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Synthesis of Dendrimers with Porphyrine Core and their Supramolecular Complexes with Fullerene C_{60}

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Dendritic branches of poly(arylether) with peripheral butyl chains have been attached to a porphyrine core. Dendrimers of first, second and third generation were synthesized. Viability to form supramolecular complexes with fullerene C_{60} was studied with two dendrimers of second and third generation. The supramolecular complexes were characterized by ^1H, ^{13}C NMR in solution, FTIR, UV-vis spectroscopy and elemental analysis.

Keywords: Dendrimers; Porphyrine; Supramolecular complex; Fullerene C_{60}

INTRODUCTION

Dendrimers are well-defined macromolecules with uniform molecular weight and nanoscopic size. These compounds have received increasing attention due to their physical and chemical properties and the viability to form supramolecular complexes [1–4]. Recently, porphyrin dimers have shown a selective fullerene binding with a high binding constant ($>10^5$ M^{-1}) [5,6]. In these supramolecular hosts for fullerenes, the conformity of the C_{60} size with the host cavity enables stable complexation between the organic hosts and C_{60}. In the last years, porphyrin-core dendrimers have been synthesized by attaching convergent Fréchet-type dendrons [7] to a porphyrin core [8–11]. Dendritic porphyrins have been synthesized using porphyrins and metalloporphyrins. The synthesized dendritic porphyrins possess a regulated nanospace with different sizes. These well defined nanospaces with peripheral n-alkyl chain dendrimers can provide cavities for inclusion of C_{60}. Furthermore, the porphyrin core in the dendritic porphyrins can interact strongly with C_{60} via a π-donor-π-acceptor interaction. In this context, we expect stable complexation of C_{60} with poly(arylether) based dendritic porphyrins.

In this paper, we report the synthesis of monodisperse poly(arylether) dendrons and dendrimers with a porphyrin core and their supramolecular complexes with fullerene C_{60}.

RESULTS AND DISCUSSION

Dendrons containing alkyl groups were prepared according to the convergent Fréchet approach [12]. Esterification of 3,5-dihydroxybenzoic acid (MeOH, H_2SO_4) (Scheme 1) followed by alkylation of the ester (**1**) (n-butyl bromide, K_2CO_3, acetone) afforded methyl 3,5-dipropyloxybenzoate. This was reduced with $LiAlH_4$ in THF at 0°C to give 3,5-dipropyloxybenzyl alcohol, which was converted into bromide (**4**) upon treatment with carbon tetrabromide in tetrahydrofuran and triphenylphosphine at 0°C. This bromide may be regarded as the first generation reagent. The reaction of bromide **4** with methyl 3,5-dihydroxybenzyl alcohol in presence of K_2CO_3 and a small amount of 18-crown-6 in boiling acetone yielded compound (3,5-bis(3,5-dibutoxybenzyloxy)-phenyl)methanol. This gave the second-generation bromide (**6**) upon treatment with carbon tetrabromide in tetrahydrofuran and triphenylphosphine at 0°C. The third-generation chloride (**8**) was obtained

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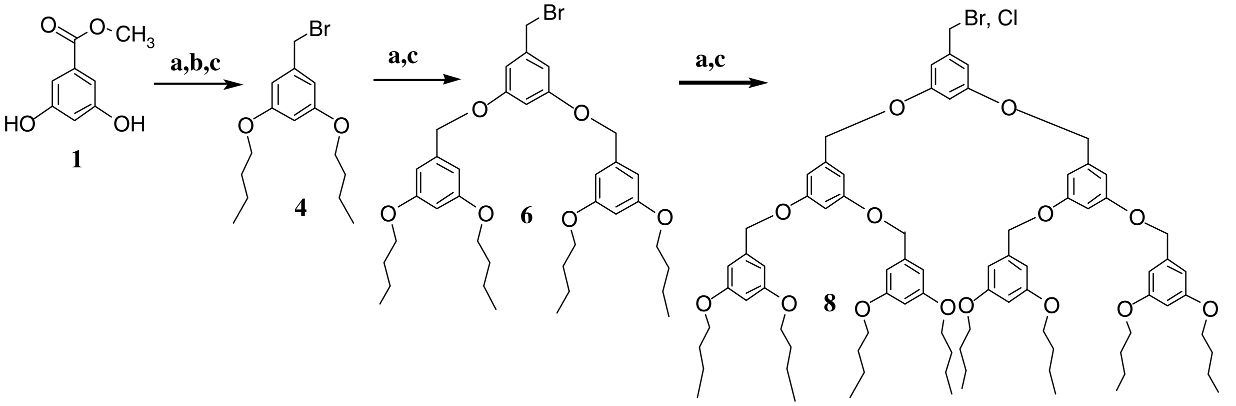


SCHEME 1 Synthesis of dendrons of first, second and third generation a) Acetone, K_2CO_3, 18-C-6; b) THF, $LiAlH_4$, 0 °C; c) CBr_4, THF, $P(Ph)_3$ and Py, CH_2Cl_2, $SOCl_2$, 0 °C.

from bromide (**6**) and 3,5 dihydroxybenzyl alcohol upon treatment with thionyl chloride (Scheme 1).

Dendrons **4**, **6** and **8** were characterized by ^{1}H- and ^{13}C-NMR, IR, FAB + mass spectrometry.

