4, C^5, C^{12}, $C^{12'}$, C^{13}, $C^{13'}$, C^{21}, $C^{21'}$, $C^{21'''}$, C^{22}, $C^{22'}$, $C^{22''}$, $C^{22'''}$), 104.42 (C2, 92.49 (C1), 103.80, 97.64, 90.02, 88.79, 82.59, 82.31 (C^8, C^9, $C^{9'}$, C^{10}, $C^{10'}$, C^{16}, $C^{16'}$, C^{17}, $C^{17'}$, $C^{17''}$, $C^{17'''}$, C^{18}, $C^{18'}$, $C^{18''}$, $C^{18'''}$).



*β,β-Bis[β′,β′-di(4″-formylphenylethynyl)styryl-4′-ethynyl]-4-ethynylstyrene (**10**)*

A solution of compound **8** (0.3 g; 0.311 mmol) and K_2CO_3 (0.35 g) in a mixture of methanol (150 ml) and benzene (150 ml) was stirred for 20 h at room temperature. The solvent was then removed under reduced pressure, and the solid was collected, washed with dilute HCl and water, and dried under vacuum. The yield was 94%. Compound characteristics were i.r. (cm^{-1}): 3240 (C≡C–H), 2840 (CH, aldehyde), 2200 (C≡C), 2110 (C≡CH), 1700 (C=O, aldehyde); ^1H n.m.r. ($CDCl_3$): 10.04–10.02 (m, 4H, H^{23}, $H^{23'}$, $H^{23''}$, $H^{23'''}$), 7.89 (d, 6H, *J* 8.4 Hz, H^5, H^{13}, $H^{13'}$), 7.87 (d, 8H, *J* 8.4 Hz, H^{21}, $H^{21'}$, $H^{21''}$, $H^{21'''}$), 7.68, 7.67 (two d, 8H, *J* 8.4 Hz, H^{20}, $H^{20'}$, $H^{20''}$, $H^{20'''}$) 7.55 (d, 2H, *J* 8.4 Hz, H^4), 7.50–7.45 (m, 4H, H^{12}, $H^{12'}$), 7.26–7.24 (m, 3H, H^7, H^{15}, $H^{15'}$), 3.11 (s, 1H, H^1); ^{13}C n.m.r.: 191.23 (C^{23}, $C^{23'}$, $C^{23''}$, $C^{23'''}$), 144.01 (C^7, C^{15}, $C^{15'}$), 136.41, 136.08, 135.90, 128.94, 128.59, 127.59, 127.69, 124.32, 123.1, 121.67 (C^3, C^6, C^{11}, $C^{11'}$, C^{14}, $C^{14'}$, C^{19}, $C^{19'}$, $C^{19''}$, $C^{19'''}$, C^{22}, $C^{22'}$, $C^{22''}$, $C^{22'''}$), 133.25, 132.76, 132.39, 132.12, 129.85, 129.73, 129.29 (C^4, C^5, C^{12}, $C^{12'}$, C^{13}, $C^{13'}$, C^{21}, $C^{21'}$, $C^{21''}$, $C^{21'''}$, C^{22}, $C^{22'}$, $C^{22''}$, $C^{22'''}$), 104.42 (C^2), 92.49 (C^1), 103.80, 97.64, 90.02, 88.79, 82.59, 82.31 (C^8, C^9, $C^{9'}$, C^{10}, $C^{10'}$, C^{16}, $C^{16'}$, C^{17}, $C^{17'}$, $C^{17''}$, $C^{17'''}$, C^{18}, $C^{18'}$, $C^{18''}$, $C^{18'''}$).

