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Transformation from rod-like to hockey-stick and bent-shaped molecule in 3,4'-disubstituted azobenzene-based mesogens

Martin Horčic,[a] Václav Kozmík,[a] Jiří Svoboda,*[a] Vladimíra Novotná*[b] and Damian Pociecha[c]

[a] *Department of Organic Chemistry, Institute of Chemical Technology, CZ-166 28 Prague 6, Czech Republic. e-mail: Jiri.Svoboda@vscht.cz*

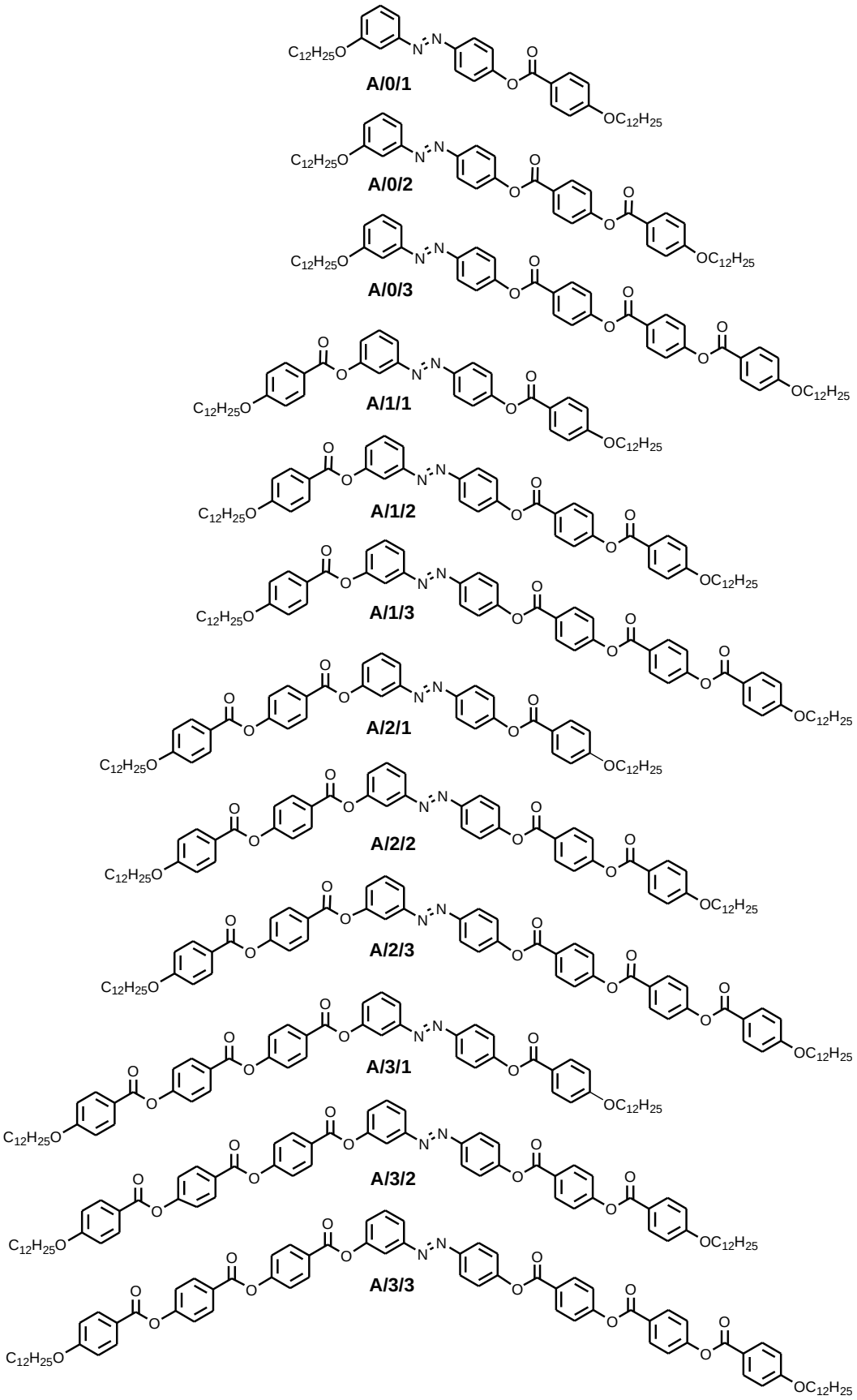
[b] *Institute of Physics, Academy of Science of the Czech Republic, Na Slovance 2, CZ-182 21 Prague 8, Czech Republic, e-mail: novotna@fzu.cz*

[c] *Laboratory of Dielectrics and Magnetics, Chemistry Department, Warsaw University, Al. Zwirki i Wigury 101, 02-089 Warsaw, Poland*