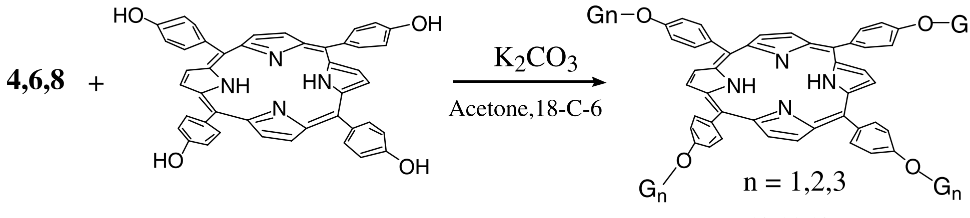
The attachment of dendrons, *viz.*, chlorides **4, 6** and **8,** to the porphyrine core was carried out in a single step (Scheme 2).

The dendrimers **10–12** were obtained from porphyrine and the dendrons **4**, **6** and **8** in acetone and K_2CO_3 at reflux for 3 days. The structures of first **10,** second **11** and third **12** generation of dendrimers were confirmed by ^{1}H and ^{13}C NMR, IR, MALDI-TOF mass spectrometry. The ^{1}H NMR spectra show in all examples one broad signal at -2.7 ppm assigned to the NH groups, one triplet for the CH_3, and two multiplets for the CH_2- peripheral groups, three singlets at 4.95 ppm, 4.97 ppm and 5.28 ppm due to the CH_2-O protons, two doublets for the aromatic protons joined to the porphyrine, one singlet at 8.87 ppm assigned to the pyrrole protons.

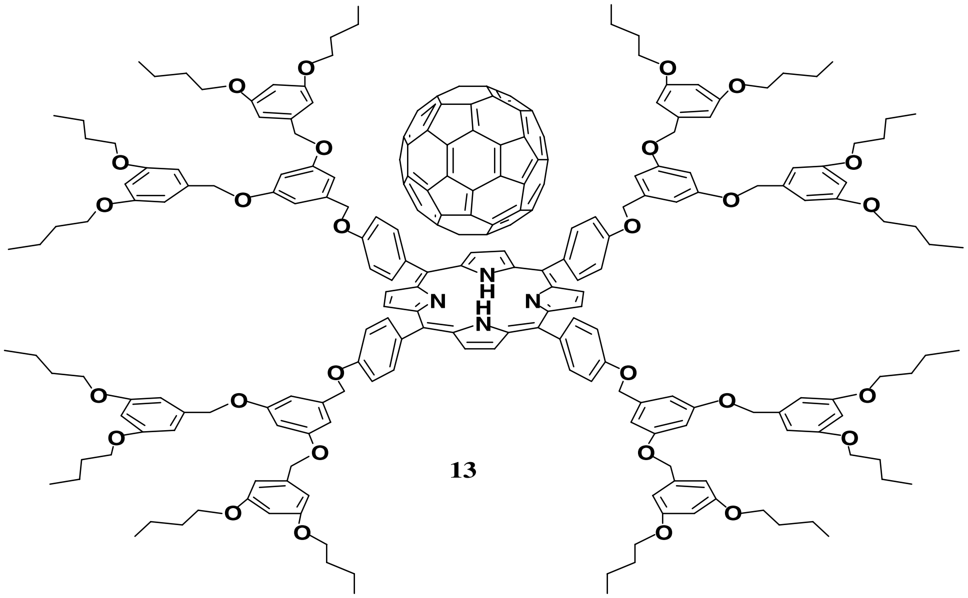
To form supramolecular complexes the dendrimers **11** and **12** were used with fullerene C_{60}. To a toluene solution of the fullerene equimolar amounts of the dendrimer **11** or **12** were added. The solvent was evaporated in vacuum and the solid was carefully washed with small quantities of toluene to remove the traces of free fullerene and dendrimer. Elemental analysis of the residual solid was consistent with the 1:1 stoichiometry (Scheme 3).

^{1}H NMR and ^{13}C NMR spectroscopy in $CDCl_3$ at room temperature of the free porphyrin and of the complexes reveals the structural changes. When fullerene is added to porphyrin-dendrimers **11** or **12**, ring current effects from the fullerene cause up field shifts in the central N-H protons (up to 0.012 ppm and 0.027 ppm). Conversely, ring current effects of the porphyrins cause down field shifts in the ^{13}C NMR in $CDCl_3$ of the fullerene. For C_{60}, the shift is 3.1 ppm for complexation by **11** and **12** (see Fig. 1). Also NMR spectroscopy studies were made using toluene-d_8 and shifts in the central N-H protons up to 0.62 ppm were observed.

The absorption spectrum of **11** or **12** in toluene solution changed upon the addition of C_{60}, and the Soret band was blue shifted from 423 nm to 411 nm (Table I) with decreasing absorption intensity, indicating electronic interaction between the porphyrin core in **11** or **12** and C_{60} (Fig. 2). However, the dendritic porphyrins, **11**, and **12**, showed spectral changes in the absorption spectra after the addition of a large excess of C_{60}. All the family emitted fluorescence at 518 nm and 652 nm, where the intensities were found to be virtually unchanged in response to the generation when normalized to a constant absorbance at the excitation wavelength. Therefore, the fluorescing property of the porphyrin core is hardly affected by the generation of the dendron subunits (no site isolation effect).



SCHEME 2 Synthesis of dendrimers of first, second and third generation.



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SCHEME 3 Supramolecular complexes between dendritic- porphyrines **13**, **14** and fullerene C_{60}.