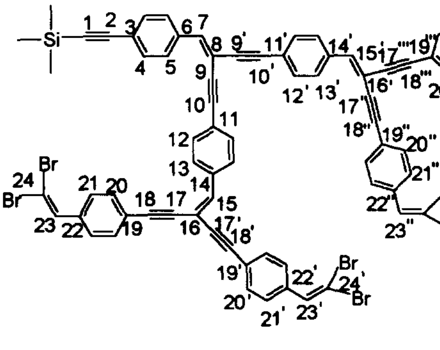


*Bis{β,β-di[β′,β′-di(4″-formylphenylethynyl)styryl-4′-ethynyl]-4-styryl}butadiyne (**11**)*

Oxygen gas was bubbled through a solution of compound **10** (0.1 g; 0.112 mmol), TMDA (1 ml) and CuCl (0.01 g) in *N*-methylpyrrolidone (20 ml) for 5 h at room temperature. The precipitate formed was filtered off, washed with dilute HCl and water, and dried under vacuum at room temperature. The yield was 51%. Compound characteristics were i.r. (cm^{-1}): 2845 (CH, aldehyde), 2200 (C≡C), 1700 (C=O, aldehyde); elemental analysis: ($C_{130}H_{70}O_8$) calc. C 88.7%, H 3.98%, found C 87.5%, H 3.77%.

*β,β-Bis[β′,β′-di(β″,β″-dibromostyryl-4″-ethynyl)styryl-4′-ethynyl]-4-ethynylstyrene (**12**)*

To a solution of CBr_4 (0.512 g; 1.54 mmol) and TPP (0.809 g; 3.08 mmol) in CH_2Cl_2 (40 ml), compound **8** (0.248 g; 0.257 mmol) was added under nitrogren. After 8 h of stirring at room temperature, the solvent was evaporated, also at room temperature. The reaction mixture was extracted with hot hexane, the solvent was evaporated, and the residue was purified by column chromatography on SiO_2 (benzene–hexane as eluent). The yield was 6%. Compound characteristics were i.r. (cm^{-1}): 2200 (C≡C), 2150 (C≡C–Si(Me)$_3$), 1600 (C=C arom); ^{1}*H* n.m.r. ($CDCl_3$): 7.96–7.83 (m, 6H, H^5, H^{13}, $H^{13'}$), 7.57–7.47 (m, 28 H, arom) 7.36–7.35 (m, 4H, H^{23}, $H^{23'}$, $H^{23''}$, $H^{23'''}$), 7.17–7.15 (m, 3H, H^7, H^{15}, $H^{15'}$), 0.26 (s, 9H, $Si(Me)_3$); ^{13}C n.m.r.: 142.5–142.0 (C^7, C^{15}, $C^{15'}$), 136.2–135.7 (C^6, C^{14}, $C^{14'}$, C^{22}, $C^{22'}$, $C^{22''}$, $C^{22'''}$, C^{23}, $C^{23'}$, $C^{23''}$, $C^{23'''}$), 132.3–127.9 (C^4, C^5, C^{12}, $C^{12'}$, C^{13}, $C^{13'}$, C^{20}, $C^{20'}$, $C^{20''}$, $C^{20'''}$, C^{21}, $C^{21'}$, $C^{21''}$ $C^{21'''}$), 124.0–122.0 (C^3, C^{11}, $C^{11'}$, C^{19}, $C^{19'}$, $C^{19''}$, $C^{19'''}$), 106.5–103.9 (C^2, C^8, C^{16}, $C^{16'}$) 95.0 (C^1), 96.0–88.0 (C^9, C^{10}, $C^{9'}$, $C^{10'}$, C^{17}, $C^{17'}$, $C^{17''}$, $C^{17'''}$, C^{18}, $C^{18'}$, $C^{18''}$, $C^{18'''}$, C^{24}, $C^{24'}$, $C^{24''}$, $C^{24'''}$).



