End functionalised liquid crystalline bent core molecules and first DAB derived dendrimers with banana shaped mesogenic units†

Dorota Kardas,[a] Makro Prehm,[a] Ute Baumeister,[b] Damian Pociecha[c], R. Amaranatha Reddy,[a] Georg H. Mehl[d] and Carsten Tschierske*[a]

[a] *Institute of Organic Chemistry, Martin-Luther University, 06120 Halle, Kurt-Mothes Str.2, Germany. Fax: +49 345 5527346; Tel: +49 345 5525664; carsten.tschierske@chemie.uni-halle.de.*
[b] *Institute of Physical Chemistry, Martin-Luther-University Halle-Wittenberg, Mühlpforte 1, D-06108 Halle, Germany*
[c] *Warsaw University, Department of Chemistry, Al. Zwirki i Wigury 101, 02089 Warsaw, Poland*
[d] *The Hull University, Department of Chemistry, Cottingham Road, HU7 6RX, Hull, UK*

Supporting Information

1. X-Ray data of compounds 1-Pfp-16, III 1-16 and 2-12, DSC traces of 1-Pfp-14 and possible structures for the $Col_{ob}P_A$ phase of 1-Pfp-16

Table S1 X-ray data for **I-Pfp16** from a Guinier film pattern (powder-like sample in a glass capillary, θ_{obs}: experimental scattering angle; d_{obs}: experimental and d_{calc}: calculated d spacing; *hk*: assigned indices)

Lattice parameters for an oblique 2D cell: a = 4.19 nm, b = 2.35 nm, γ = 94,9°

θ_{obs} (°)	d_{obs} (nm)	*hk*	d_{calc} (nm)	d_{obs}- d_{calc} (nm)
1.057	4.177	10	4.175	0.002
1.881	2.347	01	2.341	0.006
2.100	2.103	20	2.087	0.016
		$\bar{1}1$	2.129	-0.026
2.248	1.964	11	1.972	-0.008
2.950	1.497	21	1.496	0.001

Table S2 X-ray data for the amphiphile **III** (d = 9.16(2) nm at 140 °C) and for the dendrimer **1-16** (d = 9.11(5) nm at 140 °C) from Guinier film patterns (powder-like sample in a glass capillary, θ_{obs}: experimental scattering angle; d_{obs}: experimental and d_{calc}: calculated d spacing; n: order of the reflection)

Compd.	θ_{obs} (°)	d_{obs} (nm)	n	$d_{obs} \cdot n$ (nm)
III	0.963	4.587	2	9.174
	1.450	3.045	3	9.135
	1.925	2.295	4	9.180
	2.413	1.830	5	9.150
	2.900	1.523	6	9.138
1-16	0.975	4.528	2	9.056
	1.447	3.051	3	9.154
	1.937	2.280	4	9.118

Table S3 X-ray data for **2-12** from a Guinier film pattern (powder-like sample in a glass capillary, θ_{obs}: experimental scattering angle; d_{obs}: experimental and d_{calc}: calculated d spacing; hk: trial indices only based on the powder pattern)

Lattice parameters for a rectangular 2D cell: a = 7.4 nm, b = 5.6 nm

θ_{obs} (°)	d_{obs} (nm)	hk	d_{calc} (nm)	d_{obs}- d_{calc} (nm)
0.78	5.69	01	5.60	0.09
1.20	3.68	20	3.68	0.00
1.45	3.04	21	3.08	-0.04
1.60	2.76	12	2.62	0.14
1.78	2.49	30	2.45	0.04
1.96	2.25	31	2.25	0.00

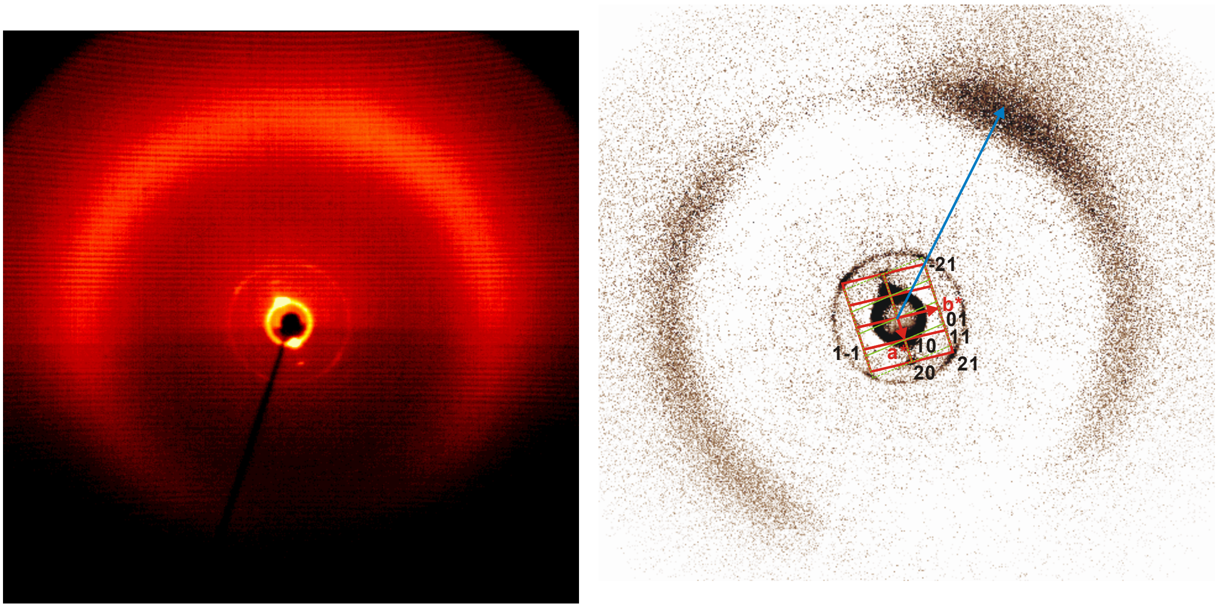


Figure S1 a) X-ray diffraction pattern of a partially aligned sample of **I-Pfp16** (drop on a glass plate) and b) *I*(80 °C) – *I*(90 °C, isotropic) pattern showing the reciprocal lattice of two main domains (red and green lines), reciprocal 2D-lattice parameters *a** and *b** and indices for the observed reflections of the main domain, and the dominant direction of the outer diffuse scattering (blue arrow).