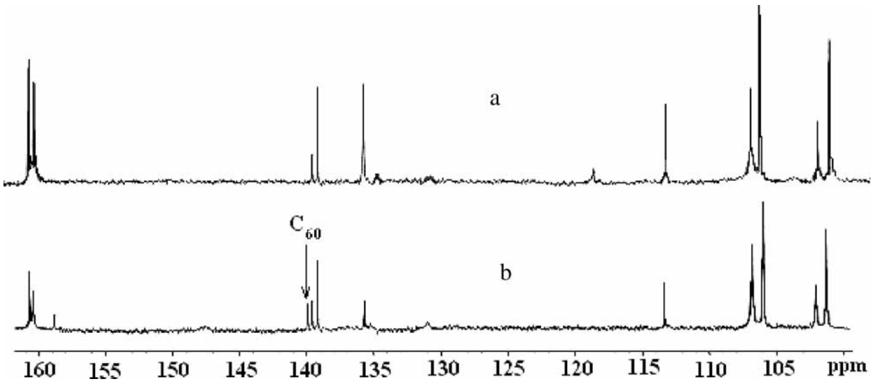

FIGURE 1 NMR ^{13}C spectra of a) third generation dendrimer **12** and b) supramolecular complex **14**, in $CDCl_3$.

CONCLUSIONS

The second and third generation of 3,5-*n*-butyloxy-periphery dendrons units can form a stable complex with C_{60}. The regulated nanospace constructed from the regulated branching system of 16 and 32 benzene rings around the porphyrin core is exactly fitted to the C_{60} size. The multipoint interaction among the

TABLE I Spectroscopic data for the supramolecular complexes **13** and **14**

Complex **13**		Complex **14**	
Wavelength (nm)	Absorbance	Wavelength (nm)	Absorbance
284	0.1015	283	0.1341
423	1.0000	411	1.0000
518	0.0405	518	0.0437
554	0.0285	554	0.0226
595	0.0131	595	0.0138
653	0.0139	652	0.0139

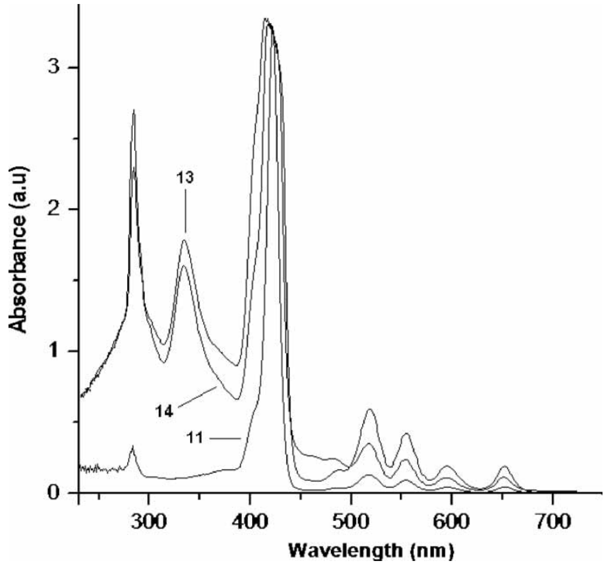

FIGURE 2 UV-Vis spectra of third generation dendrimer **11** and supramolecular complex **13** and **14**, in toluene.

curved π surface of C$_{60}$ and the planar π surface of the porphyrin core was confirmed by ^{1}H and ^{13}C NMR spectroscopy. Some weak interactions between benzene rings of the branching units of dendrimers and fullerene C$_{60}$ can also be expected.

EXPERIMENTAL SECTION

Infrared (IR) spectra were recorded on a Nicolet FT-IR Magna 700 Spectrometer. ^{1}H and ^{13}C NMR spectra for solutions in CDCl$_3$ were collected on a Varian Unity operating at 300 MHz and 75 MHz, respectively. For both ^{1}H and ^{13}C, chemical shifts are expressed in ppm relative to tetramethylsilane (Me$_4$Si δ 0.00) as the internal standard. Column chromatography was carried out on silica. Elemental analyses were performed at Galbraith Laboratories, INC. Knoxville. USA. FAB$^+$ mass spectra were taken with a JEOL JMS AX505 HA mass spectrometer. Matrix-assisted laser desorption/ionization were taken with a TofSpec spectrometer.

Methyl 3,5-dihydroxybenzoate 1

10 g (64.9 mmol) of 3,5-dihydroxybenzoic acid were dissolved in 60 mL of absolute methanol. Once dissolved, 0.5 mL of concentrated sulfuric acid was added. The reaction was heated to reflux for 18 h. After that, the solvent was evaporated to dryness to yield 10.8 g, (98%) of a white powder. UV CHCl$_3$ (nm): 251, 308.IR (cm^{-1}): 3375, 3250, 1695, 1603, 1487, 1444, 1347, 1302, 1264, 1167, 1000, 767.^{1}H-NMR (CDCl$_3$) δ (ppm): 3.85 (s, 3H, CH$_3$), 6.47 (t, $J = 2.4\,Hz$, 1H, Ar-H), 6.92 (d, $J = 2.34\,Hz$, 2H, Ar-H). ^{13}C-NMR (CDCl$_3$) δ (ppm): 52.6 (CH$_3$-O), 108.4, 108.9, 109.2 (Ar), 133.2 (Cipso), 159.7 (Ar-OH), 168.8 (C=O). EM (IE$^+$): 168 m/z. Calcd. for C: 57.14%, H: 4.80%. Found. C: 57.13, H: 4.81%.

General Procedure

A mixture of methyl 3,5-dihydroxybenzoate **1** and the 1-bromobutane or the bromides **5** and **7**, K$_2$CO$_3$, KI, in dry acetone (150 ml) was heated to reflux and stirred under nitrogen for 24 h. The mixture was allowed to cool and the precipitate was filtered, the filtrate was evaporated to dryness under reduced pressure. The residue was dissolved in diethyl ether and washed with an aqueous solution of 5% Na$_2$CO$_3$ (2 times). The product was purified (SiO$_2$; Hexane-ethyl acetate, 4:1).

