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The Synthesis of New Phthalocyanines Substituted with 12-Membered Diazadioxa Macrocycles

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Summary. A macrocyclic diazadioxa dibromo compound was synthesized by ring closure of 1,2-*bis*-(2-iodoethoxy)-4,5-dibromo-benzene and 1,4-*bis*-(*p*-tolylsulfonyl)-ethylenediamine. Its phthalonitrile derivative was obtained by cyano substitution. This diazadioxa macrocyclic dibromo derivative was directly converted into the copper(II) phthalocyanine by reaction with CuCN in tetramethyl urea. Conversion of this phthalonitrile derivative into the metal-free phthalocyanine was accomplished by refluxing with *DBU*. The zinc(II) phthalocyanine was prepared by reaction of the dinitrile derivative with $Zn(OAc)_2$ in quinoline. The lutetium *bis*-(phthalocyaninate) complex was obtained by treating the dinitrile derivative with anhydrous lutetium acetate and *DBU* in 1-hexanol. The new compounds were characterized by elemental analyses and IR, ^{1}H NMR, mass, UV/Vis, and ESR spectra.

Keywords. Diazadioxa macrocycle; Phthalonitrile; Phthalocyanine; Cyclotetramerization.

Introduction

In addition to their industrial importance as pigments, metal phthalocyanines have been extensively studied because of their interesting conductivity, catalytic, photovoltaic, and electrochromic properties [1]. The physical and chemical properties of soluble phthalocyanines (*Pc*) have recently attracted attention from materials chemists for their potential use in semiconducting materials, nonlinear optics, and other optical devices [2].

The growing use of phthalocyanines as advanced materials during the last decade has encouraged research on the synthesis of new derivatized materials which differ in the central metal ion or in the peripheral substituents. Despite this extensive interest, there are relatively few synthetic routes to phthalocyanine derivatives, covering mainly phthalonitrile derivatives and aromatic *ortho*-dibromo compounds [3]. For this reason, attention has been focused on their synthesis with new substituents.

We have previously synthesized phthalocyanines substituted with oxa and/or aza macrocycles, which are very soluble in common organic solvents and capable

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of binding alkali metal ions [4–6]. Phthalocyanines substituted with 14- or 15-membered tetraaza macrocycles provided donor sites for coordinating to transition metal ions [7, 8]. The phthalocyanines substituted with 17-membered diazatrioxa macrocycles are soluble to a certain extent, but neither alkali nor transition metal complexes could be isolated due to their low stability [9].

We describe here for the first time the preparation of a 12-membered symmetrical diazadioxa macrocycle and metal phthalocyanines containing four 12-membered diazadioxa macrocyclic units derived thereof.