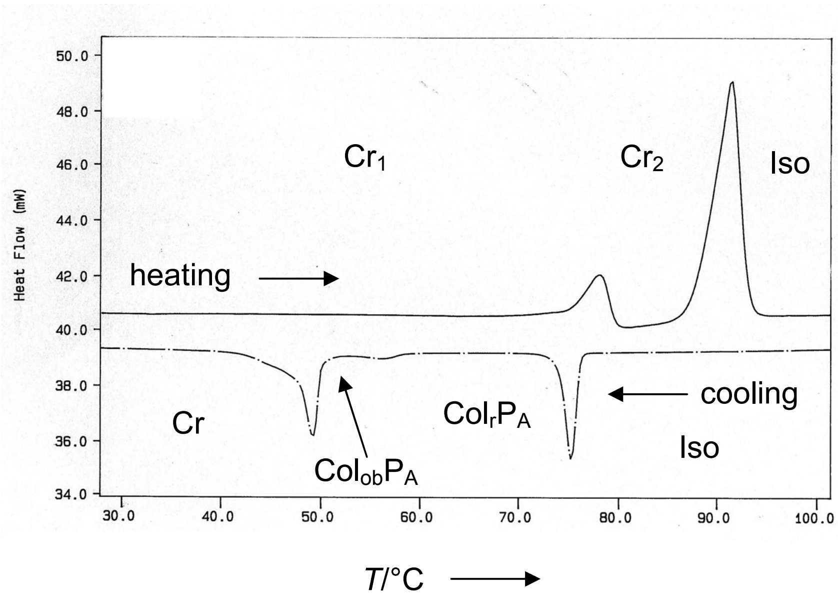
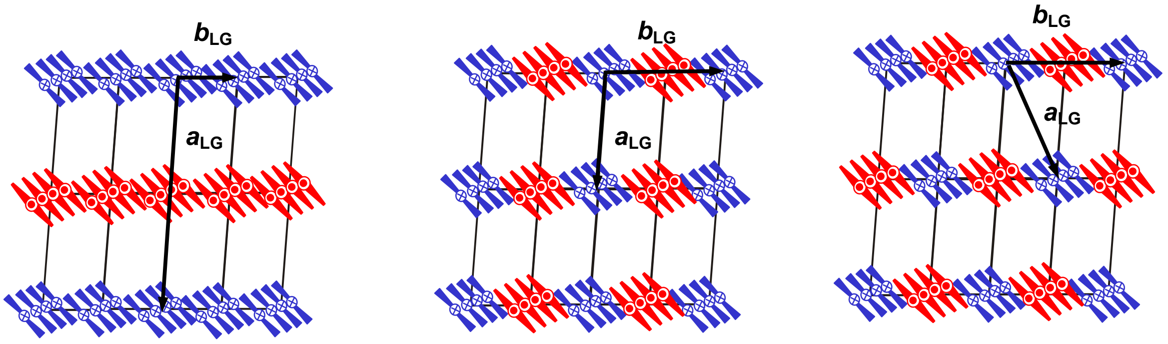


Figure S2 DSC heating and cooling traces of **1-Pfp14** (10 K min^{-1})



a) b) c)

Figure S3. Three possible organisations of the bent core molecules in the $\mathrm{Col_{ob}P_A}$ phase, taking into account the polar directions of the bent-core units in adjacent ribbons. The structure of these columnar phases with a polarisation direction along the column long axis cannot be adequately described by the 17 plane groups, because, due to the polar direction, the upper and the lower ends of the columns become different. Therefore, the 80 layer groups (LG) are used instead, which are three dimensional groups with two dimensional translations.[1] The lattice parameters of these layer groups (a_{LG} and b_{LG}) give the distance between adjacent ribbons (columns) with uniform polarisation direction (red or blue). Because conventional X-ray methods cannot distinguish the polarisation direction (identical electron density) the lattice parameters described by the layer groups can differ from the lattice parameters determined by X-ray (compare Fig. 5c in the main text and Fig. S3 a-c).

a) Uniform polarisation direction along *b* and alternating polarisation direction along *a*. This model would be in best agreement with the observed antiferroelectric switching behaviour. However, the packing of the bent units along *b* is difficult in this ribbon structure, because at the side-to-side interfaces of the ribbons there is no strictly parallel organisation of the rod-like wings of the bent core molecules. If a sinusoidal undulation of the (correlated) layers is assumed instead, then these packing constraints become less important and in this case this organisation might become the most reasonable. The facts that the cross reflections occur only with index $k = 1$ and are very weak might be hints on this type of packing. However, a similar diffraction pattern can also be expected for the other two arrangements and a sinusoidal undulation is difficult to imagine for such a short undulation wave length. The appropriate layer group for this model, taking into account the polar directions is the monoclinic/oblique one *p*112/*a* with corresponding lattice parameters $a_{\mathrm{LG}} = 8.4$ nm, $b_{\mathrm{LG}} = 2.35$ nm and $\gamma_{\mathrm{LG}} = 95°$.

b) Alternating polarisation direction along *b* and uniform polarisation direction along *a*; layer group monoclinic/oblique *p*112/*b*, $a_{\mathrm{LG}} = 4.2$ nm, $b_{\mathrm{LG}} = 4.7$ nm and $\gamma_{\mathrm{LG}} = 95°$.

c) Layer group monoclinic/oblique *p*112/*b*, $\mathrm{a_{LG}} = 4.6$ nm, $b_{\mathrm{LG}} = 4.7$ nm and $\gamma_{\mathrm{LG}} = 64.5°$.

Models b) and c) appear to be more reasonable considering the packing of the bent units along *b*, due to the parallel arrangement of the wings of the bent core units at the interfaces between adjacent ribbons. Model b) is more similar to the organisation proposed in other $\mathrm{Col_{ob}P_A}$ phases.

2. Synthesis and Analytical Data

2.1 Synthesis of compound D-I

2.1.1 Benzyl 11-(4-formylphenoxy)undecanoate

4-Hydroxybenzaldehyde (2.5 g, 20.5 mmol), benzyl 11-bromoundecanoate (8.0 g, 22.5 mmol) and K_2CO_3 (8.5 g, 61.5 mmol) were dissolved in acetonitril (200 ml). The reaction mixture was stirred under reflux for 7 h, and then cooled to room temperature. Ice-water (500 ml) was added and the solution was acidified with HCl (37%) to pH = 2-3, extracted with diethyl ether, washed with water, dried with Na_2SO_4, and the solvent was evaporated. The crude product was purified by crystallisation from ethanol. Yield: 5.0 g (62 %); colourless solid; mp: 34-36 °C; ^{1}H NMR (δ ppm, $CDCl_3$): 1.28 (s, 10H, CH_2); 1.39-1.43 (m, 2H, CH_2); 1.59-1.66 (m, 2H, $OOCCH_2CH_2$); 1.72-1.86 (m, 2H, OCH_2CH_2); 2.33 (t, 2H, $OOCCH_2$, J=7.5 Hz); 4.02 (t, 2H, OCH_2, J=6.4 Hz); 5.09 (s, 2H, OCH_2 Ph); 6.97 (d, 2H, Ar-H, J=8.8 Hz); 7.33 (s, 5H, Ar-H); 7.80 (d, 2H, Ar-H, J=8.8 Hz); 9.86 (s, 1H, CHO).

2.1.2 4-[10-(Benzyloxycarbonyl)decyloxy]benzoic acid D-I

Benzyl 11-(4-formylphenoxy)undecanoate (5.0 g, 12.6 mmol) was dissolved in acetic acid (90%, 50 ml) and a solution of CrO_3 (2.5 g, 25.2 mmol) in acetic acid (60%, 20ml) was added. The resulting solution was refluxed with stirring for 5 hours. Afterwards water (20 ml) was added and the solution was allowed to cool to room temperature and was stored overnight in a refrigerator (0-4 °C). The precipitate formed was filtered off, washed with water, and crystallised from ethanol. Yield: 4.1 g (79 %); colourless solid; mp: 90-91 °C; ^{1}H NMR (δ ppm, $CDCl_3$): 1.27 (s, 10H, CH_2); 1.39-1.42 (m, 2H, CH_2); 1.59-1.66 (m, 2H, $OOCCH_2CH_2$); 1.71-1.81 (m, 2H, OCH_2CH_2); 2.33 (t, 2H, $OOCCH_2$, J=7.5 Hz); 3.99 (t, 2H, OCH_2, J = 6.4 Hz); 5.09 (s, 2H, OCH_2Ph); 6.90 (d, 2H, Ar-H, J=8.8 Hz); 7.33 (s, 5H, Ar-H); 8.02 (d, 2H, Ar-H, J=8.8 Hz).