Measurements and sample preparation

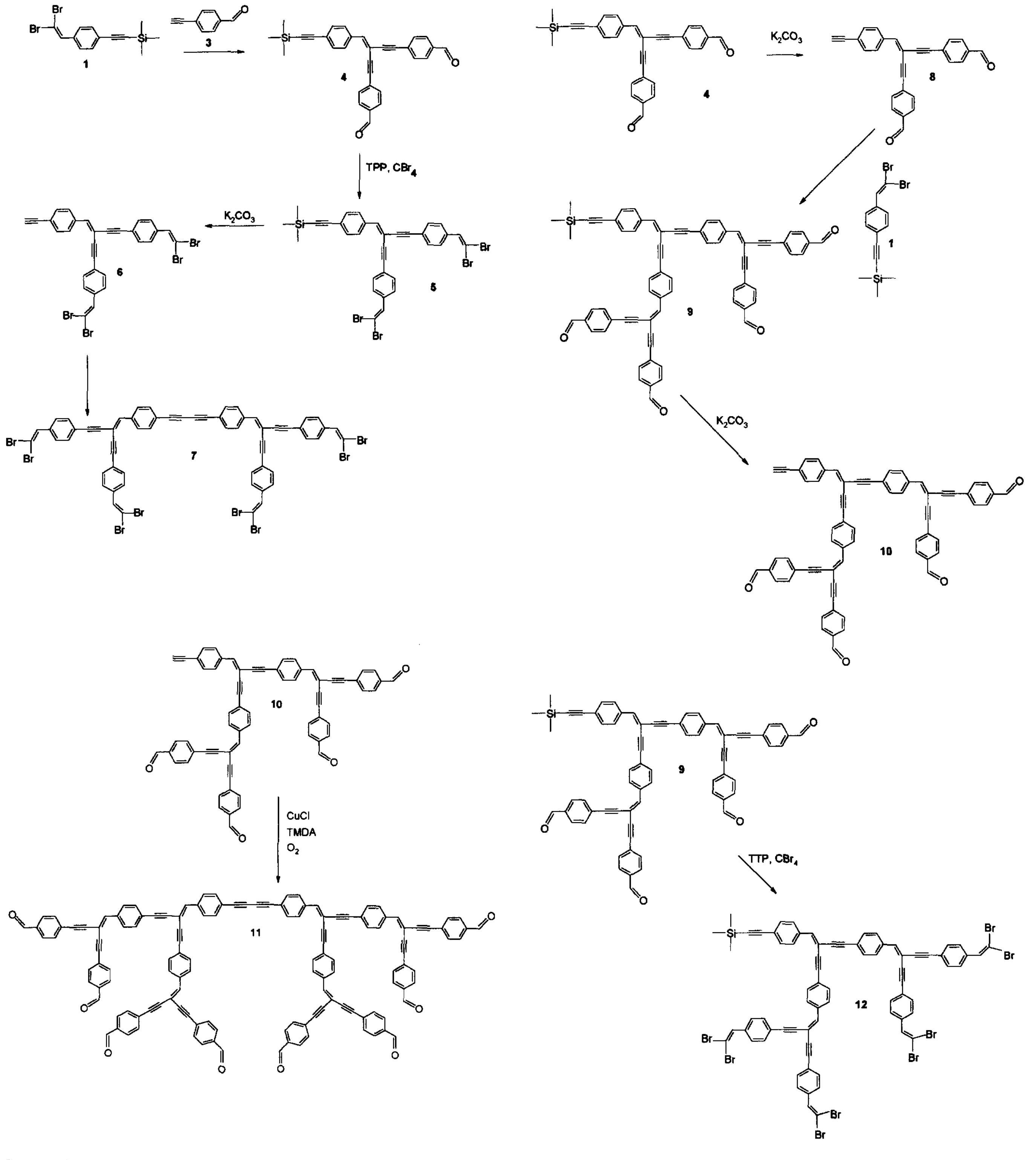
The *FT*i.r. spectra were recorded using a Nicolet 510p spectrometer. The u.v.-visible spectra were obtained in chloroform solution using a Shimadzu UV-260 spectrometer. The ^1H n.m.r. and ^{13}C n.m.r. spectra were recorded using a Varian spectrometer at 300 MHz and 75.5 MHz, respectively, in DMSO-d_6 or $CDCl_3$ with TMS as the internal standard. Emission and excitation spectra were measured with use of a Perkin-Elmer 630-10S fluorimeter, in chloroform solution.

