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Towards supramolecular nanostructured materials: Control of the self-assembly of ionic bent-core amphiphiles

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1.- Materials and General Techniques.

All chemical reagents were purschased from Aldrich and used as received. PPI-$(NH_2)_4$ (G1) and PPI-$(NH_2)_8$ (G2) were purchased from SyMO-Chem BV (Eindhoven, the Netherlands). Solvents were purified and rigorously dried over appropriate drying agents and distilled prior to use. All atmosphere-sensitive reactions were carried out under dry argon using standard Schlenk techniques. Analytical TLC was performed on 60F 254, 60A-15 mm silica gel polyester plates (SDS). Column chromatography was carried out under flash conditions using 60 Å silica gel (SDS). Silica gel type 7749 (with gypsum, Merck) was used for centrifugal force mediated preparative thin layer chromatography in conjunction with a Chromatotron form Harrison Research Europe model 8924.

All the compounds were characterized by ^{1}H-NMR, ^{13}C-NMR and FTIR. MALDI-MS experiments were performed for all the carboxylic acids to further confirm the correct synthesis of the compounds. Elemental analysis was performed to determine the purity of all the carboxylic acids prior to the preparation of the ionic dendrimers. ^{1}H-NMR spectra were recorded on spectrometers operating at 300.13 (Bruker ARX-300), 400.13 (Bruker AV-400) or 500.13 (Bruker AV-500) MHz, whereas ^{13}C-NMR spectra were recorded at 75.47, 100.5 and 125.7 MHz, respectively. Chemical shifts are given in ppm relative to TMS. NMR experiments in solution were recorded using standard pulse sequences on Bruker spectrometers. FT-IR spectra were performed in a THERMONICOLET Avatar 360 and a Bruker Tensor II using either KBr pellets or neat samples on NaCl. Elemental analyses were performed on a Perkin-Elmer 240 Analyzer. Mass spectrometry studies (MALDI+) were performed with a VG AutoSpec EBE and a Microflex (MALDI-ToF).

The mesophase identification was based on microscopic examination of the textures formed by samples between two glass plates. NIKON and OLYMPUS BH-2 polarizing microscopes equipped with a LINKAM THMS600 hot stage were used. The temperatures and enthalpies of the phase transitions were determined by calorimetric measurements performed with DSC TA Instrument Q-20 and Q-2000 systems. Thermogravimetric analysis (TGA) was performed using a TA Q5000IR instrument at a heating rate of 10 ^{0}C / min under a nitrogen atmosphere. Molecular dimensions were estimated by molecular modeling (ChemSketch3D). The X-ray investigations on non-oriented samples were carried out in Lindemann capillary tubes (diameter: 0.9 or 1 mm) using a PINHOLE (ANTON-PAAR) film camera.

TEM images were recorded in a TECNAI G^2 20 (FEI COMPANY) microscope using a work voltage of 200 kV (Advanced Microscopy Laboratory, Instituto de Nanociencia de Aragón and Servicio de Apoyo a la Investigación, Universidad de Zaragoza).

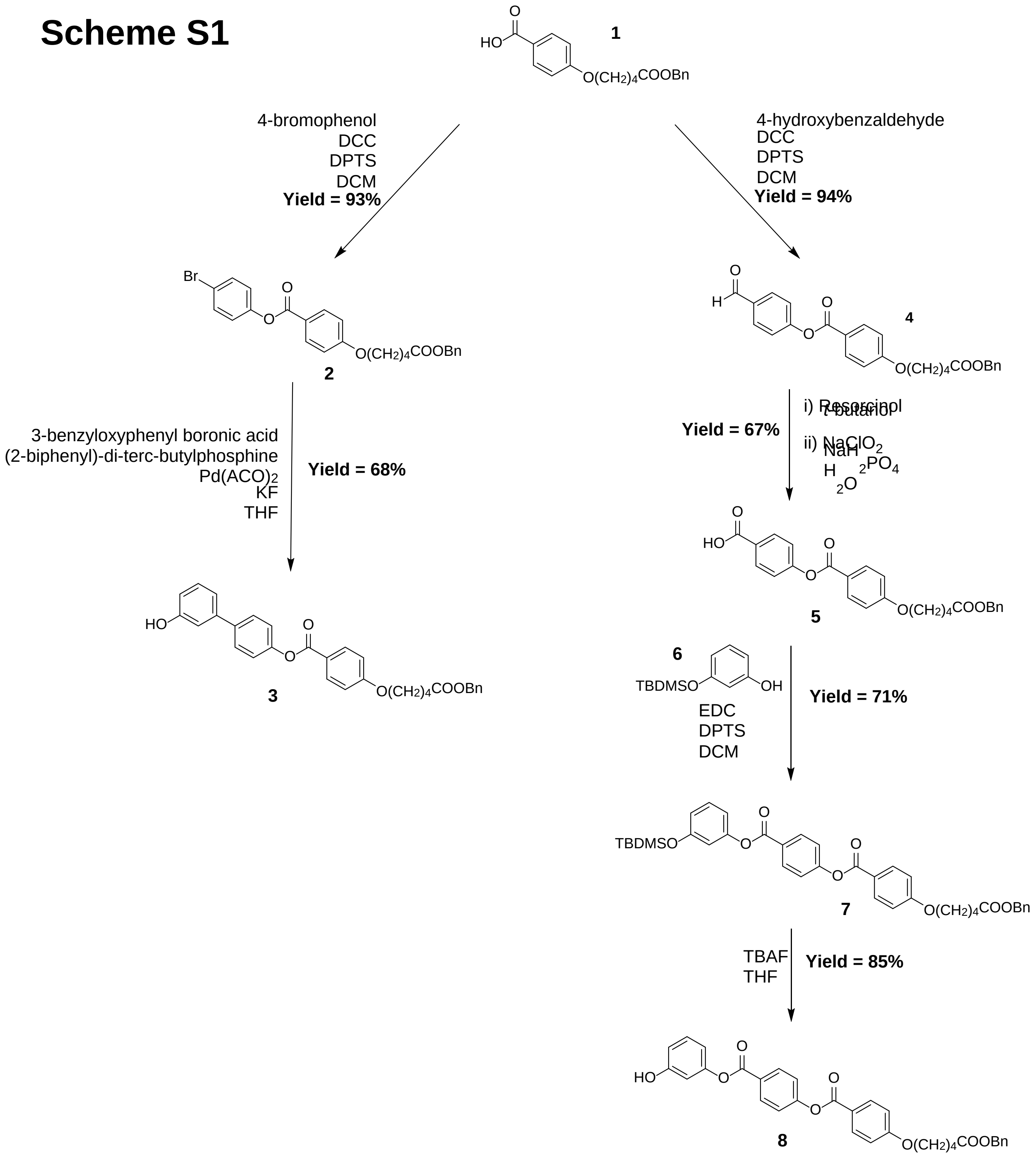
2.- Synthesis of the ionic dendrimers.

The synthesis of the new ionic dendrimers was carried out following the synthetic routes shown in Schemes S1-S7.

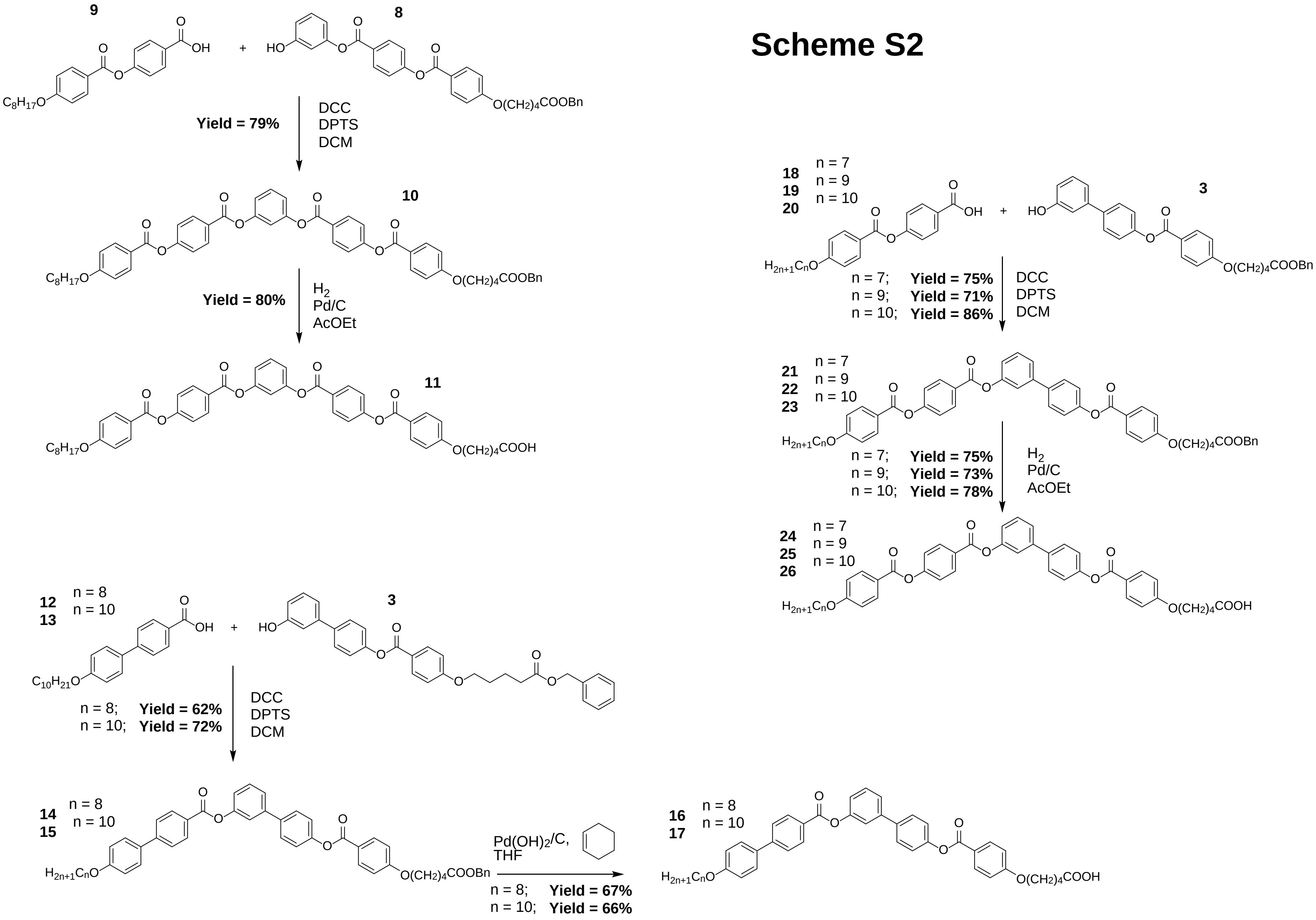
The ionic dendrimers **PPI1-B1-4-8, PPI2-B1-4-8** and **PPI2-B1-10-14** have been reported previously by us.[1,2]

Synthetic methods used in the synthesis of the rest of the intermediate compounds and their characterization data are given below. All the new ionic dendrimers were prepared following synthetic methodologies reported by us.[1,2]

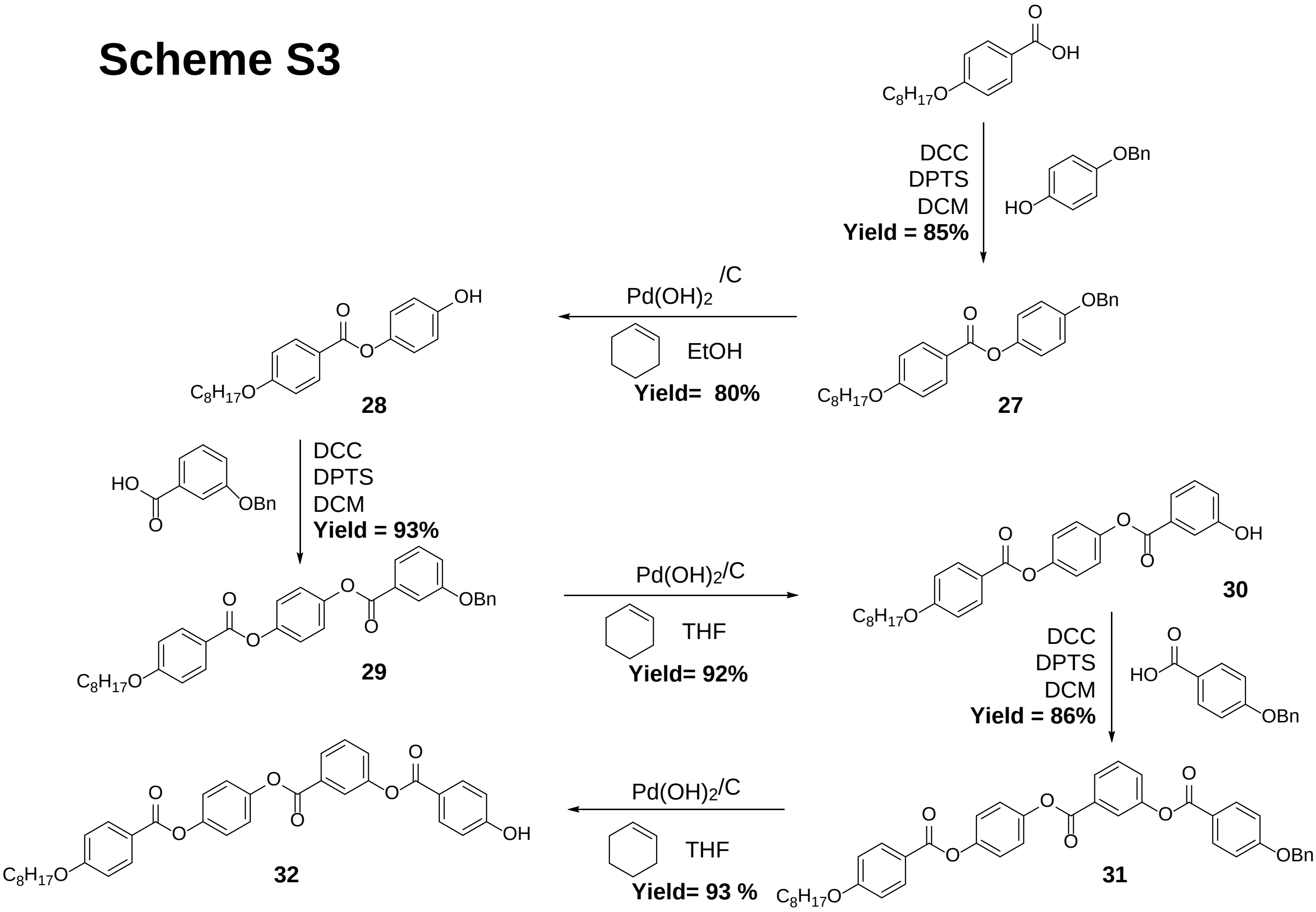
Scheme S1


1
HO
O
O(CH2)4COOBn
4-bromophenol
DCC
DPTS
DCM
Yield = 93%
4-hydroxybenzaldehyde
DCC
DPTS
DCM
Yield = 94%
Br
O
O
O(CH2)4COOBn
2
H
O
O
O
4
O(CH2)4COOBn
3-benzyloxyphenyl boronic acid
(2-biphenyl)-di-terc-butylphosphine
Pd(ACO)2
KF
THF
Yield = 68%
Yield = 67%
i) Resorcinol
t-butanol
ii) NaClO2
NaH2PO4
H2O
HO
O
O
O
5
O(CH2)4COOBn
HO
O
O
3
O(CH2)4COOBn
6
TBDMSO
OH
EDC
DPTS
DCM
Yield = 71%
TBDMSO
O
O
O
O
7
O(CH2)4COOBn
TBAF
THF
Yield = 85%
HO
O
O
O
O
8
O(CH2)4COOBn