2.2 Synthesis of compound D-IF

2.2.1 Allyl 3-fluoro-4-hydroxybenzoate

To a solution of 3-fluoro-4-hydroxybenzoic acid (4.8 g, 31.0 mmol) dissolved in freshly distilled acetonitril, DBU (4.7 g, 31.0 mmol) and allyl bromide (4.5 g, 37.0 mmol) were added slowly. The reaction mixture was heated up to 70 °C and stirred at this temperature for 4 hours. After cooling to room temperature, the mixture was poured into ice and extracted with dichloromethane, the organic layer was washed with water and brine, dried over sodium sulphate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (eluent: dichloromethane: methanol mixtures up to 5 % methanol) followed by crystallisation from hexane. Yield: 4.5 g (74 %); ^{1}H NMR (δ ppm, $CDCl_3$): 4.78 (d, 2H, CH_2, J=5.8 Hz); 5.25-5.40 (m, 2H, $CH=CH_2$); 5.95-6.05 (m, 1H, $CH=CH_2$); 6,33 (s, 1H, OH); 7.02 (t, 1H, Ar-H, J=8.6 Hz); 7.73-7.78 (m, 2H, Ar-H).

2.2.2 Allyl 4-[10-(benzyloxycarbonyl)decyloxy]-3-fluorobenzoate

To a mixture of allyl 3-fluoro-4-hydroxybenzoate (2.6 g, 13.0 mmol), potassium carbonate (1.8 g, 13.0 mmol) and Bu_4NI (37 mg, 0.1 mmol) in dry butanone, benzyl 11-bromoundecanoate (5.7 g, 16 mmol) was added slowly. The reaction mixture was heated under reflux for 4 hours. After cooling to room temperature the precipitated solid was removed by filtration and the solvent was evaporated. The crude product was purified by column chromatography (eluent: dichloromethane), followed by crystallisation from hexane. Yield: 5.6 g (95 %); ^{1}H NMR (δ ppm, $CDCl_3$): 1.27-1.34 (m, 10H, CH_2); 1.42-1.48 (m, 2H, CH_2); 1.60-1.64 (m, 2H, $OOCCH_2CH_2$); 1.82 (quintet, 2H, OCH_2CH_2, J=7.0 Hz); 2.34 (t, 2H, $OOCCH_2$, J=7.6 Hz); 4.06 (t, 2H, OCH_2, J=6.6 Hz); 4.78 (d, 2H, $H_2C=CHCH_2$, J=5.5 Hz); 5.10 (s, 2H, OCH_2Ph); 5.25-5.40 (m, 2H, $CH=CH_2$); 5.95-6.05 (m, 1H, C*H*=CH$_2$); 6.94 (t, 1H, Ar-H, *J*=8.3 Hz); 7.28-7.36 (m, 5H, Ar-H); 7.74 (dd, 2H, Ar-H, J_1=11.7 Hz, J_2=2.1 Hz); 7.80 (d, 1H, Ar-H, *J*=8.5 Hz).

2.2.3 4-[10-(Benzyloxycarbonyl)decyloxy]-3-fluorobenzoic acid D-IF

A mixture of the allyl 4-[10-(benzyloxycarbonyl)decyloxy]-3-fluorobenzoate (2.7 g, 6.0 mmol), tetrakis(triphenylphosphino)palladium (0) (16 mg, 0.1 mmol) and triphenylphosphine (52 mg, 0.2 mmol) dissolved in dichloromethane was cooled down to 0 °C and pyrrolidine was added dropwise. After stirring for 30 min at 0 °C the reaction mixture was washed with 1N HCl, followed by water, the organic layer was dried over sodium sulphate and the solvent was evaporated. The crude product was purified by crystallisation from iso-propanol. Yield: 2.2 g (90 %); ^{1}H NMR (δ ppm, acetone): 1.30-1.31 (m, 10H, CH$_2$); 1.45-1.54 (m, 2H, CH$_2$); 1.59-1.63 (m, 2H, OOCCH$_2$C*H*$_2$); 1.83 (quintet, 2H, OCH$_2$C*H*$_2$, *J*=7.1 Hz); 2.34 (t, 2H, OOCCH$_2$, *J*=7.4 Hz); 4.17 (t, 2H, OCH$_2$, *J*=6.5 Hz); 5.10 (s, 2H, OCH$_2$Ph); 7.22 (t, 1H, Ar-H, *J*=8.5 Hz); 7.35-7.37 (m, 5H, Ar-H); 7.69 (dd, 2H, Ar-H, J_1=12.0 Hz, J_2=2.1 Hz); 7.81 (d, 1H, Ar-H, *J*=8.5 Hz).

2.3 Synthesis of compound D-II

2.3.1 Benzyl 5-(4-formylphenoxy)pentanoate

Prepared according to the procedure 2.1.1 from benzyl 5-bromopentanoate (13.6 g, 50.0 mmol), 4-hydroxybenzaldehyde (5.5 g, 45.0 mmol) and K_2CO_3 (18.8 g, 136 mmol). Purification by crystallisation from ethanol. Yield: 10.4 g (73 %); colourless solid; mp: 35-36 °C; ^{1}H NMR (δ ppm, CDCl$_3$): 1.81-1.87 (m, 4H, CH$_2$); 2.44 (t, 2H, OOCCH$_2$, *J*=6.8 Hz); 4.03 (t, 2H, OCH$_2$, *J*=5.7 Hz); 5.10 (s, 2H, OCH$_2$Ph); 6.95 (d, 2H, Ar-H, *J*=8.8 Hz); 7.33 (bs, 5H, Ar-H); 7.79 (d, 2H, Ar-H, *J*=8.8 Hz); 9.86 (s, 1H, CHO).

2.3.2 4-[4-(Benzyloxycarbonyl)butoxy]benzoic acid D-II

Prepared according to the procedure 2.1.2 from benzyl 5-(4-formylphenoxy)pentanoate (10.4 g, 33.3mmol) (5.0 g, 12.6 mmol) and CrO_3 (6.6 g, 66.0 mmol). Purification by crystallisation from ethanol. Yield: 7.3 g (67 %); colourless solid; mp: 103-104 °C; ^{1}H NMR (δ ppm, CDCl$_3$): 1.83-1.86 (m, 4H, CH$_2$); 2.45 (t, 2H, OOCCH$_2$, *J*=6.9 Hz); 4.02 (t, 2H, OCH$_2$, *J*=5.8 Hz); 5.11 (s, 2H, OCH$_2$Ph); 6.89 (d, 2H, Ar-H, *J*=8.9 Hz); 7.32-7.35 (m, 5H, Ar-H); 8.03 (d, 2H, Ar-H, *J*=8.9 Hz).