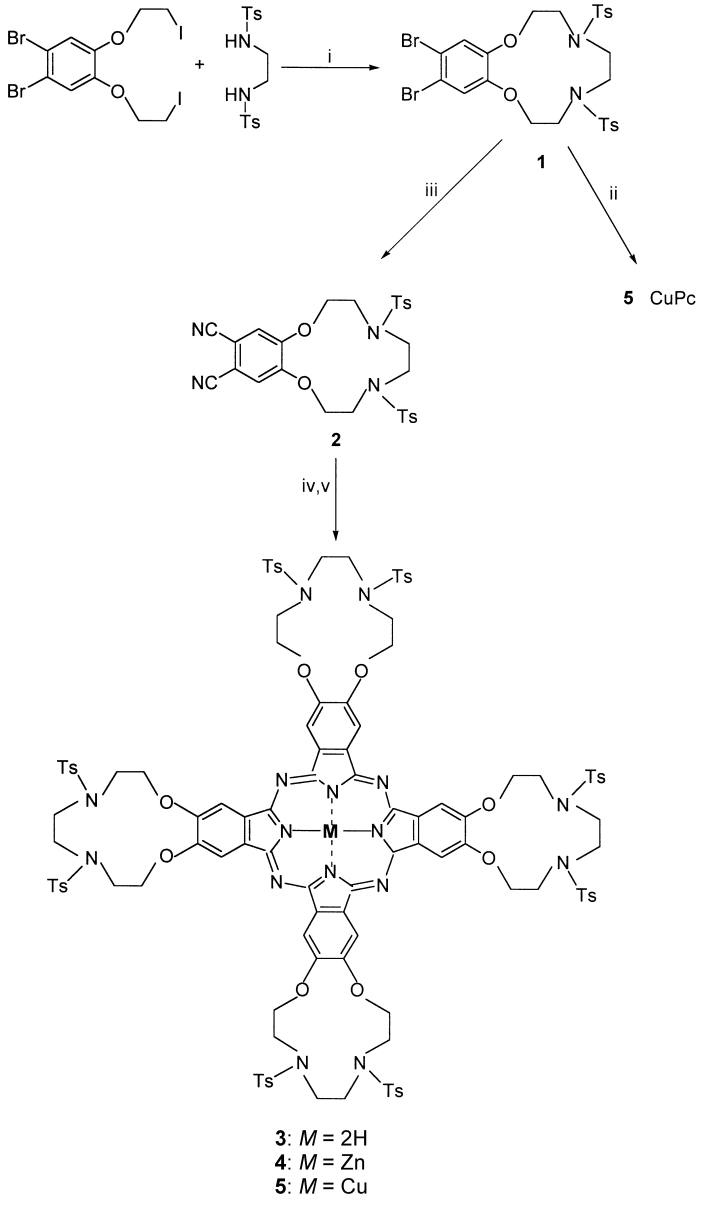
Results and Discussion

The first step in the synthetic procedure outlined in Scheme 1 is the formation of the diazadioxa macrocycle **1**. Starting from 1,4-*bis*-(*p*-tolylsulfonyl)-ethylenediamine and 1,2-*bis*-(2-iodoethoxy)-4,5-dibromo-benzene, cyclization was accomplished in *DMF* in the presence of Cs_2CO_3 as the base [7, 8]. The relatively high yield of this reaction between two bifunctional reactants indicated the template effect of the cesium ion [10]. Tosyl groups are not only effective in cyclization, but also used as protective groups for the aza functions in the cyclotetramerization to form the phthalocyanine. The dicyano derivative **2** was prepared by the *Rosenmund-von Braun* reaction, which might be considered as an intermediate step in the phthalocyanine formation. This conversion was achieved by treatment with cuprous cyanide in *DMF* at low concentrations to avoid the formation of phthalocyanine [11].

The diazadioxa macrocycle **1** was directly converted into the copper(II) phthalocyanine **5** by reaction with CuCN in tetramethyl urea. The usual synthetic routes were applied to obtain the metal-free and the divalent metal phthalocyanines. Conversion of **2** into the metal-free phthalocyanine **3** was accomplished directly by refluxing **3** in *DBU*. The reaction of **2** in a high-boiling solvent, such as quinoline, with zinc(II) acetate gave the divalent metal phthalocyanine **4**. The most characteristic feature of complexes **3–5** is their high solubility in common organic solvents like chloroform, dichloromethane, *THF*, *DMF*, and *DMSO*.

The reaction of **2** with anhydrous lutetium acetate and *DBU* in 1-hexanol gave the lutetium *bis*-(phthalocyaninate) complex **6** (Fig. 1) in 57% yield. Compound **6** is soluble in common organic solvents such as chloroform, dichloromethane, *THF*, *DMF*, and *DMSO*. All new compounds and phthalocyanines were sufficiently pure and gave satisfactory analytical results.

The spectroscopic data of the newly synthesized intermediates and phthalocyanines were in accordance with the proposed structures. Comparison of the IR spectra gave some hints to the nature of the products. In this context, we may cite the presence of SO_2 vibrations in the spectra of **1–6** at 1340 and 1140 cm^{-1}. The intense absorption band of **2** at 2213 cm^{-1}, corresponding to the C≡N groups, disappeared after its conversion into the phthalocyanines **3–6**. The band around 3300 cm^{-1} for **3** can be attributed to the NH stretching frequency of the inner core of the metal-free phthalocyanine. The ^1H NMR spectra are also consistent with the proposed structures. The aromatic protons of **1** appeared at 7.24–7.68 ppm, the CH_2O and CH_2N protons at 3.91–4.23 and 3.31–3.37 ppm. The Ar-CH_3 protons were found at 2.41 ppm. The ^1H NMR spectrum of **2** was similar to that of **1**. The