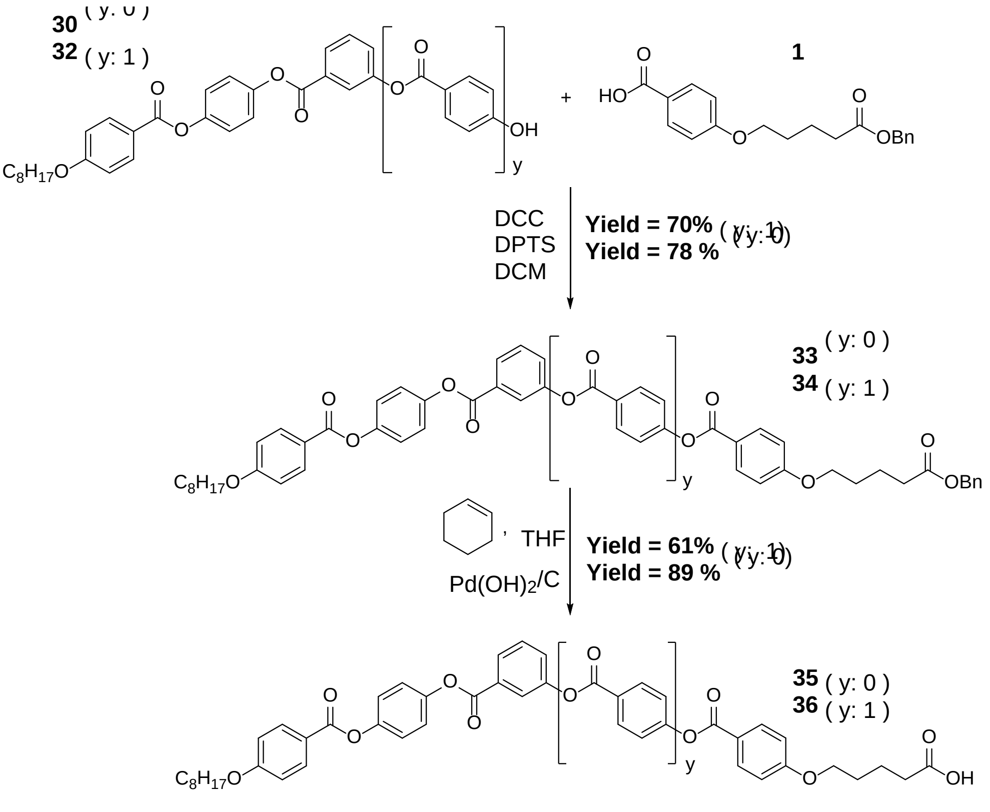
Scheme S2

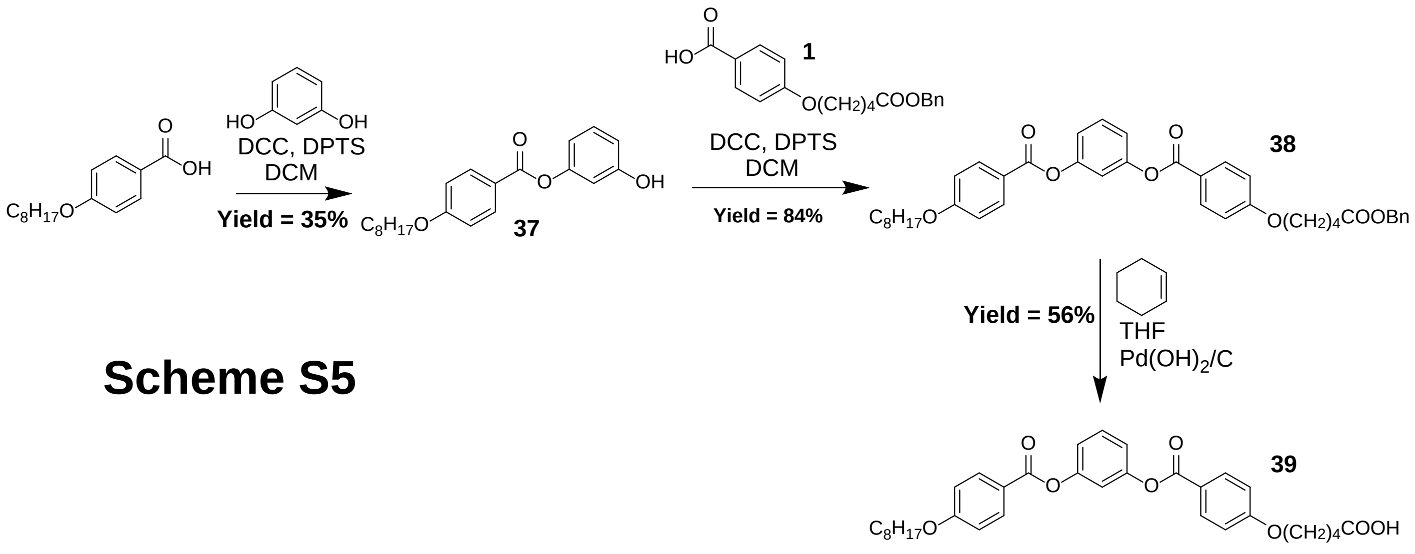

9
8
C8H17O
OH
HO
O(CH2)4COOBn
+
Yield = 79%
DCC
DPTS
DCM
10
C8H17O
O(CH2)4COOBn
Yield = 80%
H2
Pd/C
AcOEt
11
C8H17O
O(CH2)4COOH
12 n = 8
13 n = 10
C10H21O
OH
+
HO
3
n = 8; Yield = 62%
n = 10; Yield = 72%
DCC
DPTS
DCM
14 n = 8
15 n = 10
H2n+1CnO
O(CH2)4COOBn
Pd(OH)2/C,
THF
n = 8; Yield = 67%
n = 10; Yield = 66%
16 n = 8
17 n = 10
H2n+1CnO
O(CH2)4COOH
18 n = 7
19 n = 9
20 n = 10
H2n+1CnO
OH
+
HO
3
O(CH2)4COOBn
n = 7; Yield = 75%
n = 9; Yield = 71%
n = 10; Yield = 86%
DCC
DPTS
DCM
21 n = 7
22 n = 9
23 n = 10
H2n+1CnO
O(CH2)4COOBn
n = 7; Yield = 75%
n = 9; Yield = 73%
n = 10; Yield = 78%
H2
Pd/C
AcOEt
24 n = 7
25 n = 9
26 n = 10
H2n+1CnO
O(CH2)4COOH

Scheme S3

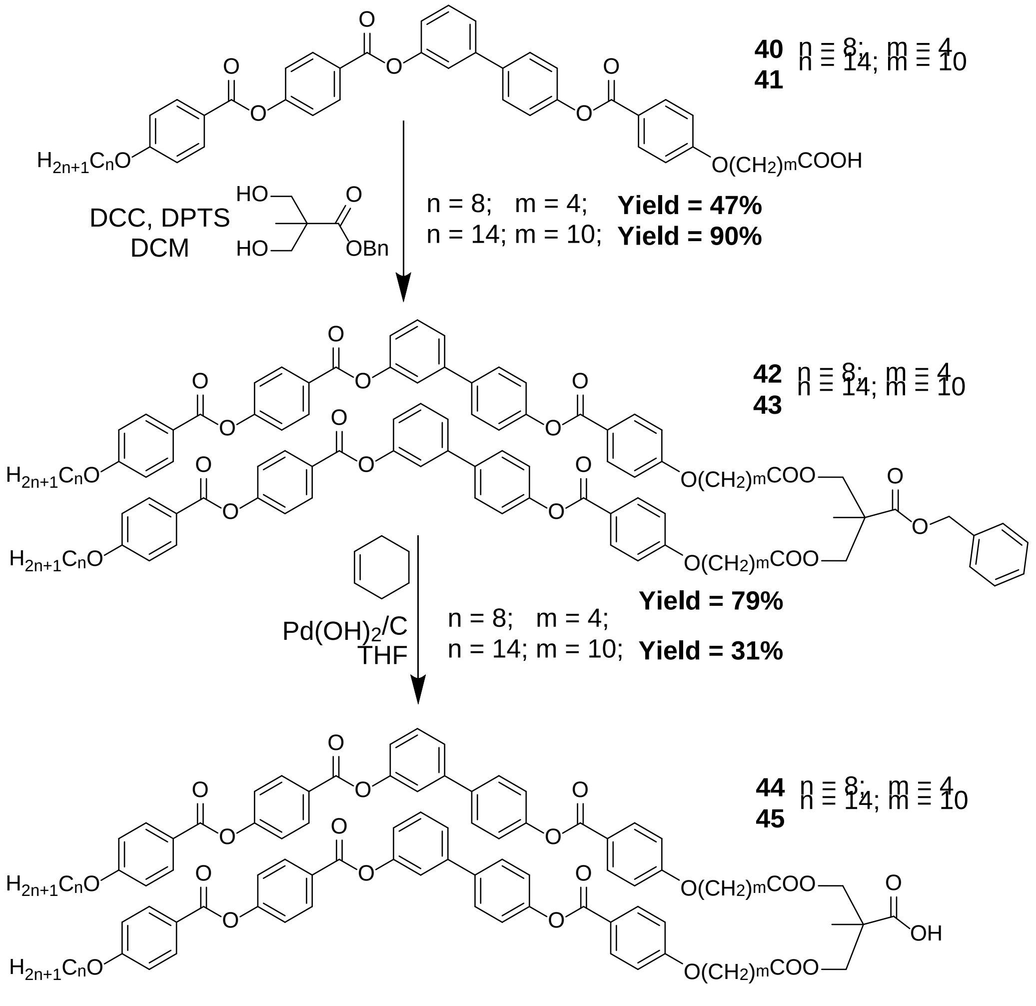


Scheme S4





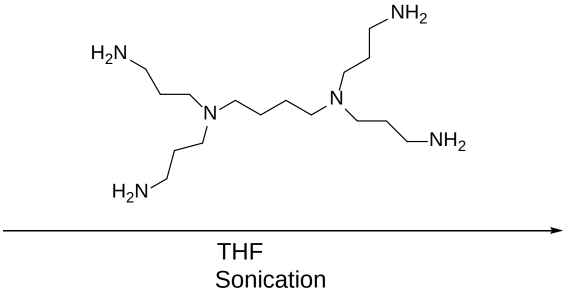
Scheme S5



Scheme S6

Scheme S7

11, 16, 17, 24, 25, 26, 35, 36, 39, 44 or **45**



PPI1-D1B1-4-8
PPI1-D1B1-10-14
PPI1-B1-4-7
PPI1-B1-4-9
PPI1-B1-4-10
PPI1-Bi-4-8
PPI1-Bi-4-10
PPI1-Bz1-4-8
PPI1-Bz-4-8
PPI1-Ph-4-8
PPI1-Ph1-4-8

Compound 2. Compound **1** (7.20 g, 21.94 mmol), 4-bromophenol (3.80 g, 21.94 mmol) and DPTS (1.90 g, 6.58 mmol) were dissolved in 25 mL of dry CH_2Cl_2 under argon atmosphere and the solution was cooled down to 0°C. DCC (6.80 g, 32.91 mmol) was slowly added and the solution was heated up to room temperature and made to react for 24 h. Then, the crude was filtered, and the solvent was evaporated. The resulting solid was purified by column chromatography (silica gel, eluent CH_2Cl_2/hexane 7/3) to obtain a white powder. Yield: 93%.
^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 1.84-1.91 (m, 4H), 2.45-.2.50 (m, 2H), 4.04-4.07 (m, 2H), 5.14 (s, 2H), 6.93-6.97 (m, 2H), 7.07-7.13 (m, 2H), 7.30-7.41 (m, 5H), 7.50-7.56 (m, 2H), 8.09-8.14 (m, 2H). **^{13}C RMN (100 MHz, CDCl$_3$):** δ (ppm) = 21.7, 28.6, 34.0, 66.4, 67.8, 114.5, 118.9, 121.4, 123.8, 128.4, 128.5, 128.7, 132.5, 132.6, 136.1, 150.2, 163.6, 164.7, 173.3. **FTIR (KBr, v: cm^{-1})**: 3090, 3066, 3037, 2926, 2873, 1731, 1605, 1512, 1483, 1257, 1196.

Compound 3. Compound **2** (3 g, 6.21 mmol), 3-hydroxyphenylboronic acid (1.28 g, 9.31 mmol), potassium fluoride (1.80 g, 31.05 mmol), (2-biphenyl)-di-tert-butyl phosphine (185 mg, 0.62 mmol) and palladium (II) acetate (112 mg, 0.50 mmol) were dissolved in 40 mL of dry THF in a Schlenk tube. The mixture was made to react under inert atmosphere for 72 h. The crude was filtered through Celite© and the solvent was evaporated. The product was purified by column chromatography (silica gel, eluent $CHCl_2$/hexane 1/1 to CH_2Cl_2) and recrystallized from ethanol to give a pure white powder.

^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 1.81-1.90 (m, 4H), 2.47 (t, *J* = 6.8 Hz, 2H), 4.07 (t, *J* = 6.8 Hz, 2H), 5.12 (s, 2H), 5.28 (bs, 1H), 6.80-6.86 (m, 1H), 6.96-7.02 (m, 2H), 7.06-7.09 (m, 1H), 7.16-7.20 (m, 2H), 7.25-7.29 (m, 2H), 7.29-7.39 (6H), 7.60-7.66 (2H), 8.11-8.17 (m, 2H). **^{13}C RMN (100 MHz, CDCl$_3$):** δ (ppm) = 21.7, 28.6, 34.0, 66.5, 67.8, 114.2, 114.4, 114.5, 119.7, 121.7, 122.2, 128.3, 128.4, 128.5, 128.7, 130.1, 132.5, 136.1, 138.5, 142.3, 150.7, 156.1, 163.5, 173.4. **FTIR (KBr, v: cm^{-1})**: 3438, 3063, 3037, 2957, 2938, 1729, 1708, 1604, 1495, 1256, 1173.

Compound 4. Compound **1** (3.60 g, 10.97 mmol), 4-hydroxybenzaldehyde (1.34 g, 10.97 mmol) and DPTS (968 mg, 3.29 mmol) were dissolved in 17 mL of dry CH_2Cl_2 under argon atmosphere and the solution was cooled down to 0°C. DCC (3.39 g, 16.46 mmol) was slowly added and the solution was heated up to room temperature and made to react for 24 h. Then, the crude was filtered, and the solvent was evaporated. The resulting solid was purified by column chromatography (silica gel, eluent CH_2Cl_2/hexane 4/6 to CH_2Cl_2) and recrystallized from ethanol to obtain a white powder. Yield: 94%. **^{1}H NMR (400 MHz, CDCl$_3$):** δ (ppm) = 1.84-1.90 (m, 4H), 2.45-.2.50 (m, 2H), 4.03-4.09 (m, 2H), 5.13 (s, 2H), 6.95-6.98 (m, 2H), 7.31-7.38 (m, 5H), 7.38-7.42 (m, 2H), 7.95-7.98 (m, 2H), 8.12-8.16 (m, 2H). **^{13}C RMN (100 MHz, $CDCl_3$):** δ (ppm) = 21.7, 28.6, 34.0, 66.4, 67.9, 114.6, 121.2, 122.7, 128.4, 128.5, 128.7, 131.4, 132.6, 134.1, 136.1, 156.0, 163.8, 164.3, 173.3, 191.1. **FTIR (KBr, ν: cm^{-1})**: 3070, 3028, 2950, 2879, 1723, 1695, 1596, 1511, 1259, 1202.

