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Supporting Information

Supramolecular Self-Organization of "Janus-like" Diblock Co-Dendrimers: Synthesis, Thermal Behavior and Phase Structure Modeling

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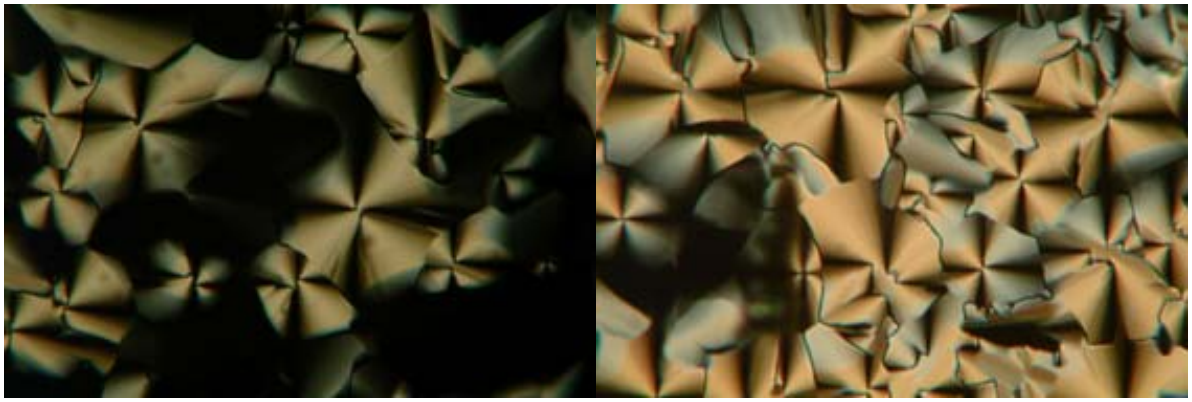
Experimental techniques

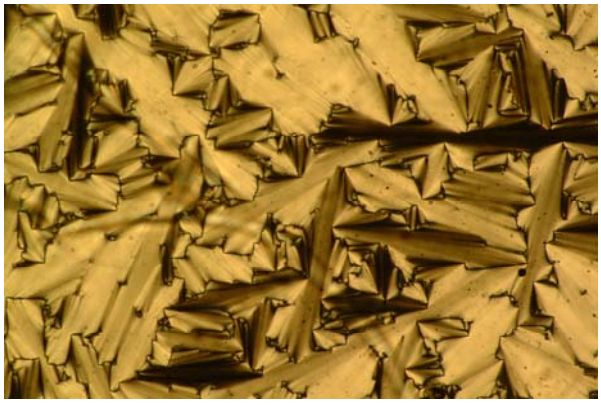
^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 300 (300 MHz) spectrometer in $CDCl_3$, CD_3OD, $(CD_3)_2CO$, DMSO-d_6, or THF-d_6 solutions. MALDI-TOF spectra were recorded on a Bruker biflex III spectrometer in a dithranol matrix (1,8,9-anthracenetriol). The optical textures of the mesophases were studied with a Leitz polarizing microscope equipped with a Mettler FP80 hot-stage and an FP80 central processor. The transition temperatures and enthalpies were measured by differential scanning calorimetry with a Perkin-Elmer DSC-7 instrument operated at a scanning rates of 2-to-10 °C min^{-1} on heating and on cooling. The apparatus was calibrated with indium (156.6 °C; 28.4 J g^{-1}) and gallium (29.8 °C) as the standards. The TGA measurements were carried out on a SDTQ 600 apparatus at scanning rate of 10 °C min^{-1}. The XRD patterns were obtained with three different experimental set-ups. In all cases, a linear monochromatic Cu-Kα_1 beam (λ = 1.5405 Å) was obtained using a sealed-tube generator (900 W) equipped with a bent quartz monochromator. In the first set, the transmission Guinier geometry was used, whereas a Debye-Scherrer-like and a flat film geometry were used in the second and third experimental set-ups, respectively. In all cases, the crude powder was filled in Lindemann capillaries of 1 mm diameter and 10 μm wall-thickness. An initial set of diffraction patterns was recorded on an image plate; periodicities up to 80 Å can be measured, and the sample temperature controlled to within ±0.3 °C from 20 to 350 °C. The second set of diffraction patterns was recorded with a curved Inel CPS 120 counter gas-filled detector linked to a data acquisition computer; periodicities up to 60 Å can be measured, and the sample temperature controlled to within ±0.05 °C from 20 to 200°C. Finally, the last set of diffraction patterns was recorded on image plate, and periodicities up to 350 Å can be measured, and the sample temperature controlled to within ±0.01 °C from 20 to 200°C. In each case, exposure times were varied from 1 to 24 h. The molecular modeling calculations were performed on an SGI Origin 200 4 CPU computer and on an SGI Octane^2 workstation using the DISCOVER 3 molecular mechanics package from Accelrys (www.accelrys.com) with the pcff force field. For both smectic and columnar models, prior to the dynamics, the systems were minimized to a gradient of 0.5 kcal mol^{-1}. The simulation then consisted of a 100 ps isotherm at 373 K in the NVT-PBC ensemble and with a 1 fs time step.

POM investigations

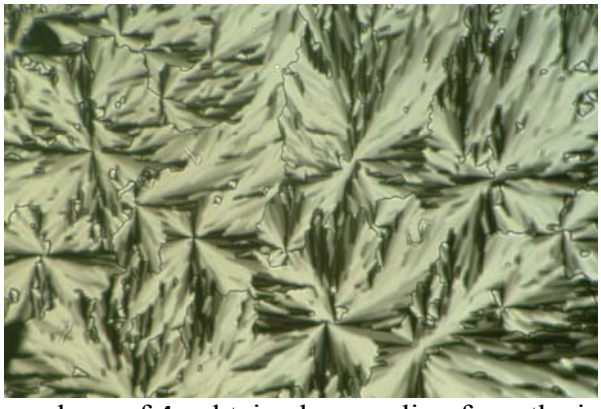
Some typical and characteristic optical textures are shown for some of the samples.



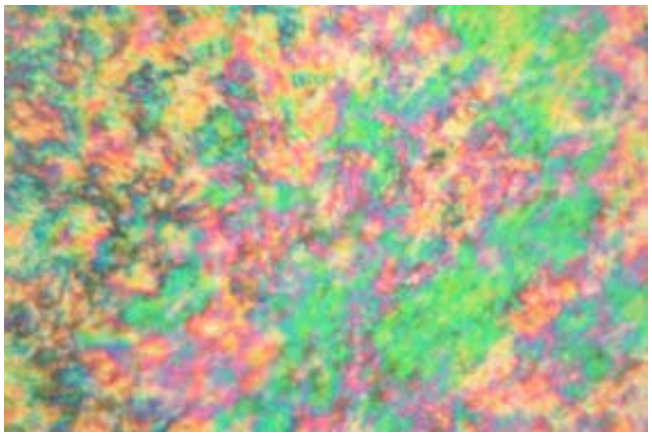
Textures of the Col_h mesophase of **1c** obtained on cooling from the isotropic liquid (72 and 53°C) showing cylindrical domains and with the presence of large homeotropic zones.



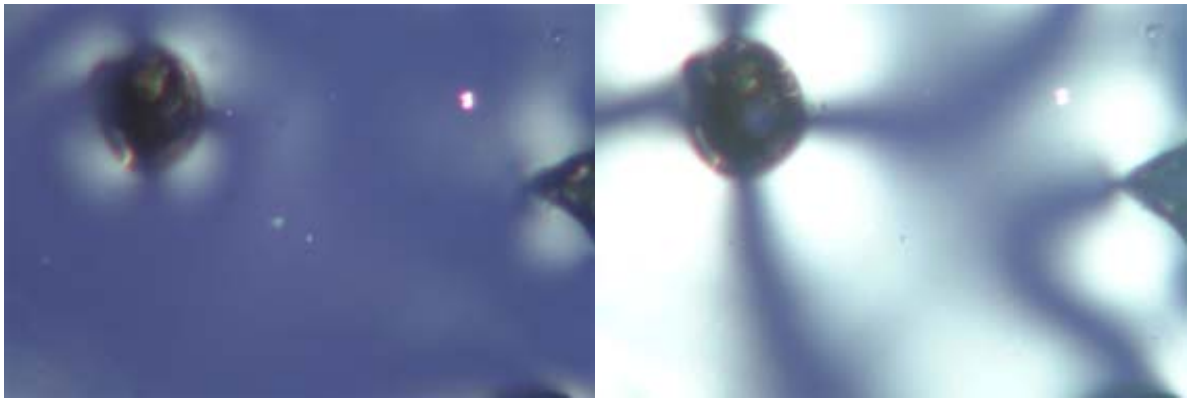
Texture of the Col_h mesophase of **2a** obtained on cooling from the isotropic liquid (50°C) showing cylindrical domains.



Texture of the Col_h mesophase of **4a** obtained on cooling from the isotropic liquid (120°C) showing cylindrical domains.



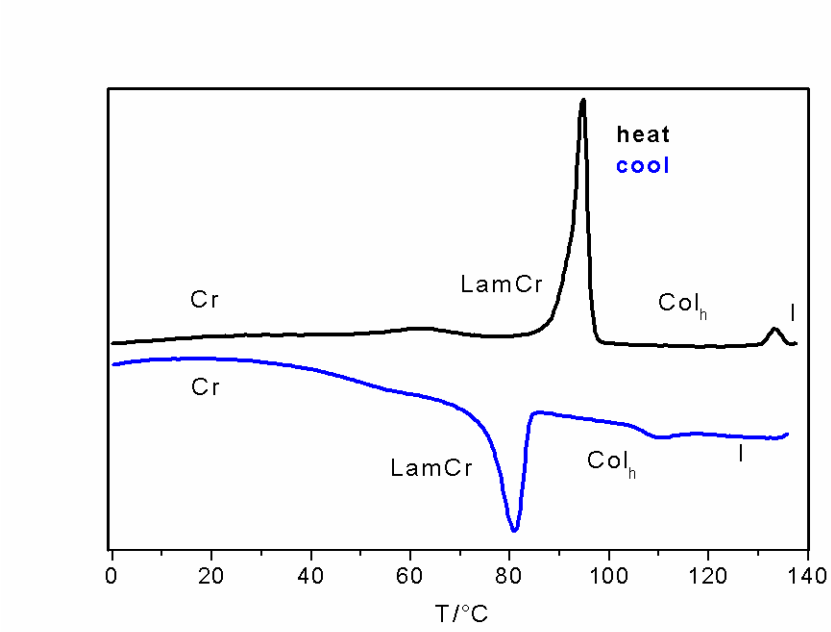
Texture of the Col_h mesophase of **5a** obtained on cooling at 30°C (supercooled Col_h phase).



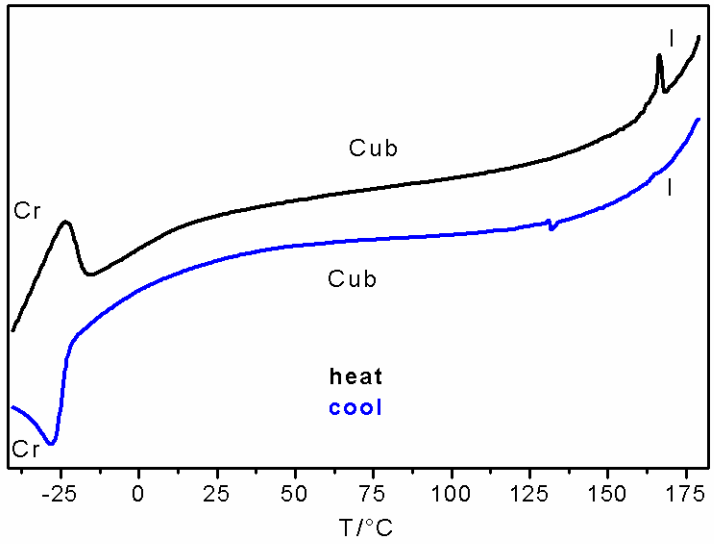
Texture of the cubic phase of **6a** obtained upon pressure on the glass-slide (50 °C).

DSC analysis

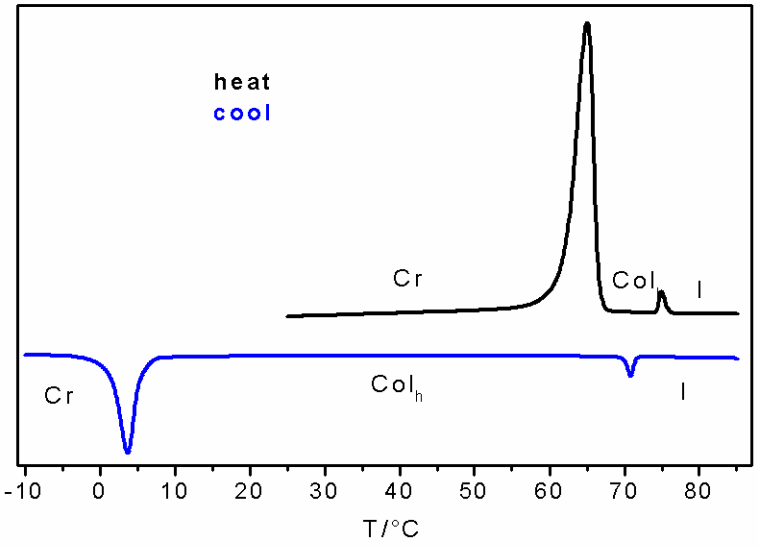
The following protocol was applied in order to obtain exploitable DSC analyses. A first sample was prepared and heated above the isotropization temperature (or close to the degradation point). Then, in order to check the transition temperatures and their reproducibility over several cycles, a new and fresh sample was heated providing that neither the isotropic liquid nor the decomposition temperatures were reached during the two first heating runs, and then cooled from the mesophase. In the last stage of the experiment, the samples were heated above these temperatures allowing the control of the thermal stability of the samples. This procedure gave exploitable DSC traces for most samples. Some representative DSC traces are shown for illustration.



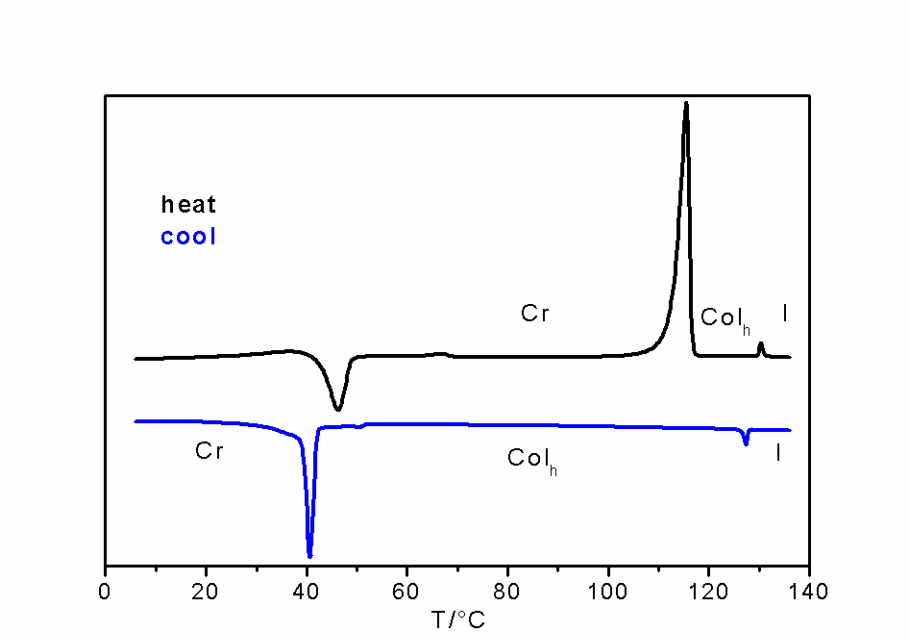
DSC traces of **5a** (second cycle, the isotropization temperature is reduced when compared to the first cycle).



DSC traces of **4b** (second cycle,).



DSC traces of **1c**



DSC traces of **1d**

Phase diagram

Mesomorphic behavior of the dendrimers studied here. Cr: crystalline phase; LamCr: lamello-crystalline phase; Col_h: hexagonal columnar phase; $Im\bar{3}m$: body-centered cubic phase; $Pm\bar{3}n$: primitive cubic phase; IL: isotropic liquid up to decomposition.

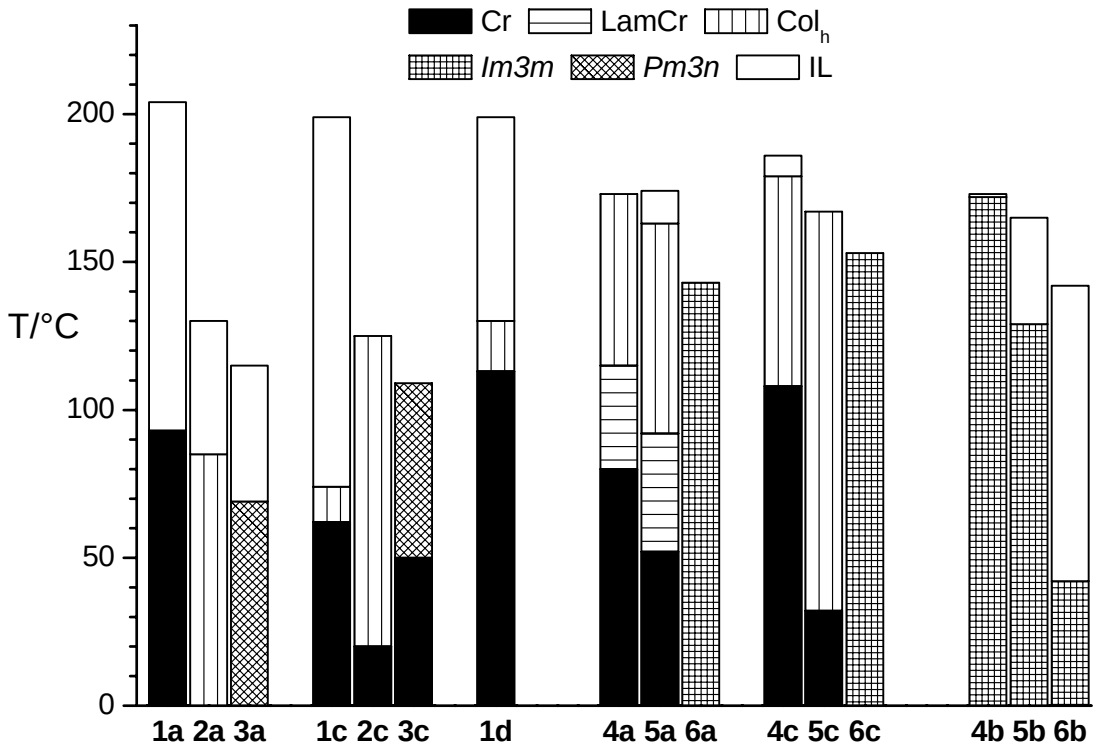


Table S1: Thermal behavior of the amphiphilic block co-dendrimers and X-ray characterization of the mesophases.