2.4 Analytical data of compounds of series I

2.4.1 Compound I–Bz14

^{1}H NMR (δ ppm, CDCl$_3$): 0.87 (t, 3H, CH$_3$, *J*=7.0 Hz); 1.26–1.36 (m, 30H, CH$_2$); 1.43–1.47 (m, 4H, CH$_2$); 1.63 (quintet, 2H, CH$_2$, *J*=7.5 Hz); 1.78–1.84 (m, 4H, CH$_2$); 2.34 (t, 2H, OOCCH$_2$, *J*=7.5 Hz); 4.03 (t, 2H, OCH$_2$, *J*=6.5 Hz); 4.04 (t, 2H, OCH$_2$, *J*=6.5 Hz); 5.10 (s, 2H, OCH$_2$Ph); 6.96 (dd, 2H, Ar-H, J_1=8.5 Hz, J_2=5.0 Hz); 6.97 (dd, 2H, Ar-H, J_1=9.5 Hz, J_2=5.0 Hz); 7.20–7.22 (m, 1H, Ar-H); 7.28 (dd, 2H, Ar-H, J_1=8.5 Hz, J_2=4.5 Hz); 7.30–7.35 (m, 5H, Ar-H); 7.35 (dd, 2H, Ar-H, J_1=8.5 Hz, J_2=4.5 Hz); 7.44 (bs, 1H, Ar-H); 7.49 (d, 2H, Ar-H, *J*=5.0 Hz); 7.64 (dd, 2H, Ar-H, J_1=8.5 Hz, J_2=5.0 Hz); 8.14 (dd, 4H, Ar-H, J_1=9.0 Hz, J_2=5.0 Hz); 8.29 (dd, 2H, Ar-H, J_1=8.5 Hz, J_2=5.0 Hz); ^{13}C NMR (δ ppm, CDCl$_3$): 14.10, 22.68, 24.93, 25.95, 25.97, 29.08, 29.19, 29.30, 29.33, 29.34, 29.44, 29.54, 29.58, 29.64, 29.66, 29.68, 31.91, 34.31, 66.05, 68.31, 68.39, 114.32, 114.43, 120.41, 120.54, 120.97, 121.48, 122.11, 122.17, 124.67, 126.87, 128.15, 128.23, 128.53, 129.84, 131.83, 132.31, 132.41, 136.15, 137.75, 142.17, 150.86, 151.33, 155.43, 163.58, 163.83, 164.31, 164.47, 164.91, 173.64; Calcd. for $C_{65}H_{76}O_{10}$: C 76.74, H 7.53 %; Found: C 76.69, H 7.27 %.

2.4.2 Compound I–H14

^{1}H NMR (δ ppm, CDCl$_3$): 0.87 (t, 3H, CH$_3$, J=7.0 Hz); 1.25–1.35 (m, 30H, CH$_2$); 1.44–1.49 (m, 4H, CH$_2$); 1.63 (quintet, 2H, CH$_2$, J=7.5 Hz); 1.78–1.84 (m, 4H, CH$_2$); 2.34 (t, 2H, OOCCH$_2$, J=7.5 Hz); 4.03 (t, 2H, OCH$_2$, J=6.5 Hz); 4.04 (t, 2H, OCH$_2$, J=6.5 Hz); 6.96 (dd, 2H, Ar-H, J_1=9.0 Hz, J_2=5.0 Hz); 6.97 (dd, 2H, Ar-H, J_1=9.0 Hz, J_2=5.0 Hz); 7.19–7.23 (m, 1H, Ar-H); 7.27 (dd, 2H, Ar-H, J_1=9.0 Hz, J_2=4.5 Hz); 7.37 (dd, 2H, Ar-H, J_1=9.0 Hz, J_2=4.5 Hz); 7.43 (bs, 1H, Ar-H); 7.49 (d, 2H, Ar-H, J=5.5 Hz); 7.63 (dd, 2H, Ar-H, J_1=8.5 Hz, J_2=4.5 Hz); 8.14 (dd, 4H, Ar-H, J_1=9.0 Hz, J_2=5.0 Hz); 8.29 (dd, 2H, Ar-H, J_1=8.5 Hz, J_2=4.5 Hz); ^{13}C NMR (δ ppm, CDCl$_3$): 14.10, 22.68, 24.66, 25.95, 25.97, 29.02, 29.08, 29.18, 29.29, 29.31, 29.35, 29.43, 29.54, 29.58, 29.64, 29.66, 29.68, 31.92, 33.73, 68.31, 68.40, 114.32, 114.43, 120.42, 120.54, 120.97, 121.48, 122.11, 122.17, 124.68, 126.87, 128.24, 129.84, 131.83, 132.31, 132.42, 137.76, 142.17, 150.86, 151.33, 155.43, 163.59, 163.84, 164.32, 164.48, 164.93, 178.36; Calcd. for $C_{58}H_{70}O_{10}$: C 75.13, H 7.61 %; Found: C 75.12, H 7.35 %.

2.4.3 Compound I–Pfp14

^{1}H NMR (δ ppm, CDCl$_3$): 0.87 (t, 3H, CH$_3$, J=7.0 Hz); 1.26–1.53 (m, 34H, CH$_2$); 1.73–1.85 (m, 6H, CH$_2$); 2.65 (t, 2H, OOCCH_2, J=7.4 Hz); 4.04 (t, 2H, OCH$_2$, J=6.4 Hz); 4.05 (t, 2H, OCH$_2$, J=6.6 Hz); 6.96 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.8 Hz); 6.98 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.6 Hz); 7.19–7.22 (m, 1H, Ar-H); 7.27 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.8 Hz); 7.37 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.4 Hz); 7.44 (bs, 1H, Ar-H); 7.49 (d, 2H, Ar-H, J=4.8 Hz); 7.64 (dd, 2H, Ar-H, J_1=8.4 Hz, J_2=4.4 Hz); 8.14 (dd, 4H, Ar-H, J_1=9.2 Hz, J_2=4.6 Hz); 8.29 (dd, 2H, Ar-H, J_1=8.4 Hz, J_2=4.6 Hz); ^{13}C NMR (δ ppm, CDCl$_3$): 14.15, 22.73, 24.81, 26.03, 28.88, 29.14, 29.33, 29.40, 29.45, 29.59, 29.63, 29.69, 29.71, 29.73, 31.96, 33.38, 68.33, 68.43, 114.29, 114.40, 120.37, 120.49, 120.97, 121.51, 122.05, 122.11, 124.61, 126.84, 128.17, 129.77, 131.76, 132.24, 132.35, 137.70, 142.11, 150.80, 151.29, 155.38, 163.50, 163.75, 164.20, 164.36, 164.78, 169.42, 172.87; Calcd. for $C_{64}H_{69}F_5O_{10}$: C 70.31, H 6.36 %; Found: C 70.63, H 6.44 %.