RESULTS AND DISCUSSION

The synthetic route to well-defined oligomers of poly(β,β-dibromo-4-ethynylstyrene) is shown in *Scheme 1*. In the case of the direct homopolymerization of (β,β-dibromo-4-ethynylstyrene, only the polymer with a β,β-dibromovinyl end group is available, while in the case of stepwise synthesis both the β,β-dibromovinyl- and formyl-terminated oligomers were synthesized and characterized.

The synthetic route to oligomers **5**, **6** and **7** consisted of two repeating steps: the Heck reaction of the β,β-dibromovinyl groups of the β,β-dibromovinylstyrene derivative **1** with 4-ethynylbenzaldehyde (**3**) to produce the formyl-terminated oligomer **4**, followed by the Wittig reaction of oligomer **4** with triphenyldibromomethylenephosphorane generated from triphenylphosphine and carbon tetrabromide to give the β,β-dibromovinyl-terminated oligomer **5**. After removing the protective trimethylsilyl group under mildly basic conditions followed by oxidative dimerization of the resulting acetylene-terminated oligomer **6**, the dimer **7** is obtained.

A different synthetic approach was applied in the preparation of the next generation of oligomers (**9**, **10** and **11**) due to the low yield and solubility problems in the step **6** → **9**. First, the protective trimethylsilyl group was removed from compound **4** to give the acetylene-terminated compound **8**. A Heck reaction of compound **1** with compound **8** gave oligomer **9** directly with a reasonably good yield. The Heck reaction of compound **9** with triphenyldibromomethylenephosphorane gave oligomer **12**