1. Synthesis

1.1 General

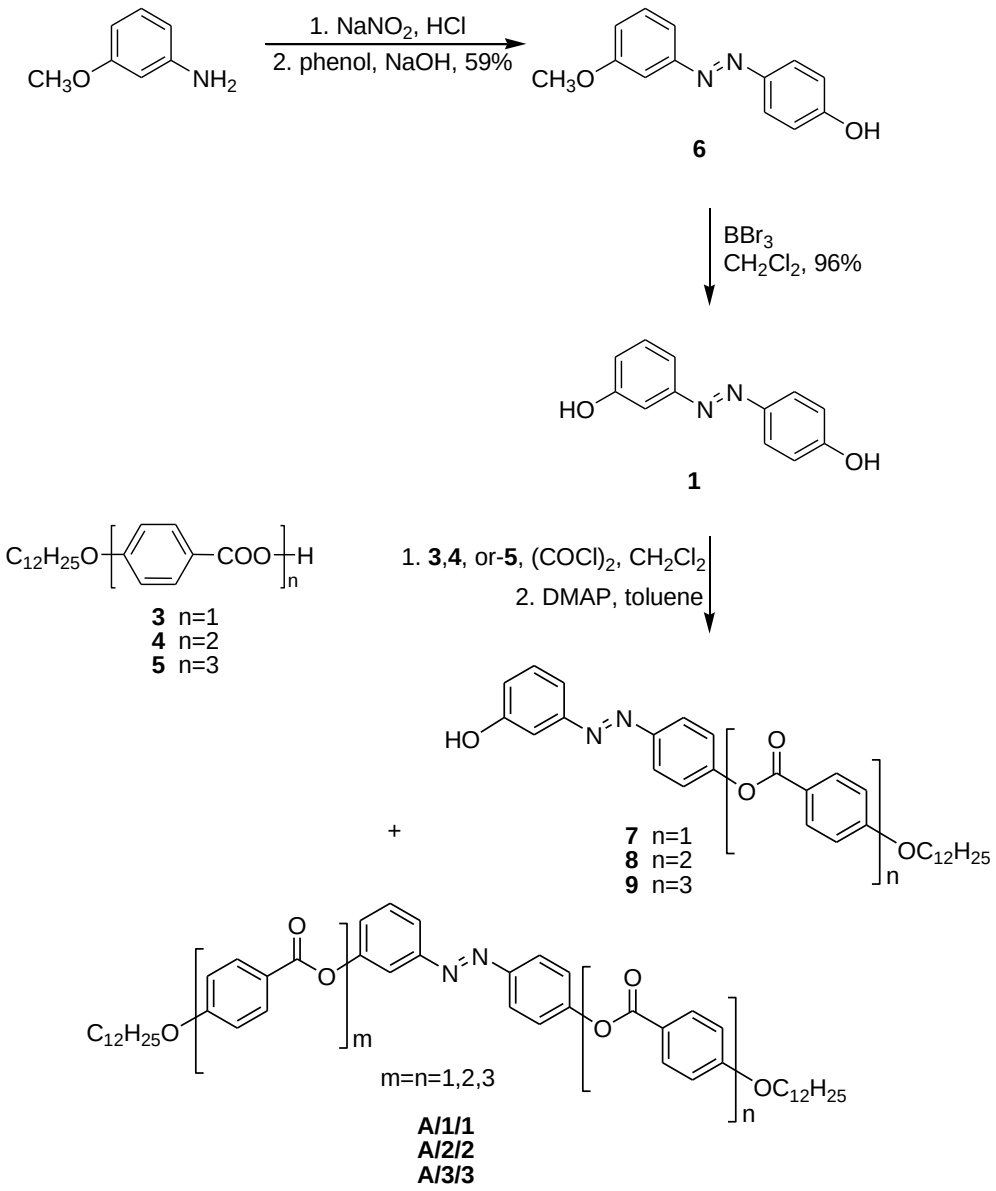
Structures of intermediates and final products were confirmed by ^{1}H NMR spectroscopy (Varian Gemini 300 HC instrument), deuteriochloroform and acetone-d_6, resp., were used as solvent and signals of the solvent served as internal standard, *J* values are given in Hz. Elemental analyses were carried out on a Perkin-Elmer 2400 instrument. Purity of all final compounds was confirmed by HPLC analysis (Tessek C18 25x4.5 RP column) and found >99.8%. Column chromatography was carried out using Merck Kieselgel 60 (60-100 μm). The experimental part summarizes synthetic procedures for the preparation of intermediates **1**, **2**, **6-14** and target compounds of the series **A/m/n**. The molecular structure of all the synthesised compounds is shown in Scheme S1.