[d_{meas} and d_{theor} are the measured and theoretical diffraction spacings (d_{theor} is deduced from the following mathematical expressions: $\langle d_{001} \rangle = \frac{1}{N_l}(\sum_l d_{00l}.l)$, where N_l is the number of 00*l* reflections observed for the smectic phase; $\langle d_{10} \rangle = \frac{1}{N_{hk}}(\sum_{h,k} d_{hk}.\sqrt{h^2+k^2+hk})$, where N_{hk} is the number of *hk* reflections observed for the Col$_h$ phase; from *a* - for $Im\bar{3}m$ and $Pm\bar{3}n$ - the lattice parameter of the cubic phase: $a = \frac{1}{N_{hkl}}(\sum_{h,k,l} d_{hkl}.\sqrt{h^2+k^2+l^2})$,where N_{hkl} is the number of *hkl* reflections observed for the cubic phase); I is the intensity of the reflection (VS: very strong, S: strong, M: medium, W: weak, VW: very weak, br: broad); 00*l*, *hk* and *hkl* are the indexations of the reflections corresponding to the lamellar, Col$_h$ and cubic phases respectively; *d* is the lamellar periodicity ($d = \langle d_{001} \rangle$), A_M is the molecular area ($A_M = \frac{V_{mol}}{d}$); *D* is the lattice parameter of the Col$_h$ phase ($D = \frac{2}{\sqrt{3}}\langle d_{10} \rangle$), *S* is the lattice area ($S = D\langle d_{10} \rangle$); V_{cell}: a^3 (volume of the cubic cell), and *h.S* (volume of an hexagonal stratum of thickness *h*, see text). The molecular volume is defined as $V_{mol} = \frac{M}{\rho 0.6022}$, *M*: molecular weight, $V_{CH_2}(T) = 26.5616 + 0.02023T$ (*T* in °C, T_0 = 25 °C), ρ is the density ($\rho = \frac{V_{CH_2}(T_0)}{V_{CH_2}(T)}$); *N*: number of molecules per V_{cell} ($N = \frac{V_{cell}}{V_{mol}}$).

Compd	Transition temperatures/°C	d_{meas}/Å	I	Indexation *hkl*			d_{theor}/Å	Mesophase parameters measured at T
				hk	*hkl*	*00l*		
1a	Cr 93 I							–
2a	G –28 Col_h–*p6mm* 85 I	34.1	VS	10			34.05	T = 50 °C
		19.6	S	11			19.65	D = 39.3 Å
		17.05	W	20			17.0	S = 1 340 Å^2
		4.6	br					
3a	G 14 Cub-$Pm\bar{3}n$ 69 I	40.75	VS		200		40.75	T = 50 °C
		36.3	VS		210		36.45	a = 81.5 Å
		32.9	VS		211		33.3	V_{cell} = 541 345 Å^3
		29.4	S		220		28.8	
		21.8	M		321		21.8	
		20.35	W		400		20.4	
		4.6	br					
4a	Cr 80 LamCr 115 Col_h–*p6mm* 173 I	32.0	VS			001	32.0	T = 90 °C
		16.0	S			002	16.0	d = 32.0 Å
								A_M = 46.2 Å^2
		39.6	VS	10			39.6	T = 130 °C
		22.8	S	11			22.85	D = 45.7 Å
		19.85	M	20			19.8	S = 1 810 Å^2
		15.0	W	21			15.0	
		4.5	br					
5a	Cr 52 LamCr 92 Col_h–*p6mm* 163 I	48.4	VS			001	48.4	T = 50 °C
		24.3	S			002	24.2	d = 48.4 Å
		12.1	S			004	12.1	A_M = 50.0 Å^2
		43.15	VS	10			43.15	T = 100 °C
		25.0	S	11			24.9	D = 49.8 Å
		21.5	S	22			21.6	S = 2 150 Å^2
		4.6	br					

6a	G 28 Cub-$Im\bar{3}m$ 143 dec.	44.75	VS		110	44.75	T = 100 °C
		31.65	S		200	31.65	a = 63.3 Å
		25.85	S		211	25.85	V_{cell} = 253 060 Å^3
		22.2	M		220	22.4	
		19.85	M		310	20.0	
		18.25	VW		222	18.25	
		16.8	W		321	16.9	
		14.7	W		411/330	14.9	
		13.0	W		422	12.9	
		12.35	W		431/510	12.4	
		11.55	W		521	11.55	
		11.2	W		440	11.2	
		4.6	br				
1b	Liquid oil						–
2b	Liquid oil						–
3b	Liquid oil						–
4b	Cr –28 Cub-$Im\bar{3}m$ 172 I	38.7	VS		110	38.7	T = 100 °C
		27.8	S		200	27.35	a = 54.7Å
		22.0	S		211	22.35	V_{cell} = 163 670 Å^3
		4.5	br				
5b	Cr –21 Cub-$Im\bar{3}m$ 129 I	42.15	VS		110	41.75	T = 50 °C
		29.1	S		200	29.5	a = 59.05Å
		23.9	S		211	24.1	V_{cell} = 205 900 Å^3
		18.9	M		310	18.7	
		4.5	br				
6b	Cr –15 Cub-$Im\bar{3}m$ 42 I						-
1c	Cr 62 Col_h–*p6mm* 74 I	34.7	VS	10		34.75	T = 50°C
		20.05	M	11		20.05	D = 40.1 Å
		17.35	W	20		17.35	S = 1 395 Å^2
		4.6	br				

2c	Cr_1 –7 Cr_2 20 Col_h–*p6mm* 125 dec	38.7	VS	10		38.55	*T* = 40°C
		22.3	M	11		22.25	*D* = 44.5 Å
		19.25	W	20		19.3	*S* = 1 715 Å^2
		4.6	br				
3c	Cr_1 –43 Cr_2 50 Cub-*Pm*$\bar{3}$*n* 109 dec	41.4	VS		200	41.45	*T* = 80°C
		37.15	VS		210	37.1	*a* = 82.9 Å
		33.8	VS		211	33.85	V_{cell} = 569 663 Å^3
		4.6	br				
4c	Cr_1 –2 Cr_2 108 Col_h–*p6mm* 179 dec	43.6	VS	10		43.6	*T* = 140°C
		25.2	S	11		25.3	*D* = 50.35 Å
		21.85	S	20		21.8	*S* = 2 195 Å^2
		4.6	br				
5c	Cr_1 15 Cr_2 32 Col_h–*p6mm* 167 dec	46.8	VS	10		46.90	*T* = 100°C
		27.1	S	11		27.1	*D* = 54.15 Å
		23.45	S	20		23.45	*S* = 2 540 Å^2
		4.6	br				
6c	G –15 Cub-*Im*$\bar{3}$*m* 153 dec	27.0	S		211	27.0	*T* = 100°C
		23.35	M		220	23.4	*a* = 66.2 Å
		21.0	M		310	20.95	V_{cell} = 290 064 Å^3
		4.6	br				
1d	Cr 113 Col_h–*p6mm* 130 I	40.8	VS	10		40.85	*T* = 60°C
		23.55	M	11		23.6	*D* = 47.1 Å
		20.45	M	20		20.4	*S* = 1 925 Å^2
		4.6	br				

Cr, Cr_1, Cr_2: crystalline phases, G: amorphous or partially crystallized solid, I: isotropic liquid, LamCr: lamellar crystalline phase, Col_h: hexagonal columnar phase, Cub: cubic phase, dec.: decomposition temperature.

Table S2: Thermal behavior of the hydrophobic esters, acids and alcohols monodendrons based on a 3,5 arborescence and a 3,5, 3,4 or 3,4,5 chain substitution pattern (dodecyloxy chains).

	3,5[a]	3,4[b]	3,4,5[b]
G^1-CO_2Me	**12a**: Cr 54 I	**12d**: Cr 54 I	**12c**: Cr 44 I
G^1-CO_2H	**13a**: Cr 120 I	**13d**:	**13c**: Cr 60 I
G^1-CH_2OH	**14a**:	**14d**: Cr 53 I	**14c**: Cr 49 I
G^2-CO_2Me	**15a**:	**15d**: Cr 76 I	**15c**: Cr 87 I
G^2-CO_2H	**16a**:	**16d**: Cr 14 Col_h 68 I	**16c**: Cr 58 I
G^2-CH_2OH	**17a**: oil	**17d**: Cr 79 [Col_h 49] I	**17c**: Cr 49 I
G^3-CO_2Me	**18a**: oil	**18d**: Cr –4 Col_h 45 I	**18c**: Cr 45 I
G^3-CO_2H	**19a**: oil	**19d**:	**19c**: Cr –5 Cub-$Pm\bar{3}n$ 93 I
G^3-CH_2OH	**20a**: oil	**20d**:	**20c**: LQC 71 Tet-$P4_2/mnm$ 72 I

Data taken from: [a] Izabela Bury, PhD thesis2004. [b] (a) Percec, V.; Ahn, C.-H.; Cho, W.-D.; Jamieson, A. M.; Kim, J.; Leman, T.; Schmidt, M.; Gerle, M.; Möller, M.; Prokhorova, S. A.; Sheiko, S. S.; Cheng, S. Z. D.; Zhang, A.; Ungar, G.; Yeardley D. J. P. *J. Am. Chem. Soc.* 1998, *120*, 8619-8631. (b) Percec, V.; Cho, W. D.; Ungar, G.; Yeardley, D. J. P. *Angew. Chem. Int. Ed*. 2000, *39*, 1597-1602; (c) Percec, V.; Cho, W. D.; Ungar, G.; Yeardley, D. J. P. *J. Am. Chem. Soc*. 2001, *123*, 1302-1315.

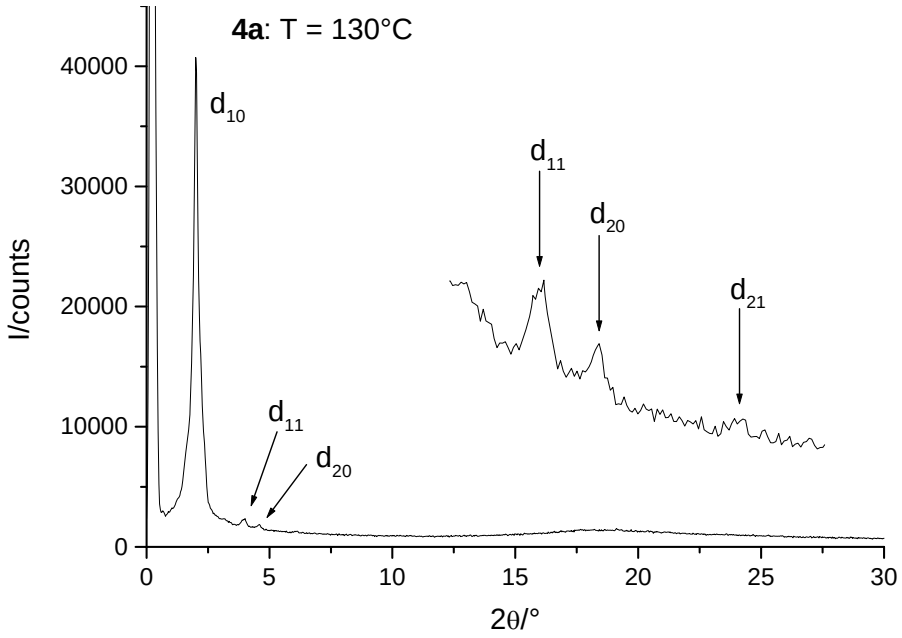
Table S3: DSC, TG data

Compounds	Temperatures [°C] et Enthalpies [kJ mol^{-1}] of the phases transitions	Decomposition temperatures [°C]
1a	Cr 93 (15.4) I	204
2a	G -28 Col_h 85 (0.6) I	130
3a	G 14 Cub 69 (1.2) I	115
4a	Cr 80 (15.2) LamCr 115 (20.2) Col_h 173 (0.3) I	180
5a	Cr 52 LamCr 92 (15.4) Col_h 163 (0.75) I	174
6a	G 28 Cub 143 dec.	143
1b	Liquid oil	112
2b	Liquid oil	98
3b	Liquid oil	81
4b	Cr -28 (85.0) Cub 172 (1.5) I	173
5b	Cr -21 (69.7) Cub 129 (0.4) I	165
6b	Cr -15 (107.2) Cub 42 (0.5)I	142
1c	Cr 62 (66.1) Col_h 74 (1.5) I	199
2c	Cr_1 -7 Cr_2 20 (42.0) Col_h 125 dec	125
3c	Cr_1 -43 Cr_2 50 (35.75) Cub 109 dec	109
4c	Cr_1 -2 Cr_2 108 (18.25) Col_h 179 dec	179
5c	Cr_1 15 Cr_2 32 (19.9) Col_h 167 dec	167
6c	G -15 Cub 153 dec	153
1d	Cr 113 (63.5) Col_h 130 (1.1) I	199

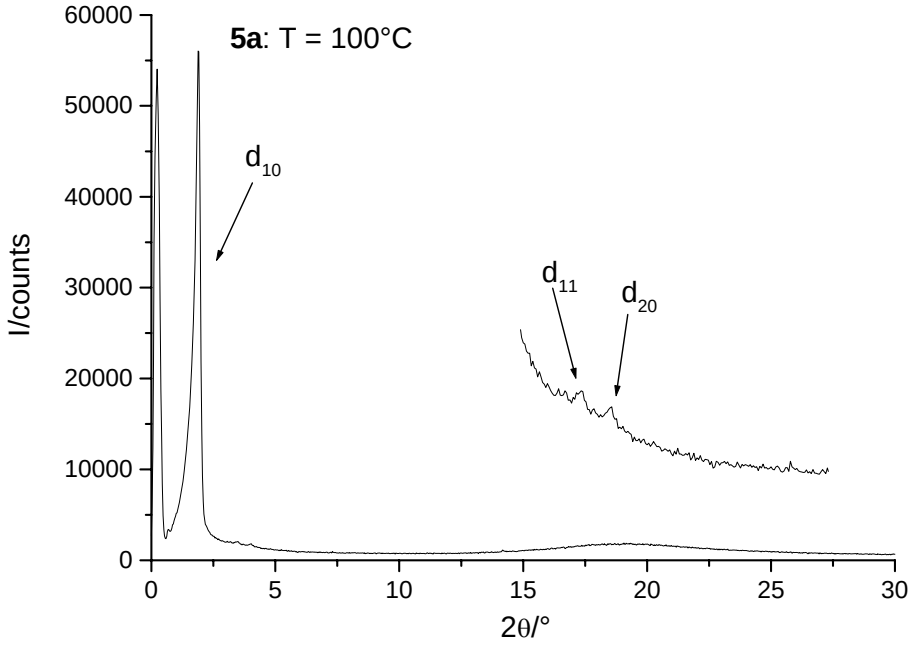
Cr, Cr_1, Cr_2: crystalline phases, G: amorphous or partially crystallized solid, I: isotropic liquid, LamCr: lamellar crystalline phase, Col_h: hexagonal columnar phase, Cub: cubic phase.