Scheme 1

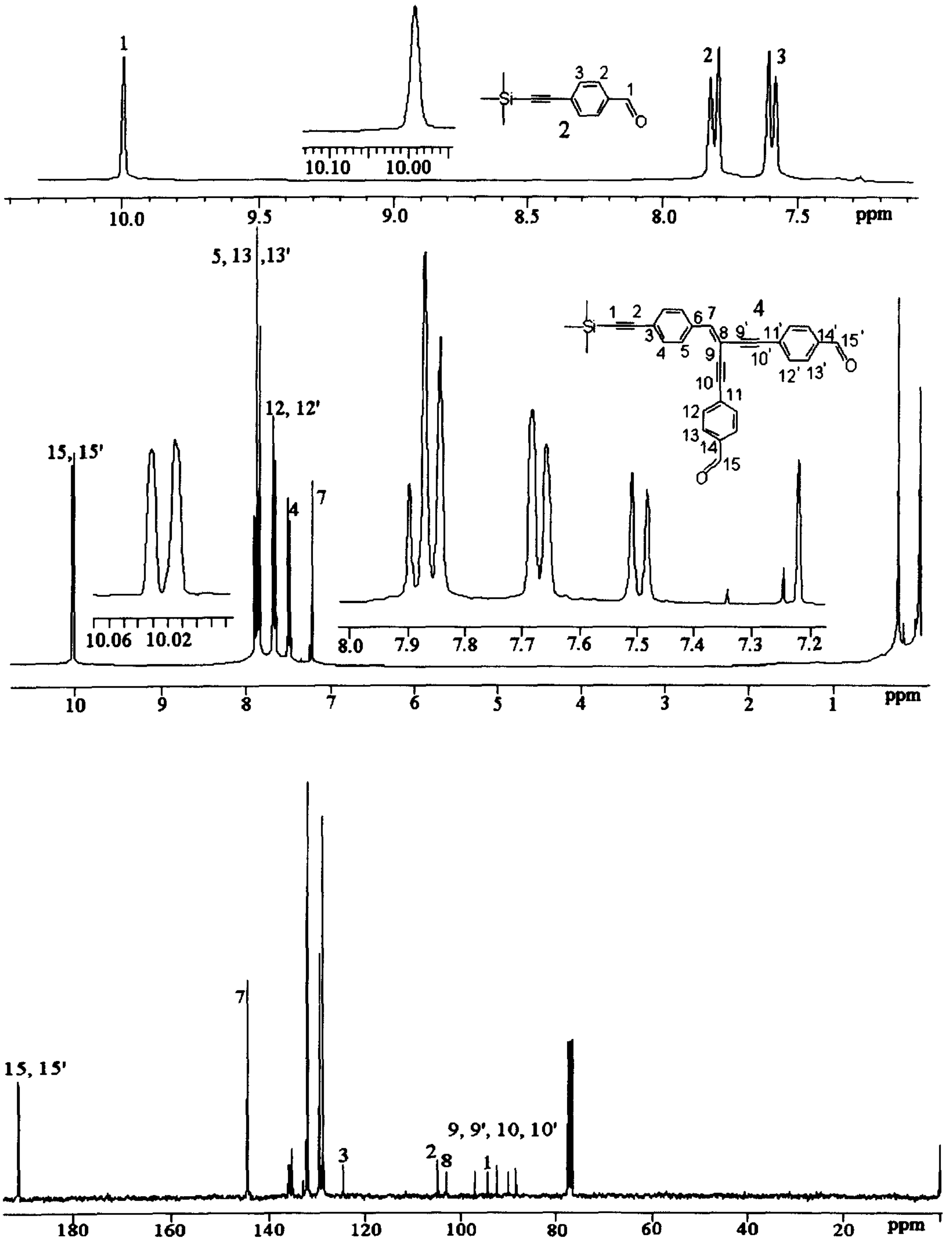


Figure 1 The ^{1}H n.m.r. spectrum of compound **2**, and the ^{1}H n.m.r. and ^{13}C n.m.r. spectra of compound **4**

containing eight bromine atoms in only 6% yield. Therefore the protective group of compound **9** was removed and the resulting oligomer **10** containing a terminal acetylene group was dimerized by an oxidative coupling reaction, producing dimer **11**.

The structure of the oligomers was confirmed by i.r. spectroscopy and ^{1}H n.m.r. and ^{13}C n.m.r. spectrometry, and, in the case of the dibromovinyl-terminated oligomers, by elemental analysis. It was impossible to measure the n.m.r. spectra of compound **11** due to its poor solubility; therefore its structure was confirmed by i.r. spectroscopy and elemental analysis. *Figure 1* shows the ^{1}H n.m.r. spectra of 4-trimethylsilylethynylbenzaldehyde (**2**) and a formyl-terminated oligomer of the first generation compound **4**, and the ^{13}C n.m.r. spectrum of the latter. The ^{1}H n.m.r. spectrum of **4** shows two signals around 10 ppm separated by 4 Hz and integrated for one proton each, corresponding to the aldehyde protons. Taking into account that the aldehyde proton of 4-trimethylsilylethynylbenzaldehyde appears as a single peak, it can be concluded that protons 15 and 15′ of compound **4** are not equivalent. From this it follows that free rotation around the C^6–C^7 bond is hampered. This conclusion is also reached from the ^{13}C n.m.r. spectrum of **4**. Thus, four different signals appeared at 97.15 ppm, 92.52 ppm, 90.13 ppm and 88.42 ppm assigned to the C^9, $C^{9\prime}$, C^{10} and $C^{10\prime}$ carbon atoms. If the C^6–C^7 bond rotated freely, there would be only two signals instead of four. The hampered rotation around the C^6–C^7 bond can be attributed to the conjugation, as will be shown in the theoretical analysis. Eventually, as can be seen from *Table 1*, the oligomers exhibit a bathochromic shift of the absorption maxima with the number of repeating units, thus proving