Compound 5. Compound **4** (4.40 g, 10.17 mmol) and resorcinol (1.79 g, 16.27 mmol) were dissolved in 150 mL of *tert*-BuOH at 35°C. A solution of $NaClO_2$ (6.05 g, 64.07 mmol) and NaH_2PO_4 (4.88 g, 40.68 mmol) in 75 mL of distilled water was slowly added to the mixture and it was stirred for 72 h. Then, the solvent was evaporated and the solid was redispersed in distilled water and a HCl 2M solution was added until pH=1 was reached. The precipitate was filtered, washed with water and recrystallized from ethanol. Yield: 66%.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.85-1.91 (m, 4H), 2.45-2.50 (m, 2H), 4.03-4.10 (m, 2H), 5.14 (s, 2H), 6.93-6.9 (m, 2H), 7.30-7.35 (m, 2H), 7.31-7.40 (m, 5H), 8.11-8.16 (m, 2H), 8.17-8.22 (m, 2H). **^{13}C RMN (100 MHz, $CDCl_3$):** δ (ppm) = 21.7, 28.6, 34.0, 66.5, 67.9, 114.5, 121.3, 122.2, 126.7, 128.4, 128.5, 128.7, 132.0, 132.6, 136.1, 155.6, 163.7, 164.4, 170.3, 173.3. **FTIR (KBr, ν: cm^{-1})**: 2952, 1734, 1689, 1599, 1506, 1422, 1251, 1207.

Compound 6. Resorcinol (1 g, 9.08 mmol) was dissolved in 5 mL of dry DMF at 0°C under Ar amtosphere. Then, imidazole (1.23 g, 18.16 mmol) was added. Finally, a solution of *tert*-butyltrimethylsilyl chloride (685 mg, 4.54 mmol) dissolved in 5 mL of dry DMF was added to the mixture. The crude was made to react for 1 h. Then, 20 mL of distilled water were added and the mixture was extracted with hexane/AcOEt 1/1 (3x 20 mL). The organic phase was washed with distilled water (2x 25 mL), dried with $MgSO_4$ anhydrous and evaporated. The solid residue was purified by column chromatography (silica gel, eluent hexane/CH_2Cl_2 4/6 to hexane/CH_2Cl_2 2/8) to obtain a yellow oil. Yield: 60%.

^{1}H RMN (400 MHz, $CDCl_3$): δ (ppm) = 0.19 (s, 6H), 0.98 (s, 9H), 4.63 (bs, 1H), 6.35 (t, *J* = 2.2 Hz, 1H), 6.41-6.45 (m, 2H), 7.07 (t, *J* = 8.0 Hz, 1H). **^{13}C RMN (100 MHz, $CDCl_3$):** δ (ppm) = 4.3, 18.3, 25.8, 107.7, 108.6, 112.9, 130.1, 156.6, 157.1. **FTIR (KBr, ν: cm^{-1})**: 3600-3100, 2929, 2858, 1592, 1472, 1294.

Compound 7. Compound **5** (630 mg, 1.40 mmol), compound **6** (314 mg, 1.40 mmol) and DPTS (123 mg, 0.42 mmol) were dissolved in 15 mL of dry CH_2Cl_2 under argon atmosphere and the solution was cooled down to 0°C. EDC (405 mg, 2.11 mmol) was slowly added and the solution was heated up to room temperature and made to react for 24 h. Then, the crude was washed with water (3x 20 mL) and brine (2x 20mL), dried with $MgSO_4$ anhydrous and evaporated. The solid residue was purified by column chromatography (silica gel, eluent CH_2Cl_2/hexane 7/3) to obtain a white powder. Yield: 71%.

^{1}H RMN (400 MHz, $CDCl_3$): δ (ppm) = 0.23 (s, 6H), 0.99 (s, 9H), 1.83-1.91 (m, 4H), 2.44-2.52 (m, 2H), 4.03-4.11 (m, 2H), 5.14 (s, 2H), 6.72-6.79 (m, 2H), 6.82-6.85 (m, 1H), 6.95-6.99 (m, 2H), 7.25-7.29 (m, 1H), 7.32-7.40 (m, 7H), 8.12-8.17 (m, 2H), 8.25-8.29 (m, 2H). **^{13}C RMN (100 MHz, $CDCl_3$):** δ (ppm) = 4.3, 18.3, 21.7, 25.8, 28.6, 34.0, 66.4, 67.9, 114.0, 114.5, 114.7, 117.8, 121.3, 122.2, 127.1, 128.4, 128.5, 128.7, 129.8, 131.9, 132.6, 136.1, 151.8, 155.4, 156.7, 163.7, 164.4, 173.3. **FTIR (KBr, ν: cm^{-1})**: 3066, 2958, 2925, 2857, 1735, 1605, 1511, 1258, 1205.

Compound 8. Compound 7 (630 mg, 0.96 mmol) was dissolved in 350 mL of a mixture of THF/MeOH 1/1. Potassium fluoride (150 mg, 2.58 mmol) was slowly added and the solution was made to react at room temperature for 40 minutes. The reaction was quenched by water addition (100 mL) and the crude was concentrated at the rotavapor. The aqueous suspension was extracted with CH_2Cl_2 (4x 75 mL) and then the organic phase was washed with water (3x 75 mL), dried with $MgSO_4$ anhydrous and evaporated. The solid residue was purified by column chromatography (silica gel, eluent from CH_2Cl_2 to CH_2Cl_2/ethyl acetate 95/5) to obtain a white powder. Yield: 85%.

^{1}H RMN (400 MHz, $CDCl_3$): δ (ppm) = 1.84-1.91 (m, 4H), 2.45-2.50 (m, 2H), 4.03-4.10 (m, 2H), 5.14 (s, 2H), 6.71-6.77 (m, 2H), 6.79-6.82 (m, 1H), 6.95-6.99 (m, 2H), 7.26-7.30 (m, 1H), 7.32-7.40 (m, 7H), 8.13-8.17 (m, 2H), 8.25-8.28 (m, 2H). **^{13}C RMN (100 MHz, $CDCl_3$):** δ (ppm) = 21.7, 28.6, 34.0, 66.5, 67.9, 109.5, 113.4, 114.0, 114.6, 121.2, 122.3, 127.0, 128.4, 128.5, 128.7, 130.3, 132.0, 132.6, 136.0, 151.9, 155.5, 156.8, 163.7, 164.5, 164.6, 173.4. **FTIR (KBr, ν: cm^{-1})**: 3500-3200, 3054, 2956, 1737, 1725, 1704, 1604, 1511, 1455, 1265.

Compound 10. Compound **8** (1 g, 1.85 mmol), compound **9** (685 mg, 1.85 mmol) and DPTS (163 mg, 0.56 mmol) were dissolved in 15 mL of dry CH_2Cl_2 under argon atmosphere and the solution was cooled down to 0°C. DCC (572 mg, 2.77 mmol) was slowly added and the solution was heated up to room temperature and made to react for 16 h. Then, the crude was filtered, and the solvent was evaporated. The resulting solid was purified by column chromatography (silica gel, eluent CH_2Cl_2 to CH_2Cl_2/AcOEt 9/1) and recrystallized from ethanol to obtain a white powder. Yield: 79%.

^{1}H RMN (400 MHz, $CDCl_3$): δ (ppm) = 0.90 (t, *J* = 6.8 Hz, 3H), 1.27-1.41 (m, 8H), 1.43-1.53 (m, 2H), 1.79-1.91 (m, 6H), 2.44-2.50 (m, 2H), 4.01-4.11 (m, 4H), 5.14 (s, 2H), 6.93-7.02 (m, 4H), 7.15-7.22 (m, 3H), 7.30-7.41 (m, 9H), 7.50 (t, *J* = 8.2 Hz, 1H), 8.12-8.17 (m, 4H), 8.26-8.30 (m, 4H). **^{13}C RMN (100 MHz, $CDCl_3$):** δ (ppm) = 14.3, 21.7, 22.8, 26.1, 28.6, 29.2, 29.4, 29.5, 31.9, 34.0, 66.4, 67.9, 68.5, 114.5, 114.6, 116.0, 119.4, 121.1, 121.3, 122.3, 128.4, 128.5, 128.7, 132.0, 132.6, 132.7, 136.1, 151.6, 155.6, 155.7, 163.7, 164.0, 164.2, 164.4, 164.5, 173.3. **FTIR (KBr, ν: cm^{-1})**: 3065, 2922, 2854, 1732, 1603, 1511, 1275.

Compound 11. Compound **10** (340 mg, 0.38 mmol) was dissolved in 25 mL of AcOEt. Three cycles of vacuum/Ar were made and Pd/C 10% wt (40 mg) was added. Again, three cycles of vacuum/Ar were made, followed by three cycles of vacuum/H_2. The mixture was made to react under H_2 atmosphere for 16 h. Then, the crude was redisolved in CH_2Cl_2, filtered through Celite© and the solvent was evaporated. The product was recrystallized from ethanol to obtain a white powder. Yield: 80%.

M.p. (°C) Cr_1 131 I 129 M 100 Cr_2 **1H RMN (400 MHz, $CDCl_3$):** δ (ppm) = 0.90 (t, *J* = 6.8 Hz, 3H), 1.27-1.42 (m, 8H), 1.43-1.52 (m, 2H), 1.79-1.93 (m, 6H), 2.48 (t, *J* = 6.8 Hz, 2H), 4.01-4.12 (m, 4H), 6.94-7.03 (m, 4H), 7.16-7.23 (m, 3H), 7.34-7.42 (m, 4H), 7.50 (t, *J* = 8.2 Hz, 1H), 8.12-8.20 (m, 4H), 8.24-8.32 (m, 4H). **^{13}C RMN (100 MHz, $CDCl_3$):** δ (ppm) = 14.2, 21.5, 22.8, 26.1, 28.6, 29.2, 29.4, 29.5, 31.9, 33.5, 67.8, 68.5, 114.5, 114.6, 116.0, 119.4, 121.1, 121.3, 122.3, 122.4, 126.8, 126.9, 130.0, 132.0, 132.6, 132.7, 151.6, 155.6, 155.7, 163.7, 164.0, 164.2, 164.3, 164.4, 164.5, 178.4. **FTIR (KBr, ν: cm^{-1})**: 3081, 3068, 2919, 2857, 1736, 1604, 1512, 1475, 1413, 1256, 1202. **MALDI-MS (ditranol/TFANa):** m/z 825.2 [M+Na]$^+$. **Elemental Analysis:** Calcd. for $C_{47}H_{46}O_{12}$: C 70.31, H 5.78; found C 70.46, H 5.93.

Compound 14. Compound **12** (300 mg, 0.92 mmol), compound **3** (447 mg, 0.92 mmol) and DPTS (81 mg, 0.28 mmol) were dissolved in 20 mL of dry CH_2Cl_2 under argon atmosphere and the solution was cooled down to 0°C. DCC (285 mg, 1.38 mmol) was slowly added and the solution was heated up to room temperature and made to react for 24 h. Then, the crude was filtered, and the solvent was evaporated. The resulting solid was purified by column chromatography (silica gel, eluent CH_2Cl_2/hexane 8/2) and recrystallized from ethanol to obtain a white powder. Yield: 62%.

^{1}H RMN (400 MHz, CD_2Cl_2): δ (ppm) = 0.90 (t, *J* = 6.8 Hz, 3H), 1.26-1.42 (m, 8H), 1.44-1.53 (m, 2H), 1.75-1.91 (m, 6H), 2.47 (t, *J* = 6.8 Hz, 2H), 4.02 (t, *J* = 6.4 Hz, 2H), 4.08 (t, *J* = 6.0 Hz, 2H), 5.11 (s, 2H), 6.95-7.05 (m, 4H), 7.25 (dt, J_1 = 6.8 Hz, J_2 = 2.4 Hz, 1H), 7.28-7.32 (m, 2H), 7.31-7.39 (m, 5H), 7.48-7.51 (m, 1H), 7.52-7.58 (m, 2H), 7.62-7.66 (m, 2H), 7.67-7.71 (m, 2H), 7.73-7.77 (m, 2H), 8.12-8.17 (m, 2H), 8.24-8.28 (m, 2H). **^{13}C RMN (100 MHz, CD_2Cl_2):** δ (ppm) = 14.4, 22.1, 23.2, 26.6, 29.1, 29.8, 29.9, 32.4, 34.3, 66.6, 68.4, 68.8, 114.9, 115.5, 121.0, 121.3, 122.2, 122.8, 125.1, 127.1, 128.1, 128.7, 128.9, 129.1, 130.4, 131.2, 132.3, 132.7, 136.9, 138.2, 142.5, 146.5, 151.6, 152.2, 160.3, 164.0, 165.3, 165.6, 173.5. **FTIR (KBr, ν: cm^{-1})**: 3064, 3034, 2921, 2853, 1730, 1604, 1256.

Compound 15. Compound **13** (108 mg, 0.30 mmol), compound **3** (151 mg, 0.30 mmol) and DPTS (26 mg, 0.09 mmol) were dissolved in 10 mL of dry CH_2Cl_2 under argon atmosphere and the solution was cooled down to 0°C. DCC (93 mg, 0.45 mmol) was slowly added and the solution was heated up to room temperature and made to react for 24 h. Then, the crude was filtered, and the solvent was evaporated. The resulting solid was purified by column chromatography (silica gel, eluent CH_2Cl_2/hexane 8/2) and recrystallized from ethanol to obtain a white powder. Yield: 72%. **^{1}H RMN (400 MHz, $CDCl_3$):** δ (ppm) = 0.89 (t, J=6,8Hz, 3H), 1.21-1.53 (m, 14H), 1.78-1.93 (m, 6H), 2.45-2.50 (m, 2H), 4.01-4.09 (m, 4H), 5.14 (s, 2H), 6.94-6.99 (m, 2H), 6.99-7.04 (m, 2H), 7.21-7.25 (m, 1H), 7.27-7.32 (m, 2H), 7.32-7.41 (m, 5H), 7.45-7.48 (m, 1H), 7.50-7.54 (m, 2H), 7.59-7.63 (m, 2H), 7.64-7.68 (m, 2H), 7.69-7.74 (m, 2H), 8.11-8.21 (m, 2H), 8.24-8.29 (m, 2H). **^{13}C RMN (100 MHz, $CDCl_3$):** δ (ppm) = 14.3, 21.7, 22.8, 26.2, 28.6, 29.4, 29.5, 29.6, 29.7, 29.7, 32.0, 34.0, 66.4, 67.8, 68.3, 114.4, 115.1, 120.6, 120.8, 121.8, 122.3, 124.8, 126.8, 126.8, 127.6, 128.4, 128.4, 128.5, 128.7, 130.0, 130.9, 132.1, 132.5, 136.1, 138.0, 142.3, 146.2, 151.0, 151.6, 159.7, 163.5, 165.1, 1165.3, 173.3. **FTIR (KBr, ν: cm^{-1})**: 3065, 3033, 2955, 2920, 2851, 1730, 1603, 1580, 1497, 1474, 1454, 1257, 1209, 1199.