Methyl 3,5-dibutoxybenzoate 2

20.96 g to yield (87%) of a yellow oil. UV CHCl$_3$ (nm): 254, 308.IR (cm^{-1}): 3907, 2936, 2940, 2873, 2768, 1725, 1598, 1448, 1352, 1327, 1299, 1234, 1170, 1068, 1052.^{1}H-NMR (CDCl$_3$) δ (ppm): 0.97 (t, 6H, CH$_3$, $J = 7.50$ Hz); 1.48 (m, 4H, CH$_2$), 1.76 (m, 4H, CH$_2$), 3.89 (s, 3H, CH$_3$-O), 3.97 (t, 4H, CH$_2$-O, $J = 6.60$), 6.36 (t, 1H, Ar-H, $J = 2.10$ Hz), 7.15 (d, 2H, Ar-H, $J = 2.40$ Hz). ^{13}C-NMR (CDCl$_3$) δ (ppm): 13.7 (CH$_3$), 19.1 (CH$_2$), 31.2 (CH$_2$), 52.1 (CH$_3$-O), 67.9 (CH$_2$-O), 106.5 (Ar), 107.6 (Ar), 131.8 (Ar$_{ipso}$), 160.1 (Ar-O), 166.9 (C=O). EM (IE$^+$): 280 m/z. Calcd. for C: 68.54%, H: 8.63%. Found; C: C: 68.53%, H: 8.63%

(3,5-Bis(3,5-dibutoxybenzyloxy)phenyl)methanol 5

3.28 g to yield (92%) of a yellow oil. UV CHCl$_3$ (nm): 243, 281.IR (cm^{-1}): 3421, 2936, 2940, 2873, 2768, 1725, 1598, 1448, 1352, 1327, 1299, 1234, 1170, 1068, 1052.^{1}H-NMṘ. (CDCl$_3$) δ̇ (ppm): 0.96 (t, 12H, CH$_3$, $J = 7.50$ Hz), 1.478 (m, 8H, CH$_2$), 1.75 (m, 8H, CH$_2$), 3.94 (t, 8H, CH$_2$-O, $J = 6.30$ Hz), 4.62 (s, 2H, CH$_2$-OH), 4.94 (s, 4H, ArCH$_2$-O), 6.40 (t, 2H, Ar-H, $J = 2.4$ Hz), 6.53 (t, 1H, Ar-H, $J = 2.4$ Hz), 6.54 (d, 4H, Ar-H, $J = 2.1$ Hz), 6.60 (d, 2H, Ar-H, $J = 2.4$ Hz). ^{13}C-NMR (CDCl$_3$) δ (ppm): 13.8 (CH$_3$), 19.2 (CH$_2$), 31.2 (CH$_2$), 65.3, 65.3 (CH$_2$-OH), 67.7 (CH$_2$-O), 70.0 (CH$_2$-O), 100.7 (Ar), 101.3 (Ar), 105.6 (Ar), 138.9 (Ar$_{ipso}$),143.3 (Ar$_{ipso}$), 160.5 (Ar-O). EM (IE$^+$): 608 m/z. Calcd. for C: 72.99, H: 8.61%. Found; 72.99, H: 8.60%

(3,5-Bis(3,5-bis(3,5-dibutoxybenzyloxy)benzyloxy)phenyl)methanol 7

3.05 g to yield (85%) of a yellow oil. UV CHCl$_3$ (nm): 244, 282 IR (cm^{-1}): 3514, 2936, 2940, 2873, 2768, 1725, 1598, 1448, 1352, 1327, 1299, 1234, 1170, 1068, 1052.^{1}H-NMṘ (CDCl$_3$) δ̇ (ppm): 0.96 (t, 24H, CH$_3$, $J = 7.32$ Hz), 1.47 (m, 16H, CH$_2$), 1.74 (m, 16H, CH$_2$), 3.93 (t, 16H, CH$_2$-O, $J = 6.50$ Hz), 4.61 (s, 2H, CH$_2$-OH), 4.94 (s, 8H, ArCH$_2$-O), 4.96 (s, 4H, ArCH$_2$-O), 6.39 (t, 4H, Ar-H, $J = 2.25$ Hz), 6.52 (t, 1H, Ar-H, $J = 2.25$ Hz), 6.54 (d, 8H, Ar-H, $J = 2.23$ Hz), 6.55 (t, 2H, Ar-H, $J = 2.33$ Hz), 6.59 (d, 2H, Ar-H, $J = 2.22$), 6.65 (d, 4H, Ar-H, $J = 2.23$). ^{13}C-NMR (CDCl$_3$) δ (ppm): 13.7 (CH$_3$), 19.2 (CH$_2$), 31.3 (CH$_2$), 65.2 (CH$_2$-OH), 67.8 (CH$_2$-O), 70.0 (CH$_2$-O), 70.2 (CH$_2$-O), 101.0 (Ar), 102.4 (Ar), 105.8 (Ar), 108.3 (Ar), 138.8 (Ar$_{ipso}$), 139.7 (Ar$_{ipso}$), 160.1 (Ar-O), 160.6 (Ar-O). EM (IE$^+$): 1320 m/z. Calcd. for C: 73.61, H: 8.24%. Found. C: 73.62, H: 8.24%.

To a suspension of LiAlH$_4$ 0.47 g (12 mmol) in 50 ml of THF under nitrogen were added **3** 5 g (18 mmol) in 50 ml of THF. The reaction mixture was continued for 24 h at room temperature. 2 ml of water were added dropwise. The mixture was filtered under zeolite and the residue washed with CH$_2$Cl$_2$. The solvent was evaporated in vacuo and the residue was chromatographed (SiO$_2$; hexane; ethylacetate 80:20).