XRD characterization

Diffractogram of the Col_h phase of **4a** (*p6mm*)



Diffractogram of the Col_h phase of **5a** (*p6mm*)



Diffractogram of the cubic phase of **6a** ($Im\bar{3}m$)

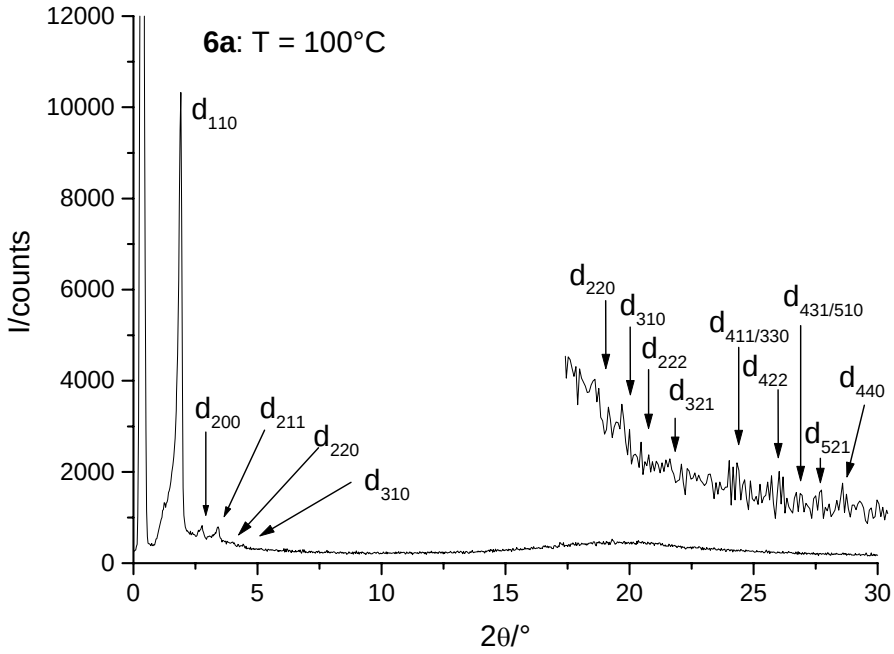
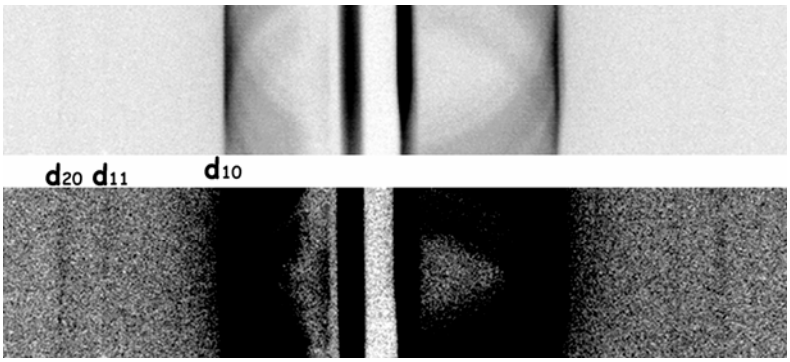


Image plates of **1c** at 50°C (Col_h-*p6mm*)



XRD diagram of **2c** at T = 40°C (Col_h-*p6mm*)

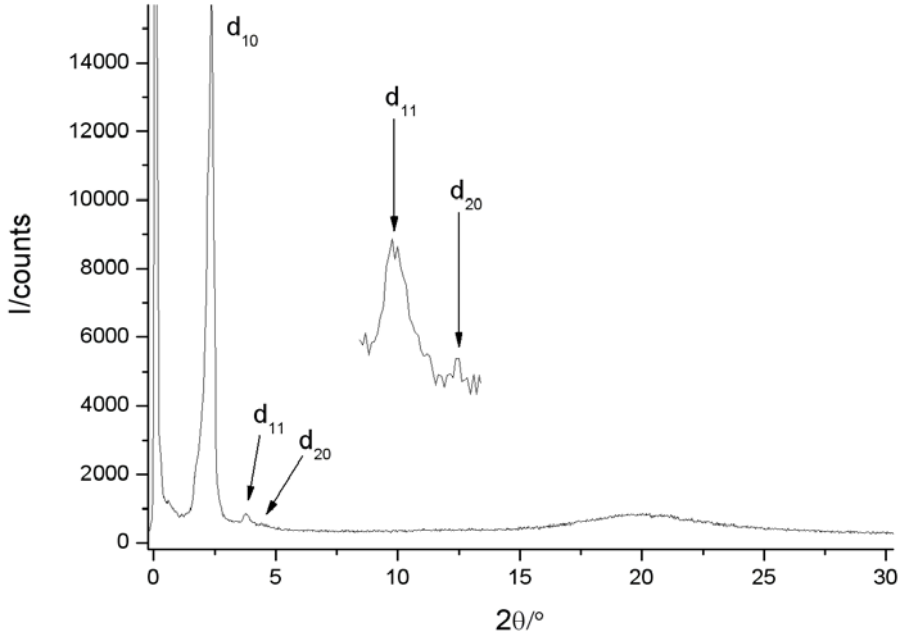
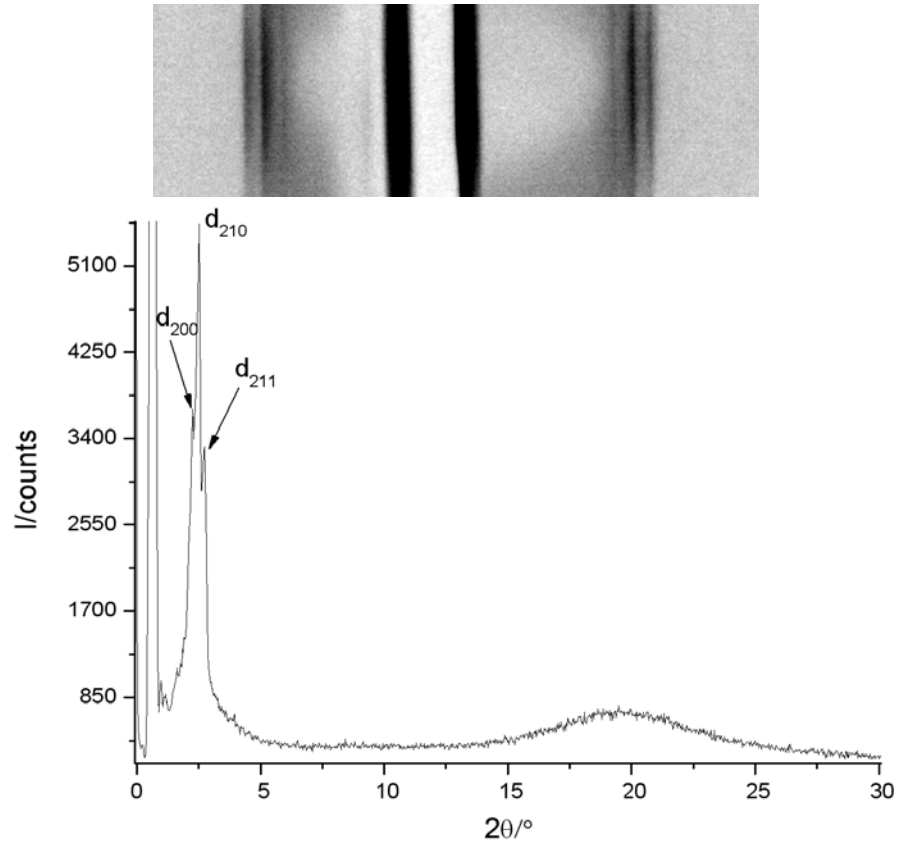
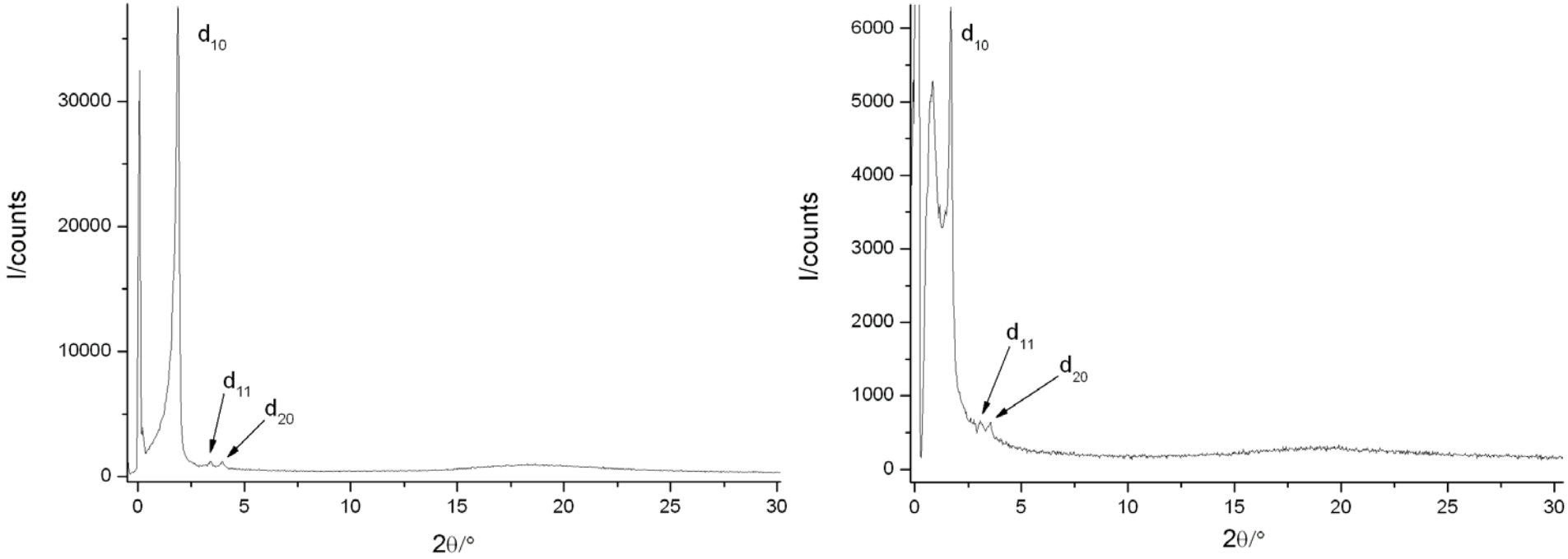


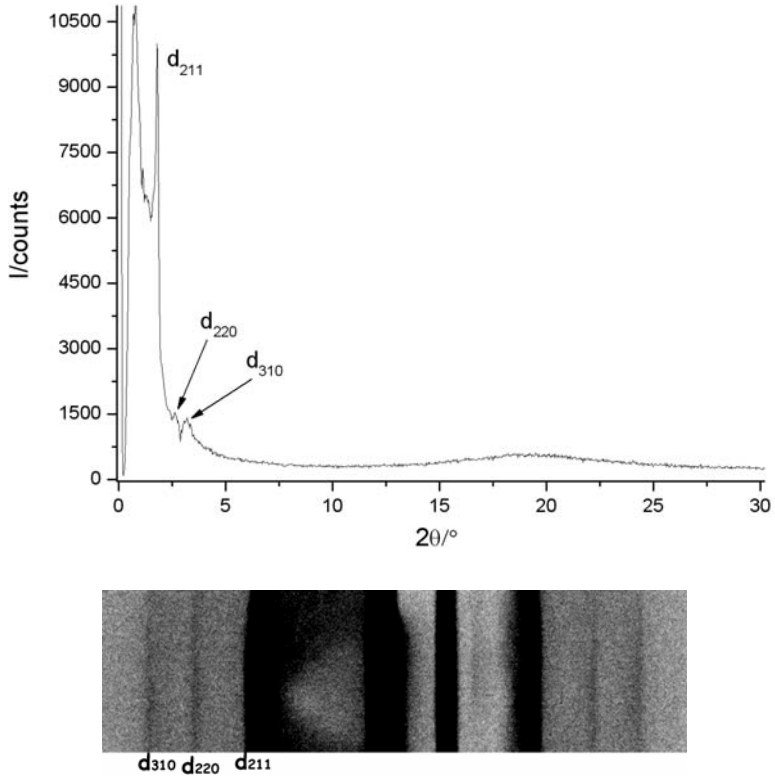
Image plate (SAXS) and XRD diagram of **3c** at T = 80°C (Cub-$Pm\bar{3}n$)



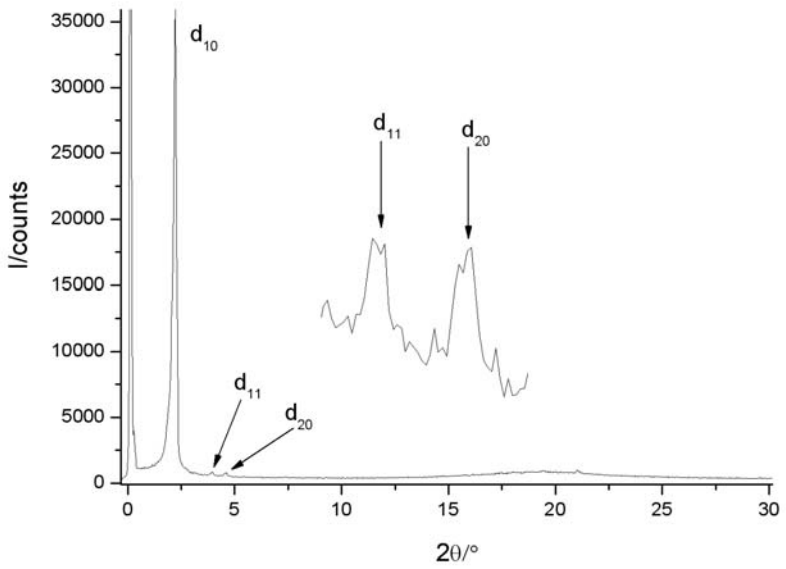
XRD diagrams of **4c** (left, T = 140°C) and **5c** (right, T = 100°C) (Col_h-*p6mm*)



XRD diagram and Image plate of **6c** (Cub-$Im\bar{3}m$) at 100°C



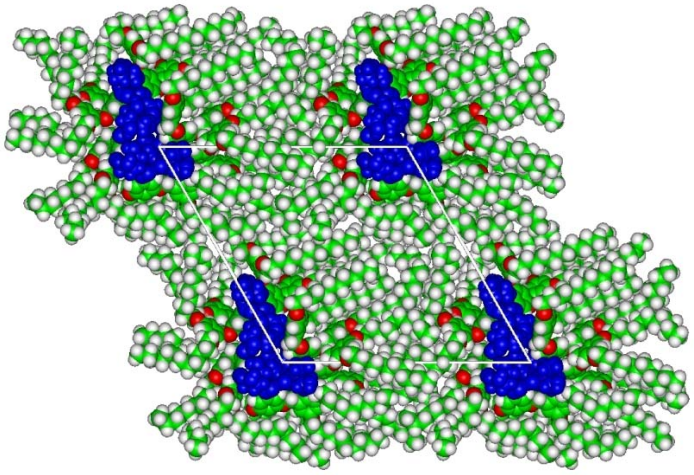
XRD diagram of **1d** at T = 60°C (Col_h-*p6mm*)



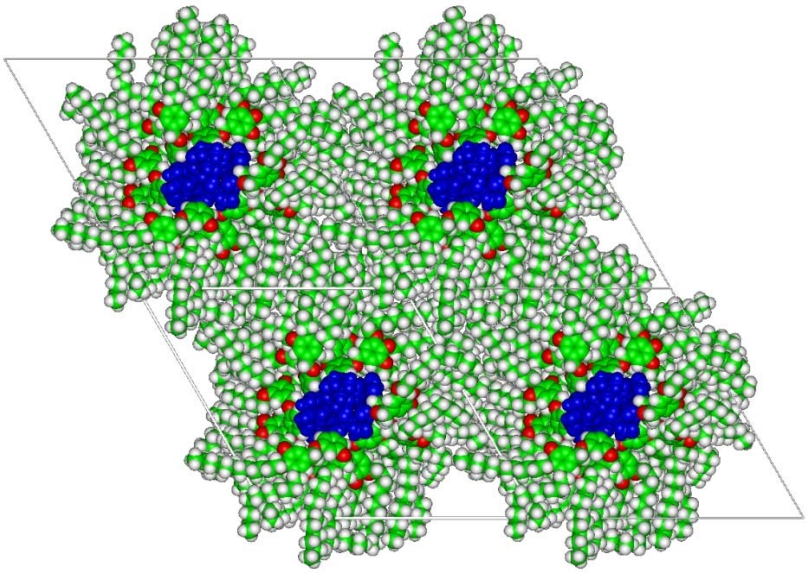
Col_h phase modeling

The following structures are represented at the same scale, and follows the description order of the text.

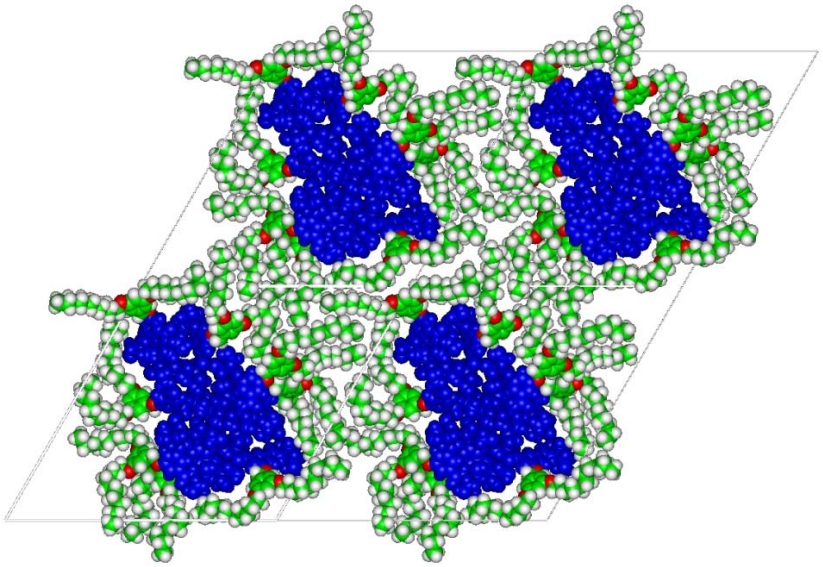
Snapshot showing the molecular self-assembling of **2a** into the hexagonal lattice of the Col_h phases (polar central core in blue).



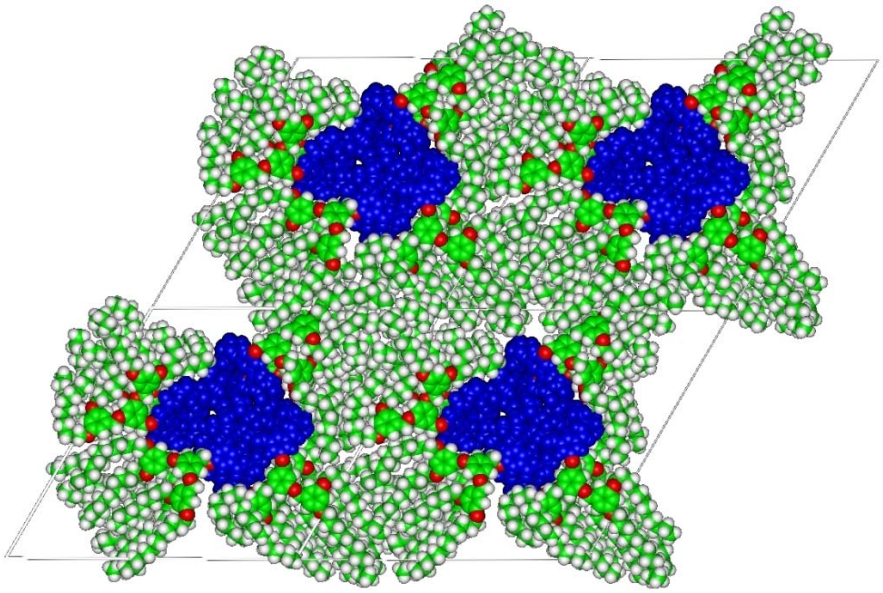
Snapshot showing the molecular self-assembling of **2c** into the hexagonal lattice of the Col_h phases (polar central core in blue).