Compound 16. Compound **14** (1.10 g, 1.37 mmol) and cyclohexene (18 mL) were dissolved in 30 mL of a THF. Then, $Pd(OH)_2/C$ 20% (110mg) was added and the reaction mixture was heated under reflux for 24 hours. The crude was filtered and the solvent was evaporated. The resulting solid was recrystallized from ethanol. Yield: 67%.

M.p. (°C) Cr 154 I.

^{1}**H-NMR (400 MHz, DMSO-d6, 373 K) δ (ppm)**: 0.89 (t, *J*= 7.2 Hz, 3H), 1.26-1.42 (m, 8H), 1.43-1.51 (m, 2H), 1.68-1.86 (m, 6H), 2.31 (t, *J*=7.2 Hz, 2H), 4.07 (t, *J* = 7.6 Hz, 2H), 4.15 (t, *J* = 6.4 Hz, 2H), 7.02-7.10 (m, 2H), 7.09-7.13 (m, 2H), 7.29-7.31 (m, 2H), 7.35-7.29 (m, 2H), 7.58 (t, *J*=8.4 Hz, 1H), 7.61-7.66 (m, 2H), 7.69-7.72 (m, 2H), 7.77-7.81 (m, 2H), 7.82-7.89 (m, 2H), 8.07-8.12 (m, 2H), 8.19-8.23 (m, 2H). ^{13}**C-NMR (100 MHz, DMSO-d6, 373 K) δ (ppm)**: 13.1, 20.7, 21.4, 25.0, 27.6, 28.0, 28.1, 28.2, 30.6, 32.9, 67.5, 67.6, 114.4, 114.9, 119.4, 120.2, 120.8, 121.7, 126.3, 125.9, 126.8, 127.4, 127.7, 129.5, 129.9, 130.6, 131.4, 136.3, 140.6, 144.8, 150.3, 151.0, 159.0, 162.9, 163.6, 164.0, 173.4. **FTIR (KBr, ν: cm^{-1})**: 2920, 2849, 1734, 1697, 1604, 1514, 1498, 1474, 1196, 1162, 1084. **MALDI-MS (ditranol/TFANa):** m/z 737.3 [M+Na]$^+$. **Elemental Analysis:** Calcd. for $C_{45}H_{46}O_8$: C 75.61, H 6.49; found C 75.73, H 6.35.

Compound 17. Compound **15** (110 mg g, 0.132 mmol) and 10 mL of cyclohexene were dissolved in 20 mL of THF under an Ar atmosphere. $Pd(OH)_2/C$ (20%) (11 mg) was added and the reaction mixture was stirred under reflux for 8 h and then cooled to room temperature. The reaction mixture was filtered and the solvent was evaporated. The product was purified by recrystallization in ethanol to give a white powder. Yield: 66%.

M.p. (°C) Cr 150 I 149 M 106 Cr. ^{1}**H RMN (400MHz, CDCl$_3$):** δ (ppm)= 0.89 (t, *J* = 7.0 Hz, 3H), 1.23-1.53 (m, 14H), 1.78-1.96 (m, 6H), 2.48 (t, *J* = 6.9 Hz, 2H), 4.02 (t, *J* = 6.6 Hz, 2H), 4.06-4.10 (m, 2H), 6.95-7.04 (m, 4H), 7.21-7.25 (m, 1H), 7.27-7.32 (m, 2H), 7.45-7.48 (m, 1H), 7.49-7.53 (m, 2H), 7.58-7.63 (m, 2H), 7.63-7.68 (m, 2H), 7.68-7.72 (m, 2H), 8.14-8.19 (m, 2H), 8.24-8.29 (m, 2H). ^{13}**C RMN (100MHz, CDCl$_3$):** δ (ppm)= 14.3, 21.5, 22.8, 26.2, 28.6, 29.5, 29.6, 29.7, 29.7, 32.1, 33.4, 67.8, 68.3, 114.4, 115.1, 120.6, 120.8, 121.8, 122.3, 124.7, 126.8, 127.6, 128.4, 128.5, 130.0, 130.9, 132.1, 132.5, 138.0, 142.3, 146.2, 150.9, 151.6, 159.7, 163.4, 165.0, 165.3, 177.9. **FTIR (KBr, ν: cm^{-1})**: 3250-2500, 3050, 2919, 2849, 1733, 1696, 1604, 1515, 1497, 1257, 1196, 1163. **MALDI-MS (ditranol/TFANa):** m/z 765.3 [M+Na]$^+$. **Elemental Analysis:** Calcd. for $C_{47}H_{50}O_8$: C 75.99, H 6.78; found C 75.55, H 6.50.

Compound 21. Compound **18** (86 mg, 0.24 mmol), compound **3** (120 mg, 0.24 mmol) and DPTS (21 mg, 0.07 mmol) were dissolved in 5 mL of dry CH_2Cl_2 under argon atmosphere and the solution was cooled down to 0°C. DCC (74 mg, 0.36 mmol) was slowly added and the solution was heated up to room temperature and made to react for 16 h. Then, the crude was filtered, and the solvent was evaporated. The resulting solid was purified by column chromatography (silica gel, eluent CH_2Cl_2) and recrystallized from ethanol to obtain a white powder. Yield: 75%.

^{1}**H RMN (400 MHz, CD$_2$Cl$_2$):** δ (ppm) = 0.91 (t, *J* = 6.8 Hz, 3H), 1.29-1.42 (m, 6H), 1.43-1.53 (m, 2H), 1.78-1.91 (m, 6H), 2.47 (t, *J* = 6.8 Hz, 2H), 4.03-4.12 (m, 4H), 5.12 (s, 2H), 6.97-7.05 (m, 4H), 7.22-7.27 (m, 1H), 7.27-7.33 (m, 2H), 7.29-7.42 (m, 5H), 7.38-7.42 (m, 2H), 7.47-7.51 (m, 1H), 7.51-7.59 (m, 2H), 7.66-7.71 (m, 2H), 8.11-8.19 (m, 4H), 8.26-8.33 (m, 2H). ^{13}**C RMN (100 MHz, CD$_2$Cl$_2$):** δ (ppm) = 14.4, 22.1, 23.2, 26.5, 29.1, 29.6, 29.7, 32.4, 34.4, 66.6, 68.4, 69.1, 114.9, 115.0, 121.0, 122.8, 122.9, 125.2, 128.6, 128.7, 128.8, 129.1, 130.4, 132.2, 132.7, 132.9, 136.9, 138.2, 142.6, 151.6, 152.1, 156.1, 164.1, 164.5, 164.8, 165.0, 165.4, 173.6. **FTIR (KBr, ν: cm^{-1})**: 3068, 2921, 2855, 1733, 1603, 1509, 1256, 1202.

Compound 22. Compound **19** (92 mg, 0.24 mmol), compound **3** (120 mg, 0.24 mmol) and DPTS (21 mg, 0.07 mmol) were dissolved in 5 mL of dry CH_2Cl_2 under argon atmosphere and the solution was cooled down to 0°C. DCC (74 mg, 0.36 mmol) was slowly added and the solution was heated up to room temperature and made to react for 24 h. Then, the crude was filtered, and the solvent was evaporated. The resulting solid was purified by column chromatography (silica gel, eluent CH_2Cl_2) and recrystallized from ethanol to obtain a white powder. Yield: 71%.

^{1}H RMN (400 MHz, CD_2Cl_2): δ (ppm) = 0.91 (t, *J* = 6.8 Hz, 3H), 1.24-1.42 (m, 10H), 1.43-1.53 (m, 2H), 1.78-1.91 (m, 6H), 2.47 (t, *J* = 6.8 Hz, 2H), 4.03-4.12 (m, 4H), 5.12 (s, 2H), 6.97-7.05 (m, 4H), 7.22-7.27 (m, 1H), 7.27-7.33 (m, 2H), 7.29-7.42 (m, 5H), 7.38-7.42 (m, 2H), 7.47-7.51 (m, 1H), 7.51-7.59 (m, 2H), 7.66-7.71 (m, 2H), 8.11-8.19 (m, 4H), 8.26-8.33 (m, 2H). **^{13}C RMN (100 MHz, CD_2Cl_2):** δ (ppm) = 14.4, 22.1, 23.3, 26.5, 29.1, 29.7, 29.8, 29.9, 30.1, 32.5, 34.4, 66.6, 68.4, 69.1, 114.9, 115.0, 121.0, 122.8, 122.9, 125.2, 128.6, 128.7, 128.8, 129.1, 130.4, 132.2, 132.7, 132.9, 136.9, 138.2, 142.6, 151.6, 152.1, 156.1, 164.1, 164.5, 164.8, 165.0, 165.4, 173.6. **FTIR (KBr, ν: cm^{-1})**: 3066, 2921, 2855, 1727, 1604, 1509, 1256, 1201.

Compound 23. Compound **20** (170 mg, 0.43 mmol), compound **3** (213 mg, 0.43 mmol) and DPTS (38 mg, 0.13 mmol) were dissolved in 5 mL of dry CH_2Cl_2 under argon atmosphere and the solution was cooled down to 0°C. DCC (132 mg, 0.64 mmol) was slowly added and the solution was heated up to 40^{o}C and made to react for 48 h. Then, the crude was filtered, and the solvent was evaporated. The resulting solid was purified by column chromatography (silica gel, eluent CH_2Cl_2) and recrystallized from ethanol to obtain a white powder. Yield: 86%.

^{1}H RMN (400 MHz, $CDCl_3$): δ (ppm) = 0.89 (t, *J* = 6.8 Hz, 3H), 1.23-1.41 (m, 12H), 1.43-1.53 (m, 2H), 1.78-1.91 (m, 6H), 2.44-2.52 (m, 2H), 4.02-4.10 (m, 4H), 5.14 (s, 2H), 6.93-7.02 (m, 4H), 7.20-7.25 (m, 1H), 7.27-7.32 (m, 2H), 7.30-7.42 (m, 5H), 7.38-7.42 (m, 2H), 7.44-7.47 (m, 1H), 7.49-7.54 (m, 2H), 7.63-7.69 (m, 2H), 8.12-8.19 (m, 4H), 8.29-8.34 (m, 2H). **^{13}C RMN (100 MHz, $CDCl_3$):** δ (ppm) = 14.3, 21.7, 22.8, 26.1, 28.7, 29.2, 29.5, 29.6, 29.7, 29.8, 32.0, 34.0, 66.4, 67.8, 68.6, 114.4, 114.6, 120.6, 121.1, 121.8, 122.3, 122.4, 124.8, 127.0, 128.3, 128.4, 128.5, 128.7, 130.0, 132.0, 132.5, 132.6, 136.1, 137.9, 142.3, 151.0, 151.5, 155.6, 163.5, 164.0, 164.5, 164.6, 165.0, 173.3. **FTIR (KBr, ν: cm^{-1})**: 3067, 2921, 2852, 1730, 1603, 1510, 1255, 1203.

Compound 24. Compound **21** (120 mg, 0.14 mmol) was dissolved in 10 mL of AcOEt. Three cycles of vacuum/Ar were made and Pd/C 10% wt (15 mg) was added. Again, three cycles of vacuum/Ar were made, followed by three cycles of vacuum/H_2. The mixture was made to react under H_2 atmosphere for 16 h. Then, the crude was redisolved in CH_2Cl_2, filtered through Celite© and the solvent was evaporated. The product was recrystallized from ethanol to obtain a white powder. Yield: 75%.

M.p. (°C) Cr 152 I **^{1}H RMN (400 MHz, CD_2Cl_2):** δ (ppm) = 0.91 (t, *J* = 6.8 Hz, 3H), 1.27-1.42 (m, 6H), 1.43-1.53 (m, 2H), 1.77-1.95 (m, 6H), 2.47 (t, *J* = 6.8 Hz, 2H), 4.02-4.14 (m, 4H), 6.96-7.06 (m, 4H), 7.22-7.27 (m, 1H), 7.28-7.34 (m, 2H), 7.38-7.42 (m, 2H), 7.47-7.51 (m, 1H), 7.51-7.60 (m, 2H), 7.65-7.73 (m, 2H), 8.11-8.19 (m, 4H), 8.27-8.33 (m, 2H). **^{13}C RMN (100 MHz, CD_2Cl_2):** δ (ppm) = 14.4, 21.9, 23.2, 26.5, 29.0, 29.6, 29.7, 32.4, 33.8, 68.4, 69.1, 114.9, 115.0, 121.0, 121.3, 121.6, 122.2, 122.8, 122.9, 125.2, 127.5, 128.7, 130.4, 132.2, 132.8, 132.9, 138.2, 142.6, 151.6, 152.1, 156.1, 164.0, 164.5, 164.8, 165.0, 165.4, 177.9. **FTIR (KBr, ν: cm^{-1})**: 2923, 2856, 1733, 1695, 1605, 1513, 1476, 1414, 1255, 1201. **MALDI-MS (ditranol/TFANa):** m/z 767.1 [M+Na]$^+$. **Elemental Analysis:** Calcd. for $C_{45}H_{44}O_{10}$: C 72.57, H 5.95; found C 72.22, H 5.60.

Compound 25. Compound **22** (120 mg, 0.14 mmol) was dissolved in 10 mL of AcOEt. Three cycles of vacuum/Ar were made and Pd/C 10% wt (15 mg) was added. Again, three cycles of vacuum/Ar were made, followed by three cycles of vacuum/H_2. The mixture was made to react under H_2 atmosphere for 16 h. Then, the crude was redisolved in THF, filtered through Celite© and the solvent was evaporated. The product was recrystallized from ethanol to obtain a white powder. Yield: 73%.

M.p. (°C) Cr 147 I **^{1}H RMN (400 MHz, CD_2Cl_2):** δ (ppm) = 0.91 (t, *J* = 6.8 Hz, 3H), 1.24-1.42 (m, 10H), 1.43-1.53 (m, 2H), 1.77-1.95 (m, 6H), 2.47 (t, *J* = 6.8 Hz, 2H), 4.02-4.14 (m, 4H), 6.96-7.06 (m, 4H), 7.22-7.27 (m, 1H), 7.28-7.34 (m, 2H), 7.38-7.42 (m, 2H), 7.47-7.51 (m, 1H), 7.51-7.60 (m, 2H), 7.65-7.73 (m, 2H), 8.11-8.19 (m, 4H), 8.27-8.33 (m, 2H). **^{13}C RMN (100 MHz, CD_2Cl_2):** δ (ppm) = 14.5, 21.9, 23.3, 26.5, 29.0, 29.7, 29.8, 29.9, 30.1, 32.5, 33.7, 68.4, 69.1, 114.9, 115.0, 121.0, 121.3, 121.6, 122.2, 122.8, 122.9, 125.2, 127.5, 128.7, 130.4, 132.2, 132.8, 132.9, 138.2, 142.6, 151.6, 152.1, 156.1, 164.0, 164.5, 164.8, 165.0, 165.4, 177.7. **FTIR (KBr, ν: cm^{-1})**: 2958, 2918, 2850, 1726, 1698, 1604, 1514, 1475, 1415, 1255, 1202. **MALDI-MS (ditranol/TFANa):** m/z 795.3 [M+Na]$^+$. **Elemental Analysis:** Calcd. for $C_{47}H_{48}O_{10}$: C 73.04, H 6.26; found C 73.31, H 6.37.