2.4.4 Compound IF-Bz14

^{1}H NMR (δ ppm, CDCl$_3$): 0.87 (t, 3H, CH$_3$, J=6.8 Hz); 1.21–1.52 (m, 34H, CH$_2$); 1.60–1.66 (m, 2H, CH$_2$); 1.77–1.90 (m, 4H, CH$_2$); 2.34 (t, 2H, OOCCH_2, J=7.4 Hz); 4.03 (t, 2H, OCH$_2$, J=6.4 Hz); 4.12 (t, 2H, OCH$_2$, J=6.6 Hz); 5.10 (s, 2H, OCH$_2$Ph); 6.96 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.8 Hz); 7.03 (t, 1H, Ar-H, J=8.4 Hz); 7.19–7.22 (m, 1H, Ar-H); 7.28 (dd, 2H, Ar-H, J_1=8.4 Hz, J_2=4.4 Hz); 7.30–7.35 (m, 5H, Ar-H); 7.37 (dd, 2H, Ar-H, J_1=8.4 Hz, J_2=4.4 Hz); 7.44 (bs, 1H, Ar-H); 7.49 (d, 2H, Ar-H, J=4.8 Hz); 7.64 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.8 Hz); 7.90 (td, 1H, Ar-H, J_1=11.6 Hz, J_2=2.0 Hz); 7.95–7.98 (m, 1H, Ar-H); 8.14 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.8 Hz); 8.30 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.4 Hz); ^{13}C NMR (δ ppm, CDCl$_3$): 14.15, 22.72, 24.98, 25.91, 26.01, 29.04, 29.14, 29.24, 29.35, 29.37, 29.39, 29.48, 29.56, 29.60, 29.68, 29.70, 29.72, 31.96, 34.36, 66.05, 68.34, 69.91, 113.53, 114.30, 117.73, 117.94, 120.35, 120.47, 121.24, 121.48, 121.94, 122.13, 124.64, 127.07, 127.45, 127.49, 128.08, 128.17, 128.47, 129.78, 131.81, 132.25, 136.12, 137.68, 142.12, 150.67, 150.67, 150.82, 151.27, 152.15, 152.25, 155.08, 163.35, 163.52, 164.29, 164.80, 173.52.

2.4.5 Compound IF-H14

^{1}H NMR (δ ppm, CDCl$_3$): 0.87 (t, 3H, CH$_3$, J=7.0 Hz); 1.25–1.31 (m, 30H, CH$_2$); 1.43–1.50 (m, 4H, CH$_2$); 1.52 – 1.65 (m, 2H, CH$_2$); 1.77–1.89 (m, 4H, CH$_2$); 2.34 (t, 2H, OOCCH_2, J=7.4 Hz); 4.03 (t, 2H, OCH$_2$, J=6.4 Hz); 4.12 (t, 2H, OCH$_2$, J=6.6 Hz); 6.96 (d, 2H, Ar-H, J=8.8 Hz); 7.03 (t, 1H, Ar-H, J=8.4 Hz); 7.19–7.23 (m, 1H, Ar-H); 7.27 (dd, 2H, Ar-H, J_1=8.4 Hz, J_2=4.8 Hz); 7.36 (dd, 2H, Ar-H, J_1=8.4 Hz, J_2=4.4 Hz); 7.44 (bs, 1H, Ar-H); 7.49 (d, 2H, Ar-H, J=5.2 Hz); 7.63 (dd, 2H, Ar-

H, J_1=8.4 Hz, J_2=4.8 Hz); 7.90 (dd, 1H, Ar-H, J_1=11.6 Hz, J_2=2 Hz); 7.96 (d, 1H, Ar-H, J=8.4 Hz); 8.14 (dd, 2H, Ar-H, J_1=9.2 Hz, J_2=Hz); 8.29 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.4 Hz); ^{13}C NMR (δ ppm, $CDCl_3$): 14.15, 22.73, 24.73, 25.91, 26.01, 27.44, 29.04, 29.07, 29.13, 29.23, 29.35, 29.39, 29.48, 29.56, 29.61, 29.68, 31.96, 33.78, 50.87, 68.33, 69.56, 113.52, 114.30, 117.73, 117.93, 120.35, 120.46, 121.46, 121.93, 122.12, 124.64, 127.07, 127.45, 128.17, 129.77, 131.81, 132.24, 137.68, 142.12, 150.82, 151.25, 152.25, 153.10, 155.08, 163.35, 163.50, 164.29, 164.81, 178.21.

2.4.6 Compound IF-Pfp14

^{1}H NMR (δ ppm, $CDCl_3$): 0.87 (t, 3H, CH_3, J=6.8 Hz); 1.25–1.48 (m, 34H, CH_2); 1.73–1.90 (m, 6H, CH_2); 2.65 (t, 2H, $OOCCH_2$, J=7.4 Hz); 4.04 (t, 2H, OCH_2, J=6.4 Hz); 4.12 (t, 2H, OCH_2, J=6.6 Hz); 6.96 (d, 2H, Ar-H, J=8.8 Hz); 7.03 (t, 1H, Ar-H, J=8.4 Hz); 7.19–7.22 (m, 1H, Ar-H); 7.27 (dd, 2H, Ar-H, J_1=8.4 Hz, J_2=4.4 Hz); 7.37 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.8 Hz); 7.44 (bs, 1H, Ar-H); 7.49 (d, 2H, Ar-H, J=5.2 Hz); 7.63 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.8 Hz); 7.90 (dd, 1H, Ar-H, J_1=11.2 Hz, J_2=2 Hz); 7.95 (d, 1H, Ar-H, J=8.8 Hz); 8.14 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.8 Hz); 8.30 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.8 Hz); ^{13}C NMR (δ ppm, $CDCl_3$): 14.13, 22.71, 24.78, 25.89, 26.00, 28.85, 29.02, 29.12, 29.31, 29.44, 29.59, 29.67, 31.94, 33.36, 68.32, 69.54, 113.53, 114.30, 117.95, 120.37, 121.49, 121.96, 122.13, 124.66, 127.51, 128.20, 129.80, 131.84, 132.27, 137.68, 142.12, 150.82, 151.27, 152.25, 153.10, 155.08, 163.35, 163.53, 164.29, 164.81; Calcd. for $C_{64}H_{68}F_6O_{10}$: C 69.18, H 6.17 %; Found: C 68.92, H 6.31 %.

2.4.7 Compound IFa-Bz14

^{1}H NMR (δ ppm, $CDCl_3$): 0.87 (t, 3H, CH_3, J=7.0 Hz); 1.19–1.36 (m, 30H, CH_2); 1.44–1.50 (m, 4H, CH_2); 1.60–1.64 (m, 2H, CH_2); 1.82–1.89 (m, 4H, CH_2); 2.34 (t, 2H, $OOCCH_2$, J=7.5 Hz); 4.11 (t, 2H, OCH_2, J=6.5 Hz); 4.12 (t, 2H, OCH_2, J=6.5 Hz); 5.10 (s, 2H, OCH_2Ph); 7.03 (dd, 1H, Ar-H, J_1=6.0 Hz, J_2=2.0 Hz); 7.20–7.22 (m, 1H, Ar-H); 7.27 (dd, 2H, Ar-H, J_1=9.0 Hz, J_2=4.5 Hz); 7.30–7.35 (m, 5H, Ar-H); 7.36 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.5 Hz); 7.44 (bs, 1H, Ar-H); 7.50 (d, 2H, Ar-H, J=4.5 Hz); 7.64 (dd, 2H, Ar-H, J_1=8.5 Hz, J_2=5.0 Hz); 7.90 (dd, 1H, Ar-H, J_1=11.5 Hz, J_2=2.5 Hz); 7.96 (dd, 1H, Ar-H, J_1=7.5 Hz, J_2=1.5 Hz); 8.29 (dd, 2H, Ar-H, J_1=9.0 Hz, J_2=4.5 Hz); ^{13}C NMR (δ ppm, $CDCl_3$): 14.14, 22.72, 24.98, 25.90, 29.03, 29.13, 29.22, 29.29, 29.35, 29.35, 29.38, 29.44, 29.55, 29.60, 29.67, 29.71, 31.95, 34.36, 66.06, 69.50, 69.57, 113.51, 114.30, 117.79, 117.94, 120.39, 121.97, 122.02, 124.67, 127.08, 127.33, 128.11, 128.25, 128.49, 129.83, 131.84, 142.05, 150.63, 164.34; Calcd. for $C_{65}H_{74}F_2O_{10}$: C 74.12, H 7.08 %; Found: C 73.89, H 7.39 %.