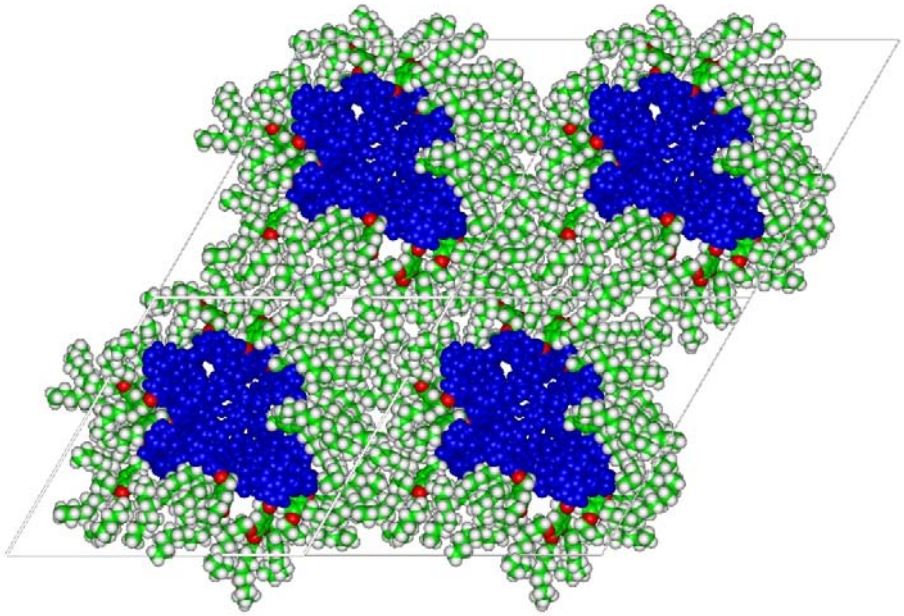
Snapshot showing the organization of **4a** in the Col_h phase (in blue – polar central core). Only one layer (6.75 Å) is represented, the apparent empty zones, being actually filled by neighbored layers.



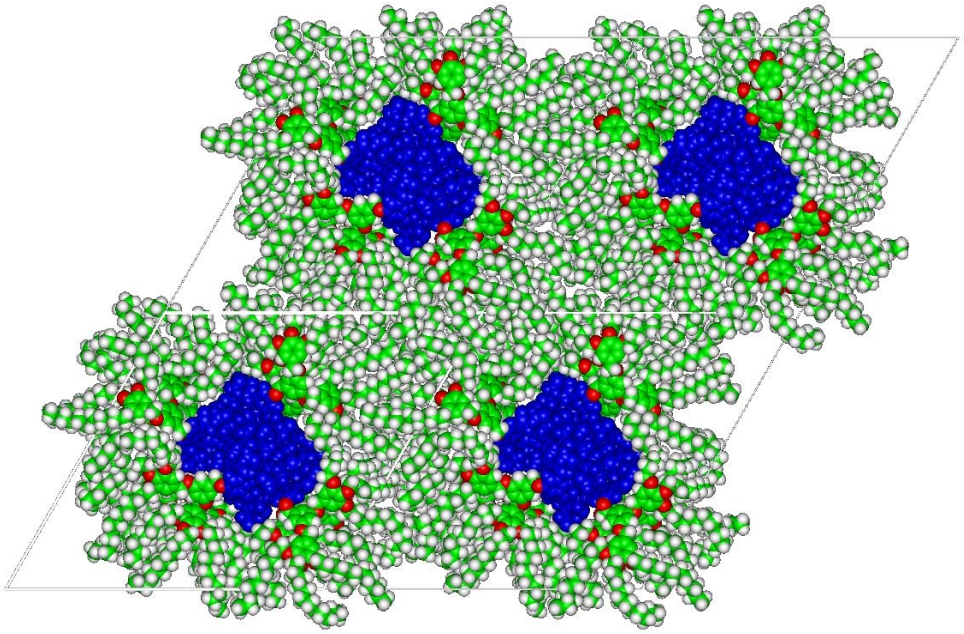
Snapshot showing the packing of **5a** after MD in the hexagonal 2D lattice of the Col_h phase (polar column in blue).



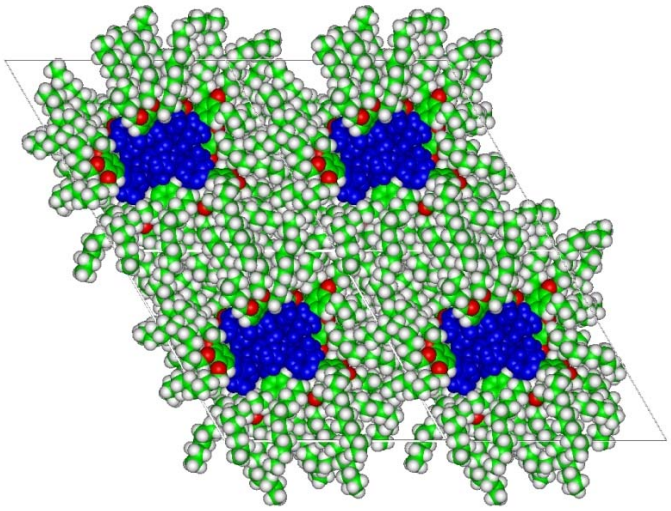
Snapshots of packing of **4c** after MD in the hexagonal 2D lattice of the Col_h phase (polar column in blue).



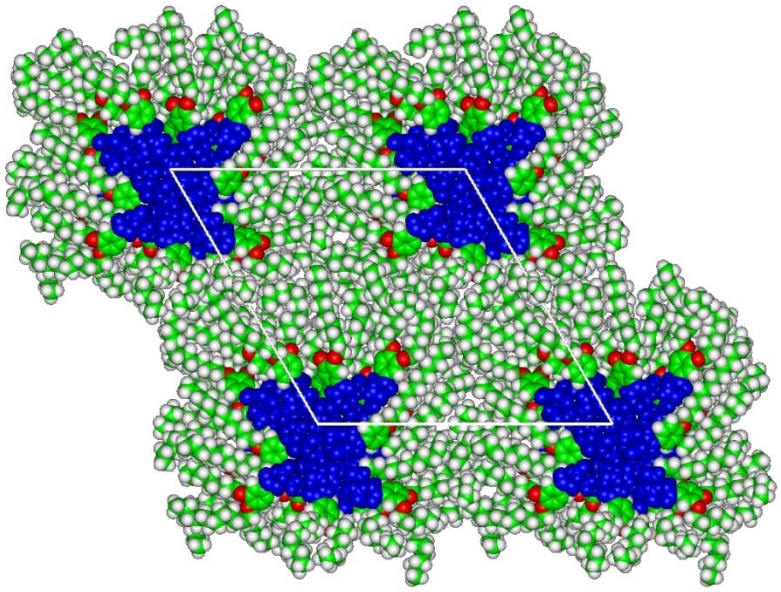
Snapshots of packing of **5c** after MD in the hexagonal 2D lattice of the Col_h phase (polar column in blue).

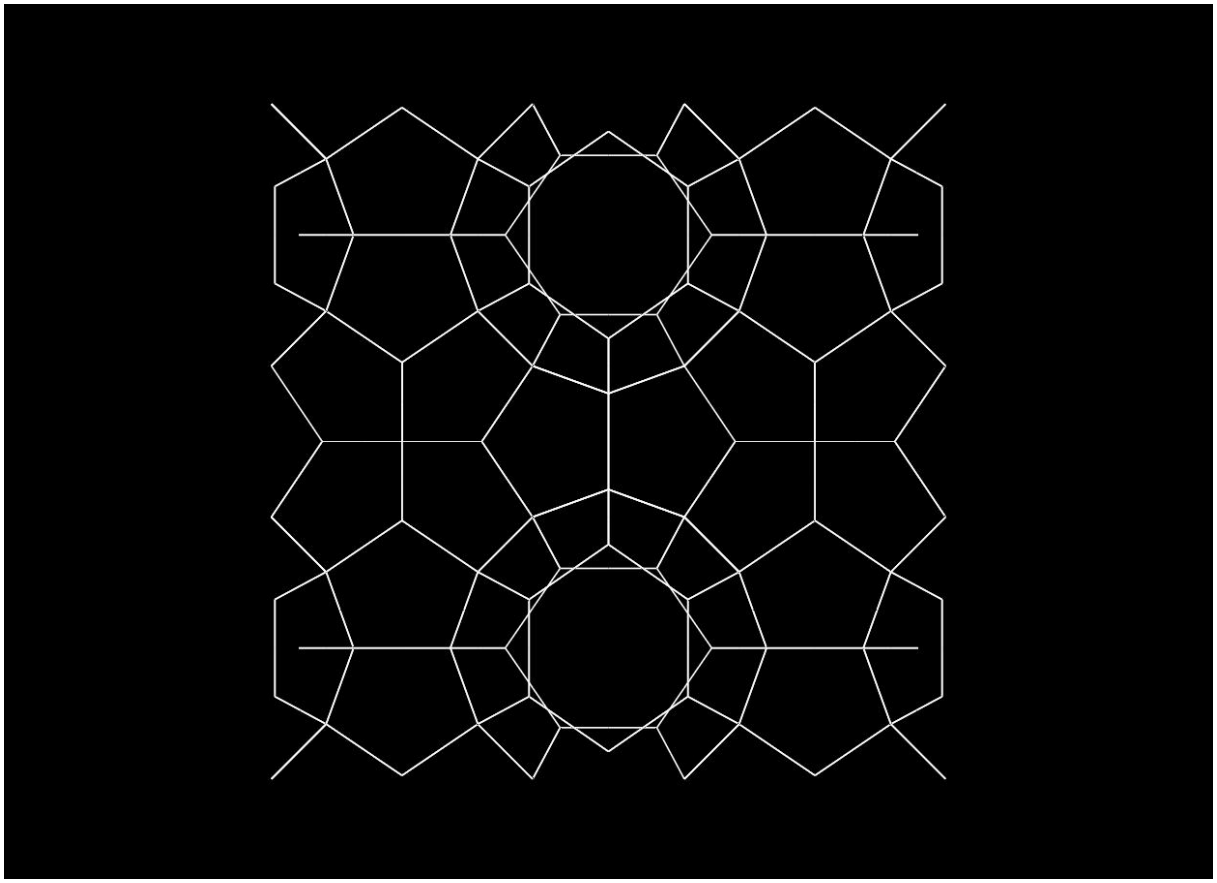


Snapshots of packing of **1c** after MD in the hexagonal 2D lattice of the Col_h phase (polar column in blue).

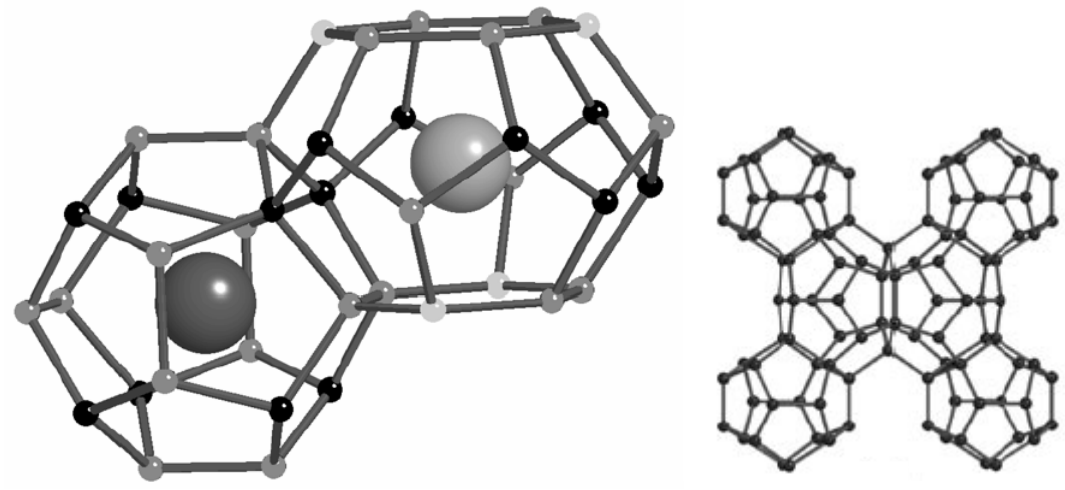


Snapshots of packing of **1d** after MD in the hexagonal 2D lattice of the Col_h phase (polar column in blue).





Projection in one plane of the cubic lattice of the network formed by the assembly of dodecahedron and tetrakaidecahedron in the cubic $Pm\bar{3}n$ phase.



Details showing the connection of one dodecahedron and one tetrakaidecahedron through one of their pentagonal face (left) and the connection between two tetrakaidecahedron through one of their hexagonal face in the $Pm\bar{3}n$ cubic structure (from Perottoni, C. A.; da Jornada, J. A. H. *J. Phys.: Condens. Matter* **2001**, *1*, 5981–5998).

General synthetic procedures

Preparation of hydrophilic dendritic parts of first and second generation

(**7**): To a solution of TRIS (8 g, 66.0 mmol) and imidazole (14.84 g, 217.9 mmol) in DMF (100 ml) under argon in –10 °C was added a solution of TBDMSCl (32.76 g, 217.9 mmol) in DMF (50 ml). The reaction was stirred at –10°C for 15 min, then allowed to warm to room temperature and stirred for 48 h. The solvent was removed and the residue was mixed with CH_2Cl_2. The white precipitate was filtrated and the residue in CH_2Cl_2 (200 ml) was washed with water (2 x 200 ml) and brine (2 x 200 ml), dried over $MgSO_4$ and filtered. The solvent was removed by under reduced pressure and the residue was dried under vacuum to give colorless oil (28.8 g, 94%). ^{1}H NMR($CDCl_3$): δ = 3.44 (6H, s), 1.47 (2H, broad), 0.89 (27H, s), 0.04 (18H, s).

(**8**): To a solution of 5-hydroxyisophthalic acid (10 g, 54.9 mmol) in DMF (70 ml) was added acetyl chloride (21.55 g, 274.5 mmol) and the reaction was heated at 57°C for 12 h. The solvent was removed under reduced pressure. The white solid was washed with CH_2Cl_2 (2 x 200 ml) and dried under vacuum to give pure product (14.7 g, 95%). ^{1}H NMR(DMSO-d_6): δ = 8.33 (1H, s), 7.88 (2H, d, ^{3}J = 1.5Hz), 3.31 (2H, b), 2.29 (3H, s). ^{13}C NMR(DMSO-d_6): δ = 169.21, 165.90, 150.73, 132.77, 127.27, 126.90, 20.87.

(**9**): A suspension of 2-mercaptobenzoxazole (13.32 g, 49.58 mmol) in 70 ml of toluene was mixed with a solution of Et_3N (6.93 ml, 49.58 mmol) in toluene (30 ml). To this mixture, was added dropwise diphenylphosphochloridate (7.5 g, 49.58 mmol) in toluene (30 ml) for 30 min at room temperature. The reaction was maintained at this temperature for 1.5 h, then the solvent was removed, and the compound crystallized several times from hexane until white (14.1 g, 74%).

(**10**): A solution of **8** (3.0 g, 13.4 mmol), condensing agent **9** (10.77 g, 28.1 mmol) and dry Et_3N (5.61 ml, 40.14 mmol) in dry THF (30 ml) was stirred for 2 h at room temperature under argon and a solution of **7** (13.65 g, 29.4 mmol) in THF (20 ml) was added. The reaction mixture was stirred for 48 h. The solvent was then removed under reduced pressure. The residue was partitioned between CH_2Cl_2 and water and the organic extract was washed with NH_4Cl (2 x 250 ml) and brine (2 x 250 ml), dried over $MgSO_4$ and filtered, and the solvent removed. The crude material was purified by flash chromatography (SiO_2, 95:5 CH_2Cl_2/Et_3N)

to give a white solid (12.45 g, 84%). ^{1}H NMR($CDCl_3$): δ = 7.95 (1H, t, ^{3}J = 1.5Hz), 7.50 (2H, d, ^{3}J = 1.5Hz), 6.35 (2H, s), 3.94 (12H, s), 2.30 (3H, s), 0.88 (54H, s), 0.05 (36H, s).

(**11**): To a solution of **10** (12.25 g, 11.0 mmol) in MeOH-water (50 ml:50 ml) was added KOH (1.23 g, 22.0 mmol) and the mixture was stirred for 12 h. MeOH was removed and the residue was partitioned between CH_2Cl_2 and water and washed with NH_4Cl (2 x 250 ml) and brine (2 x 250 ml), dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation at aspirator pressure and the product was dried under vacuum to give a white solid (9.31 g, 79%). ^{1}H NMR($CDCl_3$): δ = 7.91 (1H, s), 7.55 (1H, t, ^{3}J = 1.3Hz), 7.53 (2H, d, ^{3}J = 1.3Hz), 6.42 (2H, s), 3.95 (12H, s), 0.88 (54H, s), 0.05 (36H, s).

The preparation of the two series of dendrons of the first, second, and third generation, as well as their analytical characterization are added in the supporting information data

*Preparation of the dendrimers **1-3***

The preparation of **1a** has been selected as a representative example since the same procedure was systematically used for all the members of the series. The conditions of purification have been added when they were modified. The intermediary protected compounds have been purified as in (i).

(**1a**): (i) A solution containing **13a** (1.2 g, 2.44 mmol), **9** (1.12 g, 2.93 mmol) and dry Et_3N (0.68 ml, 4.88 mmol) in dry THF (10 ml) under argon was stirred at room temperature for 2 h. Then a solution of **7** (1.36 g, 2.93 mmol) in dry THF (10ml) was added, and the mixture was stirred for 48 h. The solvent was evaporated to dryness and the residue was partitioned between CH_2Cl_2 and water (100 ml:100 ml) and the organic extract was washed with NH_4Cl (2 x 100 ml) and brine (2 x 100 ml), dried over $MgSO_4$ and filtered, and the solvent removed. The crude material was purified by chromatography (SiO_2, eluted with 95:5 CH_2Cl_2/Et_3N) to give pale green waxy solid (1.65 g, 72%). ^{1}H NMR($CDCl_3$): δ = 6.81 (2H, d, ^{3}J = 2.3Hz), 6.54 (1H, t, ^{3}J = 2.2Hz), 6.34 (1H, s), 3.94 (10H, m), 1.75 (4H, m), 1.27 (36H, m), 0.89 (33H, m), 0.06 (18H, s). (ii) To this solution (1.5 g, 1.60 mmol) in THF (15 ml) was added the solution of TBAF (5.28 ml, 1M in THF) at 0°C and the reaction was stirred at room temperature for 12 h. The solvent was removed and the crude product was purified by chromatography (SiO_2, eluted with 90:6:4 CH_2Cl_2/MeOH/Et_3N) to give a white solid (0.49 g, 52%). ^{1}H NMR($CDCl_3$): δ = 6.98 (2H, d, ^{3}J = 2.2Hz), 6.67 (1H, t, ^{3}J = 2.2Hz), 4.05 (4H, t, ^{3}J

= 6.4Hz), 3.91 (6H, s), 1.83 (4H, m), 1.52 (3H, b), 1.36 (36H, m), 0.96 (6H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 168.79, 160.42, 135.63, 105.36, 104.87, 68.30, 62.37, 60.69, 31.87, 29.62, 29.58, 29.30, 25.97, 22.64, 14.05. Anal. cald for $C_{35}H_{63}NO_6$ (MW = 593.88 g.mol^{-1}): C: 70.78, H: 10.69, N: 2.36, O: 16.16; found: C: 70.66, H: 10.80, N: 2.32, O: 15.82. HRMS-FAB (M + Na^+) calcd for m/e 593.47 (100%), found 594.20 g.mol^{-1}.