Compound 26. Compound **23** (250 mg, 0.29 mmol) was dissolved in 20 mL of THF. Three cycles of vacuum/Ar were made and Pd/C 10% wt (25 mg) was added. Again, three cycles of vacuum/Ar were made, followed by three cycles of vacuum/H_2. The mixture was made to react under H_2 atmosphere for 24 h. Then, the crude was filtered through Celite© and the solvent was evaporated. The product was recrystallized from ethanol to obtain a white powder. Yield: 78%.

M.p. (°C) Cr 145 I **^{1}H RMN (400 MHz, $CDCl_3$):** δ (ppm) = 0.89 (t, *J* = 6.8 Hz, 3H), 1.20-1.43 (m, 12H), 1.44-1.53 (m, 2H), 1.77-1.96 (m, 6H), 2.48 (t, *J* = 6.8 Hz, 2H), 4.01-4.12 (m, 4H), 6.94-7.02 (m, 4H), 7.20-7.25 (m, 1H), 7.26-7.31 (m, 2H), 7.36-7.41 (m, 2H), 7.44-7.47 (m, 1H), 7.49-7.54 (m, 2H), 7.62-7.68 (m, 2H), 8.13-8.20 (m, 4H), 8.28-8.33 (m, 2H). **^{13}C RMN (100 MHz, $CDCl_3$):** δ (ppm) = 14.3, 21.5, 22.8, 26.1, 28.6, 29.2, 29.5, 29.6, 29.7, 29.8, 32.0, 33.5, 67.8, 68.6, 114.4, 114.6, 120.6, 120.7, 121.1, 121.9, 122.3, 122.4, 124.8, 127.0, 128.4, 130.0, 132.0, 132.5, 132.6, 137.9, 142.3, 151.0, 151.5, 155.6, 163.4, 164.0, 164.5, 164.6, 165.0, 178.1. **FTIR (KBr, ν: cm^{-1})**: 3073, 2910, 2852, 1724, 1695, 1606, 1510, 1474, 1245. **MALDI-MS (ditranol/TFANa):** m/z 809.3 [M+Na]$^+$. **Elemental Analysis:** Calcd. for $C_{48}H_{50}O_{10}$: C 73.26, H 6.40; found C 73.34, H 6.45.

Compound 27. 4-n-octyloxybenzoic acid (5.50 g, 22 mmol), 4-benzyloxy phenol (4.50 g, 22 mmol) and DPTS (2.0 g, 6.8 mmol) were dissolved in 150 mL of dry CH_2Cl_2 under argon atmosphere and the solution was cooled down to 0°C. DCC DCC (5.4 g, 26 mmol) was slowly added and the solution was heated up to room temperature and made to react for 24 h. Then, the crude was filtered, and the solvent was evaporated. The resulting solid was recrystallized from ethanol to obtain a white powder. Yield: 85%.

M.p (°C) Cr 94 SmC 99 I. **^{1}H RMN (400 MHz, $CDCl_3$):** δ, ppm = 0.92 (t, *J* = 6.8 Hz, 3H), 1.23-1.52 (m, 10H), 1.82 (q, *J*= 6.8 Hz, 2H), 4.04 (t, *J*= 6.8 Hz, 2H), 5.08 (s, 2H), 6.95-6.98 (m, 2H), 6.99-7.03 (m, 2H), 7.10-7.14 (m, 2H), 7.31-7.36 (m, 1H), 7.37-7.42(m, 2H), 7.43-7.45 (m, 2H), 8.11-8.15 (m, 2H). **^{13}C RMN (100 MHz, $CDCl_3$):** δ, ppm = 14.2, 22.8, 26.1, 29.3, 29.4, 29.5, 31.9, 68.5, 70.6, 114.4, 115.7, 121.8, 122.7, 127.6, 128.2, 128.8, 132.4, 137.1, 144.9, 156.6, 163.6, 165.4. **FTIR (KBr, ν: cm^{-1}):** 2921, 2851, 1728, 1605, 1510, 1468, 1253, 1218, 1193.

Compound 28. Compound **27** (7.8 g, 18 mmol) and 70 mL of cyclohexene were dissolved in 125 mL of ethanol. $Pd(OH)_2/C$ (20%) (800 mg) was added and the reaction mixture was stirred and heated under reflux for 8 h and then cooled to room temperature. The reaction mixture was filtered and the solvent was evaporated. The product was recrystallized from ethanol to obtain a white powder. Yield: 80%

M.p (°C) Cr 109 I (I 90 N 85 Cr). **^{1}H RMN (400 MHz, $CDCl_3$):** δ, ppm = 0.90 (t, *J* = 6,8 Hz, 3H), 1.26-1.51 (m, 10H), 1.82 (q, *J* = 6.8 Hz, 2H), 4.04 (t, *J* = 6.8 Hz, 2H), 5.53 (s, 1H), 6.77-6.80 (m, 2H), 6.95-6.98 (m, 2H), 7.03-7.02(m,2H), 8.12-8.14 (m, 2H). **^{13}C RMN (100 MHz, $CDCl_3$):** δ, ppm = 14.2, 22.8, 26.1, 29.2, 29.4, 29.5, 31.9, 68.5, 114.4, 116.3, 121.6, 122.7, 132.4, 144.5, 153.6, 163.7, 166.0. **FTIR (KBr, ν: cm^{-1}):** 3467, 2952, 2921, 2851, 1711, 1606, 1512, 1471, 1287, 1256, 1209.

Compound 29. Compound **28** (4.7 g, 14 mmol), 3-benzyloxybenzoic acid (3.2 g, 14 mmol) and DPTS (1.4 g, 4.7 mmol) were dissolved in 150 mL of dry CH_2Cl_2 under argon atmosphere and the solution was cooled down to 0°C. DCC (4.5 g, 22 mmol) was slowly added and the solution was heated up to room temperature and made to react for 24 h. Then, the crude was filtered, and the solvent was evaporated. The resulting solid was recrystallized from ethyl acetate to obtain a white powder. Yield: 93%.

M.p 132 °C. **^{1}H RMN (400 MHz, $CDCl_3$):** δ, ppm = 0.90 (t, *J* = 7.0 Hz, 3H), 1.24-1.52 (m, 10H), 1.83 (q, *J* = 7.0 Hz, 2H), 4.05 (t, *J*= 6.8 Hz, 2H), 5.16 (s, 2H), 6.96-7.00 (m, 2H), 7.24-7.30 (m, 5H), 7.33-7.37 (m, 1H), 7.39- 7.48 (m, 5H), 7.81-7.84 (m, 2H), 8.13-8.17 (m, 2H). **^{13}C RMN (100 MHz, $CDCl_3$):** δ, ppm = 14.3, 22.8, 26.1, 29.2, 29.4, 29.5, 32.0, 68.5, 70.4, 114.5, 115.8, 121.1, 121.5, 122.7, 122.9, 123.0, 127.7, 128.3, 128.8, 129.8, 130.9, 132.4, 136.6, 148.4, 148.7, 159.0, 163.8, 165.0, 165.0. **FTIR (KBr, ν: cm^{-1}):** 2911, 2851, 1728, 1609, 1513, 1505, 1267, 1183, 1168.

Compound 30. Compound **29** (6.6 g, 12 mmol) and 50 mL of cyclohexene were dissolved in 100 mL of ethanol. $Pd(OH)_2/C$ (20%) (700 mg) was added and the reaction mixture was stirred and heated under reflux for 8 h and then cooled to room temperature. The reaction mixture was filtered and the solvent was evaporated. The product was recrystallized from ethyl acetate to obtain a white powder. Yield: 92%

M.p (°C) Cr 126 N 136 I. **^{1}H RMN (400 MHz, $CDCl_3$):** δ, ppm = 0.90 (t, *J* = 6.8Hz, 3H), 1.24-1.53 (m, 10H), 1.83 (q, *J* = 7.0 Hz, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 5.70 (s, 1H), 6.96-7.00 (m, 2H), 7.10 (ddd, J_1 = 8.2 Hz, J_2 = 2.6 Hz, J_3 = 1.0 Hz, 1H), 7.23-7.28 (m, 4H), 7.37 (dd, J_1 = 8.0 Hz, J_2 = 8.0 Hz, 1H), 7.65 (dd, J_1 = 2.4 Hz, J_2 = 1.6 Hz, 1H), 7.77 (ddd, J_1 = 7.6Hz, J_2 = 1.2 Hz, J_3 = 1.2 Hz, 1H), 8.13-8.17 (m, 2H). **^{13}C RMN (100 MHz, $CDCl_3$):** δ, ppm = 14.2, 22.8, 26.1, 29.2, 29.4, 29.5, 31.9, 68.5, 114.5, 116.9, 121.1, 121.4, 122.7, 122.7, 122.9, 130.0, 130.8, 132.5, 148.4, 148.7, 156.1, 163.8, 165.1, 165.2. **FTIR (KBr, ν: cm^{-1}):** 3459, 2952, 2918, 2851, 1728, 1713, 1704, 1606, 1512, 1449, 1290, 1255, 1170.

Compound 31. Compound **30** (2.2 g, 4.8 mmol), 4-benzyloxybenzoic acid (1.1 g, 4.8 mmol) and DPTS (0.5 g, 1.7 mmol) were dissolved in 150 mL of dry CH_2Cl_2 under argon atmosphere and the solution was cooled down to 0°C. DCC DCC (1.6 g, 7.7 mmol) was slowly added and the solution was heated up to room temperature and made to react for 24 h. Then, the crude was filtered, and the solvent was evaporated. The resulting solid was recrystallized from ethyl acetate to obtain a white powder. Yield: 86%.

M.p. (°C) Cr 140 I. **^{1}H RMN (400 MHz, $CDCl_3$):** δ, ppm = 0.90 (t, J=7,0 Hz, 3H), 1.25-1.53 (m, 10H), 1.83 (q, *J* = 7.0 Hz, 2H), 4.05 (t, *J*= 6.8 Hz, 2H), 5.18 (s, 2H), 6.96-7.00 (m, 2H), 7.06-7.10 (m, 2H), 7.26-7.32 (m, 4H), 7.33-7.38 (m, 1H), 7.39-7.48 (m, 4H), 7.51 (ddd, J_1=8,0 Hz, J_2=2,4 Hz, J_3=1,2 Hz, 1H), 7.58 (dd, J_1 = 8,0 Hz, J_2 = 8,0 Hz, 1H), 8.04 (dd, J_1 = 2.0 Hz, J_2 = 2.0 Hz, 1H), 8.10-8.21 (m, 5H). **^{13}C RMN (100 MHz, $CDCl_3$):** δ, ppm = 14.3, 22.8, 26.1, 29.2, 29.4, 29.5, 29.9, 32.0, 68.5, 70.4, 114.5, 115.0, 121.5, 121.7, 122.7, 122.9, 123.8, 127.5, 127.6, 127.7, 128.4, 128.9, 129.8, 131.1, 132.5, 132.6, 136.2, 148.3, 148.8, 151.3, 163.4, 163.8, 164.4, 164.8, 164.9. **FTIR (KBr, ν: cm^{-1}):** 2939, 2916, 2856, 1744, 1720, 1610, 1514, 1505, 1254, 1184, 1165.

Compound 32. Compound **31** (2.5 g, 3.7 mmol) and 50 mL of cyclohexene were dissolved in 100 mL of THF. $Pd(OH)_2/C$ (20%) (300 mg) was added and the reaction mixture was stirred and heated under reflux for 8 h and then cooled to room temperature. The reaction mixture was filtered and the solvent was evaporated. The product was recrystallized from ethanol to obtain a white powder. Yield: 93%

M.p. (°C) Cr 191 I. **^{1}H RMN (400 MHz, $CDCl_3$):** δ, ppm = 0.90 (t, *J* = 6.8 Hz, 3H), 1.22-1.53 (m, 10H), 1.83 (q, *J*= 6.8 Hz, 2H), 4.05 (t, *J*= 6.8 Hz, 2H), 6.01 (s, 1H), 6.88-6.92 (m, 2H), 6.96-7.00 (m, 2H), 7.27-7.31 (m, 4H), 7.50 (ddd, J_1 = 8.0 Hz, J_2 = 2.4 Hz, J_3 = 1.2 Hz, 1H), 7.58 (dd, J_1 = 8.0 Hz, J_2 = 8.0 Hz, 1H), 8.04 (dd, J_1 = 2.0 Hz, J_2 = 2.0 Hz, 1H), 8.09-8.18 (m, 5H). **^{13}C RMN (100 MHz, $CDCl_3$):** δ, ppm =14.2, 22.8, 26.1, 29.2, 29.4, 29.5, 31.9, 68.5, 114.5, 115.7, 121.4, 121.5, 122.7, 122.9, 123.8, 127.5, 127.7, 129.9, 131.0, 132.5, 132.8, 148.3, 148.8, 151.3, 160.9, 163.8, 164.5, 164.9, 165.2. **FTIR (KBr, ν: cm^{-1}):** 3366, 2924, 2853, 1729, 1700, 1608, 1591, 1511, 1259, 1185, 1165.

Compound 33. Compound **30** (1.8 g, 3.1 mmol), compound **1** (1.0 g, 3.1 mmol) and DPTS (0.4 g, 1.4 mmol) were dissolved in 100 mL of dry CH_2Cl_2 under argon atmosphere and the solution was cooled down to 0°C. DCC DCC (1.1 g, 5.3 mmol) was slowly added and the solution was heated up to room temperature and made to react for 24 h. Then, the crude was filtered, and the solvent was evaporated. The resulting solid was recrystallized from ethyl acetate to obtain a white powder. Yield: 70%.

^{1}H RMN (400 MHz, $CDCl_3$): δ, ppm = 0.90 (t, *J* = 6.8 Hz, 3H), 1.23-1.54 (m, 10H), 1.79-1.91 (m, 6H), 2.48 (t, *J* = 7.0 Hz, 2H), 4.01-4.10 (m, 4H), 5.14 (s, 2H), 6.96-7.01 (m, 4H), 7.27-7.30 (m, 4H), 7.32-7.42 (m, 7H), 7.53 (ddd, J_1 = 8.0 Hz, J_2 = 2.4 Hz, J_3 = 1.2 Hz, 1H), 7.61 (dd, J_1 = 8.0 Hz, J_2 = 8.0 Hz, 1H), 8.08 (dd, J_1 = 2.0 Hz, J_2 = 1.6 Hz, 1H), 8.13-8.17 (m, 5H), 8.29-8.33 (m, 2H). **^{13}C RMN (100 MHz, $CDCl_3$):** δ, ppm = 14.2, 21.7, 22.8, 26.1, 28.6, 29.2, 29.4, 29.5, 31.9, 34.0, 66.4, 67.9, 68.5, 114.5, 114.6, 121.3, 121.5, 122.4, 122.7, 122.9, 123.7, 126.6, 127.4, 127.9, 128.4, 128.4, 128.7, 129.9, 131.2, 132.1, 132.5, 132.6, 136.1, 148.2, 148.8, 151.2, 155.7, 163.7, 163.8, 164.3, 164.4, 164.4, 165.0, 173.3. **FTIR (KBr, ν: cm^{-1}):** 2939, 2923, 2858, 1732, 1604, 1511, 1472, 1259, 1184, 1160.