2.4.8 Compound IFb-Bz14

^{1}H NMR (δ ppm, $CDCl_3$): 0.87 (t, 3H, CH_3, J=6.4 Hz); 1.25–1.28 (m, 30H, CH_2); 1.42–1.49 (m, 4H, CH_2); 1.63 (quintet, 2H, CH_2, J=7.4 Hz); 1.77–1.89 (m, 4H, CH_2); 2.34 (t, 2H, $OOCCH_2$, J=7.6 Hz); 4.03 (t, 2H, OCH_2, J=6.6 Hz); 4.13 (t, 2H, OCH_2, J=6.4 Hz); 5.10 (s, 2H, OCH_2Ph); 6.82 (dd, 1H, H_a, J_1=6.0 Hz, J_2=1.6 Hz); 6.96 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.8 Hz); 7.19–7.22 (m, 1H, Ar-H); 7.27 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.4 Hz); 7.30–7.35 (m, 5H, Ar-H); 7.38 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.8 Hz); 7.44 (bs, 1H, Ar-H); 7.49 (d, 2H, Ar-H, J=5.2 Hz); 7.63 (dd, 2H, Ar-H, J_1=8.4 Hz, J_2=4.8 Hz); 7.84 (dd, 1H, Ar-H, J_1=6.0 Hz, J_2=2.0 Hz); 8.14 (dd, 2H, Ar-H, J_1=9.2 Hz, J_2=4.8 Hz); 8.29 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.8 Hz); ^{13}C NMR (δ ppm, $CDCl_3$): 14.12 22.71 24.97 25.82, 25.99, 28.96, 29.12, 29.22, 29.33, 29.36, 29.46, 29.52, 29.57, 29.66, 31.94, 34.35, 66.05, 68.33, 70.07, 108.55, 110.77, 114.31, 120.31, 120.36, 120.47, 121.47, 121.94, 122.13, 124.64, 127.05, 127.21, 128.09, 128.18, 128.48, 129.79, 131.82, 132.26, 136.13, 137.69, 142.13, 142.70, 150.84, 151.27, 153.42, 154.76, 161.31, 163.54, 164.29, 164.82, 173.55; Calcd. for $C_{65}H_{74}F_2O_{10}$: C 74.12, H 7.08 %; Found: C 74.37, H 7.36 %.

2.4.9 Compound IFc–Bz14

^{1}H NMR (δ ppm, CDCl$_3$): 0.87 (t, 3H, CH$_3$, J=6.4 Hz); 1.25–1.34 (m, 30H, CH$_2$); 1.44–1.49 (m, 4H, CH$_2$); 1.61–1.65 (m, 2H, CH$_2$); 1.81–1.89 (m, 4H, CH$_2$); 2.34 (t, 2H, OOCCH_2, J=7.6 Hz); 4.10 (t, 2H, OCH$_2$, J=6.6 Hz); 4.13 (t, 2H, OCH$_2$, J=6.4 Hz); 5.10 (s, 2H, Ar-H); 6.82 (m, 1H, Ar-H); 7.02 (t, 1H, Ar-H, J=8.4 Hz); 7.20–7.22 (m, 1H, Ar-H); 7.27 (dd, 2H, Ar-H, J_1=8.4 Hz, J_2=4.4 Hz); 7.30–7.35 (m, 5H, Ar-H); 7.38 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.8 Hz); 7.43 (bs, 1H, Ar-H); 7.49 (d, 2H, Ar-H, J=5.2 Hz); 7.64 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.8 Hz); 7.84 (m, 1H, Ar-H); 7.90 (dd, 1H, Ar-H, J_1=11.6 Hz, J_2=2.0 Hz); 7.94–7.97 (m, 1H, Ar-H); 8.29 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.4 Hz); ^{13}C NMR (δ ppm, CDCl$_3$): 14.20, 22.78, 25.04, 25.89, 25.95, 29.03, 29.09, 29.19, 29.27, 29.36, 29.43, 29.50, 29.58, 29.64, 29.73, 32.00, 34.41, 66.07, 69.52, 70.11, 108.54, 109.98, 110.76, 113.48, 117.68, 117.88, 120.35, 120.51, 121.91, 121.97, 124.62, 127.00, 127.16, 127.27, 128.05, 128.20, 128.44, 129.77, 131.77, 136.09, 137.86, 141.99, 150.56, 151.22, 151.83, 153.07, 154.70, 161.25, 163.87, 164.21, 169.12, 173.46; Calcd. for $C_{65}H_{73}$ F_3O_{10}: C 72.87, H 6.87 %; Found: C 72.61, H 6.88 %.

2.5 Analytical data of compounds of series II

2.5.1 Compound II-Bz12

^{1}H NMR (δ ppm, CDCl$_3$): 0.87 (t, 3H, CH$_2$, J=6.8 Hz); 1.26-1.38 (m, 16H, CH$_2$; 1.43-1.48 (m, 2H, CH$_2$); 1.79-1.84 (m, 2H, CH$_2$); 1.85-1.87 (m, 4H, CH$_2$); 2.44-2.46 (m, 2H, OOCCH$_2$); 4.04 (t, 4H, OCH$_2$, J=6.5 Hz); 5.11 (s, 2H, OCH$_2$Ph); 6.94 (d, 2H, Ar-H, J = 8.9 Hz); 6.97 (d, 2H, Ar-H, J=9.2 Hz); 7.19-7.21 (m, 1H, Ar-H), 7.27 (d, 2H, Ar-H, J=8.6 Hz); 7.32-7.35 (m, 5H, Ar-H); 7.37 (d, 2H, Ar-H, J=8.8 Hz); 7.44 (bs, 1H, Ar-H), 7.49 (d, 2H, Ar-H, J=5.1 Hz); 7.63 (d, 2H, Ar-H, J=8.8 Hz); 8.14 (dd, 4H, Ar-H, J_1=8.9 Hz, J_2=1.8 Hz); 8.29 (d, 2H, Ar-H, J=8.8 Hz).

2.5.2 Compound II-H12

^{1}H-NMR (δ ppm, CDCl$_3$): 0.87 (t, 3H, CH$_3$, J=6.8 Hz); 1.26-1.35 (m, 16H, CH$_2$); 1.43-1.48 (m, 2H, CH$_2$); 1.78-1.87 (m, 6H, CH$_2$); 2.46 (t, 2H, OOCCH$_2$, J=6.9 Hz); 4.04 (t, 4H, OCH$_2$, J=6.6 Hz); 6.95 (d, 2H, Ar-H, J=9.0 Hz); 6.97 (d, 2H, Ar-H, J=9.0 Hz); 7.19-7.21 (m, 1H, Ar-H); 7.26 (d, 2H, Ar-H, J=8.6 Hz); 7.36 (t, 2H, Ar-H, J=8.8 Hz); 7.44 (bs, 1H, Ar-H); 7.48 (d, 2H, Ar-H, J=5.1 Hz); 7.62 (d, 2H, Ar-H, J=8.6 Hz); 8.14 (d, 4H, Ar-H, J=8.6 Hz); 8.28 (d, 2H, Ar-H, J=8.8 Hz).