(**1b**): (i) From **13b** (1.0 g, 0.714 mmol), **9** (0.33 g, 0.857 mmol), Et_3N (0.2 ml, 1.43 mmol) and **7** (0,4 g, 0.857 mmol). CC (SiO_2, eluted with CH_2Cl_2/Et_3N, 95:5). Pale green oil (1.23 g, 93%). ^{1}H NMR($CDCl_3$): δ = 6.80 (2H, d, ^{3}J = 2.2Hz), 6.55 (1H, t, ^{3}J = 2.2Hz), 6.36 (1H, s), 3.97 (6H, s), 3.94 (4H, s), 3.47 (12H, s), 3.36 (12H, t, ^{3}J = 6.5Hz), 1.52 (12H, m), 1.25 (108H, m), 0.88 (45H, m), 0.05 (18H, s). (ii) CC (SiO_2, eluted with 90:6:4 CH_2Cl_2/MeOH/Et_3N). Colorless oil (0.79 g, 87%). ^{1}H NMR($CDCl_3$): δ = 7.17 (1H, t, ^{3}J = 2.1Hz), 6.87 (2H, d, ^{3}J = 2.1Hz), 6.63 (1H, s), 3.97 (4H, s), 3.78 (6H, s), 3.61 (3H, b), 3.48 (12H, s), 3.38 (12H, t, ^{3}J = 6.5Hz), 1.52 (12H, m), 1.25 (108H, m), 0.88 (18H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 168.81, 160.66, 135.43, 105.75, 104.44, 71.58, 69.21, 67.47, 62.05, 61.91, 45.21, 31.92, 29.71, 29.61, 29.37, 26.19, 22.68, 14.09. Anal. calcd for $C_{93}H_{179}NO_{12}$ (MW = 1503.42 g.mol^{-1}): C: 74.30, H: 12.00, N: 0.93, O: 12.77; found: C: 74.31, H: 12.13, N: 1.13, O: 12.51. HRMS-FAB (M + Na^+) calcd for m/e 1503.35 (100%), found 1502.9 g.mol^{-1}.

(**1c**): (i) From **13c** (1.2 g, 1.78 mmol), **9** (0.82 g, 2.14 mmol), Et_3N (0.5 ml, 3.56 mmol) and **7** (0.99 g, 2.14 mmol). CC (SiO_2, eluted with CH_2Cl_2/Et_3N, 95:5). Pale green waxy solid (1.3 g, 65%). ^{1}H NMR($CDCl_3$): δ = 6.89 (2H, s), 6.30 (1H, s), 3.96 (6H, m), 3.94 (6H, m), 1.80 (6H, m), 1.27 (54H, m), 0.89 (36H, m), 0.06 (18H, s). (ii) CC (SiO_2, eluted with CH_2Cl_2/MeOH/Et_3N, 90:6:4) and crystallization from methanol. White solid (0.72 g, 87%). ^{1}H NMR($CDCl_3$): δ = 7.18 (1H, s), 6.96 (2H, s), 4.00 (6H, m), 3.75 (6H, s), 1.77 (9H, m), 1.27 (54H, m), 0.88 (9H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 168.63, 153.11, 141.64, 128.34, 105.67, 73.52, 69.34, 62.32, 60.67, 31.89, 30.27, 29.60, 29.33, 26.05, 22.65, 14.07. Anal. cald for $C_{47}H_{87}NO_7$ (MW = 778.2 g.mol^{-1}): C: 72.54, H: 11.27, N: 1.80, O 14.39; found: C: 72.28, H: 11.32, N: 1.84, O: 14.21. HRMS-FAB calcd for m/e 777.65 (100%), found 778.5 g.mol^{-1}.

(**1d**): (i): From **13d** (1.2 g, 2.44 mmol), **9** (1.12 g, 2.93 mmol), Et_3N (0.68 ml, 4.88 mmol) and **7** (1.36 g, 2.93 mmol). CC (SiO_2, eluted with CH_2Cl_2/Et_3N, 95:5). Pale yellow oil (1.60 g, 70%). ^{1}H NMR($CDCl_3$): δ = 7.30 (1H, d, ^{3}J = 2.0Hz), 7.19 (1H, dd, ^{3}J = 2.0Hz, ^{3}J = 8.3Hz), 6.84 (1H, d, ^{3}J = 8.3Hz), 6.32 (1H, s). 3.97 (10H, m), 1.82 (4H, m), 1.27 (36H, s), 0.89 (33H, m), 0.06 (18H, s). (ii) CC (SiO_2, eluted with CH_2Cl_2/MeOH/Et_3N, 92:4:4) and crystallized

from methanol. White solid (0.89 g, 94%). ^{1}H NMR($(CD_3)_2CO$): δ = 7.42 (1H, d, ^{3}J = 2.2Hz), 7.37 (1H, dd, ^{3}J = 2.2Hz, ^{3}J = 8.3Hz), 7.23 (1H, s), 7.00 (1H, d, ^{3}J = 8.3Hz), 4.55 (3H, t, ^{3}J = 6.1Hz), 4.05 (4H, m); 3.75 (6H, d, ^{3}J = 6.1Hz), 1.79 (4H, m), 1.28 (36H, m), 0.86 (6H, t, ^{3}J = 6.7Hz). ^{13}C NMR(THF-d_6): δ = 165.43, 150.42, 147.12, 125.43, 117.94, 111.23, 110.29, 67.03, 66.77, 60.26, 60.18, 24.22, 23.01, 22.73, 22.21, 21.93, 20.73, 11.61. Anal. cald for $C_{35}H_{63}NO_6$ (MW = 593.88 g.mol^{-1}): C: 70.78, H: 10.69, N: 2.36, O: 16.16; found: C: 70.44, H: 10.77, N: 2.35, O: 16.25. HRMS-FAB calcd for m/e 593.47 (100%), found 594.30 g.mol^{-1}.

(**2a**): (i) From **16a** (0.75 g, 0.7 mmol), **9** (0.32 g, 0.84 mmol), Et_3N (0.19 ml, 1.4 mmol) and **7** (0.39 g, 0.84 mmol). CC (SiO_2, eluted with CH_2Cl_2/hexane/Et_3N, 65:30:5). Pale yellowish sticky paste (0.92 g, 87%). ^{1}H NMR($CDCl_3$): δ = 6.94 (2H, d, ^{3}J = 2.3Hz), 6.69 (1H, s), 6.54 (4H, d, ^{3}J = 2.3Hz), 6.41 (2H, t, ^{3}J = 2.2Hz), 6.35 (1H, s), 4.95 (4H, s), 3.94 (14H, m), 1.77 (8H, m), 1.27 (72H, m), 0.88 (39H, m), 0.05 (18H, s). (ii) CC (SiO_2, eluted with 88:6:4 CH_2Cl_2/MeOH/Et_3N). Amorphous solid (0.53 g, 76%). ^{1}H NMR($CDCl_3$): δ = 7.19 (1H, s), 6.99 (2H, d, ^{3}J = 2.2Hz), 6.74 (1H, t, ^{3}J = 2.1Hz), 6.55 (4H, d, ^{3}J = 2.2Hz), 6.41 (2H, t, ^{3}J = 2.1Hz), 4.98 (4H, s), 3.94 (6H, t, ^{3}J = 6.5Hz), 3.76 (6H, b), 1.77 (8H, m), 1.27 (72H, m), 0.88 (12H, t, ^{3}J = 6.7Hz). ^{13}C NMR ($CDCl_3$): δ = 168.46, 160.50, 160.01, 138.40, 135.88, 106.11, 105.79, 105.59, 100.89, 70.35, 68.06, 62.07, 61.58, 31.89, 29.65, 29.61, 29.24, 26.03, 22.66, 14.09. Anal. calcd. for $C_{73}H_{123}NO_{10}$ (MW = 1174.76 g.mol^{-1}): C: 74.64, H: 10.55, N: 1.19, O: 13.62; found C: 74.24, H: 10.58, N: 1.06, O: 13.51. HRMS-FAB (M + Na^+) calcd for m/e 1173.91 (100%), found 1174.4 g.mol^{-1}.

(**2b**): (i) From **16b** (0.74 g, 0.256 mmol), **9** (0.12 g, 0.307 mmol), Et_3N (0.07ml, 0.512 mmol) and **7** (0.14 g, 0.307 mmol). CC (SiO_2, eluted with CH_2Cl_2/Et_3N, 95:5). Pale green oil (0.77 g, 90%). ^{1}H NMR($CDCl_3$): δ = 6.97 (2H, d, ^{3}J = 2.2Hz), 6.74 (1H, s), 6.56 (4H, d, ^{3}J = 2.0Hz), 6.45 (2H, s), 6.37 (1H, s); 4.91 (4H, s), 3.98 (8H, s), 3.95 (6H, s), 3.49 (24H, s), 3.38 (24H, t, ^{3}J = 6.5Hz), 1.52 (24H, m), 1.25 (216H, m), 0.87 (63H, m), 0.06 (18H, s). (ii) CC (SiO_2, eluted with 90:6:4 CH_2Cl_2/MeOH/Et_3N). Colorless oil (0.38 g, 61%). ^{1}H NMR($CDCl_3$): δ = 7.12 (1H, s), 6.98 (2H, d, ^{3}J = 2Hz), 6.79 (1H, t, ^{3}J = 2Hz), 6.57 (4H, d, ^{3}J = 2Hz), 6.45 (2H, t, ^{3}J = 2Hz), 4.98 (4H, s), 3.94 (8H, s), 3.88 (3H, t,^{3}J = 6.0Hz), 3.72 (6H, d, ^{3}J = 6.0Hz), 3.49 (24H, s), 3.38 (24H, t, ^{3}J = 6.6Hz), 1.52 (24H, m), 1.25 (216H, m), 0.88 (36H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 168.20, 160.77, 160.10, 138.25, 135.93, 106.44, 106.01, 105.96, 101.13, 71.61, 70.57, 69.34, 67.24, 62.92, 61.50, 45.21, 31.93, 29.71, 29.61, 29.37, 26.20, 22.68, 14.09. Anal. calcd for $C_{189}H_{355}NO_{22}$ (MW = 2993.83 g.mol^{-1}): C: 75.82, H: 11.95, N:

0.47, O 11.76; found: C: 75.72, H: 11.97, N: 0.26, O: 11.78. MALDI-TOF calcd for m/e 2993.68 (100%), found 2994.77g.mol^{-1}.

(**2c**): (i): From **16c** (0.8 g, 0.555 mmol), **9** (0.26 g, 0.667 mmol), Et_3N (0.16 ml, 1.11 mmol) and **7** (0.31g, 0.667 mmol). CC: (SiO_2, eluted with CH_2Cl_2/Et_3N, 95:5). Pale green oil (0.86 g, 82%). ^{1}H NMR($CDCl_3$): δ = 6.96 (2H, d, ^{3}J = 2.2Hz), 6.71 (1H, t, ^{3}J = 2.2Hz), 6.60 (4H, s), 6.36 (1H, s), 4.92 (4H, s), 3.94 (12H, m), 3.75 (6H, s), 1.77 (12H, m), 1.27 (108H, s), 0.88 (45H, m), 0.05 (18H, s). (ii) CC (SiO_2, eluted with CH_2Cl_2/MeOH/Et_3N, 92:4:4). Waxy solid (0.43 g, 65%). ^{1}H NMR($CDCl_3$): δ = 7.16 (1H, s), 7.00 (2H, d, ^{3}J = 2.2Hz), 6.76 (1H, t, ^{3}J = 2.2Hz), 6.62 (4H, s), 4.95 (4H, s), 3.97 (18H, m), 3.76 (3H, t, ^{3}J = 6.6Hz), 1.77 (12H, m), 1.27 (108H, m), 0.88 (18H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 168.47, 160.03, 153.30, 138.10, 135.96, 131.13, 106.31, 106.12, 105.59, 73.39, 70.78, 69.14, 62.06, 61.74, 31.87, 30.30, 29.61, 29.32, 26.09, 22.64, 14.05. Anal. calcd for $C_{97}H_{171}NO_{12}$ (MW = 1543.4 g.mol^{-1}): C: 75.49, H: 11.17, N: 0.91; found: C: 75.67, H: 11.05, N: 1.12. MALDI-TOF calcd for m/e 15432.28 (100%), found 1566.86 g.mol^{-1}.

(**3a**): (i): From **19a** (0.55 g, 0.246 mmol), **9** (0.11 g, 0.295 mmol), Et_3N (0.05 ml, 0.492 mmol) and **7** (0.14 g, 0.295 mmol). CC (SiO_2, eluted with CH_2Cl_2/hexane/Et_3N, 45:50:5). Pale sticky paste (0.51 g, 78%). ^{1}H NMR($CDCl_3$): δ = 6.96 (2H, d, ^{3}J = 2.2Hz), 6.72 (1H, t, ^{3}J = 2.2Hz), 6.68 (4H, d, ^{3}J = 2.2Hz), 6.56 (10H, m), 6.41 (4H, t, ^{3}J = 2.2Hz), 6.36 (1H, s), 4.98 (4H, s), 4.95 (8H, s), 3.93 (22H, m), 1.75 (16H, m), 1.26 (144H, m), 0.88 (51H, m), 0.05 (18H, s). (ii) CC (SiO_2, eluted with 94:2:4 CH_2Cl_2/MeOH/Et_3N). Amorphous solid (0.37 g, 86%). ^{1}H NMR($CDCl_3$): δ = 7.20 (1H, s), 7.00 (2H, d, ^{3}J = 2Hz), 6.75 (1H, t, ^{3}J = 2H), 6.68 (4H, d, ^{3}J = 2.2Hz), 6.57 (2H, t, ^{3}J = 2.2H), 6.55 (8H, d, ^{3}J = 2.2H), 6.40 (4H, t, ^{3}J = 2.2Hz), 5.01 (4H, s), 4.95 (8H, s), 3.93 (16H, t, ^{3}J = 6.5Hz), 3.75 (6H, b), 3.59 (3H, b), 1.75 (16H, m), 1.26 (144H, m), 0.88 (24H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 168.31, 160.48, 160.15, 159.93, 138.79, 138.65, 136.01, 106.43, 106.15, 105.72, 101.64, 100.78, 70.16, 68.66, 62.73, 61.66, 31.91, 29.67, 29.61, 29.35, 26.05, 22.68, 14.11. Anal. calcd for $C_{149}H_{243}NO_{18}$ (MW = 2336.52 g.mol^{-1}): C: 76.59, H: 10.48, N: 0.60, O: 12.33; found: C: 76.53, H: 10.51, N: 0.40, O: 12.25. MALDI-TOF calcd for m/e 2335.82 (100%), found 2336.98 g.mol^{-1}.

(**3b**): (i) From **19b** (0.59 g, 0.1 mmol), **9** (0.05 g, 0.121 mmol), Et_3N (0.03 ml, 0.2 mmol) and **7** (0.06g, 0.121 mmol). CC (SiO_2, eluted with CH_2Cl_2/Et_3N, 95:5). Pale yellow oil (0.31 g, 49%). ^{1}H NMR($CDCl_3$): δ = 6.99 (2H, d, ^{3}J = 2.1Hz), 6.78 (1H, t, ^{3}J = 2.1Hz), 6.72 (4H, d, ^{3}J = 2.0Hz), 6.63 (2H, t, ^{3}J = 2.0Hz), 6.58 (8H, d, ^{3}J = 1.9Hz), 6.46 (4H, t, ^{3}J = 1.9Hz), 6.36 (1H, s), 4.98 (4H, s), 4.91 (8H, s), 3.90 (6H, s), 3.95 (16H, s), 3.49 (48H, s), 3.38 (48H, t, ^{3}J =

6.5Hz), 1.52 (48H, m), 1.24 (432H, m), 0.85 (99H, m), 0.59 (18H, s). (ii) flash GPC (SiO_2, eluted with THF). Oil (0.24 g, 86%). ^{1}H NMR($CDCl_3$): δ = 7.23 (1H, s), 7.05 (2H, d, ^{3}J = 2Hz), 6.81 (1H, t, ^{3}J = 2Hz), 6.72 (4H, d, ^{3}J = 1.8Hz), 6.63 (2H, t, ^{3}J = 1.8Hz), 6.58 (8H, d, ^{3}J = 1.8Hz), 6.46 (4H, t, ^{3}J = 1.8Hz), 5.02 (4H, s), 4.92 (8H, s), 3.95 (16H, s), 3.74 (6H, s), 3.49 (48H, s), 3.38 (48H, t, ^{3}J = 6.5Hz), 1.52 (51H, m), 1.24 (432H, m), 0.87 (72H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ =. 168.15, 161.15, 160.74, 160.34, 160.18, 138.63, 138.26, 136.13, 106.56, 106.36, 105.49, 101.43, 100.89, 71.58, 70.46, 70.34, 69.36, 67.25, 63.29, 61.45, 45.25, 31.93, 29.72, 29.65, 29.38, 26.21, 22.69, 14.10. Anal. calcd for $C_{381}H_{707}NO_{42}$ (MW = 5974.67 g.mol^{-1}): C: 76.59, H: 11.93, N: 0.23, O: 11.25; found: C: 76.71, H: 11.98, N: 0.37, O:11.27. MALDI-TOF calcd for m/e 5974.34 (100%), found 5976.95 g.mol^{-1}.