Scheme S1 Structure of the studied materials **A/m/n**

1.2 Synthesis of the parent central unit 1 and materials A/m/n (m=n=1,2,3)

The central unit **1** was prepared by a standard azocoupling reaction of *m*-anisidine with phenol and subsequent deprotection of the methoxy group in the formed azo dye **6** with boron tribromide (Scheme S2). Compounds **A/m/n** with identical lengthening arms (i.e. m=n=1,2,3) were obtained by acylation of **1** with acid chlorides (freshly prepared from acids **3-5** and oxalyl chloride) in the presence of dimethylaminopyridine (DMAP) in toluene. In addition, products of monoacylation **7** and **8**, resp., were also isolated in analytical purity and used as important intermediates in the synthesis of non-symmetrical intermediates. This was not for intermediate **9**, synthesis of which is described in Scheme S3 (see below).



Scheme S2 Synthesis of the central unit **1** and compounds **A/m/n** (m=n=1,2,3)

***(E)-4-((3-Methoxyphenyl)diazenyl)phenol* (6)**

To a mixture of *m*-anisidine (15.0 g; 122 mmol) in 35% aq. hydrochloric acid (33 mL) and water (60 mL), a solution of sodium nitrite (8.63 g; 125 mmol) in water (35 mL) was added drop wise under stirring at 0-5 °C. After 15 min, the solution of the diazonium salt was neutralized with an aq. solution of potassium carbonate to pH~7. Phenol (11.5 g; 122 mmol) in 5% aq. NaOH (4.88 g; 122 mmol) was added drop wise, the formed thick slurry was diluted with acetone (15 mL), after stirring for 15 min the mixture was acidified with 6 M hydrochloric acid to pH~3 and extracted with *tert*-butyl methyl ether (4 × 140 mL). The combined organic solution was washed with brine (60 mL) and dried with anhydrous magnesium sulfate. The solvent was removed and the crude product purified by column chromatography (toluene/*tert*-butyl methyl ether 12/1). The product was crystallized from toluene to yield 16.5 g (59%) of **6**, m.p. 120-122 °C. ^{1}H NMR ($CDCl_3$): 3.89 (s, 3 H, CH_3O), 5.20 (s, 1 H, OH), 6.94 (d, 2 H, J = 8.8), 7.01 (dd, 1 H, ^{3}J = 8.2, ^{4}J = 2.5), 7.38-7.43 (m, 2 H), 7.51 (d, 1 H, J = 7.7), 7.88 (d, 2 H, J = 9.1).

***(E)-3,4'-(Diazene-1,2-diyl)diphenol* (1)**

Boron tribromide (26 mL; 280 mmol) was added drop wise to a solution of **6** (16.0 g; 70 mmol) in dry dichloromethane (250 mL) at -78 °C for 4 h in an argon atmosphere. The mixture was poured on crushed ice and water (500 mL) and the solid was filtered off. The filtrate was separated and the aq. layer was extracted with chloroform (4 × 150 mL). The organic solution was dried with anhydrous magnesium sulfate and the solvent evaporated. The combined solid was purified by column chormatography (toluene/*tert*-butyl methyl ether 4/1) and crystallized from toluene. Yield 14.4 g (96%) of **1**, m.p. 210-212 °C. ^{1}H NMR (acetone-d_6): 6.97 (m, 1 H), 7.01 (d, 2 H, J = 9.1), 7.34-7.44 (m, 3 H), 7.84 (d, 2 H, J = 8.8), 8.65 (s, 1 H, OH), 9,10 (s, 1 H, OH). Elemental analysis: for $C_{12}H_{10}N_2O_2$ (214.23) calculated: 67.28% C, 4.71% H, 13.08% N; found: 67.11%. 4.70% H, 12.77% N.

General procedure for acylation of diphenol 1

A mixture of acid **3-5** (2.5 mmol), oxalyl chloride (10 mmol) and dichloromethane (50 mL) was stirred at room temperature for 12 h and subsequently heated to reflux for 5 h. After cooling the solution was evaporated, the residue was diluted with dry toluene (15 mL) and re-evaporated. The formed acid chloride was dissolved in toluene (20 mL), and added to a solution of diphenol **1** (0.50 g; 2.33 mmol) and DMAP (280 mg; 2.33 mmol) in dry toluene

(70 mL) at 70 °C and then refluxed for 2.5 h. After cooling to room temperature, water (20 mL) was added, the mixture stirred for 10 min and separated. The aqueous layer was extracted with chloroform (3 × 40 mL), the combined organic solution was dried with anhydrous magnesium sulfate and evaporated. The mixture of products was separated by column chromatography (toluene/*tert*-butyl methyl ether/triethylamine 20/1/0.03). The fractions containing the products **A/m/n** were combined, evaporated and recrystallized from cyclohexane. Compound **7** was obtained from the combined fractions by a triple crystallization from toluene.