2.5.3 Componud II-Pfp12

^{1}H-NMR (δ ppm, CDCl$_3$): 0.87 (t, 3H, CH$_3$, J=6.8 Hz); 1.26-1.37 (m, 16H, CH$_2$); 1.43-1.50 (m, 2H, CH$_2$); 1.78-1.85 (m, 2H, CH$_2$); 1.94-2.02 (m, 4H, CH$_2$); 2.78 (t, 2H, OOCCH$_2$, J=6.9 Hz); 4.04 (t, 2H, OCH$_2$, J=6.5 Hz); 4.11 (t, 2H, OCH$_2$, J=5.7 Hz); 6.98 (d, 4H, Ar-H, J=8.9 Hz); 7.19-7.22 (m, 1H, Ar-H); 7.28 (d, 2H, Ar-H, J=8.8 Hz); 7.37 (d, 2H, Ar-H, J=8.8 Hz); 7.44 (bs, 1H, Ar-H); 7.49 (d, 2H, Ar-H, J=5.1 Hz); 7.64 (d, 2H, Ar-H, J=8.6 Hz); 8.14 (d, 2H, Ar-H, J=8.8 Hz); 8.16 (d, 2H, Ar-H, J=8.8 Hz); 8.29 (d, 2H, Ar-H, J=8.6 Hz).

2.5.4 Compound II–Bz14

^{1}H NMR (δ ppm, CDCl$_3$): 0.87 (t, 3H, CH$_3$, J=7.0 Hz); 1.26–1.49 (m, 20H, CH$_2$); 1.78–1.85 (m, 2H, CH$_2$); 1.86–1.88 (m, 4H, CH$_2$); 2.46 (t, 2H, OOCCH_2, J=7.2 Hz); 4.04 (t, 2H, OCH$_2$, J=6.4 Hz); 4.05 (t, 2H, OCH$_2$, J=6.6 Hz); 5.12 (s, 2H, OCH$_2$Ph); 6.95 (dd, 2H, Ar-H, J_1=9.2 Hz, J_2=4.8 Hz); 6.97 (dd, 2H, Ar-H, J_1=9.2 Hz, J_2=4.8 Hz); 7.20–7.22 (m, 1H, Ar-H); 7.28 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.8 Hz); 7.30–7.35 (m, 5H, Ar-H); 7.37 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.4 Hz); 7.44 (t, 1H, Ar-H, J=1.2 Hz); 7.49 (d, 2H, Ar-H, J=4.8 Hz); 7.64 (dd, 2H, Ar-H, J_1=8.4 Hz, J_2=4.8 Hz); 8.14

(dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.6 Hz); 8.14 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.6 Hz); 8.29 (dd, 2H, Ar-H, J_1=8.4 Hz, J_2=4.6 Hz); ^{13}C NMR (δ ppm, $CDCl_3$): 14.16, 21.63, 22.73, 26.03, 28.55, 29.14, 29.40, 29.59, 29.63, 29.69, 29.71, 29.73, 31.96, 33.90, 66.27, 67.70, 68.42, 114.27, 114.40, 120.38, 120.50, 120.96, 121.65, 122.06, 122.12, 124.63, 126.84, 128.17, 128.53, 129.78, 131.77, 132.27, 132.36, 137.72, 142.10, 150.79, 151.28, 155.37, 163.26, 163.76, 164.22, 164.38, 164.77, 173.00.

2.5.5 Compound II–H14

^{1}H NMR (δ ppm, $CDCl_3$): 0.89 (t, 3H, CH_3, J=7.0 Hz); 1.26–1.38 (m, 20H, CH_2); 1.43–1.49 (m, 2H, CH_2); 1.78–1.91 (m, 6H, CH_2); 2.46 (t, 2H, $OOCCH_2$, J=6.8 Hz); 4.04 (t, 2H, OCH_2, J=6.6 Hz); 4.07 (t, 2H, OCH_2, J=6.5 Hz); 6.96 (dd, 2H, Ar-H, J_1=9.0 Hz, J_2=5.0 Hz); 6.97 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.4 Hz); 7.19–7.22 (m, 1H, Ar-H); 7.28 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.4 Hz); 7.37 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.4 Hz); 7.43 (bs, 1H, Ar-H); 7.49 (d, 2H, Ar-H, J=5.2 Hz); 7.63 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.4 Hz); 8.14 (dd, 2H, Ar-H, J_1 =8.8 Hz, J_2=4.4 Hz); 8.15 (dd, 2H, Ar-H, J_1 =8.8 Hz, J_2=4.4 Hz); 8.29 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.4 Hz); ^{13}C NMR (δ ppm, $CDCl_3$): 14.14, 21.41, 22.73, 26.03, 28.49, 29.14, 29.39, 29.59, 29.62 29.68, 29.71, 29.72, 31.96, 33.37, 67.68, 68.43, 114.27, 114.41, 120.36, 120.49, 120.98, 121.73, 122.04, 122.09, 124.60, 126.85, 128.17, 129.76, 131.75, 132.26, 132.35, 137.72, 142.09, 150.79, 151.29, 155.37, 163.21, 163.76, 164.20, 164.36, 164.74, 177.92; Calcd. for $C_{52}H_{58}O_{10}$: C 74.09, H 6.93 %; Found: C 74.14, H 6.90 %.

2.5.6 Compound II–Pfp14

^{1}H NMR (δ ppm, $CDCl_3$): 0.87 (t, 3H, CH_3, J=7.0 Hz); 1.25–1.53 (m, 22H, CH_2);1.82 (quintet, 2H, CH_2, J=6.4 Hz); 1.95–2.04 (m, 4H, CH_2); 2.78 (t, 2H, $OOCCH_2$, J=7.8 Hz); 4.04 (t, 2H, OCH_2, J=6.6 Hz); 4.11 (t, 2H, OCH_2, J=6.4 Hz); 6.97 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.6 Hz); 6.98 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.6 Hz); 7.18–7.22 (m, 1H, Ar-H); 7.28 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.8 Hz); 7.37 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.4 Hz); 7.44 (bs, 1H, Ar-H); 7.49 (d, 2H, Ar-H, J=4.8 Hz); 7.64 (dd, 2H, Ar-H, J_1=8.4 Hz, J_2=4.8 Hz); 8.14 (dd, 2H, Ar-H, J_1=9.2 Hz, J_2=4.6 Hz); 8.16 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.8 Hz)); 8.29 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.8 Hz); ^{13}C NMR (δ ppm, $CDCl_3$): 14.14, 21.58, 22.72, 26.01, 28.28, 29.13, 29.38, 29.58, 29.61, 29.68, 29.70, 29.71, 31.95, 32.96, 67.48, 68.43, 114.29, 114.43, 120.40, 120.54, 120.99, 121.87, 122.09, 122.13, 124.65, 126.87, 128.23, 129.82, 131.80, 132.34, 132.39, 137.78, 142.13, 151.32, 155.42, 163.17, 163.80, 164.27, 164.42, 164.78, 169.09.