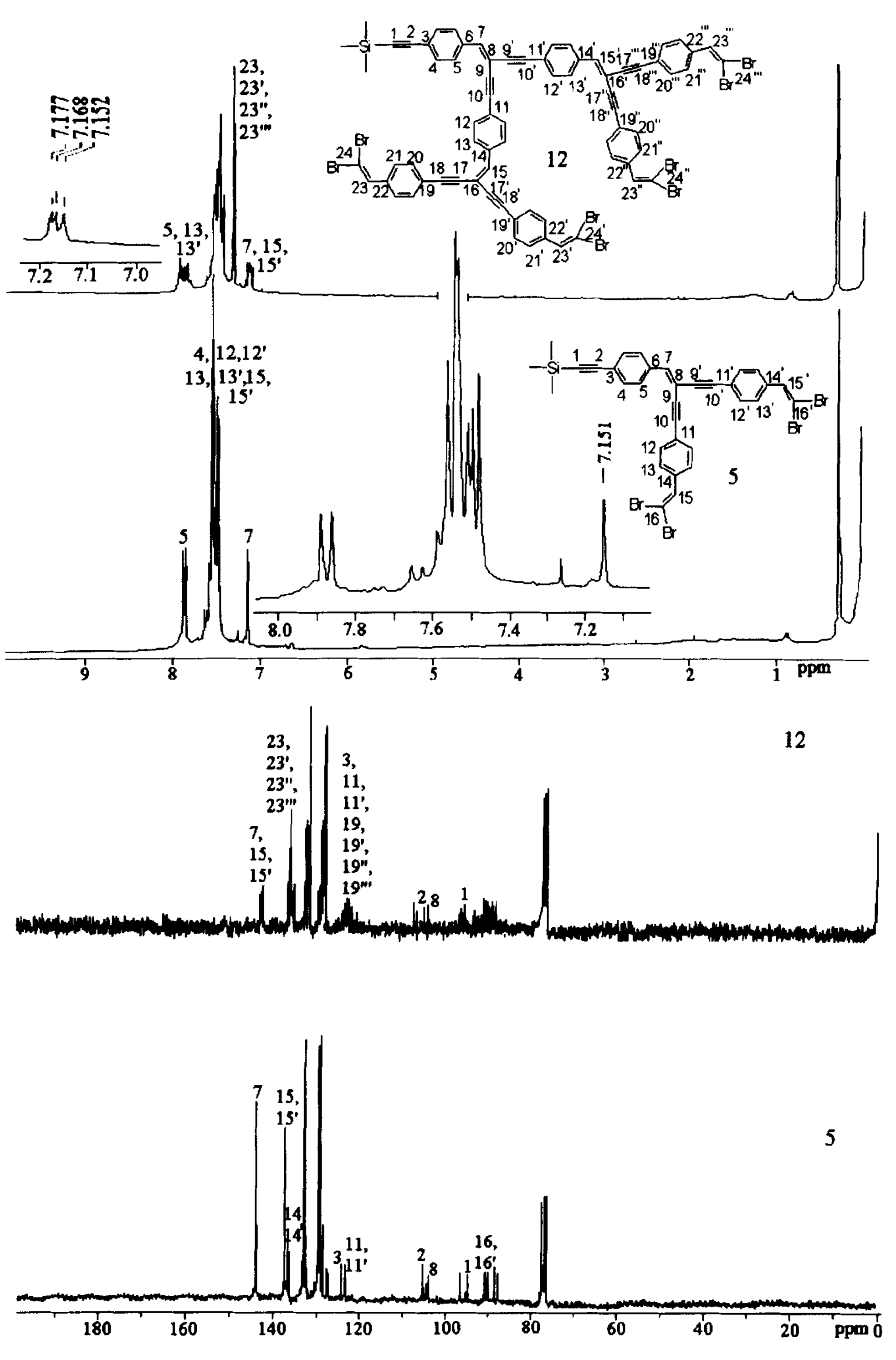


Figure 2 The ^{1}H n.m.r. and ^{13}C n.m.r. spectra of compounds **5** and **12**.

this hypothesis. *Figure 2* shows the ^{1}H n.m.r. and ^{13}C n.m.r. spectra of the dibromovinyl-terminated oligomers (**5** and **12**) of the first and the second generations, respectively. The spectra are similar to each other, reflecting the similarity in their chemical structures. However, it is noteworthy that in the ^{1}H n.m.r. spectrum of oligomer **5** one signal appears at 7.15 ppm corresponding to the H^{7} proton, while in the spectrum of **12** can be distinguished three close peaks at 7.18 ppm, 7.17 ppm and 7.15 ppm, each integrated for one proton. These signals should be assigned to H^{7}, H^{15} and $H^{15\prime}$, again proving hampered rotation around the C^{6}–C^{7} due to conjugation. AM1[9] semiempirical calculations were carried out on structure **8** showing that the C^{6}–C^{7} bond is partially double. This phenomenom can be visualized as a consequence of the electronic resonance between the triple bond and the aromatic ring. The calculated activation energy of the rotation around the C^{6}–C^{7} bond is 5.9 kcal mol^{-1}, which explains the n.m.r. data.