(E)-4-((3-Hydroxyphenyl)diazenyl)phenyl 4-(dodecyloxy)benzoate **(7**). Yield 8%, m.p. 135 °C. ^{1}H NMR ($CDCl_3$): 0.88 (t, 3 H, *J* = 6.7, CH_3), 1.27-1.48 (m, 18 H, $(CH_2)_9$), 1.83 (m, 2 H, $\underline{CH_2}CH_2O$), 4.05 (t, 2 H, *J* = 6.6, CH_2O), 5.15 (s, 1 H, OH), 6.96-7.00 (m, 3 H), 7.35-7.42 (m, 4 H), 7.54 (d, 1 H, *J* = 7.9), 7.98 (d, 2 H, *J* = 8.8), 8.16 (d, 2 H, *J* = 8.8). Elemental analysis: for $C_{31}H_{38}N_2O_4$ (502.66) calculated: 74.08% C, 7.62% H, 5.57% N; found: 73.96% C, 7.55% H, 5.48% N.

(E)-3-((4-(4-(Dodecyloxy)benzoyloxy)phenyl)diazenyl)phenyl 4-(dodecyloxy)benzoate **(A/1/1)**. Yield 29%. ^{1}H NMR ($CDCl_3$): 0.88 (t, 6 H, *J* = 6.6, 2 × CH_3), 1.27-1.50 (m, 36 H, 2 × $(CH_2)_9$), 1.83 (m, 4 H, 2 × $\underline{CH_2}CH_2O$), 4.05 (t, 4 H, *J* = 6.6, 2 × CH_2O), 6.98 (d, 4 H, *J* = 8.8), 7.32-7.38 (m, 3 H), 7.58 (dd, 1 H, *J* = 7.9), 7.78 (s, 1 H, *J* = 2.1), 7.87 (d, 1 H, *J* = 7.9), 8.00 (d, 2 H, *J* = 8.8), 8.16 (d, 2 H, *J* = 8.5), 8.17 (d, 2 H, *J* = 8.8). Elemental analysis: for $C_{50}H_{66}N_2O_6$ (791.09) calculated: 75.91% C, 8.41% H, 3.54% N; found: 75.80% C, 8.30% H, 3.48% N.

By the same way, compounds **8** and **A/2/2**, **A/3/3**, were obtained, see Scheme S2.