2.6 Analytical data of compounds of compound III

^{1}H NMR (δ ppm, $CDCl_3$): 0.87 (t, 3H, CH_3, J=6.8 Hz); 1.12–1.30 (m, 34H, CH_2); 1.44–1.49 (m, 4H, CH_2); 1.61–1.63 (m, 2H, CH_2); 1.77–1.85 (m, 4H, CH_2); 2.21 (t, 2H, $OOCCH_2$, J=7.4 Hz); 2.65 (bs, 2H, OH); 3.43–3.49 (m, 2H, NCH_2); 3.50–3.58 (m, 2H, CH_2OH); 3.74–3.75 (m, 1 H, NCH_2CH); 4.03 (t, 2H, OCH_2, J=6.5 Hz); 4.04 (t, 2H, OCH_2, J=6.6 Hz); 4.05 (t, 2H, OCH_2, J=6.4 Hz); 6.96 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.4 Hz); 6.97 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.4 Hz); 7.20–7.22 (m, 1H, Ar-H); 7.28 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.8 Hz); 7.37 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.4 Hz); 7.44 (bs, 1H, Ar-H); 7.49 (d, 2H, Ar-H, J=4.4 Hz); 7.63 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.4 Hz); 8.14 (dd, 4H, Ar-H, J_1=8.8 Hz, J_2=4.8 Hz); 8.28 (dd, 2H, Ar-H, J_1=8.8 Hz, J_2=4.4 Hz); ^{13}C NMR (δ ppm, $CDCl_3$): 14.08, 22.71, 25.75, 26.05, 29.16, 29.19, 29.30, 29.32, 29.38, 29.48, 29.59, 29.62, 29.69, 29.71, 29.73, 31.97, 36.58, 42.49, 63.81, 68.43, 68.52, 71.31, 114.43, 114.52, 120.39, 120.49, 121.16, 121.68, 122.04, 122.11, 124.60, 126.97, 128.18, 129.76, 131.76, 132.27, 132.37, 137.77, 142.17, 150.96, 151.44, 155.50, 163.60, 163.86, 164.19, 164.36, 164.80, 172.7; Calcd. for $C_{63}H_{81}N_1O_{11}$: C 73.58, H 7.94, N 1.36 %; Found: C 73.60, H 7.98, N 1.31 %.

2.7 Analytical data of dendrimers 1-12 and 2-12

2.7.1 First generation dendrimer 1-12

Synthesised according to the procedure for compound **1-16** (main text) from DAB-1 dendrimer (40 mg, 0.12 mmol), **II-Pfp12** (0.5 g, 0.51 mmol) and TEA (5ml). Purification by repeated crystallisation from MeOH/EtOH/CHCl$_3$ (10:9:2). Yield: 0.32 g (72 %); slightly yellow solid; ^{1}H-NMR (δ ppm, CDCl$_3$): 0.87 (t, 12H, CH$_3$, J=6.8 Hz); 1.26-1.37 (m, 76H, CH$_2$); 1.43-1.48 (m, 12H, CH$_2$); 1.64-1.73 (m, 8H, CH$_2$); 1.79-1.83 (m, 26H, CH$_2$); 2.25 (bs, 8H, NHCOC*H*$_2$); 2.36-2.49 (m, 12H, NCH$_2$); 3.28 (d, 8H, NHC*H*$_2$, J=5.9 Hz); 4.03 (t, 16H, OCH$_2$, J=6.5 Hz); 6.59 (bs, 4H, NH); 6.92 (d, 8H, Ar-H, J=8.9 Hz); 6.96 (d, 8H, Ar-H, J=8.9 Hz); 7.18-7.20 (m, 4H, Ar-H); 7.24 (d, 8H, Ar-H, J=8.6); 7.35 (d, 8H, Ar-H, J=8.8); 7.42 (bs, 4H, Ar-H); 7.46 (d, 8H, Ar-H, J=5.3 Hz); 7.61 (d, 8H, Ar-H, J=8.8 Hz); 8.11 (d, 8H, Ar-H, J=8.8 Hz), 8.14 (d, 8H, Ar-H, J=8.9 Hz); 8.27 (d, 8H, Ar-H, J=8.8 Hz); ^{13}C NMR (δ ppm, CDCl$_3$): 14.12, 22.38, 22.71, 26.02, 27.02, 28.75, 29.13, 29.36, 29.58, 29.61, 29.66, 29.67, 31.94, 36.15, 38.20, 67.90, 68.43, 114.08, 114.43, 120.36, 121.00, 121.72, 122.07, 122.10, 124.61, 126.86, 128.18, 129.80, 131.77, 132.29, 132.37, 137.73, 142.05, 150.79, 151.32, 155.40, 163.29, 163.79, 164.24, 164.39, 164.75, 172.74; ESI-MS: molecular weight calc. for $C_{216}H_{248}N_6O_{36}$: m/z: 1753.2 $[M+2H]^{2+}$; found: m/z: 1752.9 $[M+2H]^{2+}$; Calcd. for $C_{216}H_{248}N_6O_{36}$: C 74.03, H 7.13, N 2.40 %; Found: C 74.17, H 7.06, N 2.43 %.

2.7.2 Second generation dendrimer 2-12

Synthesised according to the procedure for compound **1-16** (main text) from DAB-2 dendrimer (47 mg, 0.06 mmol), **II-Pfp12** (0.5 g, 0.51 mmol) and TEA (5ml). Purification by repeated crystallisation from MeOH/EtOH/CHCl$_3$ (3:9:1). Yield: 0.23 g (54 %); colourless solid; ^{1}H-NMR (δ ppm, CDCl$_3$): 0.87 (t, 24H, CH$_3$, J=6.8 Hz); 1.25-1.35 (m, 128H, CH$_2$); 1.42-1.48 (m, 24H, CH$_2$); 1.61 (bs, 16H, CH$_2$); 1.77-1.82 (m, 52H, CH$_2$); 2.26 (bs, 16H, C*H*$_2$CONH); 2.39 (bs, 36H, NH$_2$); 3.26 (d, 16H, NHC*H*$_2$, J=5.6 Hz); 4.02 (t, 32H, OCH$_2$, J=6.5 Hz); 6.90 (d, 16H, Ar-H, J=8.8 Hz); 6.96 (d, 24H, Ar-H, NHCO, J=8.8 Hz); 7.16-7.19 (m, 8H, Ar-H); 7.22 (d, 16H, Ar-H, J=8.6 Hz); 7.34 (d, 16H, Ar-H, J=8.6 Hz); 7.41 (bs, 8H, Ar-H); 7.44 (d, 16H, Ar-H, J=5.1 Hz); 7.59 (d, 16H, Ar-H, J=8.6 Hz); 8.09 (d, 16H, Ar-H, J=8.9 Hz); 8.12 (d, 16H, Ar-H, J=8.9 Hz); 8.26 (d, 16H, Ar-H, J=8.8 Hz); ^{13}C NMR (δ ppm, CDCl$_3$): 14.12, 22.40, 22.71, 26.01, 27.09, 28.76, 29.13, 29.36, 29.57, 29.60, 29.65, 29.67, 31.93, 36.06, 37.95, 67.88, 68.42, 114.28, 114.42, 120.33, 120.98, 121.68, 122.06, 122.10, 124.59, 126.83, 128.15, 129.80, 131.76, 132.27, 132.37, 137.69, 141.99, 150.76, 151.31, 155.39, 163.29, 163.78, 164.23, 164.39, 164.74, 172.93; ESI-MS: molecular weight calc. for $C_{440}H_{512}N_{14}O_{72}$: m/z: 1788.3 $[M+4H]^{4+}$; found: m/z:1788.7 $[M+4H]^{4+}$; Calcd. for $C_{440}H_{512}N_{14}O_{72}$: C 73.92, H 7.22, N 2.74 %; Found: C 73.88, H 7.27, N 2.81 %.

Reference

1 V. Kopsky and D. B. Litvin, *International Tables of Crystallography, Vol. E, Subperiodic groups*, Kluwer Academic Pub., Dordrecht, **2002**.