(3,5-dibutoxyphenyl)methanol 3

4.43 g to yield (98%) of a white powder. UV $CHCl_3$ (nm): 244, 281 IR (cm^{-1}): 3359, 3286, 2965, 2922, 2873, 1455, 1384, 1346. ^{1}H-NMṘ ($CDCl_3$) δ̇ (ppm): 0.96 (t, 6H, CH_3, *J* = 7.50 Hz); 1.47 (m, 4H, CH_2), 1.75 (m, 4H, CH_2), 3.93 (t, 4H, CH_2-O, *J* = 6.60 Hz), 4.60 (s, 2H, CH_2-OH), 6.37 (t, 1H, Ar-H, *J* = 2.40 Hz), 6.49 (d, 2H, Ar-H, *J* = 2.10 Hz). ^{13}C-NMṘ ($CDCl_3$) δ̇ (ppm): 13.8 (CH_3), 19.2 (CH_2), 31.2 (CH_2), 65.3 (CH_2-OH), 67.7 (CH_2-O), 100.5 (Ar), 105.0 (Ar), 143.1 (Ar$_{ipso}$), 160.5 (Ar-OH). EM (IE^{+}): 252 m/z. Calcd. for C: 71.39, H: 9.59%. Found. C: 71.39, H: 9.58%

A mixture (3 mmol) of **3**, **5** or **7**, and (3.5 mmol) of carbon tetrabromide were dissolved in 100 mL of anhydrous THF. This mixture was cooled to 0 °C and immediately, (3.5 mmol) triphenylphosfine were added. The reaction was carried out under nitrogen in an ice bath for 8 h. After this period, the solvent was evaporated and the resulting oil was dry supported and purified in a silica gel column using a mixture of hexane-dichloromethane 2:1 as eluent.

1-(bromomethyl)-3,5-dibutoxybenzene **4.** 4.25 g to yield (85%). UV $CHCl_3$ (nm): 246, 291 IR (cm^{-1}): 3359, 3286, 2965, 2922, 2873, 1455, 1384, 1346, 943. ^{1}H-NMṘ ($CDCl_3$) δ̇ (ppm): 0.97 (t, 6H, CH_3, *J* = 7.32 Hz); 1.48 (m, 4H, CH_2), 1.75 (m, 4H, CH_2), 3.93 (t, 4H, CH_2-O, *J* = 6.45 Hz), 4.40 (s, 2H, CH_2-Br), 6.37 (t, 1H, Ar-H, *J* = 2.04 Hz), 6.51 (d, 2H, Ar-H, *J* = 2.34 Hz). ^{13}C-NMṘ ($CDCl_3$) δ̇ (ppm): 13.8 (CH_3), 19.2 (CH_2), 31.2 (CH_2), 33.7 (CH_2-Br), 67.7 (CH_2-O), 101.4 (Ar), 107.3 (Ar), 139.5 (Ar$_{ipso}$), 160.4 (Ar-O). EM (IE^{+}): 314 m/z. Calcd. for C: 57.15, H: 7.35%. Found. C: 57.15, H: 7.35%.

5,5′-(5-(bromomethyl)-1,3-phenylene)bis(oxy)bis (methylene)bis(1,3-dibutoxybenzene) 6

3.05 g to yield (83%). UV $CHCl_3$ (nm): 284, 244. IR (cm^{-1}): 3359, 3286, 2965, 2922, 2873, 1455, 1384, 1346, 949. ^{1}H-NMṘ ($CDCl_3$) δ̇ (ppm): 0.96 (t, 12H, CH_3, *J* = 7.50 Hz), 1.47 (m, 8H, CH_2), 1.75 (m, 8H, CH_2), 3.94 (t, 8H, CH_2-O, *J* = 6.51 Hz), 4.40 (s, 2H, CH_2-Br), 4.93 (s, 4H, ArCH_2-O), 6.40 (t, 2H, Ar-H, *J* = 2.26 Hz), 6.53 (t, 1H, Ar-H, *J* = 2.25 Hz), 6.54 (d, 4H, Ar-H, *J* = 2.27 Hz), 6.62 (d, 2H, Ar-H, *J* = 2.23 Hz).^{13}C-NMR ($CDCl_3$) δ̇ (ppm): 13.7 (CH_3), 19.2 (CH_2), 31.3 (CH_2), 33.4 (CH_2-Br), 67.8 (CH_2-O), 70.2 (CH_2-O), 101.1 (Ar), 102.4 (Ar), 105.8 (Ar), 108.3 (Ar), 138.8 (Ar$_{ipso}$), 139.7 (Ar$_{ipso}$), 160.1 (Ar-O), 160.6 (Ar-O). EM (IE^{+}): 670 m/z. Calcd. for C: 66.16, H: 7.65%. Found. C: 66.15, H: 7.65%.

5,5′,5″,5″-(5,5′-(5-(bromomethyl)-1,3-phenylene)bis(oxy)bis(methylene)bis(benzene-5,3,1-triyl))tetrakis(oxy)tetrakis(methylene)tetrakis(1,3-dibutoxybenzene) **8**. To yield (5%). UV $CHCl_3$ (nm): 282, 249 IR (cm^{-1}): 3359, 3286, 2965, 2922, 2873, 1455, 1384, 1346, 949. ^{1}H-NMṘ ($CDCl_3$) δ̇ (ppm): 0.96 (t, 24H, CH_3, *J* = 7.32 Hz), 1.47 (m, 16H, CH_2), 1.74 (m, 16H, CH_2), 3.93 (t, 16H, CH_2-O, *J* = 6.50 Hz), 4.41 (s, 2H, CH_2-Br), 4.95 (s, 8H, ArCH_2-O), 4.96 (s, 4H, ArCH_2-O), 6.40 (t, 4H, Ar-H, *J* = 2.25 Hz), 6.47 (t, 1H, Ar-H, *J* = 2.25 Hz), 6.55 (d, 8H, Ar-H, *J* = 2.23 Hz), 6.56 (t, 2H, Ar-H, *J* = 2.33 Hz), 6.62 (d, 2H, Ar-H, *J* = 2.22), 6.66 (d, 4H, Ar-H, *J* = 2.23). EM (IE^{+}): 1382 m/z. Calcd. for C: 70.26, H: 7.79%. Found. C: 70.25, H: 7.78%.