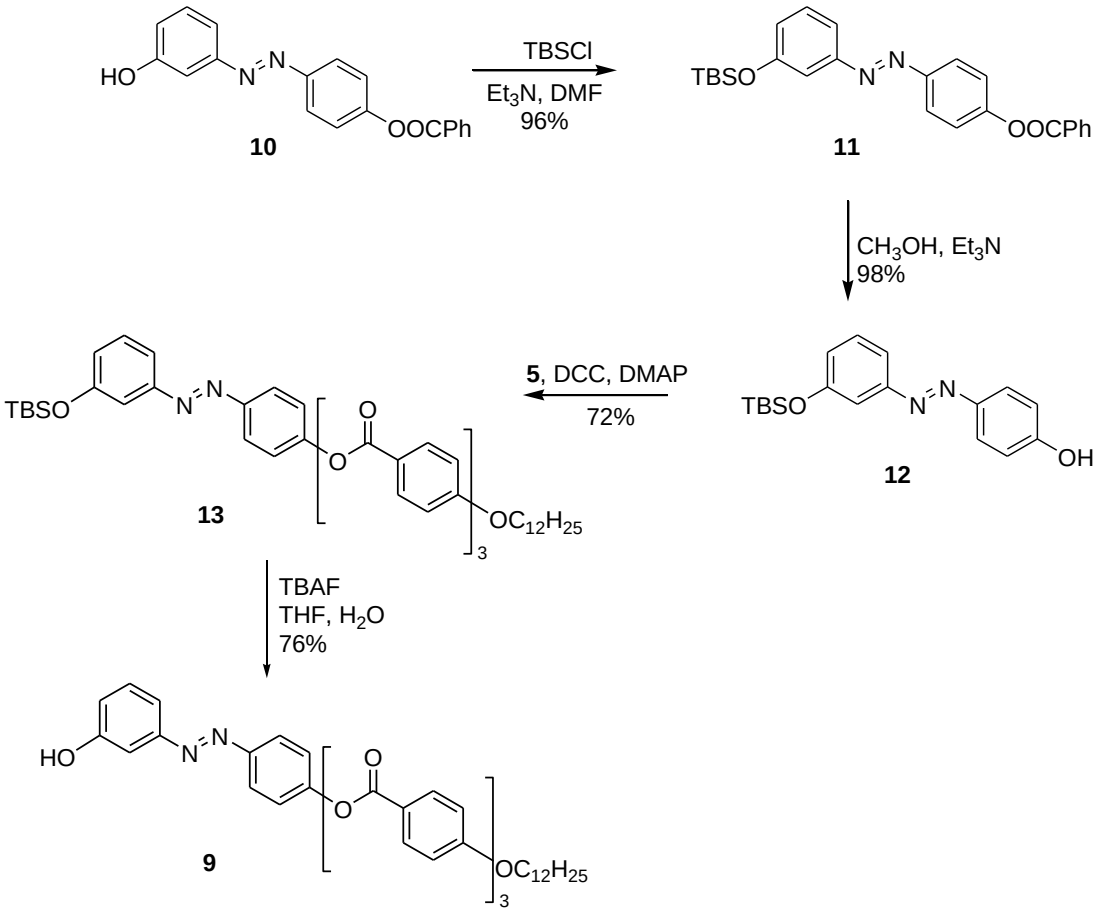
(E)-4-((4-((3-Hydroxyphenyl)diazenyl)phenoxy)carbonyl)phenyl 4-(dodecyloxy)benzoate **(8)**. Yield 15%, m.p. 152-153 °C (toluene). ^{1}H NMR ($CDCl_3$): 0.88 (t, 3 H, *J* = 6.7, CH_3), 1.27-1.48 (m, 18 H, $(CH_2)_9$), 1.83 (m, 2 H, $\underline{CH_2}CH_2O$), 4.06 (t, 2 H, *J* = 6.6, CH_2O), 5.03 (s, 1 H, OH), 6.99 (m, 3 H), 7.38-7.44 (m, 6 H), 7.56 (d, 1 H, *J* = 8.2), 8.01 (d, 2 H, *J* = 8.8), 8.16 (d, 2 H, *J* = 9.1), 8.30 (d, 2 H, *J* = 8.8). Elemental analysis: for $C_{38}H_{42}N_2O_6$ (622.77) calculated: 73.29% C, 6.80% H, 4.50% N; found: 73.11% C, 6.67% H, 4.41% N.

(E)-4-((3-((4-(4-(4-(Dodecyloxy)benzoyloxy)benzoyloxy)phenyl)diazenyl)phenoxy)-carbonyl)phenyl 4-(dodecyloxy)benzoate **(A/2/2)**. Yield 19%. ^{1}H NMR ($CDCl_3$): 0.88 (t, 6 H, J = 6.7, 2 × CH_3), 1.27-1.48 (m, 36 H, 2 × $(CH_2)_9$), 1.83 (m, 4 H, 2 × $\underline{CH_2}CH_2O$), 4,06 (t, 4 H, J = 6.6, 2 × CH_2O), 6.99 (d, 4 H, J = 8.8), 7.36-7.42 (m, 5 H), 7.61 (dd, 1 H, J = 7.9), 7.81 (d, 1 H, ^{4}J = 2.1), 7.91 (d, 1 H, J = 8.5), 8.03 (d, 2 H, J = 8.8), 8.16 (d, 4 H, J = 8.5), 8.30 (d, 2 H, J = 8.8), 8.32 (d, 2 H, J = 8.8). Elemental analysis: for $C_{64}H_{74}N_2O_{10}$ (1031.31) calculated: 74.54% C, 7.23% H, 2.72% N; found: 74.50% C, 7.21% H, 2.59% N.

(E)-4-((4-((3-((4-(4-(4-(4-(Dodecyloxy)benzoyloxy)benzoyloxy)benzoyloxy)phenyl)diazenyl)-phenoxy)carbonyl)phenoxy)carbonyl)phenyl 4-(dodecyloxy)benzoate **(A/3/3)**. The first column chromatography was performed in a mixture of toluene/*tert*-butyl methyl ether/triethylamine 20/1/0.03 and the product was rechromatographed in the chloroform/methanol/triethylamine 99/1/0.03 solvent system, yield 7%. ^{1}H NMR ($CDCl_3$): 0.88 (t, 6 H, J = 6.6, 2 × CH_3), 1.27-1.48 (m, 36 H, 2 × $(CH_2)_9$), 1.83 (m, 4 H, 2 × $\underline{CH_2}CH_2O$), 4.06 (t, 4 H, J = 6.6, 2 × CH_2O), 6.99 (d, 4 H, J = 9.1), 7.37-7.43 (m, 11 H), 7.62 (dd, 1 H, ^{3}J = 8.2, ^{3}J = 7.9), 7.82 (s, 1 H), 7.91 (d, 1 H, J = 8.8), 8.04 (d, 2 H, J = 9.1), 8.16 (d, 4 H, J = 8.8), 8.30-8.35 (m, 8 H). Elemental analysis: for $C_{78}H_{82}N_2O_{14}$ (1271.53) calculated: 73.68% C, 6.50% H, 2.20% N; found: 73.59% C, 6.49% H, 2.12% N.