Scheme 1. *i*, Cs_2CO_3, *DMF*; *ii*, CuCN, tetramethyl urea; *iii*, CuCN, *DMF*; *iv*, *DBU*, 1-pentanol; *v*, quinoline, anhydrous $Zn(O_2CMe)_2$

aromatic protons resonated at 7.44–7.85 ppm, the CH_2O and CH_2N protons at 4.28–4.37 and 3.31–3.38 ppm, and the Ar-CH_3 protons at 2.41 ppm. The ^{1}H NMR spectrum of **3** was similar to that of **4** with the only difference that the NH protons of **3** showed a peak at −4.3 ppm as a result of the 18-π electron system of the phthalocyanine ring [4, 12]. ^{1}H NMR measurements of **5** were precluded owing to its paramagnetic nature.

Only few NMR data concerning lutetium *bis*-(phthalocyaninates) are available from the literature [13, 14], most of them dealing with the reduced forms [15, 16]. For all neutral forms, the paramagnetism of LuPc_2 perturbs the signals of protons

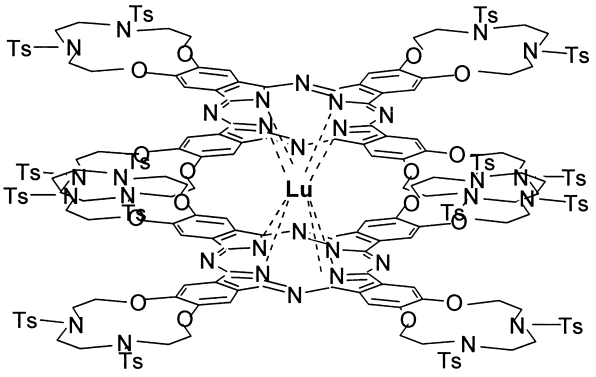


Fig. 1. Proposed structure for the lutetium *bis*-(phthalocyaninate) complex **6**

located in the vicinity of the aromatic core. The good solubility of the lutetium complex **6** in chloroform enabled us to record its ^{1}H NMR spectrum. The broad signals which were observed in the aromatic region could be attributed to the aromatic protons in the substituent. Whereas the OCH_2 protons were found at 4.28–3.62 ppm, the NCH_2 protons and tosyl CH_3 protons resonated at 3.34–3.26 and 2.17 ppm, respectively. This interpretation is also consistent with the integration values.

The phthalocyanines **3**–**5** displayed typical electronic spectra with two strong absorption bands, one of them in the UV region at about 300–350 nm (B-band), and the other one in the visible part at 600–700 nm (Q-band). The characteristic Q-band transition of copper phthalocyanine with D_{4h} symmetry is observed as a single band of high intensity at 678 nm [6]. Gradual increases in the concentration resulted in a lowering of the intensity of the Q-band at 678 nm together with a slight increase in the absorbtion at 654 nm denoting the formation of aggregated species [4]. The D_{2h} symmetry of the metal-free phthalocyanine **3** is verified by the two absorptions in the visible region at 678 and 647 nm.

The electronic spectrum of the zinc(II) phthalocyanine **4** contained a Q-band at 676 nm and a *Soret* band at 340 nm. Any increase in concentration resulted in the aggregation of phthalocyanine molecules, which was accompanied by a shift of the Q-band with some decrease in intensity. The UV/ Vis spectrum of the lutetium *bis*-(phthalocyanine) **6** showed a Q-band at 677 nm, a *Soret* band at 343 nm, and a typical radical phthalocyanine anion band as a shoulder in the 400–500 nm region [17, 18, 19–22].

A close investigation of the mass spectra of **1**–**5** confirmed the proposed structures. FAB mass spectroscopy has been extensively used to characterize various sandwich complexes [13, 15, 23–26]. However, the spectra of lutetium sandwich complexes vary drastically with the matrix used [25, 26]. Thus, FAB-MS gave only fragmentation peaks for the present compound.