Compound 34. Compound **32** (1.5 g, 3.2 mmol), compound **1** (1.1 g, 3.2 mmol) and DPTS (0.3 g, 1.0 mmol) were dissolved in 100 mL of dry CH_2Cl_2 under argon atmosphere and the solution was cooled down to 0°C. DCC DCC (1.0 g, 4.8 mmol) was slowly added and the solution was heated up to room temperature and made to react for 24 h. Then, the crude was filtered, and the solvent was evaporated. The resulting solid was recrystallized from ethyl acetate to obtain a white powder. Yield: 78%.

^{1}H RMN (400 MHz, CDCl$_3$): δ, ppm = 0.90 (t, *J* = 6.8 Hz, 3H), 1.26-1.52 (m, 10H), 1.79-1.91 (m, 6H), 2.47 (t, *J* = 7.0 Hz, 2H), 4.03-4.08 (m, 4H), 5.13 (s, 2H), 6.95-7.00 (m, 4H), 7.27-7.30 (m, 4H), 7.31-7.41 (m, 5H), 7.51 (ddd, J_1 = 8.0 Hz, J_2 = 2.4 Hz, J_3 = 1.2 Hz, 1H), 7.58 (dd, J_1 = 8.0 Hz, J_2 = 8.0 Hz, 1H), 8.05 (dd, J_1 = 1.8 Hz, J_2 = 1.8 Hz, 1H), 8.11-8.18 (m, 5H). **^{13}C RMN (100MHz, CDCl$_3$):** δ, ppm = 14.2, 21.7, 22.8, 26.1, 28.6, 29.2, 29.4, 29.5, 31.9, 34.0, 66.4, 67.9, 68.5, 114.5, 114.5, 121.4, 121.5, 122.7, 122.9, 123.8, 127.5, 127.7, 128.4, 128.4, 128.7, 129.8, 131.1, 132.5, 132.6, 136.1, 148.3, 148.8, 151.4, 163.7, 163.8, 164.4, 164.9, 165.0, 173.3. **FTIR (KBr, ν: cm^{-1}):** 2951, 2911, 2849, 1733, 1716, 1606, 1512, 1471, 1250, 1182, 1166.

Compound 35. Compound **33** (1.8 g, 2.0 mmol) and 50 mL of cyclohexene were dissolved in 100 mL of THF. $Pd(OH)_2/C$ (20%) (200 mg) was added and the reaction mixture was stirred and heated under reflux for 8 h and then cooled to room temperature. The reaction mixture was filtered and the solvent was evaporated. The product was recrystallized from ethyl acetate to obtain a white powder. Yield: 61%.

M.p. (°C) Cr 153 I. **^{1}H RMN (400 MHz, CDCl$_3$):** δ, ppm = 0.90 (t, *J*= 6.8 Hz, 3H), 1.27-1.52 (m, 10H), 1.79-1.95 (m, 6H), 2.48 (t, *J* = 7.0 Hz, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 4.09 (t, *J* = 6.0 Hz, 2H), 6.96-7.01 (m, 4H), 7.27-7.31 (m, 4H), 7.38-7.41 (m, 2H), 7.53 (ddd, J_1 = 8.0 Hz, J_2 = 2.4 Hz, J_3 = 1.2 Hz, 1H), 7.61 (dd, J_1 = 7.8 Hz, J_2 = 7.8 Hz, 1H), 8.07 (dd, J_1 = 1.8 Hz, J_2 = 1.8 Hz, 1H), 8.12-8.19 (m, 5H), 8.29-8.32 (m, 2H). **^{13}C RMN (100 MHz, CDCl$_3$):** δ, ppm = 14.2, 21.5, 22.8, 26.1, 28.5, 29.2, 29.4, 29.5, 31.9, 33.5, 67.9, 68.5, 114.5, 114.6, 121.3, 121.5, 122.3, 122.7, 122.9, 123.7, 126.6, 127.4, 127.9, 129.9, 131.2, 132.1, 132.5, 132.6, 148.2, 148.8, 151.2, 155.7, 163.7, 163.8, 164.3, 164.4, 164.4, 165.0, 178.6. **FTIR (KBr, ν: cm^{-1}):** 3150-2500, 3050, 2923, 2857, 1734, 1605, 1511, 1480, 1257, 1211, 1184. **MALDI-MS (ditranol/TFANa):** m/z 825.5 [M+Na]$^+$. **Elemental Analysis:** Calcd. for $C_{47}H_{46}O_{12}$: C 70.31, H 5.78; found C 69.92, H 5.91.

Compound 36. Compound **34** (1.9 g, 2.5 mmol) and 50 mL of cyclohexene were dissolved in 100 mL of THF. $Pd(OH)_2/C$ (20%) (200 mg) was added and the reaction mixture was stirred and heated under reflux for 8 h and then cooled to room temperature. The reaction mixture was filtered and the solvent was evaporated. The product was recrystallized from ethanol to obtain a white powder. Yield: 89%. **M.p.** (°C) Cr 142 I. **^{1}H RMN (400MHz, CDCl$_3$):** δ, ppm = 0.90 (t, *J*= 6.8 Hz, 3H), 1.25-1.53 (m, 10H), 1.79-1.95 (m, 6H), 2.48 (t, *J* = 6.8 Hz, 2H), 4.05 (t, *J* = 6.8 Hz, 2H), 4.08 (t, *J* = 6.0 Hz Hz, 2H), 6.94-7.02 (m, 4H), 7.27-7.31 (m, 4H), 7.51 (ddd, J_1 = 8.2 Hz, J_2 = 2.2 Hz, J_3 = 1.2 Hz, 1H), 7.58 (dd, J_1 = 7.8 Hz, J_2 = 7.8 Hz, 1H), 8.05 (dd, J_1 = 1.8 Hz, J_2 = 1.8 Hz, 1H), 8.09-8.20 (m, 5H). **^{13}C RMN (100MHz, CDCl$_3$):** δ, ppm = 14.2, 21.5, 22.8, 26.1, 28.6, 29.2, 29.4, 29.5, 31.9, 33.5, 67.8, 68.5, 114.5, 114.5, 121.4, 121.5, 122.7, 122.9, 123.8, 127.5, 127.7, 129.8, 131.1, 132.5, 132.6, 148.3, 148.8, 151.3, 163.6, 163.8, 164.4, 164.9, 165.0, 178.7. **FTIR (KBr, ν: cm^{-1}):** 3150-2500, 3050, 2954, 2920, 1729, 1609, 1510, 1283, 1254, 1196. **MALDI-MS**

(ditranol/TFANa): m/z 705.3 [M+Na]$^+$. **Elemental Analysis:** Calcd. for $C_{40}H_{42}O_{10}$: C 70.37, H 6.20; found C 70.16, H 6.30.

Compound 37. 4-*n*-octyloxybenzoic acid (7.5 g, 30 mmol), resorcinol (5.0 g, 45.4 mmol) and DPTS (8.3 g, 30 mmol) were dissolved in 250 mL of dry CH_2Cl_2 under argon atmosphere and the solution was cooled down to 0°C. DCC (9.3 g, 45 mmol) was slowly added and the solution was heated up to room temperature and made to react for 24 h. Then, the crude was filtered, and the solvent was evaporated. The resulting solid was purified by column chromatography (silica gel, eluent CH_2Cl_2/ethanol 10/1) to obtain a white powder. Yield: 35%.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 6.8 Hz, 3H), 1.26-1.50 (m, 10H), 1.82 (q, *J* = 6.8 Hz, 2H), 4.04 (t, *J* = 6.8 Hz, 2H), 6.70 (dd, J_1 = 2.4 Hz, J_2 = 1.0 Hz, 1H), 6.72 (dd, J_1 = 2.0 Hz, J_2 = 1.0 Hz, 1H), 6.74 (dd, J_1 = 2.0 Hz, J_2 = 1.0 Hz, 1H), 6.93-6.99 (m, 2H), 7.22-7.24 (m, 1H), 8.11-8.16 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 14.1, 22.6, 24.8, 6.0, 29.1, 29.2, 29.3, 31.8, 33.8, 68.3, 109.5, 113.2, 113.7, 114.3, 121.3, 130.0, 132.3, 151.8, 156.8, 163.6, 165.4. **FTIR (KBr, ν: cm^{-1}):** 3409, 2920, 2853, 1735, 1624, 1604, 1510, 1256, 1158.

Compound 38. Compound **37** (800 mg, 2.4 mmol), compound **1** (800 mg, 2.4 mmol) and DPTS (700 mg, 2.4 mmol) were dissolved in 50 mL of dry CH_2Cl_2 under argon atmosphere and the solution was cooled down to 0°C. DCC (800 mg, 3.7 mmol) was slowly added and the solution was heated up to room temperature and made to react for 24 h. Then, the crude was filtered, and the solvent was evaporated. The resulting solid was purified by column chromatography (silica gel, eluent CH_2Cl_2) to obtain a white powder. Yield: 84%.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.7 Hz, 3H), 1.28-1.50 (m, 10H), 1.78-1.89 (m, 6H), 2.47 (t, *J* = 7.0 Hz, 2H), 4.02-4.06 (m, 4H), 5.13 (s, 2H), 6.94 (ddd, J_1 = 8.1 Hz, J_2 = 2.8 Hz, J_3 = 2.0 Hz, 2H), 6.92-7.00 (m, 2H), 7.12-7.16 (m, 3H), 7.33-7.38 (m, 5H), 7.43-7.48 (m, 1H), 8.11-8.15 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 14.1, 21.5, 22.6, 24.8, 26.0, 29.1, 29.2, 29.3, 30.9, 31.8, 33.8, 66.3, 68.3, 109.5, 113.2, 113.7, 114.3, 114.3, 114.3, 114.3, 119.1, 121.3, 128.3, 128.6, 130.0, 132.3, 132.3, 151.8, 156.9, 163.6, 165.6. **FTIR (KBr, ν: cm^{-1}):** 2920, 2851,1727, 1604, 1509, 1256.

Compound 39. Compound **38** (800 mg, 1.5 mmol) and 30 mL of cyclohexene were dissolved in 30 mL of THF. $Pd(OH)_2/C$ (20%) (100 mg) was added and the reaction mixture was stirred and heated under reflux for 8 h and then cooled to room temperature. The reaction mixture was filtered and the solvent was evaporated. The product was recrystallized from ethyl acetate to obtain a white powder. Yield: 56%. **M.p.** (°C) Cr 104 I. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 0.89 (t, *J* = 7.1 Hz, 3H), 1.25-1.52 (m, 10H), 1.80-1.92 (m, 6H), 2.43-2.51 (m, 2H), 4.00-4.11 (m, 4H), 6.92-7.00 (m, 4H), 7.12 (d, *J* = 2.1 Hz, 1H), 7.14-7.16 (m, 2H), 7.43-7.48 (m, 1H), 8.09-8.14 (m, 4H). **^{13}C RMN (100 MHz, $CDCl_3$):** δ = 14.1, 21.4, 22.7, 26.0, 28.4, 29.1, 29.2, 31.8, 113.6, 114.3, 114.3, 116.0, 119.2, 121.5, 122.6, 132.3, 151.6, 167.9, 178.4. **FTIR (KBr, ν: cm^{-1}):** 3300-3000, 2917, 2850, 1729, 1699, 1604, 1512, 1256. **MALDI-MS (ditranol/TFANa):** m/z = 585.5 [M + Na]$^+$. **Elemental Analysis:** Calcd. for $C_{33}H_{38}O_8$: C 70.44, H 6.81; Found: C 70.54, H 6.80.

Compound 42. Compound **40** (1.0 g, 1.3 mmol), benzyl 2,2-di(hydroxymethyl)propanoate (130 mg, 0.6 mmol) and DPTS (380 mg, 1.3 mmol) were dissolved in 50 mL of dry CH_2Cl_2 under argon atmosphere and the solution was cooled down to 0°C. DCC (400 mg, 1.9 mmol) was slowly added and the solution was heated up to room temperature and made to react for 24 h. Then, the crude was filtered, and the solvent was evaporated. The resulting solid was purified by column chromatography (silica gel, eluent CH_2Cl_2/AcOEt 95/5) to obtain a white powder. Yield: 47%.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.0 Hz, 6H), 1.26-1.52 (m, 23H), 1.77-1.87 (m, 12H), 2.35 (t, *J* = 7.0 Hz, 4H), 4.02-4.07 (m, 8H), 4.27 (dd, J_1 = 11.1 Hz, J_2 = 11.1 Hz, 4H), 5.18 (s, 2H), 6.98 (d, *J* = 8.9 Hz, 4H), 7.00 (d, *J* = 8.9 Hz, 4H), 7.21-7.24 (m, 2H), 7.28 (d, *J* = 8.7 Hz, 4H), 7.31-7.36 (m, 5H), 7.38 (d, *J* = 8.8 Hz, 4H), 7.45 (s, 2H), 7.50 (d, *J* = 5.0 Hz, 4H), 7.65 (d, *J* = 8.7 Hz, 4H), 8.16 (dd, J_1 = 8.9 Hz, J_2 = 1.0 Hz, 8H), 8.30 (d, *J* = 8.8 Hz, 4H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 14.1, 17.9, 21.4, 22.6, 26.0, 28.4, 29.1, 29.2, 29.3, 31.8, 33.6, 46.4, 65.4, 114.3, 114.4, 120.4, 120.9, 121.7, 122.1, 122.2, 124.7, 126.8, 128.1, 128.2, 128.4, 128.6, 129.8, 131.8, 132.3, 132.4, 135.5, 137.8, 142.1, 150.8, 151.3, 155.4, 163.3, 163.8, 164.5, 172.5, 172.7. **FTIR (KBr, ν: cm^{-1}):** 2924, 2859, 1731, 1728, 1604, 1579, 1254.

Compound 43. Compound **41** (1.2 g, 1.3 mmol), benzyl 2,2-di(hydroxymethyl)propanoate (130 mg, 0.6 mmol) and DPTS (380 mg, 1.3 mmol) were dissolved in 50 mL of dry CH_2Cl_2 under argon atmosphere and the solution was cooled down to 0°C. DCC (400 mg, 1.9 mmol) was slowly added and the solution was heated up to room temperature and made to react for 24 h. Then, the crude was filtered, and the solvent was evaporated. The resulting solid was purified by column chromatography (silica gel, eluent CH_2Cl_2/AcOEt 95/5) to obtain a white powder. Yield: 90%.

^{1}H NMR (400 MHz, $CDCl_3$):): δ = δ = 0.88 (t, *J* = 7.0 Hz, 6H), 1.20-1.52 (m, 71H), 1.75-1.89 (m, 12H), 2.24 (t, *J* = 7.4 Hz, 4H), 4.02-4.07 (m, 8H), 4.24 (dd, J_1 = 13.7 Hz, J_2 = 13.7 Hz, 4H), 5.16 (s, 2H), 6.96-7.00 (m, 8H), 7.19-7.24 (m, 2H), 7.27-7.42 (m, 13H), 7.45 (s, 2H), 7.50 (d, *J* = 5.2 Hz, 4H), 7.65 (d, *J* = 8.6 Hz, 4H), 8.16 (dd, *J* = 8.9 Hz, J = 1.1 Hz, 8H), 8.30 (d, *J* = 8.8 Hz, 4H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = δ = 14.1, 17.8, 21.4, 22.6, 26.0, 28.4, 29.1, 29.2, 29.3, 31.8, 33.6, 65.4, 66.8, 67.6, 68.4, 114.3, 114.4, 120.4, 120.5, 120.9, 122.1, 122.2, 124.7, 126.8, 128.1, 128.2, 128.4, 128.6, 129.8, 131.8, 132.3, 132.4, 135.5, 137.7, 142.1, 150.8, 151.3, 155.4, 163.3, 163.8, 164.5, 172.7. **FTIR (KBr, ν: cm^{-1}):** 2924, 2857, 1730, 1728, 1604, 1579, 1254.