Compound **7** was added to a mixture of pyridine (1.5 ml) and CH_2Cl_2 (150 ml) and cooled at 0°C under nitrogen and vigorously stirred for 20 min. thionyl chloride (20.29 mmol) was added dropwise, the reaction was continued for 4 h at room temperature and the solvent was evaporated in vacuo. The product was washed with a mixture hexane: ethyl acetate, the solvent was evaporated to give 5,5′,5″,5″-(5,5′-(5-(chloromethyl)-1,3-phenylene) bis (oxy)bis (methylene)bis(benzene-5,3,1-triyl))tetrakis(oxy)tetrakis (methylene)tetrakis(1,3-dibutoxybenzene) **8′.** 3.04 g to yield (75%). UV $CHCl_3$ (nm): 282, 249 IR (cm^{-1}): 3359, 3286, 2965, 2922, 2873, 1455, 1384, 1346, 949. ^{1}H-NMṘ ($CDCl_3$) δ̇ (ppm): 0.96 (t, 24H, CH_3, *J* = 7.32 Hz), 1.47 (m, 16H, CH_2), 1.74 (m, 16H, CH_2), 3.93 (t, 16H, CH_2-O, *J* = 6.50 Hz), 4.50 (s, 2H, CH_2-Cl), 4.95 (s, 8H, ArCH_2-O), 4.96 (s, 4H, ArCH_2-O), 6.40 (t, 4H, Ar-H, *J* = 2.25 Hz), 6.50 (t, 1H, Ar-H, *J* = 2.25 Hz), 6.54 (d, 8H, Ar-H, *J* = 2.23 Hz), 6.56 (t, 2H, Ar-H, *J* = 2.33 Hz), 6.61 (d, 2H, Ar-H, *J* = 2.22), 6.66 (d, 4H, Ar-H, *J* = 2.23). ^{13}C-NMR ($CDCl_3$) δ̇ (ppm): 13.8 (CH_3), 19.2 (CH_2), 31.3 (CH_2), 33.4 (CH_2-Cl), 67.7 (CH_2-O), 70.2 (CH_2-O), 100.9 (Ar), 101.7 (Ar), 105.7 (Ar), 106.4 (Ar), 107.7 (Ar), 138.9 (Ar$_{ipso}$), 139.5 (Ar$_{ipso}$), 160.1 (Ar-O), 160.5 (Ar-O).EM (IE^{+}): 1338 m/z. Calcd. for C:72.59, H: 8.05%. Found. C: 72.59, H: 8.04%.

A mixture of 1 mmol of the respective monochloride generation of dendron **4**, **6** or **8′**, potassium carbonate (21.2 mmol) and 18-crown-6 (0.56 g, 2.12 mmol) in dry acetone (80 ml) was heated to reflux and stirred vigorously under nitrogen for 20 min. The porphyrine **11** (0.110 mmol) dissolved in dry acetone (40 ml) was added dropwise and the reaction was continued for 48 h. The mixture was allowed to cool and the precipitate was filtered. The filtrate was evaporated to dryness under reduced pressure. The residue dissolved in diethyl ether was washed with an aqueous solution of 5% Na_2CO_3 (3 times). The organic layer was dried and evaporated to dryness and reprecipitation with dichloromethane–methanol.

Dendrimer 10

195 mg to yield 82%. UV $CHCl_3$ (nm): 423, 483, 518, 554, 595, 652 IR (cm^{-1}): 2955, 2931, 2870, 1599, 1237, 1171. ^{1}H-NMṘ ($CDCl_3$) δ̇ (ppm): -2.75 (s, 2H, N-H), 1.01 (t, 24H, CH_3, *J* = 7.50 Hz), 1.53 (m, 16H, CH_2), 1.82 (m, 16H, CH_2), 4.04 (t, 16H, CH_2-O, *J* = 6.30 Hz),

5.28 (s, 8H, ArCH$_2$-O), 6.50 (t, 4H, Ar-H, *J* = 2.40 Hz), 6.76 (d, 8H, Ar-H, *J* = 2.40 Hz), 7.35 (d, 8H, Ar-H, *J* = 8.40 Hz), 8.12 (d, 8H, Ar-H, *J* = 8.40 Hz), 8.86 (s, 8H, pyrrole-H). ^{13}C-NMR (CDCl$_3$) δ̇ (ppm): 13.8 (CH$_3$), 19.3 (CH$_2$), 31.3 (CH$_2$), 67.8 (CH$_2$-O), 70.4 (ArCH$_2$-O), 101.0 (Ar), 105.9 (Ar), 113.1 (py), 119.7 (Ar$_{ipso}$), 134.9 (Ar), 135.6 (Ar), 139.2 (Ar$_{ipso}$), 158.6 (Ar-O), 160.6 (Ar-O). FAB + : 1614 m/z. Calcd. for C: 77.29, H: 7.36%. Found. 77.28, H: 7.34%.