The free radical nature of the green LuPc_2 complex was confirmed by its ESR spectrum [27]. The spectrum of a solid sample of **6** at room temperature, which shows a strong signal at $g = 2.007$ with a bandwidth of 10 G, confirmed the presence of an unpaired spin and is consistent with the occurrence of a phthalocyanine radical [28] (Fig. 2). Probably, both phthalocyanine ligands are symmetrically

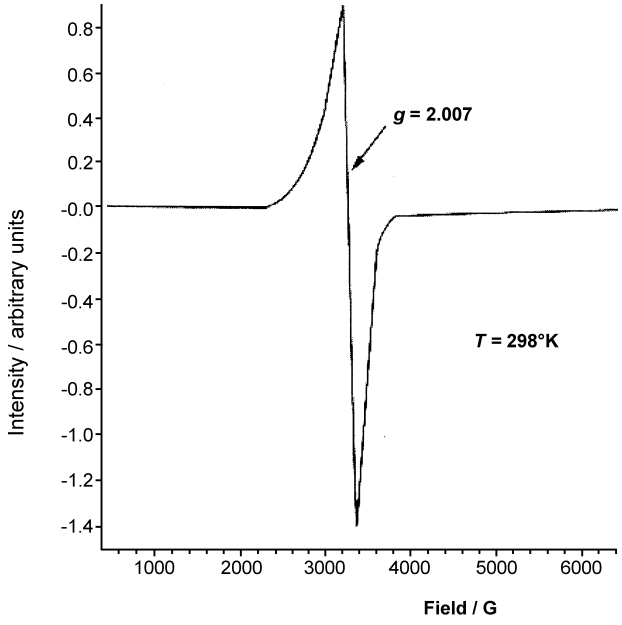


Fig. 2. X-Band ESR spectrum of the lutetium *bis*-(phthalocyaninate) complex **6**

attached to the central metal atom. An intramolecular charge transfer with the free electron hopping between the two phthalocyanine rings has been suggested for the green form of LuPc_2 [29, 30].

Experimental

IR spectra were recorded on a ATI Unicom-Mattson 1000 spectrophotometer using KBr pellets, electronic spectra on a ATI Unicom UV/ Vis spectrometer UV2. Elemental analyses were performed by the instrumental analysis laboratory of the TUBİTAK Marmara Research Centre. Their results agreed favourably with the calculated values. ^{1}H NMR spectra: Bruker 200 MHz spectrometer; mass spectra: VG Zabspec GS-MS spectrometer; ESR spectra: Bruker 380 EMX spectrometer operated at X-band. 1,2-*Bis*-(2-iodoetoxy)-4,5-dibromo benzene [31] and 1,4-*bis*-(*p*-tolyl sulfonyl)-ethylenediamine [32] were prepared according to reported procedures.

2,3-Dibromo-8,11-bis-(p-tolylsulfonyl)-6,7,8,9,10,11,12,13-octahydro-5,14-dioxa-8,11-diaza-benzocyclododecene (**1**; $C_{26}H_{28}O_6N_2S_2Br_2$)

1,4-*Bis*-(*p*-tolylsulfonyl)-ethylenediamine (0.73 g, 2 mmol) was dissolved in 200 cm^3 *DMF* containing 1.36 g finely ground anhydrous Cs_2CO_3 (4.2 mmol) and stirred at room temperature for 15 min under N_2. A solution of 1.15 g 1,2-*bis*-(2-iodo-ethoxy)-4,5-dibromo-benzene (2 mmol) in 80 cm^3 *DMF* was added dropwise over a period of 5 h. After stirring the reaction mixture for a further 24 h at room temperature, 500 cm^3 ice-water was added. The white solid which precipitated upon addition of 60 drops of concentrated HCl was collected by filtration and washed with H_2O to neutral. The wet solid was dissolved in 30 cm^3 CH_2Cl_2, and the solution was dried over Na_2SO_4. After the volume of the filtrate was reduced to 10 cm^3, 15 cm^3 petroleum ether were added. Finally, the crystalline white product was filtered and dried *in vacuo*.

Yield: 0.96 g (70%); m.p.: 179°C; IR (KBr): $\nu = 3106$ (CH aromatic), 2928–2850 (CH aliphatic), 1340, 1140 (Ar-CH_3), 640 (C-Br) cm^{-1}; ^{1}H NMR (*DMSO*-d_6, δ, 200 MHz): 2.41 (s, 6H, Ar-CH_3),

3.34 (t, $J = 6.4$ Hz, 8H, NCH_2), 4.13 (t, $J = 6.2$ Hz, 4H, OCH_2), 7.46 (t, $J = 6.2$ Hz, 10H, aromatic H) ppm; MS (EI): $m/z = 687$ (M^+).