(**3c**): (i) From **19c** (0.74 g, 0.249 mmol), **9** (0.11 g, 0.299 mmol), Et_3N (0.07 ml, 0.498 mmol) and **7** (0.139 g, 0.299 mmol). CC (SiO_2, eluted with CH_2Cl_2/hexane/Et_3N, 65:30:5). Colorless waxy solid (0.48 g, 56%). ^{1}H NMR($CDCl_3$): δ = 6.97 (2H, d, ^{3}J = 2.2Hz), 6.73 (1H, t, ^{3}J = 2.2Hz), 6.70 (4H, d, ^{3}J = 2.0Hz), 6.62 (8H, m), 6.56 (2H, t, ^{3}J = 2.0Hz), 6.36 (1H, s), 4.99 (4H, s), 4.91 (8H, s), 3.97 (24H, m), 3.92 (6H, s), 1.77 (24H, m), 1.26 (216H, m), 0.88 (63H, m), 0.05 (18H, s). (ii) CC (SiO_2, eluted with CH_2Cl_2/MeOH/Et_3N, 94:2:4). Glassy solid (0.19 g, 47%). ^{1}H NMR($CDCl_3$): δ = 7.23 (1H, s), 6.97 (2H, d, ^{3}J = 2.2Hz), 6.75 (1H, t, ^{3}J = 2.2Hz), 6.69 (4H, d, ^{3}J = 2.2Hz), 6.61 (8H, s), 6.60 (2H, t, ^{3}J = 2.2Hz), 5.01 (4H, s), 4.95 (8H, s), 3.96 (24H, m), 3.76 (6H, s), 1.77 (27H, m), 1.27 (216H, m), 0.88 (36H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 168.11, 160.20, 159.95, 153.29, 138.67, 137.94, 136.17, 131.56, 106.41, 106.19, 105.33, 101.74, 73.46, 70.61, 70.22, 69.13, 63.22, 61.45, 31.90, 30.32, 29.63, 26.11, 22.67, 14.07. Anal. calcd for $C_{197}H_{339}NO_{22}$ (MW = 3073.79 g.mol^{-1}): C: 76.98, H: 11.12, N: 0.46; found: C: 77.18, H: 11.39, N: 0.61. MALDI-TOF calcd for m/e 3073.55 (100%), found 3097.30 g.mol^{-1}.

*Preparation of the dendrimers **4-6***

The preparation of **4a** has been selected as a representative example since the same procedure was systematically used for all the members of the series. The conditions of purification have been added when they were modified. The intermediary protected compounds have been purified as (i). All the compounds were obtained as amorphous solids.

(**4a**): (i) To **14a** (0.7 g, 1.47 mmol), **11** (1.74 g, 1.62 mmol) and PPh_3 (0.42 g, 1.62 mmol) in dry THF (15 ml) under argon, DIAD was added (0.32 ml 1.62 mmol) dropwise to the solution cooled at 0°C. The reaction was refluxed for 48 h. The solvent was removed and the residue

was partitioned between CH_2Cl_2 and water, the organic extract was washed with NH_4Cl (2 x 100 ml) and brine (2 x 100 ml), dried over $MgSO_4$ and filtered, and the solvent was evaporated to dryness. The crude product was purified by chromatography (eluted 65:30:5 CH_2Cl_2/hexane/Et_3N) to give a pale green glassy solid (1.84 g, 82%). ^{1}H NMR($CDCl_3$): δ = 7.64 (1H, s), 7.41 (2H, d, ^{3}J = 1.3Hz), 6.55 (2H, d, ^{3}J = 2.2Hz), 6.41 (1H, t, ^{3}J = 2.2Hz), 6.32 (2H, s), 5.01 (2H, s), 3.94 (16H, m), 1.77 (4H, m), 1.27 (36H, m), 0.88 (60H, m), 0.05 (36H, s). (ii) To this solution (1.75 g, 1.14 mmol) in THF (10 ml) was added the solution of TBAF (8.54 ml, 1M in THF) at 0°C and the reaction was stirred at room temperature for 12 h. The solvent was removed and the crude product was purified by flash CC (SiO_2, eluted with 88:6:4 CH_2Cl_2/MeOH/Et_3N) to give a white solid (0.88 g, 90%). ^{1}H NMR(MeOD): δ = 7.88 (1H, t, ^{3}J = 1.5Hz), 7.67 (2H, d, ^{3}J = 1.5Hz), 6.66 (2H, d, ^{3}J = 2.2Hz), 6.46 (1H, t, ^{3}J = 2.2Hz), 5.18 (2H, s), 4.01 (4H, t, ^{3}J = 6.4Hz), 3.94 (12H, s), 1.80 (4H, m), 1.51 (6H, b), 1.36 (36H, m), 0.96 (6H, t, ^{3}J = 6.7Hz). ^{13}C NMR(MeOD): δ = 168.08, 160.03, 158.37, 138.27, 136.05, 117.60, 116.10, 104.92, 100.00, 69.47, 67.18, 62.24, 60.59, 31.20, 28.91, 28.89, 28.63, 25.29, 21.87, 12.58. Anal. calcd for $C_{47}H_{78}N_2O_{11}$ (MW = 847.13 g.mol^{-1}): C: 66.64, H: 9.28, N: 3.31, O: 20.78; found: C: 66.56, H 9.40, N 3.25, O 20.05. HRMS-FAB (M + Na^+) calcd for m/e 846.56 (100%), found 847.3 g.mol^{-1}.

(**4b**): (i) From **14b** (1.0 g, 0.721 mmol), **11** (1.1 g, 0.865 mmol), PPh_3 (0.23 g, 0.865 mmol), and DIAD (0.17 ml, 0.865 mmol). CC (SiO_2, eluted with CH_2Cl_2/hexane/Et_3N, 65:30:5). Pale green sticky paste (1.1 g, 63%). ^{1}H NMR($CDCl_3$): δ = 7.66 (1H, s), 7.43 (2H, d, ^{3}J = 1.3Hz), 6.54 (2H, d, ^{3}J = 2.0Hz), 6.45 (1H, t, ^{3}J = 2.0Hz), 6.33 (2H, s), 4.96 (2H, s), 3.95 (16H, m), 3.49 (12H, s), 3.38 (12H, t, ^{3}J = 6.6Hz), 1.52 (12H, m), 1.25 (108H, m), 0.87 (72H, m), 0.05 (36H, s). (ii) CC (SiO_2, eluted with 88:6:4 CH_2Cl_2/MeOH/Et_3N), to give an amorphous wax (0.57 g, 76%) .^{1}H NMR($CDCl_3$): δ = 7.76 (1H, s), 7.51 (2H, d, ^{3}J = 1.2Hz), 7.28 (2H, s), 6.56 (2H, d, ^{3}J = 2Hz), 6.45 (1H, t, ^{3}J = 2Hz), 5.06 (2H, s), 4.10 (6H, b), 3.92 (4H, s), 3.75 (12H, s), 3.48 (12H, s), 3.38 (12H, t, ^{3}J = 6.6Hz), 1.52 (12H, m), 1.25 (108H, m), 0.88 (18H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 167.75, 160.79, 159.23, 137.62, 135.80, 117.78, 117.13, 106.12, 101.07, 71.61, 70.69, 69.27, 67.94, 67.21, 62.49, 62.11, 53.37, 43.18, 31.90, 29.70, 29.58, 29.35, 26.17, 22.67, 14.08. Anal. calcd for $C_{105}H_{194}N_2O_{17}$ (MW = 1756.67 g.mol^{-1}): C: 71.79, H: 11.13, N: 1.59, O: 15.48; found: C: 71.42, H: 11.16, N: 11.42, O: 15.50. MALDI-TOF calcd for m/e 1756.44 (100%), found 1757.44 g.mol^{-1}.

(**4c**): (i) From **14c'** (0.89 g, 1.31 mmol), K_2CO_3 (1.81 g, 13.1 mmol) and **11** (1.83 g, 1.7 mmol) in 20 ml of DMF. The brut product is crystallized twice from acetone, and a white

vitreous solid is obtained (1.24 g, 55%). ^{1}H NMR($CDCl_3$): δ = 7.65 (1H, s), 7.43 (2H, s), 6.61 (2H, s), 6.32 (2H, s), 4.97 (2H, s), 3.98 (18H, m), 1.78 (6H, m), 1.27 (54H, m), 0.88 (63H, m), 0.06 (36H, s). (ii) CC (SiO_2, eluted in CH_2Cl_2/MeOH/Et_3N, 88:8:4). White vitreous solid (0.32 g, 53%). ^{1}H NMR(DMSO-d_6): δ = 7.76 (1H, s), 7.54 (2H, s), 7.38 (2H, s), 6.73 (2H, s), 5.05 (2H, s), 4.72 (6H, t, ^{3}J = 5.6Hz), 3.91 (4H, t, ^{3}J = 5.8Hz), 3.78 (2H, t, ^{3}J = 6.3Hz), 3.68 (12H, d, ^{3}J = 5.6Hz), 1.68 (6H, m), 1.21 (54H, m), 0.82 (9H, t, ^{3}J = 6.7Hz). ^{13}C NMR(DMSO-d_6): δ = 168.45, 159.86, 154.45, 138.90, 138.44, 133.43, 120.61, 118.06, 74.07, 71.86, 70.13, 64.73, 62.22, 33.34, 31.29, 31.13, 30.83, 27.71, 24.05, 15.54. Anal. calcd for $C_{59}H_{102}N_2O_{12}$ (MW = 1031.45 g.mol^{-1}): C: 68.70, H: 9.97, N: 2.71, O: 18.61; found: C: 68.41, H: 10.06, N: 2.72, O: 18.13. MALDI-TOF calcd for m/e 1030.74 (100%), found 1031.73 g.mol^{-1}.

(**5a**): (i) From **17a** (0.8 g, 0.756 mmol), **11** (0.96 g, 0.908 mmol), PPh_3 (0.24 g, 0.908 mmol) and DIAD (0.18 ml, 0.908 mmol). CC (SiO_2, eluted with CH_2Cl_2/Et_3N, 95:5). Pale green solid (1.1 g, 69%). ^{1}H NMR($CDCl_3$): δ = 7.65 (1H, t, ^{3}J = 1.3Hz), 7.43 (2H, d, ^{3}J = 1.3Hz), 6.68 (2H, d, ^{3}J = 2.1Hz), 6.58 (1H, t, ^{3}J = 2.1Hz), 6.57 (4H, d, ^{3}J = 2.2Hz), 6.41 (2H, t, ^{3}J = 2.2Hz), 6.32 (2H, s), 5.03 (2H, s), 4.95 (4H, s), 3.94 (20H, m), 1.77 (8H, m), 1.27 (72H, m), 0.88 (66H, m), 0.05 (36H, s). (ii) CC (SiO_2, eluted with 88:6:4 CH_2Cl_2/MeOH/Et_3N) to give an amorphous solid (0.35 g, 55%). ^{1}H NMR($CDCl_3$): δ = 7.68 (1H, s), 7.48 (2H, s), 7.33 (2H, s), 6.64 (2H, d, ^{3}J = 2Hz), 6.54 (5H, m), 6.39 (2H, t, ^{3}J = 2.1Hz), 5.00 (2H, s), 4.91 (4H, s), 3.91 (8H , t, ^{3}J = 6.5Hz), 3.74 (12H, b), 3.12 (6H, b), 1.75 (8H, m), 1.26 (72H, m), 0.88 (12H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 167.89, 160.42, 160.11, 158.85, 138.70, 138.12, 135.70, 117.77, 116.82, 106.36, 105.80, 101.69, 100.72, 70.11, 68.02, 62.57, 62.20, 31.89, 29.66, 29.58, 29.26, 26.04, 22.66, 14.08. Anal. calcd for $C_{85}H_{138}N_2O_{15}$ (MW = 1428.01 g.mol^{-1}): C: 71.49, H: 9.74, N: 1.96, O: 16.81; found: C: 71.54, H: 9.85, N: 2.01, O: 16.23. MALDI-TOF calcd for m/e 1427.01, found 1428.56 g.mol^{-1}.

(**5b**): (i) From **17b** (0.7 g, 0.243 mmol), **11** (0.31 g, 0.292 mmol), PPh_3 (0.08 g, 0.292 mmol) and DIAD (0.06 ml, 0.292 mmol). CC (SiO_2, eluted with CH_2Cl_2/hexane/Et_3N, 65:30:5). Pale green sticky paste (0.5 g, 52%). ^{1}H NMR($CDCl_3$): δ = 7.66 (1H, t, ^{3}J = 1.3Hz), 7.45 (2H, d, ^{3}J = 1.3Hz), 6.70 (2H, d, ^{3}J = 2.1Hz), 6.64 (1H, t, ^{3}J = 2.1Hz), 6.58 (4H, d, ^{3}J = 2.0Hz), 6.46 (2H, t, ^{3}J = 2.0Hz), 6.33 (2H, s), 5.03 (2H, s), 4.91 (4H, s), 3.96 (20H, s), 3.49 (24H, s), 3.38 (24H, t, ^{3}J = 6.5Hz), 1.52 (24H, m), 1.25 (216H, m), 0.88 (90H, m), 0.06 (36H, s). (ii) CC (SiO_2, eluted with 88:6:4 CH_2Cl_2/MeOH/Et_3N) to give a wax (0.28 g, 74%). ^{1}H NMR($CDCl_3$): δ = 7.79 (1H, s), 7.57 (2H, d, ^{3}J = 1.3Hz), 7.33 (2H, s), 6.70 (2H, d, ^{3}J = 2Hz), 6.63 (1H, t, ^{3}J = 2Hz), 6.58 (4H, d, ^{3}J = 2Hz), 6.46 (2H, t, ^{3}J = 2Hz), 5.11 (2H, s), 4.92 (4h, s),

3.95 (8H, s), 3.86 (6H, b), 3.77 (12H, s), 3.49 (24H, s), 3.38 (24H, t, ^3J = 6.5Hz), 1.52 (24H, m), 1.25 (216H, m), 0.88 (36H, t, ^3J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 167.66, 160.70, 160.34, 159.24, 138.17, 138.07, 135.91, 117.13, 106.40, 106.29, 101.52, 100.87, 71.55, 70.32, 69.31, 67.19, 62.86, 61.98, 45.20, 31.91, 29.70, 29.60, 29.36, 26.19, 22.67, 14.08. Anal. calcd for $C_{201}H_{370}N_2O_{27}$ (MW = 3247.09 g.mol^{-1}): C: 74.35, H: 11.49, N: 0.86, O: 13.30; found C: 74.25, H: 11.64, N: 0.86, O: 13.14. MALDI-TOF calcd for m/e 3246.77 (100%), found 3247.38 g.mol^{-1}.

(**5c**): (i) From **17c** (1.0 g, 0.701 mmol), **11** (1.75 g, 0.841 mmol), PPh_3 (0.22 g, 0.841 mmol) and DIAD (0.17 ml, 0.841 mmol). CC (SiO_2, eluted with CH_2Cl_2/Et_3N, 95:5). Pale green vitreous solid (1.5 g, 86%). ^1H NMR($CDCl_3$): δ = 7.64 (1H, s), 7.43 (2H, s), 6.69 (2H, s), 6.62 (5H, m), 6.32 (2H, s), 5.05 (2H, s), 4.90 (4H, s), 3.95 (24H, m), 1.77 (12H, m), 1.27 (108H, m), 0.88 (72H, m), 0.05 (36H, s). (ii) CC (SiO_2, eluted with CH_2Cl_2/MeOH/Et_3N, 90:6:4). White glassy solid (0.48 g, 47%). ^1H NMR($CDCl_3$): δ = 7.84 (1H, s), 7.57 (2H, s), 7.50 (1H, s), 6.68 (2H, d, ^3J = 2.0Hz), 6.61 (6H, m), 5.06 (2H, s), 4.91 (4H, s), 3.95 (12H, m), 3.77 (12H, s), 1.76 (18H, m), 1.26 (108H, m), 0.87 (18H, t, ^3J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 168.21, 160.10, 158.98, 153.18, 138.55, 137.83, 135.61, 131.51, 117.97, 117.70, 106.15, 101.68, 73.34, 70.49, 70.11, 69.02, 62.94, 58.66, 31.84, 30.27, 29.61, 29.29, 26.05, 22.58, 14.00. Anal. calcd for $C_{109}H_{186}N_2O_{17}$ (MW = 1796.65 g.mol^{-1}): C: 72.87, H: 10.43, N: 1.56; found: C: 72.64, H: 10.80, N: 1.39. MALDI-TOF calcd for m/e 1796.38 (100%), found 1797.66 g.mol^{-1}.

(**6a**): (i) From **20a** (0.7 g, 0.315 mmol), **11** (0.41 g, 0.378 mmol), de PPh_3 (0.1 g, 0.378 mmol) and DIAD (0.07 ml, 0.378 mmol). CC (SiO_2, eluted with CH_2Cl_2/hexane/Et_3N, 55:40:5). Pale green oil (0.65 g, 63%). ^1H NMR($CDCl_3$): δ = 7.65 (1H, s), 7.45 (2H, s), 6.71 (6H, d, ^3J = 2.0Hz), 6.61 (1H, s), 6.56 (10H, m), 6.41 (4H, d, ^3J = 2.2Hz), 6.33 (2H, s), 5.04 (2H, s), 4.98 (4H, s), 4.95 (8H, s), 3.93 (28H, m), 1.77 (16H, m), 1.26 (144H, m), 0.88 (78H, m), 0.05 (36H, s). (ii) CC (SiO_2, eluted with 94:4:4 CH_2Cl_2/MeOH/Et_3N) to give viscous paste (0.42 g, 84%). ^1H NMR($CDCl_3$): δ = 7.74 (1H, s), 7.57 (2H, s), 7.32 (2H, s), 6.67 (4H, d, ^3J = 2Hz), 6.60 (5H, m), 6.55 (8H, d, ^3J = 2.2Hz), 6.40 (4H, t, ^3J = 2.2Hz), 5.07 (2H, s), 4.96 (4H, s), 4.93 (8H, s), 3.92 (16H, t, ^3J = 6.6Hz), 3.75 (12H, b), 1.75 (22H, m), 1.26 (144H, m), 0.88 (24H, t, ^3J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 167.72, 160.45, 160.13, 160.10, 159.00, 138.92, 138.82, 138.26, 135.79, 117.71, 117.04, 106.42, 105.76, 101.59, 100.76, 76.57, 70.28, 70.11, 68.03, 63.02, 62.04, 53.37, 52.33, 31.89, 29.64, 29.60, 29.32, 26.03, 22.65, 14.08. Anal. calcd for $C_{161}H_{258}N_2O_{23}$ (MW = 2589.77 g.mol^{-1}): C: 74.67, H: 10.04, N: 1.08, O: 14.21; found: C:

74.64, H: 10.19, N: 1.12, O: 13.70. MALDI-TOF calcd for m/e 2588.91 (100%), found 2590.94 g.mol^{-1}.