1.3 Synthesis of the intermediate 9

Due to different reactivity of the hydroxylic groups of **1**, we succeeded in a selective protection of the 4'-hydroxylic group of **1** by benzoylation (Scheme S3). Subsequently the second hydroxylic group of benzoate **10** was protected by silylation with *tert*-butyldimethylsilyl chloride (TBSCl) and the protectiong benzoate group of **11** was removed by transesterification with methanol. Finally, acylation of phenol **12** with acid **5** in the presence of dicyclohexycarbodiimide (DCC) and DMAP left the protected derivative **13**, the TBS group of which was removed with tetrabutylammonium fluoride (TBAF) in wet THF to yield the target intermediate **9**.



Scheme S3 Synthesis of intermediate **9**

***(E)-4-((3-Hydroxyphenyl)diazenyl)phenyl benzoate* (10).** The compound was obtained by a direct acylation of **1** with benzoyl chloride by the procedure shown above. Yield 41%, m.p. 181 °C. ^{1}H NMR ($CDCl_3$): 5.03 (s, 1 H, OH), 6.98 (d, 1 H, *J* = 7.9), 7.37-7.43 (m, 4 H), 7.54 (m, 3 H), 7.67 (m, 1 H), 8.00 (d, 2 H, *J* = 9.1), 8.24 (d, 2 H, *J* = 8.5). Elemental analysis: for $C_{19}H_{14}N_2O_3$ (318.34) calculated: 71.69% C, 4.43% H, 8.80% N; found: 71.58% C, 4.46% H, 8.70% N.

***(E)-4-((3-(tert-Butyldimethylsilyloxy)phenyl)diazenyl)phenyl benzoate* (11)**

A solution of TBSCl (0.19 g; 1.26 mmol) in dry DMF (5 mL) was added drop wise to a mixture of **10** (0.20 g; 0.63 mmol), triethylamine (0.13 mL; 0.95 mmol) and dry DMF (12 mL) at room temperature in an argon atmosphere. The mixture was stirred at room temperature for 21 h, diluted with water (35 mL), the deposited solid was filtered and washed with water (2 × 15 mL). The solid was dissolved in dichloromethane (35 mL), the solution was washed with brine (15 mL) and dried with anhydrous magnesium sulfate. After removing the solvent, the crude product was purified by column chromatography (toluene) to yield 262

mg (96%) of **11**, m.p. 110-111 °C. ^{1}H NMR ($CDCl_3$): 0.26 (s, 6 H, 2 × CH_3), 1.02 (s, 9 H, $(CH_3)_3C$), 6.97 (dd, 1 H, ^3J = 8.1, ^4J = 2.5), 7.35-7.40 (m, 4 H), 7.54 (m, 3 H), 7.67 (m, 1 H), 8.01 (d, 2 H, J = 8.8), 8.23 (d, 2 H, J = 7.0). Elemental analysis: for $C_{25}H_{28}N_2O_3Si$ (432.60) calculated: 69.41% C, 6.52% H, 6.48% N; found: 69.40% C, 6.49% H, 6.33% N.

***(E)-4-((3-(tert-Butyldimethylsilyloxy)phenyl)diazenyl)phenol* (12)**

To a solution of silyl derivative **11** (316 mg; 0.73 mmol) in dry methanol (70 mL), triethylamine (0.61 ml; 4.4 mmol) was added and the mixture was stirred at room temperature in an argon atmosphere for 26 h. After evaporation, the product was purified by column chromatography (toluene). 235 mg (98%) of **12** as a red oil. ^{1}H NMR ($CDCl_3$): 0.24 (s, 6 H, 2 × CH_3), 1.01 (s, 9 H, $(CH_3)_3C$), 5.18 (s, 1 H, OH), 6.94 (m, 3 H), 7.32-7.37 (m, 2 H), 7.50 (d, 1 H, J = 7.9), 7.87 (d, 2 H, J = 8.5). Elemental analysis: for $C_{18}H_{24}N_2O_2Si$ (328.49) calculated: 65.82% C, 7.36% H, 8.53% N; found: 65.70% C, 7.41% H, 8.47% N.