8,11-Bis-(p-tolylsulfonyl)-6,7,8,9,10,11,12,13-octahydro-5,14-dioxa-8,11-diaza-benzocyclododecene-2,3-dicarbonitrile (**2**; $C_{28}H_{28}O_6N_4S_2$)

Compound **1** (0.8 g, 1.16 mmol), 0.31 g CuCN (3.48 mmol), and 5 cm^3 anhydrous *DMF* were refluxed at 160°C for 24 h under N_2. After cooling to room temperature the dark brown mixture was poured into 25 cm^3 NH_4OH (25%), and air was passed through the solution for 24 h. The creamy coloured precipitate was filtered off, washed with H_2O until the filtrate was neutral, and dried *in vacuo* at 50°C. This crude product was dissolved in CH_2Cl_2, filtered, and the filtrate was evaporated to dryness. Recrystallization from EtOH gave a creamy coloured product. Compound **2** is soluble in $CHCl_3$, CH_2Cl_2, *THF*, *DMF*, and *DMSO*.

Yield: 0.27 g (40%); m.p.: 196°C; IR (KBr): $\nu = 3100$ (CH aromatic), 2928–2850 (CH aliphatic), 2213 (C≡N), 1340 and 1140 (Ar-CH_3) cm^{-1}; ^{1}H NMR (*DMSO*-d_6, δ, 200 MHz): 2.41 (s, 6H, Ar-CH_3), 3.34 (t, $J = 6.6$ Hz, 8H, NCH_2), 4.33 (t, $J = 6.4$ Hz, 4H, OCH_2), 7.44–7.85 (m, 10H, aromatic H) ppm; MS (EI): $m/z = 580$ (M^+).

4,7-Bis-(p-tolylsulfonyl)-2,3,5,6,8,9,17,18,20,21,23,24,31,32,34,35,37,38,46,47,49,50,52,53-tetracosahydro-61H,63H-tetrakis-((4,7)-diaza-(1,10)-dioxa)-cyclodecine [5,6-b:5^1,6^1-k:5^{11},6^{11}-t:5 ^{111},6^{111}-c$_1$]phthalocyanine (**3**; $C_{112}H_{114}O_{24}N_{16}S_8$)

A mixture of 0.12 g **2** (0.2 mmol) and 0.03 cm^3 *DBU* in 7 cm^3 1-pentanol was refluxed under N_2 for 5 h. After cooling to room temperature, 10 cm^3 of EtOH were added. The dark-green precipitate was filtered, washed several times successively with hot H_2O, hot EtOH, hot MeOH, hot ethyl acetate, and diethyl ether in order to remove the unreacted organic materials, and dried. Compound **3** is soluble in $CHCl_3$, CH_2Cl_2, *THF*, *DMF*, and *DMSO*.

Yield: 0.047 g (39%); IR (KBr): $\nu = 3300$ (NH), 3100 (CH aromatic), 2928–2850 (CH aliphatic), 1340 and 1140 (Ar-CH_3) cm^{-1}; ^{1}H NMR (*DMSO*-d_6, δ, 200 MHz): 7.27–6.67 (m, 40H, aromatic H), 4.23 (t, $J = 6.0$ Hz, 16H, OCH_2), 2.91 (t, $J = 6.2$ Hz, 32H, NCH_2), 2.22 (s, 24H, tosyl CH_3), −4.3 (s, 2H, NH) ppm; MS (FAB): $m/z = 2322$ [M^+].

4,7-Bis-(p-tolyl sulfonyl)-2,3,5,6,8,9,17,18,20,21,23,24,31,32,34,35,37,38,46,47,49,50,52,53-tetracosahydro-61H,63H-tetrakis-((4,7)-diaza-(1,10)-dioxa)-cyclodecine [5,6-b:5^1,6^1-k:5^{11},6^{11}-t:5^{111},6^{111}-c$_1$]phthalocyaninato zinc(II) (**4**; $C_{112}H_{112}O_{24}N_{16}S_8Zn$)

A mixture of 0.120 g **2** (0.2 mmol), 0.01 g, anhydrous zinc acetate (0.05 mmol), and 0.5 cm^3 quinoline was heated and stirred at 180–190°C for 20 h under N_2. After cooling to room temperature, the dark-green mixture was diluted with 5 cm^3 EtOH and filtered. The product was washed with 2×20 cm^3 hot H_2O, 3×20 cm^3 EtOH, 2×20 cm^3 MeOH, and 2×20 cm^3 ethyl acetate and dried. Compound **4** is soluble in $CHCl_3$, CH_2Cl_2, *DMF* pyridine, and *DMSO*.