(**6b**): (i) From **20b** (0.75 g, 0.128 mmol), **11** (0.17 g, 0.154 mmol), PPh_3 (0.04 g, 0.154 mmol) and DIAD (0.03 g, 0.154 mmol). CC (SiO_2, eluted with CH_2Cl_2/hexane/Et_3N, 65:30:5). Pale green sticky paste (0.57 g, 65%). ^{1}H NMR($CDCl_3$): δ = 7.66 (1H, s), 7.45 (2H, d, ^{3}J = 1.2Hz), 6.74 (4H, d, ^{3}J = 2.0Hz), 6.68 (1H, t, ^{3}J = 2.0Hz), 6.64 (2H, t, ^{3}J = 2.1Hz), 6.58 (10H, d, ^{3}J = 2.0Hz), 6.45 (4H, t, ^{3}J = 1.9Hz), 6.32 (2H, s), 5.04 (2H, s), 4.97 (4H, s), 4.91 (8H, s), 3.95 (28H, s), 3.48 (48H, s), 3.37 (48H, t, ^{3}J = 6.5Hz), 1.50 (48H, m), 1.24 (432H, m), 0.87 (126H, m), 0.079 (36H, s). (ii) GPC (SiO_2, eluted with THF). Colourless paste (0.21 g, 42%). ^{1}H NMR($CDCl_3$): δ = 7.84 (1H, s), 7.55 (2H, d, ^{3}J = 1.2Hz), 7.34 (2H, s), 6.71 (4H, t, ^{3}J = 2.3Hz), 6.65 (1H, t, ^{3}J = 1.9Hz), 6.62 (2H, t, ^{3}J = 1.8Hz), 6.58 (10H, m), 6.46 (4H, s), 5.11 (2H, s), 4.99 (4H, s), 4.91 (8H, s), 3.95 (16H, s), 3.87 (6H, b), 3.74 (12H, s), 3.49 (48H, s), 3.38 (48H, t, ^{3}J = 6.5Hz), 1.50 (48H, m), 1.24 (432H, m), 0.87 (72H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 167.59, 161.16, 160.71, 160.35, 160.30, 159.13, 138.80, 138.28, 135.97, 117.93, 117.15, 106.39, 101.43, 100.80, 71.57, 70.30, 69.33, 67.21, 63.32, 62.01, 45.23, 31.92, 29.71, 29.63, 29.36, 26.20, 22.67, 14.08. Anal. calcd for $C_{393}H_{722}O_{47}N_2$ (MW = 6227.92 g.mol^{-1}): C: 75.79, H: 11.68, N: 0.45, O: 12.07; found: C: 76.17, H: 11.85, N: 0.61, O: 12.18. MALDI-TOF calcd for m/e 6227.43 (100%), found 6227.50 g.mol^{-1}.

(**6c**): (i) From **20c** (1.61 g, 0.544 mmol), **11** (0.70 g, 0.653 mmol), PPh_3 (0.17 g, 0.653 mmol) and DIAD (0.13 ml, 0.653 mmol). CC (SiO_2, eluted with CH_2Cl_2/Et_3N, 65:30:5). Pale green oil (1.42 g, 65%). ^{1}H NMR($CDCl_3$): δ = 7.64 (1H, s), 7.44 (2H, s), 6.72 (6H, m), 6.62 (11H, m), 6.37 (2H, s), 5.04 (2H, s), 4.98 (4H, s), 4.91 (8H, s), 3.97 (36H, m), 1.77 (24H, m), 1.26 (216H, m), 0.87 (90H, m), 0.05 (36H, s). (ii) CC (SiO_2, eluted with CH_2Cl_2/MeOH/Et_3N, 92:4:4). White sticky paste (0.29 g, 27%). ^{1}H NMR($CDCl_3$): δ = 7.79 (1H, s), 7.55 (2H, d, ^{3}J = 1.1Hz), 7.34 (2H, s), 6.69 (4H, d, ^{3}J = 2.0Hz), 6.59 (11H, m), 6.58 (2H, t, ^{3}J = 2.0Hz), 5.09 (2H, s), 4.99 (4H, s), 4.91 (8H, s), 3.95 (24H, m), 3.76 (12H, s), 1.77 (24H, m), 1.27 (216H, m), 0.88 (36H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 167.76, 160.13, 158.99, 153.22, 152.69, 138.93, 138.36, 137.90, 135.75, 131.54, 117.65, 117.20, 106.39, 106.22, 101.58, 73.39, 70.51, 70.06, 69.05, 62.86, 62.22, 31.86, 30.30, 29.60, 29.31, 26.10, 22.62, 14.03. Anal. calcd for $C_{209}H_{354}N_2O_{27}$ (MW = 3327.04 g.mol^{-1}): C: 75.45, H: 10.72, N: 0.84; found: C: 74.74, H: 10.92, N: 0.88. MALDI-TOF calcd for m/e 3326.65 (100%), found 3349.82 g.mol^{-1}.

Preparation of the hydrophobic monodendrons of the first generation

(**12a**): A mixture of methyl 3,5–dihydroxybenzoate (11.0 g, 65.42 mmol) in DMF (100 ml), K_2CO_3 (36.2 g, 261.92 mmol) was heated to 60°C and dodecylbromide (35.88 g, 143.96 mmol) in DMF (50 ml) added. The reaction was heated for 24 h at 80°C. K_2CO_3 was filtered off over celite and DMF was removed. The residue was partitioned between CH_2Cl_2 and water and the organic extract was washed with NH_4Cl (2 x 50ml) and brine (2 x 50ml), dried over $MgSO_4$ and filtered, and the solvent was evaporated to dryness. The crude product was purified by two successive crystallization in acetone to give a white solid (32.3 g, 98%). ^{1}H NMR($CDCl_3$): δ = 7.16 (2H, d, ^{3}J = 2.3Hz), 6.64 (1H, t, ^{3}J = 2.3Hz), 3.97 (4H, t, ^{3}J = 6.5Hz), 3.90 (3H, s), 1.78 (4H, m), 1.27 (36H, m), 0.88 (6H, t, ^{3}J = 6.6Hz). ^{13}C NMR($CDCl_3$): δ = 166.90, 160.11, 131.75, 107.56, 106.49, 68.23, 52.06, 31.89, 29.60, 29.56, 22.65, 14.06.

(**12b**): (i) A solution of pentaerythritol (30 g, 220 mmol) and NaOH (350.4 g, 8.82 mol) in water (500 ml) was stirred for 1 h at 80°C. Dodecylbromide (219.72 g, 882.0 mmol) and tetrabutylammonium bromide (TBAB**,** 28.23 g, 88.0 mmol) were added and stirred under the control of TLC for 3 h. The solution was cooled to room temperature and mixed with CH_2Cl_2 (500 ml) and the organic extract was washed with NH_4Cl (2 x 500ml), brine (2 x 500ml), dried over $MgSO_4$, filtered and the solvent was evaporated to dryness. The crude product was purified by chromatography (SiO_2, 7:3 CH_2Cl_2/hexane) to give colourless oil (66.39 g, 47%). ^{1}H NMR($CDCl_3$): δ = 3.71 (2H, d, ^{3}J = 6.1Hz), 3.37 (12H, m), 3.16 (1H, t, ^{3}J = 6.1Hz), 1.54 (6H, m), 1.26 (54H, m), 0.87 (9H, t, ^{3}J = 6.6Hz). ^{13}C NMR($CDCl_3$): δ = 71.71, 71.46, 65.59, 44.71, 29.71, 29.68, 29.34, 26.17, 22.66, 14.05. (ii) To a solution of the alcohol (27.6 g, 43.12 mmol), methyl 3,5–dihydroxybenzoate (3.29 g, 19.59 mmol) and PPh_3 (11.29 g, 43.12 mmol) in dry THF (50 ml), diisopropyl azodicarboxylate was added slowly under argon (DIAD 8.49 ml, 43.12 mmol) at 0°C. The reaction was refluxed for 48 h. The solvent was removed and the residue was partitioned between CH_2Cl_2 and water, the organic extract was washed with NH_4Cl (2 x 250ml) and brine (2 x 250ml), dried over $MgSO_4$ and filtered, and the solvent was evaporated to dryness. The crude product was purified by chromatography (SiO_2, 1:1 CH_2Cl_2/hexane) to give a white powder (24.07 g, 87%). ^{1}H NMR($CDCl_3$): δ = 7.17 (2H, d, ^{3}J = 2.3Hz), 6.67 (1H, t, ^{3}J = 2.3Hz), 3.97 (4H, s), 3.89 (3H, s), 3.48 (12H, s), 3.38 (12H, t, ^{3}J = 6.5Hz), 1.52 (12H, m), 1.25 (108H, m), 0.88 (18H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 166.99, 160.34, 131.53, 107.92, 106.51, 71.56, 69.29, 67.50, 52.01, 45.25, 31.93, 29.71, 29.62, 29.38, 26.21, 22.69, 14.09.

(**12c**): As **12a**. Methyl 3,4,5–trihydroxybenzoate (10.0 g, 54.3 mmol), K_2CO_3 (75.0 g, 542.26 mmol) and bromododecane (48.8 g, 195.8 mmol) in 150 ml DMF. A white solid was obtained after two crystallization from acetone (33 g, 88%). ^{1}H NMR($CDCl_3$): δ = 7.25 (2H, s), 4.03 (6H, t, ^{3}J = 4.1Hz), 3.89 (3H, s), 1.81 (6H, m), 1.27 (54H, m), 0.88 (9H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 166.85, 152.77, 142.31, 124.60, 107.92, 73.41, 69.09, 52.01, 31.90, 30.30, 29.60, 29.34, 26.05, 22.66, 14.05.

(**12d**): As **12a**. Methyl 3,4–dihydroxybenzoate (11.0 g, 65.42 mmol), K_2CO_3 (36.2 g, 261.92 mmol), and bromododecane (35.88 g, 143.96 mmol) in 150 ml DMF. A white solid was obtained after two crystallization from acetone (30 g, 91%). ^{1}H NMR($CDCl_3$): δ = 7.63 (1H, dd, ^{3}J = 2.0Hz, ^{3}J = 8.3Hz), 7.54 (1H, d, ^{3}J = 2.0Hz), 6.86 (1H, d, ^{3}J = 8.3Hz), 4,05 (4H, m), 3.88 (3H, s), 1.83 (4H, m), 1.27 (36H, m), 0.88 (6H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 166.90, 153.14, 148.45, 123.46, 122.33, 114.17, 111.83, 69.18, 68.91, 51.79, 31.89, 29.66, 29.59, 29.33, 25.97, 22.64, 14.05.

(**13a**): To the solution of **12a** (4 g, 7.92 mmol) in MeOH/water (15 ml:15 ml) was added KOH (4.44 g, 79.2 mmol) and the mixture was stirred for 12 h at 60°C. The solution was concentrated and cooled to 0°C and a solution of 6 M HCl was added drop by drop to observe the precipitation of white solid, which was filtered, washed with water and dried under vacuum to give pure product (3.77 g, 97%). ^{1}H NMR(DMSO-d_6): δ = 7.16 (2H, d, ^{3}J = 2.4Hz), 6.62 (1H, t, ^{3}J = .4Hz), 3.99 (4H, t, ^{3}J = 6.5Hz), 1.76 (4H, m), 1.27 (36H, m), 0.86 (6H, t, ^{3}J = 6.7Hz).

(**13b**): As **13a**. **12b** (1.5 g, 1.06 mmol) in MeOH/water (20 ml:20 ml), KOH (0.89 g, 15.59 mmol). MeOH was removed and the residue was partitioned between CH_2Cl_2 and water and washed with NH_4Cl (2 x 200ml) and brine (2 x 200ml), dried over $MgSO_4$ and filtered. The solvent was removed and the product was dried under vacuum to give a white powder (1.27 g, 92%). ^{1}H NMR($CDCl_3$): δ = 7.23 (2H, d, ^{3}J = 2.3Hz), 6.71 (1H, t, ^{3}J = 2.3Hz), 3.98 (4H, s), 3.50 (12H, s), 3.38 (12H, t, ^{3}J = 6.5Hz), 1.52 (12H, m), 1.25 (108H, m), 0.88 (18H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 171.81, 160.42, 130.82, 108.55, 107.23, 71.61, 69.29, 67.56, 45.28, 31.95, 29.73, 29.63, 29.39, 26.23, 22.70, 14.11.

(**13c**): As **13a**. **12c** (5.0 g, 7.255 mmol), KOH (4.07 g, 72.55 mmol)**.** White solid (4.55 g, 93%). ^{1}H NMR(DMSO-d_6): δ = 7.06 (2H, s), 3.88 (4H, t, ^{3}J = 6.3Hz), 3.75 (2H, t, ^{3}J = 6.8Hz), 1.67 (6H, m), 1.22 (54H, m), 0.81 (9H, t, ^{3}J = 6.4Hz).

(**13d**) As **13a**. **12d** (4.0 g, 7.92 mmol), KOH (4.44 g, 79.2 mmol). White solid (3.81 g, 98%). ^{1}H NMR (DMSO-d_6): δ = 7.41 (2H, large), 6.90 (1H, large), 3.94 (4H, m), 1.68 (4H, m), 1.22 (36H, s), 0.81 (6H, t, ^{3}J = 6.5Hz).

(**14a**, **14b**, **14c**): To a solution of the corresponding ester benzoate (**12a**: 25.0 g, 49.52 mmol; **12b**: 21.0 g, 14.84 mmol; **12c**: 26.2 g, 38.02 mmol) in dry THF (*ca*. 100 ml) was slowly added the solution of $LiAlH_4$ 1M in THF (37.12 ml, 11.13 ml, and 28.5 ml, respectively) at 0°C. The reaction was stirred at room temperature for 12 h. The excess of $LiAlH_4$ was neutralized by 10 ml of MeOH and 20 ml of water was added. THF was evaporated and the residue was purified by flash chromatography (SiO_2, 7:3 CH_2Cl_2/hexane) to give a white solid (**14a**: 23.23 g, 98%; **14c**: 23.5 g, 93%) or colorless oil (**14b**: 19.2 g, 94%). **14a**: ^{1}H NMR($CDCl_3$): δ = 6.51 (2H, d, ^{3}J = 2.3Hz), 6.38 (1H, t, ^{3}J = 2.3Hz), 4.62 (2H, d, ^{3}J = 6.0Hz), 3.94 (4H, t, ^{3}J = 6.5Hz), 1.77 (4H, m), 1.63 (1H, t, ^{3}J = 6.0Hz), 1.27 (36H, m), 0.87 (6H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 160.48, 143.19, 105.01, 100.51, 68.02, 65.34, 31.90, 29.64, 29.61, 29.32, 26.03, 22.66, 14.07. **14b**: ^{1}H NMR($CDCl_3$): δ = 6.50 (2H, d, ^{3}J = 2.1Hz), 6.41 (1H, t, ^{3}J = 2.1Hz), 4.60 (2H, d, ^{3}J = 6.2Hz), 3.94 (4H, s), 3.48 (12H, s), 3.38 (12H, t, ^{3}J = 6.6Hz), 1.52 (12H, m), 1.25 (108H, m), 0.88 (18H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 160.76, 142.84, 105.13, 100.81, 71.56, 69.37, 67.24, 65.49, 45.21, 31.93, 29.71, 29.63, 29.37, 26.21, 22.68, 14.08. **14c**: ^{1}H NMR($CDCl_3$): δ = 6.56 (2H, s), 4.60 (2H, d, ^{3}J = 6.0Hz), 3.95 (6H, m), 1.77 (6H, m), 1.61 (1H, t, ^{3}J = 6.0Hz), 1.27 (54H, m), 0.87 (9H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 153.15, 137.37, 136.14, 105.19, 73.38, 69.00, 65.47, 31.90, 30.29, 29.63, 29.34, 26.08, 22.66, 14.06.

(**14c'**): To a CH_2Cl_2 solution (100 ml) containing **14c** (19.0 g, 28.74 mmol) and DMF (catalytic amount), a solution of $SOCl_2$ (3.76 g, 31.61 mmol) in 50 ml of CH_2Cl_2 was added dropwise at room temperature, and the mixture stirred for 12 h. After evaporation of the solvent, a pale yellow solid was obtained, and used without further purification.

Preparation of the dendrons of the second and third generation

Dendrons with an ester function

(**15a**, **15b**): To a solution of the corresponding benzilic alcohol (**14a**: 19.0g, 39.85 mmol; **14b**: 17.4 g, 12.55 mmol), methyl 3,5–dihydroxybenzoate (3.19 g, 18.97 mmol; 1.0 g, 5.97 mmol) and PPh_3 (10.44 g, 39.85 mmol, 3.27 g, 12.55 mmol) in dry THF (*ca*. 50–70 ml) was added slowly under argon DIAD (7.85 ml, 39.85 mmol; 2.46 ml, 12.55 mmol,) at 0 °C. The reaction

was refluxed for 48-60 h. The solvent was removed and the residue was partitioned between CH_2Cl_2 and water, the organic extract was washed with NH_4Cl (2 x 250ml) and brine (2 x 250ml), dried over $MgSO_4$ and filtered, and the solvent was evaporated to dryness. The crude product was purified by chromatography (SiO_2, eluted with 1:1 CH_2Cl_2/hexane) to give a white powder (**15a**: 17.06 g, 83%) or a colorless oil (**15b**: 12.6 g, 73%). **15a**: ^{1}H NMR($CDCl_3$): δ = 7.28 (2H, d, ^{3}J = 2.4Hz), 6.79 (1H, t, ^{3}J = 2.4Hz), 6.56 (4H, d, ^{3}J = 2.2Hz), 6.42 (2H, t, ^{3}J = 2.2Hz), 4.99 (4H, s), 3.93 (11H, m), 1.77 (8H, m), 1.27 (72H, m), 0.88 (12H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 166.69, 160.51, 159.74, 138.56, 131.96, 108.35, 107.15, 105.68, 100.89, 70.26, 68.03, 52.15, 31.90, 29.65, 29.61, 29.33, 26.03, 22.66, 14.07. **15b**: ^{1}H NMR($CDCl_3$): δ = 7.30 (2H, d, ^{3}J = 2.3Hz), 6.84 (1H, t, ^{3}J = 2.3Hz), 6.57 (4H, d, ^{3}J = 2.1Hz), 6.45 (2H, t, ^{3}J = 2.1Hz), 4.95 (4H, s), 3.95 (8H, s), 3.91 (3H, s), 3.49 (24H, s), 3.38 (24H, t, ^{3}J = 6.5Hz), 1.52 (24H, m), 1.25 (216H, m), 0.88 (36H, t, ^{3}J = 6.7Hz). ^{13}C NMR ($CDCl_3$): δ = 166.75, 160.74, 159.89, 138.08, 131.94, 108.22, 106.94, 106.15, 101.04, 71.56, 70.42, 69.35, 67.24, 52.14, 45.23, 31.94, 29.72, 29.64, 29.38, 26.21, 22.69, 14.01.