***(E)-4-((4-((4-((3-(tert-Butyldimethylsilyloxy)phenyl)diazenyl)phenoxy)carbonyl)phenoxy)-carbonyl)phenyl 4-(dodecyloxy)benzoate* (13)**

A mixture of silyl derivative **12** (557 mg; 1.7 mmol), acid **5** (1.28 g; 2.3 mmol), DCC (615 mg; 3 mmol) and DMAP (5 mg) in dry dichloromethane (220 mL) was stirred at room temperature for 3.5 h and the excess of DCC was decomposed by addition of water (15 mL). After 15 min, the layers were separated and the organic solution was washed subsequently with water (3 x 70 mL), brine (40 mL) and dried with anhydrous magnesium sulfate. After evaporation, the residue was chromatographed (toluene) to yield 1.043 g (72%) of **13**, m.p. 131-133 °C. ^{1}H NMR ($CDCl_3$): 0.26 (s, 6 H, 2 x CH_3), 0.88 (t, 3 H, J = 6.7, CH_3), 1.02 (s, 9 H, $(CH_3)_3C$), 1.27-1.49 (m, 18 H, $(CH_2)_9$), 1.83 (m, 2 H, $\underline{CH_2}CH_2O$), 4.06 (t, 2 H, J = 6.4, CH_2O), 6.98 (m, 3 H), 7.35-7.43 (m, 8 H), 7,56 (d, 1 H, J = 8.5), 8.02 (d, 2 H, J = 9.1), 8.16 (d, 2 H, J = 8.8), 8.30 (d, 2 H, J = 8.8), 8.33 (d, 2 H, J = 8.8). Elemental analysis: for $C_{51}H_{60}N_2O_8Si$ (857.14) calculated: 71.47% C, 7.06% H, 3.27% N; found: 71.44% C, 7.00% H, 3.20% N.

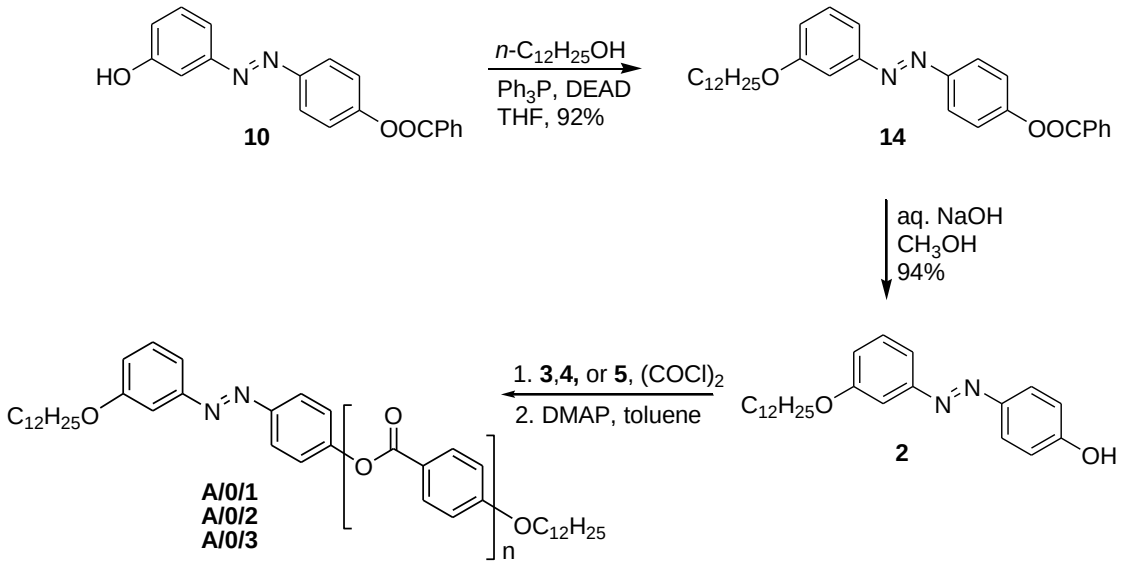
***(E)-4-((4-((4-((3-Hydroxyphenyl)diazenyl)phenoxy)carbonyl)phenoxy)carbonyl)phenyl 4-(dodecyloxy)benzoate* (9)**