Table 1 presents the positions of the long-wave absorption, emission and excitation maxima of the oligomers. As can be seen, both series of oligomers, dibromovinyl-terminated (**1**, **5**, **12** and **7**) and formyl-terminated (**2**, **4**, **11** and **9**), exhibit a bathocromic shift of the absorption maxima with molecular weight due to the expansion of conjugation. Formyl-terminated oligomers show slightly red-shifted absorption maxima compared to the respective

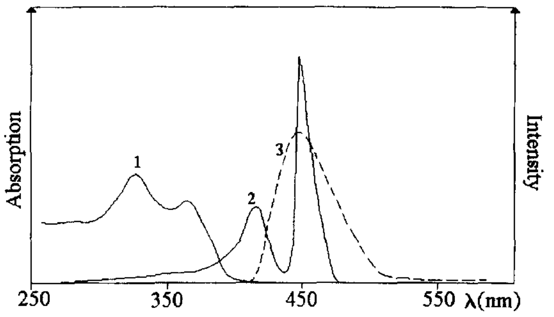


Figure 3 Absorption (**1**), excitation (**2**) and emission (**3**) spectra of compound **4** ($\lambda_{(ex)} = 350$ nm, $\lambda_{(em)} = 443$ nm in chloroform solution)

Table 1 Absorption, emission and excitation maxima of the oligomers in $CHCl_3$ solution

Compound	λ(max) (nm)		
	Absorption	Emission[a]	Excitation[b]
1	295	-	-
5	367	440	408,440
12	383	499	465
7	409	476	392,480
2	295	-	-
4	377	443	415,440
11	390	478	447,480
9	399	473	445,475

[a] The emission spectra were measured at λ = 350 nm [b] The excitation spectra were measured at the respective emission maximum of each compound

dibromovinyl derivatives, which may be related to a charge-transfer contribution due to the electron withdrawing nature of the formyl group. It is interesting to note that poly(β,β-dibromo-4-ethynylstyrene) prepared by the direct Heck polymerization of β,β-dibromo-4-ethynylstyrene[6] with an M_w of 70 000 according to g.p.c. exhibited a long-wave absorption maximum at 377 nm, which lies between the values for the first and second generations of dibromovinyl-terminated oligomers (367 nm and 383 nm, respectively). This may be explained either by steric hindrance in the poly(β,β-dibromo-4-ethynylstyrene) molecules, preventing them from having large conjugated fragments, or by incomplete branching during the polymerization leading to conjugation defects.

All compounds except **1** and **2** were found to be blue emitters peaking at 440–500 nm when excited at 350 nm, with the positions of the emission maxima correlated with those of absorption. The positions of the emission maxima of the obtained oligomers of the second generation lie close to that of poly(β,β-dibromo-4-ethynylstyrene) (500 nm). It is noteworthy that the excitation spectra of all oligomers except **12** exhibited two peaks (*Table 1*). The first is relatively broad and lies close to that of absorption. This peak is due to emission from the S_1 state. The second maximum, however, is very sharp and intense. It is located very close to the emission maximum of the respective compound and its origin is not yet clear. *Figure 3* shows the absorption excitation and emission spectra of the oligomer **4** as an example.

CONCLUSIONS

Well-defined dendritic oligomers of poly(β,β-dibromo-4-ethynylstyrene) of the first and second generations have been prepared by stepwise synthesis and characterized. It was found from the n.m.r. analysis and by theoretical calculations that free rotation around formal single bonds is hampered by conjugation. All oligomers were found to be blue emitters with their emission maxima correlating with the number of repeating units. All dendrimers except dendrimer **12** showed two maxima in the excitation spectra. The first is due to emission from the S_1 state. The second maximum is located close to the emission maximum of the respective compound, and its origin is not yet clear.

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