(**15c**): this ester was prepared differently. A solution containing methyl 3,5–dihydroxybenzoate (2.19 g, 13.06 mmol) and K_2CO_3 (21.66 g, 156.72 mmol) in 100 ml of DMF was stirred at 70°C for 1 h and **14c'** (19.52 g, 28.74 mmol) added. After 6 h, the reaction was completed, K_2CO_3 was filtered through celite and the DMF evaporated. The brut was dissolved in CH_2Cl_2 (150 ml), washed with water (2 x 150 ml), NH_4Cl (2 x 50 ml), and brine (2 x 50 ml), dried over $MgSO_4$, and filtered. The compound was purified by chromatography (SiO_2, eluted with CH_2Cl_2/hexane, 7:3) and a white solid obtained (15.94 g, 84%). ^{1}H NMR($CDCl_3$): δ = 7.30 (2H, d, ^{3}J = 2.2Hz), 6.81 (1H, t, ^{3}J = 2.2Hz), 6.62 (4H, s), 4.95 (4H, s), 3.96 (15H, m), 1.77 (12H, m), 1.27 (108H, m), 0.88 (18H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 166.75, 159.75, 153.30, 138.00, 131.96, 131.23, 108.29, 107.16, 106.18, 73.40, 70.69, 69.09, 52.27, 31.90, 30.39, 29.61, 29.33, 26.06, 22.68, 14.11.

The same Mitsunobu procedure as for **15a** was employed for the preparation of the other ester dendritic derivatives **18a**, **18b** and **18c**, starting from the benzilic alcohol **17a**, **17b** and **17c** and methyl 3,5-dihydroxybenzoate.

(**18a**, **18b**, **18c**): **17** (**17a**: 10.0 g, 9.45 mmol; **17b**: 7.73 g, 2.86 mmol; **17c**: 7.0 g, 4.91 mmol), methyl 3,5–dihydroxybenzoate (0.75 g, 4.5 mmol; 0.23 g, 1.35 mmol; 0.393 g, 2.337 mmol) and PPh_3 (2.48 g, 9.45 mmol; 0.75 g, 2.86 mmol; 1.28 g, 4.91 mmol) in dry THF (*ca*. 50-100 ml) was added slowly under argon DIAD (1.86 ml, 9.45 mmol; 0.56 ml, 2.86 mmol; 0.97 ml,

4.91 mmol). CC (SiO_2, eluted with CH_2Cl_2/hexane 1:1 for **18a** and **18b**, and 7:3 for **18c**). **18a**: colorless oil (8.02 g, 80%); ^{1}H NMR($CDCl_3$): δ = 7.29 (2H, d, ^{3}J = 2.4Hz), 6.80 (1H, t, ^{3}J = 2.4Hz), 6.68 (4H, d, ^{3}J = 2.1Hz), 6.58 (2H, t, ^{3}J = 2.1Hz), 6.56 (8H, d, ^{3}J = 2.2Hz),, 6.40 (4H, t, ^{3}J = 2.2Hz), 5.01 (4H, s), 4.95 (8H, s), 3.93 (19H, m), 1.75 (16H, m), 1.26 (144H, m), 0.88 (24H, t, ^{3}J = 6.6Hz). ^{13}C NMR($CDCl_3$): δ = 166.68, 160.49, 160.15, 159.69, 138.84, 138.75, 132.01, 108.36, 107.08, 106.34, 105.69, 101.64, 100.79, 70.15, 68.03, 53.37, 52.22, 31.90, 29.66, 29.60, 29.34, 26.05, 22.67, 14.10. **18b**: colorless oil (4.61 g, 58%). ^{1}H NMR($CDCl_3$): δ = 7.33 (2H, d, ^{3}J = 2.2Hz), 6.87 (1H, t, ^{3}J = 2.2Hz), 6.73 (4H, d, ^{3}J = 2Hz), 6.63 (2H, t, ^{3}J = 2Hz), 6.58 (8H, d, ^{3}J = 2Hz), 6.45 (4H, t, ^{3}J = 2Hz), 5.01 (4H, s), 4.92 (8H, s), 3.95 (16H, s), 3.90 (3H, s), 3.49 (48H, s), 3.38 (48H, t, ^{3}J = 6.6Hz), 1.52 (48H, m), 1.24 (432H, m), 0.88 (72H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 166.68, 160.73, 160.32, 159.89, 138.65, 138.31, 132.02, 108.44, 106.79, 106.42, 106.34, 101.46, 100.88, 71.55, 70.38, 70.30, 67.23, 64.08, 52.13, 45.23, 31.94, 29.73, 29.65, 29.39, 26.22, 22.69, 14.10. **18c**: waxy solid (6.21 g, 89%). ^{1}H NMR($CDCl_3$): δ = 7.30 (2H, d, ^{3}J = 2.2Hz), 6.82 (1H, t, ^{3}J = 2.2Hz), 6.70 (4H, d, ^{3}J = 2.0Hz), 6.62 (10H, m), 5.02 (4H, s), 4.91 (8H, s), 3.93 (27H, m), 1.77 (24H, m), 1.26 (216H, m), 0.88 (36H, t, ^{3}J = 6.6Hz). ^{13}C NMR($CDCl_3$): δ = 166.67, 160.21, 159.73, 153.30, 138.76, 138.04, 132.08, 131.50, 108.36, 107.08, 106.38, 106.28, 101.61, 70.59, 70.20, 69.11, 52.20, 31.92, 30.35, 29.65, 29.36, 26.13, 22.68, 14.10.

Dendrons with an alcohol function

The same procedure used for the preparation of the derivatives **14** was utilized for the other benzyl ether dendrimers of the second **17a**, **17b**, **17c** and third generation **20a, 20b**, **20c** starting from the corresponding ester precursors **15a**, **15b**, **15c**, and **18a**, **18b**, **18c** respectively. They were all obtained as colorless oils except **15c** and **18c** which were recovered as white solids.

(**17a**, **17b**, **17c**): **15** (**15a**: 13.0 g, 11.97 mmol; **15b**: 11.0 g, 3.78 mmol; **15c**: 12.0 g, 8.251 mmol), $LiAlH_4$-1M (8.98 ml; 2.83 ml; 6.19 ml). CC (SiO_2: eluted with CH_2Cl_2/hexane 7:3). **17a**: 12.18 g, 96%. ^{1}H NMR($CDCl_3$): δ = 6.62 (2H, d, ^{3}J = 2.2Hz), 6.55 (5H, m), 6.40 (2H, d, ^{3}J = 2.3Hz), 4.96 (4H, s), 4.64 (2H, d, ^{3}J = 6Hz), 3.94 (8H, t, ^{3}J = 6.6Hz), 1.77 (8H, m), 1.63 (1H, t, ^{3}J = 6Hz), 1.27 (72H, m), 0.88 (12H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 160.42, 160.05, 143.42, 138.96, 105.61, 105.56, 101.22, 100.70, 69.98, 67.98, 65.10, 31.87, 29.63, 29.60, 29.31, 26.02, 22.64, 14.05. **17b**: 10.1 g, 93%. ^{1}H NMR($CDCl_3$): δ = 6.63 (2H, d, ^{3}J = 2.2Hz), 6.57 (5H, m), 6.45 (2H, t, ^{3}J = 2.1Hz), 4.92 (4H, s), 4.63 (2H, s), 3.95 (8H, s), 3.49

(24H, s), 3.38 (24H, t, ^3J = 6.5Hz), 1.52 (24H, m), 1.25 (216H, m), 0.88 (36H, t, ^3J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 160.70, 160.28, 143.33, 138.45, 106.13, 105.61, 101.11, 100.94, 71.56, 70.24, 69.35, 67.22, 65.35, 45.21, 31.94, 29.72, 29.63, 29.39, 26.21, 22.69, 14.11. **17c**: 10.94 g, 93%. ^1H NMR($CDCl_3$): δ = 6.54 (2H, d, ^3J = 2.0Hz), 6.52 (4H, s), 6.47 (1H, t, ^3J = 2.0Hz), 4.82 (4H, s), 4.55 (2H, s), 3.87 (12H, m), 1.71 (12H, m), 1.18 (108H, m), 0.80 (18H, t, ^3J = 6.8Hz). ^{13}C NMR($CDCl_3$): δ = 160.11, 153.24, 143.38, 137.87, 131.60, 106.11, 105.59, 101.15, 73.39, 70.45, 69.04, 65.23, 31.89, 29.73, 29.63, 29.34, 26.05, 22.64, 14.09.

(**20a**, **20b**, **20c**): **18** (**18a**: 4.4 g, 1.96 mmol; **18b**: 2.69 g, 0.46 mmol; **18c**: 3.5 g, 1.17 mmol), $LiAlH_4$-1M (1.47 ml; 0.34 ml; 0.88 ml). CC (SiO_2: eluted with CH_2Cl_2/hexane 7:3). **20a**: 3.34 g, 77%. ^1H NMR($CDCl_3$): δ = 6.67 (4H, d, ^3J = 2.2Hz), 6.60 (2H, d, ^3J = 2.1Hz), 6.55 (11H, m), 6.40 (4H, t, ^3J = 2.2Hz), 4.98 (4H, s), 4.95 (8H, s), 4.63 (2H, d, ^3J = 5.6Hz), 3.93 (16H, t, ^3J = 6.6Hz), 1.76 (16H, m), 1.26 (144H, m), 0.88 (24H, t, ^3J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 160.47, 160.11, 160.04, 143.47, 139.20, 138.90, 106.25, 105.69, 101.53, 101.19, 100.78, 70.44, 68.03, 65.25, 31.91, 29.66, 29.61, 29.35, 26.05, 22.68, 14.11. **20b**: 2.45 g, 91%. ^1H NMR($CDCl_3$): δ = 6.71 (4H, d, ^3J = 2.2Hz), 6.64 (2H, t, ^3J = 2.2Hz), 6.62 (3H, s), 6.58 (8H, d, ^3J = 2Hz), 6.45 (4H, t, ^3J = 2Hz), 4.98 (4H, s), 4.92 (8H, s), 4.63 (2H, d, ^3J = 6Hz), 3.95 (16H, s), 3.49 (48H, s), 3.38 (48H, t, ^3J = 6.5Hz), 1.80 (1H, t, ^3J = 6Hz), 1.52 (48H, m), 1.24 (432H, m), 0.87 (72H, t, ^3J = 6.7Hz). ^{13}C NMR($CDCl_3$) δ = 160.73, 160.29, 143.48, 139.11, 138.37, 135.75, 125.49, 106.33, 105.81, 101.38, 100.97, 100.84, 71.56, 70.29, 70.17, 69.37, 67.24, 65.27, 45.25, 31.94, 29.73, 29.65, 29.39, 26.22, 22.69, 14.10. **20c**: 2.74 g, 79%. ^1H NMR($CDCl_3$): δ = 6.68 (4H, d, ^3J = 2.0Hz), 6.60 (8H, s), 6.58 (3H, m), 6.51 (2H, t, ^3J = 2.0Hz), 4.98 (4H, s), 4.91 (8H, s), 4.61 (2H, d, ^3J = 6.25Hz), 3.94 (24H, m), 1.95 (1H, t, ^3J = 6.25Hz), 1.76 (24H, m),1.26 (216H, m), 0.88 (36H, t, ^3J = 6.8Hz). ^{13}C NMR($CDCl_3$): δ = 160.13, 159.95, 153.26, 145.81, 143.83, 139.23, 137.87, 134.27, 131.55, 106.11, 101.33, 100.68, 73.40, 70.53, 69.91, 69.05, 65.09, 31.90, 29.66, 29.62, 29.34, 26.01, 22.64, 14.10.

Dendrons with an acid function

The acids **16** and **19** were prepared as the acids **13** from the ester **15** and **18**, respectively. The acids **16** and **19c** were obtained as white powder, whereas the acids **19a** and **19b** as yellowish oils.

(**16a**, **16b**, **16c**): **15** (**15a**: 3.0 g, 2.76 mmol; **15b**: 1.29 g, 0.444 mmol; **15c**: 3.0 g, 2.063 mmol), KOH (1.55 g, 27.63 mmol; 0.49 g, 8.88 mmol; 1.16 g, 20.63 mmol). **16a**: 2.55 g, 86%, ^1H NMR($CDCl_3$): δ = 7.35 (2H, d, ^3J = 2.3Hz), 6.84 (1H, t, ^3J = 2.3Hz), 6.56 (4H, d, ^3J

= 2.1Hz), 6.42 (2H, t, ^{3}J = 2.1Hz), 5.00 (4H, s), 3.94 (8H, t, ^{3}J = 6.5Hz), 1.77 (8H, m), 1.27 (72H, m), 0.88 (12H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 171.82, 160.53, 159.81, 138.45, 131.13, 108.89, 108.06, 105.74, 100.97, 70.33, 68.07, 31.91, 29.66, 29.60, 29.34, 26.05, 22.67, 14.09. **16b**: 1.17 g, 92%, ^{1}H NMR($CDCl_3$): δ = 7.36 (2H, d, ^{3}J = 2.2Hz), 6.87 (1H, t, ^{3}J = 2.2Hz), 6.59 (4H, d, ^{3}J = 2Hz), 6.46 (2H, t, ^{3}J = 2Hz), 4.95 (4H, s), 3.96 (8H, s), 3.49 (24H, s), 3.38 (24H, t, ^{3}J = 6.5Hz), 1.52 (24H, m), 1.24 (216H, m), 0.88 (36H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 171.09, 160.74, 159.94, 137.91, 131.14, 108.68, 107.69, 106.36, 101.03, 71.56, 70.50, 69.34, 67.24, 45.23, 31.93, 29.72, 29.63, 29.39, 26.21, 22.69, 14.10. **16c**: 2.79 g, 94%. ^{1}H NMR($CDCl_3$): δ = 7.05 (2H, s), 6.62 (1H, s), 6.52 (4H, s), 4.95 (1H, s), 4.71 (4H, s), 3.90 (12H, m), 1.68 (12H, m), 1.26 (108H, m), 0.85 (18H, t, ^{3}J = 6.7Hz). **^{13}C RMN** ($CDCl_3$): δ = 173.00, 166.74, 159.35, 153.11, 137.59, 131.94, 131.25, 106.23, 106.07, 73.40, 70.69, 69.09, 52.27, 31.90, 30.39, 29.61, 29.33, 26.06, 22.68, 14.11.

(**19a**, **19b**, **19c**): **18** (**18a**: 2.5 g, 1.12 mmol; **18b**: 1.3 g, 0.22 mmol; **18c**: 2.4 g, 0.804 mmol), KOH (0.62 g, 11.12 mmol; 0.74 g, 13.2 mmol; 0.45 g, 8.04 mmol). **19a**: 2.28 g, 92%. ^{1}H NMR($CDCl_3$): δ = 7.35 (2H, d, ^{3}J = 2.4Hz), 6.84 (1H, t, ^{3}J = 2.4Hz), 6.69 (4H, d, ^{3}J = 2.2Hz), 6.56 (10H, m), 6.40 (4H, t, ^{3}J = 2.2Hz), 5.01 (4H, s), 4.96 (8H, s), 3.93 (16H, t, ^{3}J = 6.6Hz), 1.75 (16H, m), 1.26 (144H, m), 0.88 (24H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 171.51, 160.50, 160.18, 159.78, 138.87, 138.67, 131.25, 108.89, 107.93, 106.43, 105.69, 101.75, 100.82, 70.17, 68.03, 31.93, 30.42, 29.63, 29.37, 26.07, 22.69, 14.12. **19b**: 1.18 g, 91%. ^{1}H NMR($CDCl_3$): δ = 7.25 (2H, s), 6.83 (1H, t, ^{3}J = 2.2Hz), 6.67 (4H, d, ^{3}J = 2Hz), 6.59 (2H, t, ^{3}J = 2Hz), 6.55 (8H, d, ^{3}J = 1.8Hz), 6.44 (4H, s), 5.04 (4H, s), 4.92 (8H, s), 3.94 (16H, s), 3.49 (48H, s), 3.38 (48H, t, ^{3}J = 6.6Hz), 1.52 (48H, m), 1.24 (432H, m), 0.87 (72H, t, ^{3}J = 6.7Hz). ^{13}C NMR($CDCl_3$): δ = 167.59, 161.16, 160.71, 160.27, 159.76, 138.91, 138.47, 108.86, 107.89, 106.29, 106.07, 101.56, 100.83, 71.58, 70.39, 70.26, 69.37, 67.20, 45.25, 31.94, 29.73, 29.63, 29.39, 26.21, 22.69, 14.10. **19c**: 2.03 g, 85%. ^{1}H NMR($CDCl_3$): δ = 7.34 (2H, d, ^{3}J = 2.4Hz); 6.86 (1H, t, ^{3}J = 2.4Hz), 6.70 (4H, d, ^{3}J = 2.2Hz), 6.62 (10H, m), 5.02 (4H, s), 4.92 (8H, s), 3.97 (24H, m), 1.77 (24H, m), 1.26 (216H, m), 0.88 (36H, t, ^{3}J = 6.6Hz). ^{13}C NMR($CDCl_3$): δ = 170.66, 166.23, 160.49, 159.82, 153.30, 138.60, 138.06, 131.50, 131.12, 108.85, 107.86, 106.51, 106.29, 101.72, 73.40, 70.58, 70.32, 69.13, 31.90, 30.35, 29.63, 29.34, 26.11, 22.67, 14.07.