Compound 44. Compound **42** (400 mg, 0.2 mmol) and 25 mL of cyclohexene were dissolved in 25 mL of THF. $Pd(OH)_2$/C (20%) (50 mg) was added and the reaction mixture was stirred and heated under reflux for 8 h and then cooled to room temperature. The reaction mixture was filtered and the solvent was evaporated. The product was purified by column chromatography (silica gel, eluent CH_2Cl_2/AcOEt 95/5) to give a white powder. Yield: 79%.

M.p. (°C) Cr 141 I. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 0.89 (t, *J* = 6.9 Hz, 6H), 1.23-1.56 (m, 23H), 1.75-1.90 (m, 12H), 2.42-2.45 (m, 4H), 4.05 (dt, J_1 = 6.9 Hz, J_2 = 2.7 Hz, 8H), 4.28 (dd, J_1 = 11.3 Hz, J_2 = 11.2 Hz, 4H), 6.98 (dd, J_1 = 8.8 Hz, J_2 = 8.4 Hz, 8H), 7.20-7.25 (m, 2H), 7.28 (d, *J* = 8.8 Hz, 4H), 7.38 (d, *J* = 8.6 Hz, 4H), 7.45 (s, 2H), 7.49 (d, *J* = 4.7 Hz, 4H), 7.64 (d, *J* = 8.5 Hz, 4H), 8.15 (d, *J* = 8.6 Hz, 8H), 8.30 (d, *J* = 8.6 Hz, 4H). **^{13}C RMN (75 MHz, $CDCl_3$):** δ = 14.1, 17.8, 21.2, 21.5, 22.6, 26.0, 28.4, 29.1, 29.2, 29.3, 30.3, 31.8, 33.6, 34.2, 46.1, 65.1, 67.6, 68.4, 114.3, 114.4, 120.4, 120.9, 121.7, 122.1, 125.5, 126.8, 128.2, 129.8, 131.8, 132.3, 132.4, 137.7, 142.1, 150.8, 151.3, 155.4, 163.3, 163.8, 164.3, 164.5, 164.8, 172.7. **FTIR (KBr, ν: cm^{-1}):** 3300-3000, 2916, 2850, 1728, 1699, 1605, 1513, 1256. **MALDI-MS (ditranol/TFANa):** m/z = 1628.6 [M + Na] $^+$. **Elemental Analysis:** Calcd. for $C_{97}H_{98}O_{22}$: C 72.10, H 6.11; Found: C 72.13, H 5.98.

Compound 45. Compound **43** (1.0 g, 0.5 mmol) and 50 mL of cyclohexene were dissolved in 50 mL of THF. $Pd(OH)_2/C$ (20%) (600 mg) was added and the reaction mixture was stirred and heated under reflux for 8 h and then cooled to room temperature. The reaction mixture was filtered and the solvent was evaporated. The product was purified by column chromatography (silica gel, eluent CH_2Cl_2/AcOEt 95/5) and recrystallized from ethyl acetate to give a white powder. Yield: 31%.

M.p. (°C) Cr 121 I. **^{1}H NMR (300 MHz, CDCl$_3$):** δ = 0.89 (t, *J* = 7.2 Hz, 6H), 1.23-1.52 (m, 71H), 1.73-1.92 (m, 12H), 2.24 (t, *J* = 7.4 Hz, 4H), 4.05 (dt, J_1 = 7.0 Hz, J_2 = 2.5 Hz, 8H), 4.24 (dd, J_1 = 11.1 Hz, J_2 = 11.1 Hz, 4H), 6.98 (dd, J_1 = 9.0 Hz, J_2 = 8.8Hz, 8H), 7.19-7.26 (m, 2H), 7.26-7.32 (m, 4H), 7.37 (d, *J* = 8.8 Hz, 4H), 7.45 (s, 2H), 7.50 (d, *J* = 5.0 Hz, 4H), 7.64 (d, *J* = 8.7 Hz, 4H), 8.15 (d, *J* = 8.9 Hz, 8H), 8.30 (d, *J* = 8.7 Hz, 4H). **^{13}C RMN (75 MHz, CDCl$_3$):** δ = 14.1, 17.8, 21.2, 21.5, 22.7, 26.0, 28.5, 29.1, 29.2, 29.3, 30.3, 31.8, 33.6, 34.2, 65.1, 67.6, 68.4, 114.3, 114.4, 120.4, 120.6, 121.0, 121.7, 122.1, 122.2, 124.7, 125.5, 126.9, 128.2, 129.9, 131.8, 132.4, 135.8, 137.8, 142.1, 150.8, 151.3, 155.4, 163.3, 163.8, 164.5, 172.8. **FTIR (KBr, ν: cm^{-1}):** 3300-3000, 2916, 2850, 1726, 1697, 1604, 1513, 1256. **MALDI-MS (ditranol/TFANa):** m/z = 1997.2 [M + 2Na] $^+$. **Elemental Analysis:** Calcd. for $C_{121}H_{146}O_{22}$: C 74.43, H 7.54; Found: C 74.33, H 7.26.

General procedure for the synthesis of ionic dendrimers

The amine-terminated PPI dendrimer was dissolved in dried THF and was added to a solution of the corresponding acid in the same solvent, using a 1:1 stoichiometry between the acid and each of the N-terminal amine groups present in the dendrimer. The mixture was sonicated for 15 min and the solvent was evaporated. The dendrimers were further dried under vacuum for 2 days.

Dendrimer PPI1-D1B1-4-8. M.p. (°C) Cr 93 Col$_r$ 158 I. **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 0.90 (t, J = 6.9 Hz, 24H), 1.20-1.25 (m, 12H), 1.26-1.47 (m, 80H), 1.43-1.57 (m, 16H), 1.75-1.94 (m, 56H), 2.37-2.48 (m, 16H), 2.90-3.16 (m, 8H), 3.95-4.10 (m, 32H), 4.15-4.43 (m, 16H), 6.98 (dd, J = 9.1 Hz, J = 9.1 Hz, 32H), 7.20-7.23 (m, 8H), 7.24-7.28 (m, 16H), 7.38 (dd, J = 8.8 Hz, J = 1.9 Hz, 16H), 7.43-4.46 (m, 8H), 7.49 (d, J = 5.1 Hz, 16H), 7.63 (d, J = 8.6 Hz, 16H), 8.17 (dd, J = 8.9 Hz, J = 5.3 Hz, 32H), 8.31 (dd, J = 8.7 Hz, J = 1.8 Hz, 16H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ =14.1, 21.0, 22.6, 26.0, 28.5, 29.1, 29.2, 29.3, 30.3, 31.8, 33.8, 67.7, 68.4, 114.3, 114.4, 120.4, 120.5, 121.0, 121.7, 122.1, 122.1, 126.8, 128.2, 129.8, 131.8, 132.3, 132.4, 137.7, 142.1, 150.8, 151.3, 155.4, 163.3, 163.8, 164.3, 164.5, 164.8, 173.1. **FTIR (KBr, ν: cm^{-1}):** 3300-3000, 2930, 2871, 1735, 1605, 1579, 1510, 1476, 1445, 1256, 1209, 1065.

Dendrimer PPI1-D1B1-10-14. M.p. (°C) Cr 106 SmCP 141 I. **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 0.91 (t, J = 7.0 Hz, 24H), 1.21 (m, 12H), 1.25-1.43 (m, 272H), 1.42-1.55 (m, 16H), 1.75-1.93 (m, 56H), 2.36-2.47 (m, 16H), 2.96-3.15 (m, 8H), 4.00-4.10 (m, 32H), 4.28 (m, 16H), 6.97 (dd, J = 9.1 Hz, J = 9.1 Hz, 32H), 7.19-7.23 (m, 8H), 7.24-7.28 (m, 16H), 7.37 (dd, J = 8.8 Hz, J = 1.9 Hz, 16H), 7.43-

4.45 (m, 8H), 7.48 (d, J = 5.0 Hz, 16H), 7.62 (d, J = 8.6 Hz, 16H), 8.16 (dd, J = 8.9 Hz, J = 5.3 Hz, 32H), 8.29 (dd, J = 8.7 Hz, J = 1.8 Hz, 16H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 14.1, 21.5, 21.6, 22.5, 22.6, 26.0, 26.2, 28.5, 29.1, 29.2, 29.3, 30.3, 31.8, 31.9, 33.8, 67.7, 68.4, 114.3, 114.4, 120.4, 120.5, 121.0, 121.7, 122.1, 122.1, 126.8, 128.8, 129.8, 131.7, 132.3, 132.3, 137.6, 142.0, 150.7, 151.3, 155.4, 163.3, 163.8, 164.5, 164.8, 172.6. **FTIR (KBr, ν: cm^{-1}):** 3400-3000, 2932, 2871, 1730, 1606, 1578, 1511, 1476, 1446, 1256, 1208, 1065.

Dendrimer PPI1-B1-4-7. M.p. (°C) Cr 99 Col$_r$ 140 I.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, *J*= 6.8 Hz, 12H), 1.27-1.41 (m, 28H), 1.42-1.53 (m, 8H), 1.74-1.90 (m, 32H), 2.31-2.38 (m, 8H), 2.42 (bs, 4H), 2.53 (bs, 8H), 3.04 (bs, 8H), 4.00-4.08 (m, 16H), 6.92-7.00 (m, 16H), 7.18-7.23 (m, 4H), 7.23-7.29 (m, 8H), 7.34-7.40 (m, 8H), 7.42-7.45 (m, 4H), 7.46-7.51 (m, 8H), 7.60-7.66 (m, 8H), 8.10-8.18 (m, 16H), 8.26-8.32 (m, 8H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 14.2, 22.4, 22.8, 26.1, 28.9, 29.2, 29.3, 31.9, 35.7, 68.1, 68.5, 114.4, 114.6, 120.5, 120.7, 121.1, 121.7, 122.3, 122.4, 124.8, 127.0, 128.4, 130.0, 132.0, 132.5, 132.6, 137.9, 142.2, 150.9, 121.5, 155.6, 163.5, 164.0, 164.5, 164.6, 165.0, 178.9. **FTIR (KBr, ν: cm^{-1}):** 3700-3150, 2944, 2929, 2856, 1732, 1640, 1607, 1574, 1546, 1513, 1475, 1444, 1259, 1204, 1162.

Dendrimer PPI1-B1-4-9. M.p. (°C) Cr 100 Col$_r$ 141 I

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J*= 6.8 Hz, 12H), 1.22-1.40 (m, 44H), 1.43-1.52 (m, 8H), 1.78-1.90 (m, 32H), 2.37-2.41 (m, 8H), 2.55 (bs, 4H), 2.66 (bs, 8H), 3.07 (bs, 8H), 4.00-4.09 (m, 16H), 6.92-7.01 (m, 16H), 7.19-7.24 (m, 4H), 7.26-7.30 (m, 8H), 7.36-7.40 (m, 8H), 7.42-7.46 (m, 4H), 7.47-7.52 (m, 8H), 7.61-7.67 (m, 8H), 8.11-8.19 (m, 16H), 8.26-8.34 (m, 8H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 14.3, 22.1, 22.8, 26.1, 28.8, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 32.0, 35.1, 68.0, 68.5, 114.3, 114.4, 114.6, 120.6, 121.1, 121.7, 122.3, 127.0, 128.4, 130.0, 132.0, 132.5, 132.6, 137.9, 142.3, 151.0, 151.5, 155.6, 163.5, 164.0, 164.5, 164.7, 165.0, 178.5. **FTIR (KBr, ν: cm^{-1}):** 3650-3200, 2918, 2851, 1729, 1640, 1605, 1579, 1543, 1514, 1474, 1444, 1256, 1204, 1160.

Dendrimer PPI1-B1-4-10. M.p. (°C) Cr 105 Col$_r$ 144 I.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J*= 6.8 Hz, 12H), 1.19-1.38 (m, 52H), 1.43-1.51 (m, 8H), 1.76-1.90 (m, 32H), 2.31-2.37 (m, 8H), 2.40 (bs, 4H), 2.52 (bs, 8H), 3.07 (bs, 8H), 4.00-4.08 (m, 16H), 6.64 (bs, 12H), 6.92-7.02 (m, 16H), 7.18-7.23 (m, 4H), 7.23-7.30 (m, 8H), 7.33-7.40 (m, 8H), 7.42-7.45 (m, 4H), 7.46-7.52 (m, 8H), 7.59-7.66 (m, 8H), 8.10-8.19 (m, 16H), 8.26-8.33 (m, 8H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 14.3, 22.6, 22.8, 26.1, 29.0, 29.2, 29.5, 29.6, 29.7, 32.0, 36.4, 68.1, 68.5, 114.4, 114.6, 120.5, 120.7, 121.1, 121.7, 122.2, 122.3, 124.8, 130.0, 132.0, 132.4, 132.6, 137.9, 142.2, 150.9, 151.4, 155.5, 163.6, 164.0, 164.5, 164.6, 165.0, 179.6. **FTIR (KBr, ν: cm^{-1}):** 3500-3300, 2919, 2852, 1733, 1651, 1605, 1511, 1473, 1444, 1254, 1212.

Dendrimer PPI1-Bi-4-8. M.p. (°C) Cr 122 HNFs 165 I. **^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm)**: 0.89 (t, *J*= 6.8 Hz, 12H), 1.22-1.53 (m, 44H), 1.72-1.89 (m, 32H), 2.20-2.33 (m, 8H), 2.40 (bs, 4H), 2.52 (bs, 8H), 3.00 (bs, 8H), 3.96-4.06 (m, 16H), 5.76 (bs, 12H), 6.87-6.95 (m, 8H), 6.96-7.03 (m, 8H), 7.18-7.26 (m, 12H), 7.40-7.49 (m, 12H), 7.54-7.64 (m, 16H), 7.65-7.71 (m, 8H), 8.08-8.15 (m, 8H), 8.20-8.27 (m, 8H). **^{13}C-NMR (100 MHz, $CDCl_3$, 323K) δ (ppm)**: 14.0. 21.6, 22.6, 26.1, 28.6, 29.2, 29.3, 29.4, 29.7, 30.8, 31.8, 33.4, 67.8, 68.3, 114.4, 115.2, 120.5, 120.6, 122.0, 122.1, 124.6, 126.7, 127.7, 128.2, 128.4, 129.8, 130.8, 132.2, 132.4, 137.9, 142.2, 146.2, 151.0, 151.7, 159.8, 163.4, 164.8, 165.1. **FTIR (KBr, ν: cm^{-1})**: 3500-3300, 2922, 2854, 1728, 1604, 1579, 1516, 1473, 1448, 1399, 1254, 1169, 1078.

Dendrimer PPI1-Bi-4-10. M.p. (°C) Cr 112 HNFs 168 I. **^{1}H RMN (400MHz, DMSO-d^6):** δ (ppm)= 0.86 (t, J=7,1Hz, 12H), 1.20-1.48 (m, 60H), 1.61-1.84 (m, 32H), 2.31 (t, J=7,2Hz, 8H), 2.89-2.97 (m, 4H), 3.06-3.14 (m, 8H), 3.17-3.25 (m, 8H), 4.03 (t, J=6,5Hz, 8H), 4.11 (t, J=6,3Hz, 8H), 7.04-7.10 (m, 8H), 7.10-7.16 (m, 8H), 7.30-7.36 (m, 4H), 7.36-7.41 (m, 8H), 7.55-7.63 (m, 4H), 7.65-7.70 (m, 8H), 7.72-7.78 (m, 8H), 7.79-7.84 (m, 8H), 7.87-7.91 (m, 8H), 8.07-8.13 (m, 8H), 8.17-8.24 (m,8H). **FTIR (KBr, ν: cm^{-1}):** 3500-3400; 2927, 2852; 1733, 1689; 1607, 1549, 1511, 1445, 1395.