Dendrimer 11

345 mg to yield 77%. UV CHCl$_3$ (nm): 423, 483, 518, 554, 595, 652. IR (cm^{-1}): 2958, 2933, 2871, 1597, 1458, 1170. ^{1}H-NMṘ (CDCl$_3$) δ̇ (ppm): -2.76 (s, 2H, N-H), 0.97 (t, 48H, CH$_3$, *J* = 7.50 Hz), 1.48 (m, 32H, CH$_2$), 1.76 (m, 32H, CH$_2$), 3.97 (t, 32H, CH$_2$-O, *J* = 6.60 Hz), 5.05 (s, 16H, ArCH$_2$-O), 5.27 (s, 8H, ArCH$_2$-O), 6.43 (t, 8H, Ar-H, *J* = 2.40 Hz), 6.62 (d, 16H, Ar-H, *J* = 2.2 Hz), 6.66 (t, 4H, Ar-H, *J* = 2.40 Hz), 6.88 (d, 8H, Ar-H, *J* = 2.20 Hz), 7.36 (d, 8H, Ar-H, *J* = 8.60 Hz), 8.15 (d, 8H, Ar-H, *J* = 8.60 Hz), 8.88 (s, 8H, pyrrole-H). ^{13}C-NMṘ (CDCl$_3$) δ̇ (ppm): 13.9 (CH$_3$), 19.3 (CH$_2$), 29.7 (CH$_2$), 31.3 (CH$_2$), 67.9 (CH$_2$-O), 70.1 (ArCH$_2$-O), 100.9 (Ar), 101.7 (Ar), 105.6 (Ar), 106.4 (Ar), 113.0 (Ar), 138.8 (Ar$_{ipso}$), 139.9 (Ar$_{ipso}$), 160.1 (Ar-O), 160.6 (Ar-O). Maldi-Tof: 3039 m/z. Calcd. for C: 75.81, H: 7.62%. Found. C: 75.81, H: 7.63%.

Dendrimer 12

556 mg to yield 64%. UV CHCl$_3$ (nm): 423, 483, 518, 554, 595, 652 IR (cm^{-1}): 2958, 2933, 2871, 1597, 1458, 1170. ^{1}H-NMṘ (CDCl$_3$) δ̇ (ppm): -2.75 (s, 2H, N-H), 0.90–0.98 (m, 96H, CH$_3$), 1.38–1.51 (m, 64H, CH$_2$), 1.66–1.77 (m, 64H, CH$_2$), 3.89–3.96 (m, 64H, CH$_2$-O), 4.97 (s, 32H, ArCH$_2$-O), 5.02 (s, 16H, ArCH$_2$-O), 5.28 (s, 8H, ArCH$_2$-O), 6.75–6.40 (m,4H, Ar-H), 6.55–6.61 (m, 16H, Ar-H), 6.66 (d, 8H, Ar-H, *J* = 2.4 Hz), 6.73 (d, 32H, Ar-H, *J* = 2.1 Hz), 6.89 (d, 16H, Ar-H, *J* = 2.1 Hz), 7.37 (d, 8H, Ar-H, *J* = 8.7 Hz), 8.13 (d, 8H, Ar-H, *J* = 8.4 Hz), 8.87 (s, 8H, pyrrole-H). ^{13}C-NMṘ (CDCl$_3$) δ̇ (ppm): 13.8 (CH$_3$), 19.2 (CH$_2$), 31.2 (CH$_2$), 67.7 (CH$_2$-O), 70.0 (ArCH$_2$-O), 100.8 (Ar), 101.6 (Ar), 105.7 (Ar), 106.5 (Ar), 113.0 (py), 135.6 (Ar), 139.0 (Ar$_{ipso}$), 139.4 (Ar$_{ipso}$), 160.2 (Ar-O), 160.5 (Ar-O). Maldi-Tof: 5889 m/z. Calcd. for C: 75.00, H: 7.76%. Found. C: 75.01, H: 7.74%.

Complexes 13 and 14

A solution (50 ml) of **11** or **12** (0.138 mmol) in toluene was added to a toluene solution of C$_{60}$ (0.138 mmol), and the mixture was stirred vigorously at 80 °C for 3.0 days. After this period, the solvent was evaporated to dryness and the solid obtained was carefully washed with small quantities of toluene.