Yield: 0.052 g (43%); IR (KBR): $\nu = 3106$ (CH aromatic), 2928–2850 (CH aliphatic), 1340 and 1140 (Ar-CH_3) cm^{-1}; ^{1}H NMR (*DMSO*-d_6, δ, 200 MHz): 7.68–6.77 (m, 40H, aromatic H), 4.43 (t, $J = 6.0$ Hz, 16H, OCH_2), 3.49 (t, $J = 6.1$ Hz, 32H, NCH_2), 2.17 (s, 24H, tosyl CH_3) ppm; MS (FAB): $m/z = 2386$ (M^+).

4,7-Bis-(p-tolylsulfonyl)-2,3,5,6,8,9,17,18,20,21,23,24,31,32,34,35,37,38,46,47,49,50,52,53-tetracosahydro-61H,63H-tetrakis-((4,7)-diaza-(1,10)-dioxa)-cyclodecine [5,6-b:5^1,6^1-k:5^{11},6^{11}-t:5^{111},6^{111}-c$_1$]phthalocyaninato copper(II) (**5**; $C_{112}H_{112}O_{24}N_{16}S_8Cu$)

A mixture of 0.120 g **1** (0.175 mmol), 41 mg CuCN (0.461 mmol), and 0.5 cm^3 *tmu* was heated and stirred at 180–190°C for 24 h under N_2. After cooling to room temperature, the dark-green mixture

was diluted with 10 cm^3 EtOH, and the crude product was precipitated. It was filtered off and washed with hot H_2O, hot EtOH, and diethyl ether. The precipitate was refluxed with a solution of 0.35 g NaCN in 15 cm^3 H_2O to remove the excess of CuCN and filtered. The dark-green product was washed with hot H_2O, hot EtOH, and diethyl ether and dried. Compound **5** is soluble in $CHCl_3$, CH_2Cl_2, *DMF*, and *DMSO*.

Yield: 0.050 g (42%); IR (KBr): $\nu = 3110$ (CH aromatic), 2972–2850 (CH aliphatic), 1340 and 1140 (Ar-CH_3) cm^{-1}; MS (FAB): $m/z = 2384$ (M^+).

Bis-(4,7-bis-(p-tolylsulfonyl)-2,3,5,6,8,9,17,18,20,21,23,24,31,32,34,35,37,38,46,47,49,50,52,53-tetracosahydro-61H,63H-tetrakis-((4,7)-diaza-(1,10)-dioxa)-cyclodecine [5,6-b:5^1,6^1-k:5^{11},6^{11}-t:5^{111},6^{111}-c_1]phthalocyaninato lutetium(III) (**6**; $C_{224}H_{224}O_{48}N_{32}S_{16}Lu$)

A mixture of 0.203 g **2** (0.35 mmol), 15 mg anhydrous lutetium(III) acetate (0.043 mmol), and 0.21 cm^3 *DBU* (0.522 mmol) in 1 cm^3 1-hexanol was heated and stirred at 160°C for 20 h under N_2. After cooling to room temperature, the crude product was diluted with 5 cm^3 EtOH, filtered, dissolved in $CHCl_3$, and filtered again. The filtrate was evaporated to dryness, and the residue was washed several times successively with hot H_2O, EtOH, MeOH, and ethyl acetate. Finally, it was dried *in vacuo*. Compound **6** is soluble in $CHCl_3$, CH_2Cl_2, *THF*, *DMF*, and *DMSO*.

Yield: 0.117 g (57%); IR (KBr): $\nu = 3060$ (CH aromatic), 2976–2850 (CH aliphatic), 1340 and 1140 (Ar-CH_3) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ, 200 MHz): 8.22–6.96 (m, 80H, aromatic H), 4.28–3.62 (m, 32H, OCH_2), 3.34–3.26 (m, 64H, NCH_2), 2.17 (s, 48H, tosyl CH_3) ppm.

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