Dendrimer PPI1-Bz1-4-8. M.p. (°C) Cr 137 M 145 I. **^{1}H RMN (400MHz, CDCl$_3$):** δ, ppm = 0.89 (t, J=7,1Hz, 12H), 1.20-1.53 (m, 44H), 1.73-1.92 (m, 32H), 2.34 (t, J=6,8Hz, 8H), 2.38-2.67 (bs, 4H), 2.88-3.20 (bs, 8H), 3.33-3.57 (bs, 8H), 3.98-4.13 (m, 16H), 6.93-6.98 (m, 16 H), 7.26-7.30 (m, 16H), 7.34-7.37 (m, 8H), 7.46-7.54 (m, 4H), 7.58 (dd, J=8,0Hz, J=8,0Hz, 4H), 8.02-8.08 (m, 4H), 8.09-8.18 (m, 20 H), 8.25-8.27 (m, 8H). **^{13}C RMN (100MHz, CDCl$_3$):** δ, ppm = 14.2, 22.5, 22.8, 24.7, 26.1 29.0, 29.3, 29.4, 29.5, 29.9, 32.0, 36.1, 39.5, 68.1,68.5, 114.5, 114.5, 115.8, 121.2, 121.5, 122.3, 122.7, 122.9, 123.7, 123.8, 126.6, 127.4, 127.9,129.9, 131.2, 132.0, 132.5, 132.6, 132.8, 148.2, 148.8, 151.1, 155.7, 163.8, 164.3, 164.3, 164.4, 165.0, 179.2. **FTIR (KBr, ν: cm^{-1}):** 3500-3400, 2925, 2852, 1734, 1707, 1559, 1510, 1540, 1446, 1400.

Dendrimer PPI1-Bz-4-8. M.p. (°C) Cr 117 I. **^{1}H RMN (400MHz, CDCl$_3$):** δ, ppm = 0.90 (t, J=7,0Hz, 12H), 1.25-1.54 (m, 44H), 1.73-1.92 (m, 32H), 2.36 (t, J=6,8Hz, 8H), 2.37-2.71 (bs, 4H), 2.80-3.12 (bs, 8H), 3.30-3.51 (bs, 8H), 3.97-4.11 (m, 16H), 6.93-6.97 (m, 16 H), 7.26-7.32 (m, 16H), 7.44-7.51 (m, 4H), 7.56 (dd, J=8,0Hz, J=8,0Hz, 4H), 7.99-8.02 (m, 4H), 8.09-8.19 (m, 20 H). **^{13}C RMN (100MHz, CDCl$_3$):** δ, ppm = 14.2, 22.3, 22.8, 26.1, 28.9, 29.2, 29.4, 29.5, 31.9, 35.5, 68.1, 68.5, 114.4, 114.5, 114.5, 116.2, 121.3, 121.5, 122.7, 122.8, 122.9, 123.8, 127.5, 127.7, 129.8, 131.1, 132.3, 132.5, 132.5, 148.3, 148.8, 151.3, 163.7, 163.8, 164.4, 164.8, 165.0, 178.9. **FTIR (KBr, ν: cm^{-1}):** 3500-3400, 2927, 2852, 1732, 1607, 1511, 1549, 1444, 1395.

Dendrimer PPI1-Ph-4-8. M.p. (°C) Cr 112 I. **^{1}H NMR (500 MHz, CDCl$_3$):** δ = 0.89 (t, J = 7.1 Hz, 12H), 1.20-1.40 (m, 36H), 1.41-1.50 (m, 8H), 1.65-1.90 (m, 32H), 2.15-2.55 (m, 8H), 2.85-3.10 (bs, 4H), 3.32-3.42 (bs, 8H), 3.72-3.78 (bs, 8H), 3.80-4.04 (m, 16H), 5.60-6.10 (m, 12H), 6.92 (dd, J = 8.9 Hz, J = 8.9 Hz, 16H), 7.08-7.14 (m, 12H), 7.42 (dd, J = 8.2 Hz, J = 8.2 Hz, 4H), 8.09 (dd, J = 14.4 Hz, J = 8.9 Hz, 16H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ = 14.1, 22.5, 22.6, 26.0, 28.9, 29.1, 29.2, 29.3, 31.8, 36.4, 68.3, 67.9, 114.3, 114.3, 115.9, 119.1, 121.2, 121.3, 129.7, 132.3, 151.5, 151.6, 163.4, 163.6, 164.5, 164.6, 179.5. **FTIR (KBr, ν: cm^{-1}):** 3400-3000, 2929, 2876, 1730, 1610, 1578, 1512, 1478, 1445, 1257, 1200.

Dendrimer PPI1-Ph1-4-8. M.p. (°C) Cr 103 Col$_r$ 150 I.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J*= 6.8 Hz, 12H), 1.25-1.40 (m, 36H), 1.42-1.51 (m, 8H), 1.73-1.91 (m, 32H), 2.30-2.39 (m, 8H), 2.41 (bs, 4H), 2.52 (bs, 8H), 3.04 (bs, 8H), 3.98-4.09 (m, 16H), 6.90-7.03 (m, 16H), 7.13-7.22 (m, 12H), 7.30-7.41 (m, 16H), 7.41-7.49 (m, 4H), 8.07-8.19 (m, 16H), 8.21-8.31 (m, 16H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 14.2, 22.4, 22.8, 26.1, 28.9, 29.2, 29.4, 29.5, 31.9, 68.1, 68.5, 114.5, 114.6, 115.9, 119.4, 121.1, 121.2, 122.3, 126.7, 126.8, 130.0, 132.0, 132.6, 151.5, 155.5, 155.6, 163.7, 164.0, 164.2, 164.3, 164.4, 164.5, 179.2. **FTIR (KBr, ν: cm^{-1}):** 3550-3300, 2921, 2857, 1735, 1605, 1548, 1510, 1473, 1452, 1258, 1205.

3.- X-ray diffraction parameters of the mesophases formed by the ionic dendrimers

Dendrimer*	Mesophase	D [Å]	Miller indexes (hkl)	Parameters [Å]
PPI1-D1B1-4-8	Col$_r$	56.9	001	a = 44.2 b = 56.9
		28.5	002	
		20.6	021	
		14.3	004	
PPI1-D1B1-10-14	Col$_r$	57.8	001	a = 58.3 b = 62.0
		29.1	002	
		21.7	022	
		16.9	032	
PPI1-B1-4-7	Col$_r$	54.5	001	a = 55.0 b = 57.2
		27.7	002	
		19.8	022	
PPI1-B1-4-9	Col$_r$	58.6	001	a = 58.6 b = 56.8
		29.3	002	
		20.4	022	
PPI1-B1-4-10	Col$_r$	58.3	001	a = 58.3 b = 57.0
		29.2	002	
		26.0	012	
		20.4	022	
PPI1-Ph1-4-8	Col$_r$	55.2	001	a = 55.2 b = 63.0
		27.6	002	
		20.8	022	
		16.7	032	
PPI1-Bi-4-8	HNFs	40.1	002	c = 80.3
		26.8	003	
		20.2	004	
		16.1	005	
		11.4	007	
PPI1-Bi-4-10	HNFs	42.5	002	c = 84.5
		28.0	003	

* The short range of temperatures of PPI1-Bz1-4-8 mesophase did not allow its characterization.

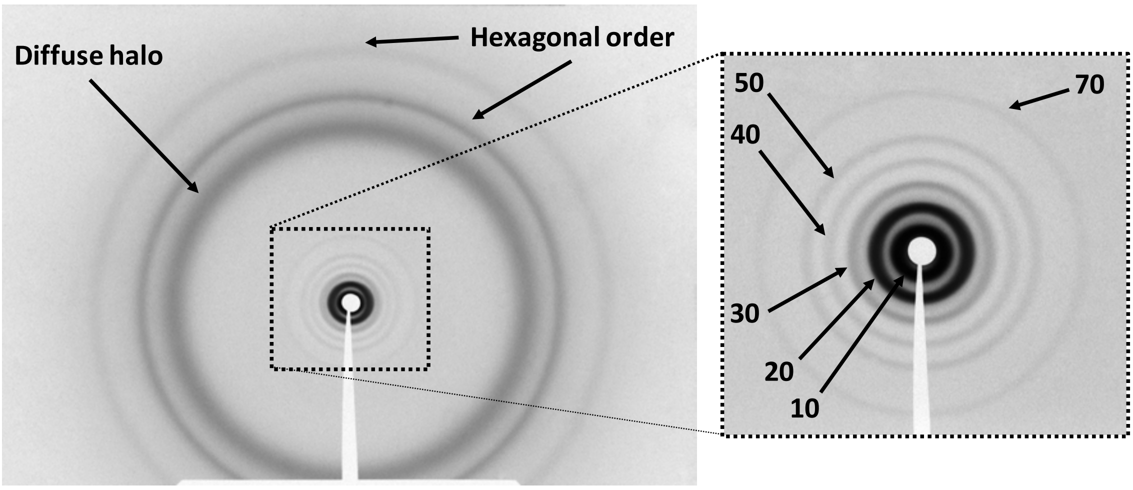


Figure S1. Example of X-ray pattern of HNFs mesophase (**PPI1-Bi-4-8**) Inset: magnification of small angle region).

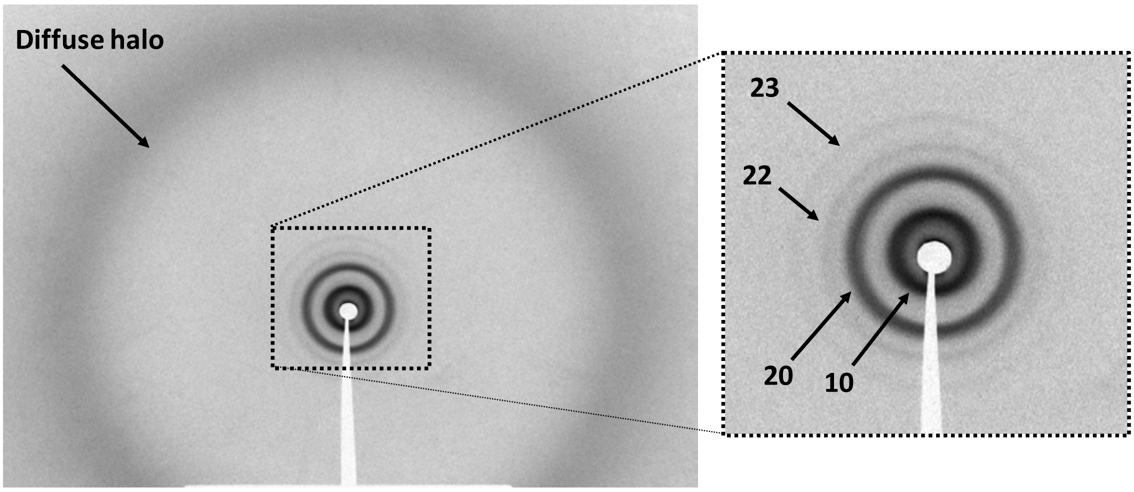
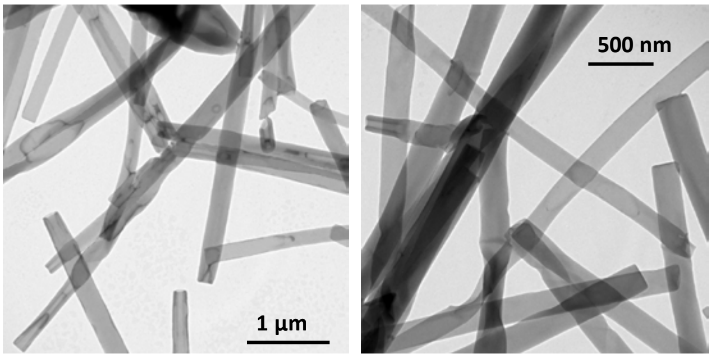


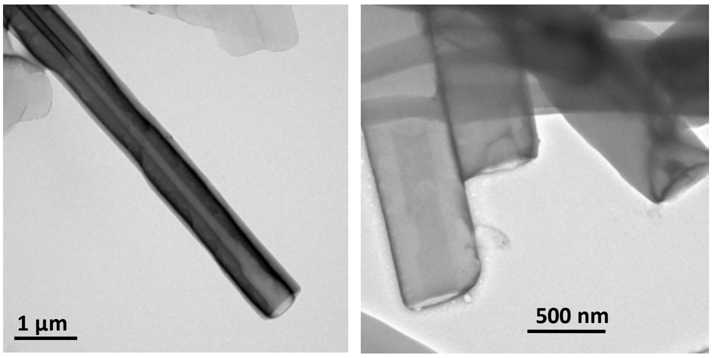
Figure S2. Example of X-ray pattern of Col$_r$ mesophase of (**PPI1-D1B1-10-14**) Inset: magnification of small angle region.

4.- Additional TEM images of the chiral aggregates of the ionic dendrimers

PPI1-Ph1-4-8



PPI1-B1-4-7



PPI1-Bi-4-8

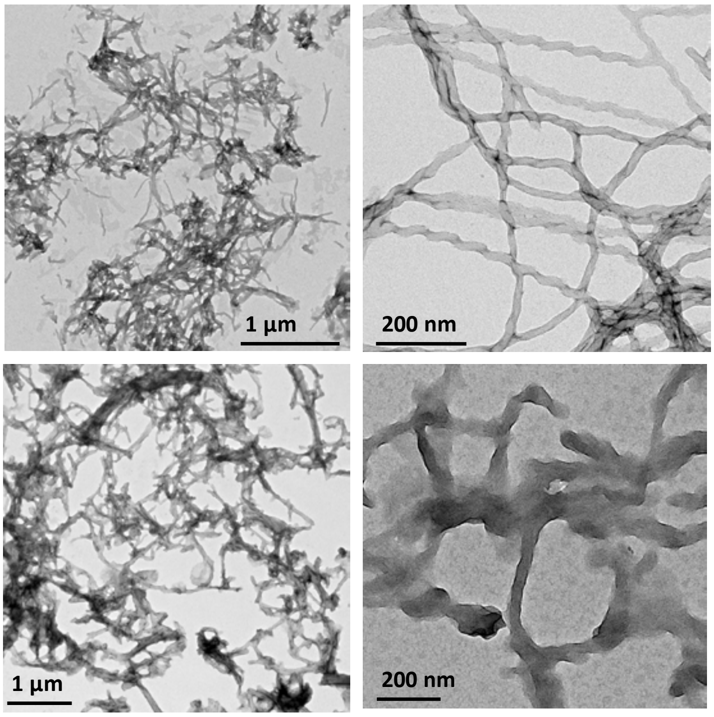


Figure S3. Additional TEM images of the chiral aggregates of the ionic dendrimers

5.- References

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[2] M. Cano, A. Sánchez-Ferrer, J. L. Serrano, N. Gimeno, M. B. Ros, *Angew. Chem. Int. Ed.* **2014**, 53, 13449.