Supramolecular Complex 13

^{1}H-NMṘ (CDCl$_3$) δ̇ (ppm): −2.73 (s, 2H, N-H), 0.96 (t, 48H, CH$_3$, *J* = 7.50 Hz), 1.48 (m, 32H, CH$_2$), 1.76 (m, 32H, CH$_2$), 3.91 (t, 32H, CH$_2$-O, *J* = 6.60 Hz), 5.05 (s, 16H, ArCH$_2$-O), 5.27 (s, 8H, ArCH$_2$-O), 6.44 (t, 8H, Ar-H, *J* = 2.40 Hz), 6.53 (d, 16H, Ar-H, *J* = 2.2 Hz), 6.66 (t, 4H, Ar-H, *J* = 2.4 Hz), 6.88 (d, 8H, Ar-H, *J* = 2.20 Hz), 7.33 (d, 8H, Ar-H, *J* = 8.60 Hz), 8.13 (d, 8H, Ar-H, *J* = 8.60 Hz), 8.88 (s, 8H, pyrrole-H). ^{13}C-NMṘ (CDCl$_3$) δ̇ (ppm): 13.7 (CH$_3$), 19.3 (CH$_2$), 29.7 (CH$_2$), 31.4 (CH$_2$), 67.9 (CH$_2$-O), 70.5 (ArCH$_2$-O), 101.3 (Ar), 102.1 (Ar), 105.6 (Ar), 106.0 (Ar), 106.9 (Ar), 113.0 (Ar$_{ipso}$), 113.3 (Py), 119.7 (Ar), 131.0 (pho), 135.2 (Ar$_{ipso}$), 135.6 (Ar), 139.2 (Ar$_{ipso}$), 139. 6 (C$_{60}$), 158.8 (Ar-O), 160.5 (Ar-O), 160.7 (Ar-O). ^{1}H-NMṘ (Toluene-d$_8$) δ̇ (ppm): −2.12 (s, 2H, N-H), 0.84 (t, 48H, CH$_3$, *J* = 7.40 Hz), 1.36 (m, 32H, CH$_2$), 1.59 (m, 32, CH$_2$), 3.69 (t, 32H, CH$_2$-O), 4.89 (t, 16H, ArCH$_2$-O, *J* = 11.7 Hz), 4.93 (s, 8H, ArCH$_2$-O), 6.54 (t, 8H, Ar-H, *J* = 1.9 Hz), 6.72 (d, 16H, Ar-H, *J* = 2.4 Hz), 6.82 (br, 4H, Ar-H), 6.97 (s, 16H, Ar-H), 7.20 (d, 8H, Ar-H, *J* = 8.7 Hz), 8.06 (d, 8H, Ar-H, *J* = 8.4 Hz), 9.02 (s, 8H, pyrrole-H). ^{13}C-NMR (Toluene-D$_8$) δ̇ (ppm): 13.9 (CH$_3$), 19.6 (CH$_2$), 31.7 (CH$_2$), 67.7 (CH$_2$-O), 70.4 (ArCH$_2$-O), 101.3 (Ar), 102.2 (Ar), 106.0 (Ar), 107.0 (Ar), 113.5 (py), 136.0 (Ar), 137.4 (Ar), 139.8 (Ar$_{ipso}$), 140.17 (C$_{60}$), 161.0 Ar-O), 161.2 (Ar-O). $C_{252}H_{230}N_4O_{28}$; Calcd. for C: 80.44, H: 6.16%. Found. C: 80.44, H: 6.15%.

Supramolecular Complex 14

^{1}H-NMṘ (CDCl$_3$) δ̇ (ppm): −2.74 (s, 2H, N-H), 0.91–0.99 (m, 96H, CH$_3$), 1.39–1.51 (m, 64H, CH$_2$), 1.67–1.76 (m, 64H, CH$_2$), 3.89–3.98 (m, 64H, CH$_2$-O), 4.98 (s, 32H, ArCH$_2$-O), 5.08 (s, 16H, ArCH$_2$-O), 5.28 (s, 8H, ArCH$_2$-O), 6.40 (br, 4H, Ar-H), 6.56–6.99 (br, 16H, Ar-H), 6.74 (br, 8H, Ar-H), 6.90 (d, 32H, Ar-H, *J* = 2.1 Hz), 6.97 (d, 16H, Ar-H), 7.23 (d, 8H, Ar-H, *J* = 8.4 Hz), 8.13 (d, 8H, Ar-H, *J* = 8.4 Hz), 8.88 (s, 8H, pyrrole-H). ^{13}C-NMṘ (CDCl$_3$) δ̇ (ppm): 13.7 (CH$_3$), 19.2 (CH$_2$), 31.4 (CH$_2$), 67.9 (CH$_2$-O), 70.1 (ArCH$_2$-O), 70.4 (ArCH$_2$-O), 101.3 (Ar), 101.7 (Ar), 102.0 (Ar), 105.5 (Ar), 106.0 (Ar), 106.8 (Ar), 106.9 (Ar), 113.0 (Ar), 113.3 (py), 119,7 (Ar), 131.0 (Ar), 135.2 (Ar), 135.6 (Ar), 139.2(Ar$_{ipso}$), 139.4 (Ar$_{ipso}$), 139.6 (C$_{60}$), 158.8 (Ar-O), 160.4 Ar-O), 160.7 (Ar-O). ^{1}H-NMṘ (Toluene-d$_8$) δ̇ (ppm): -2.14 (s, 2H, N-H), 0.83 (t, 96H, CH$_3$, *J* = 7.40 Hz), 1.29–1.36 (m, 64H, CH$_2$), 1.50–1.57 (m, 64H, CH$_2$), 3.62–3.68 (m, 64H, CH$_2$-O), 4.83 (s, 32H, ArCH$_2$-O), 4.87 (s, 16H, ArCH$_2$-O), 4.99 (s, 8H, ArCH$_2$-O), 6.49 (s, 4H, Ar-H), 6.66 (s, 16H, Ar-H), 6.75 (m, 4H, Ar-H), 6.85 (s, 4H, Ar-H), 6.97 (s, 32H, Ar-H), 7.01 (s, 8H, Ar-H), 7.09 (s, 16H, Ar-H), 7.26 (d, 8H, Ar-H, *J* = 9.0 Hz), 8.11 (d, 8H, Ar-H, *J* = 7.8 Hz), 9.03 (s, 8H, pyrrole-H). ^{13}C-NMR (Toluene-D$_8$) δ̇ (ppm): 13.9 (CH$_3$), 19.2 (CH$_2$), 31.7 (CH$_2$), 67.6 (CH$_2$-O), 70.3 (ArCH$_2$-O), 101.3 (Ar), 102.1 (Ar), 106.0 (Ar), 106.8 (Ar), 106.9 (Ar), 119,7 (Ar), 137.4 (Ar), 139.7 (Ar_{ipso}), 140.12 (C_{60}), 160.9 (Ar-O), 161.1 (Ar-O). $C_{428}H_{454}N_4O_{60}$; Calcd. for C: 77.72, H: 6.92%. Found. C: 77.75, H: 6.92%.

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