A 1 M solution of TBAF (0.29 mL; 0.29 mmol) in THF was added to a solution of **13** (983 mg; 1.15 mmol) in THF (105 mL) and water (13 mL) and the mixture was stirred at room

temperature for 4 h. The mixture was diluted with water (80 mL) and THF was evaporated. The solid was filtered and the aqueous solution was extracted with chloroform (3 × 80 mL), the organic solution was combined with the solid and evaporated. The crude product was purified by multiple washing with hot chloroform and acetone to remove all the other impurities and crystallized from toluene. Yield 647 mg (76%) of **9**, m.p. 212-215 °C. ^{1}H NMR ($CDCl_3$, 50 °C): 0.90 (t, 3 H, *J* = 6.7, CH_3), 1.29-1.47 (m, 18 H, $(CH_2)_9$), 1.83 (m, 2 H, $\underline{CH_2}CH_2O$), 4.07 (t, 2 H, *J* = 6.4, CH_2O), 4.90 (s, 1 H, OH), 7.00 (m, 3 H), 7.41 (m, 8 H), 7.56 (d, 1 H, *J* = 7.3), 8.00 (d, 2 H, *J* = 8.5), 8.16 (d, 2 H, *J* = 8,2), 8.30 (m, 4 H). Elemental analysis: for $C_{45}H_{46}N_2O_8$ (742.88) calculated: 72.76% C, 6.24% H, 3.77% N; found: 72.63% C, 6.22% H, 3.68% N.

1.4 Synthesis of materials A/0/n (n=1,2,3)

To obtain materials **A/0/n (n=1,2,3)** with the dodecyl alkyl chain in the left arm only, we utilized the benzoate **10**. Because a base catalyzed alkylation yielded a complex mixture of products, the dodecyl chain was introduced in a Mitsunobu reaction with *n*-dodecanol, triphenylphosphine (Ph_3P) and diethyl azodicarboxylate (DEAD) (Scheme S4). In the next step, the benzoate **14** was hydrolyzed in a base catalyzed reaction and the phenol **2** was acylated with acids **3**-**5** as above to yield the compounds **A/0/n (n=1,2,3)**.



Scheme S4 Synthesis of materials **A/0/n**

***(E)-4-((3-(Dodecyloxy)phenyl)diazenyl)phenyl benzoate* (14)**

Diethyl azodicarboxylate (366 mg; 0.33 mL; 2.1 mmol) was added to a solution of **10** (450 mg; 1.41 mmol), *n*-dodecanol (527 mg; 2.83 mmol) and triphenylphosphine (551 mg; 2.1 mmol) in dry THF (55 mL) at 0 °C in an argon atmosphere. The mixture was stirred at 0 °C for 2 h and at room temperature for 15 h. The reaction was quenched by addition of water (0.1 mL) and after stirring for 0.5 h, the mixture was evaporated. The residue was dissolved in a cyclohexane/toluene mixture (3/1) and triphenylphosphine oxide was filtered off. The filtrate was evaporated, the product was purified by column chromatography (toluene) and crystallization from cyclohexane to give rise to 629 mg (92%) of benzoate **14**, m.p. 82-83 °C. ^{1}H NMR ($CDCl_3$): 0.88 (t, 3 H, J = 6.7, CH_3), 1.27-1.48 (m, 18 H, $(CH_2)_9$), 1.83 (m, 2 H, $\underline{CH_2}CH_2O$), 4.06 (t, 2 H, J = 6.6, CH_2O), 7.04 (dd, 1 H, ^3J = 8.1, ^4J = 2.6), 7.37-7.45 (m, 4 H), 7.54 (m, 3 H), 7.67 (m, 1 H), 8.01 (d, 2 H, J = 8.8), 8.23 (d, 2 H, J = 7.0). Elemental analysis: for $C_{31}H_{38}N_2O_3$ (486.66) calculated: 76.51% C, 7.87% H, 5.76% N; found: 76.44% C, 7.79% H, 5.48% N.

***(E)-4-((3-(Dodecyloxy)phenyl)diazenyl)phenol* (2)**

A solution of sodium hydroxide (196 mg; 5 mmol) in water (20 mL) was added to a solution of benzoate **14** (597 mg; 1.23 mmol) in a mixture of methanol (20 mL) and dioxane (60 mL). The mixture was stirred at room temperature for 1 h, acidified with 5% aq. hydrochloric acid to pH~7 and diluted with water (150 mL). The solid was filtered and dissolved in dichloromethane (100 mL), washed with brine (40 mL) and dried with anhydrous magnesium sulfate. After removing the solvent, the product was purified by column chromatography (toluene/*tert*-butyl methyl ether 20/1) and crystallised from toluene. Yield: 443 mg (94%) of phenol **2**, m.p. 84-85 °C. ^{1}H NMR ($CDCl_3$): 0.88 (t, 3 H, J = 6.7, CH_3), 1.27-1.48 (m, 18 H, $(CH_2)_9$), 1.82 (m, 2 H, $\underline{CH_2}CH_2O$), 4.04 (t, 2 H, J = 6.4, CH_2O), 6.94 (d, 2 H, J = 8.8), 7.00 (dd, 1 H, ^3J = 8.2,^4J = 2.5), 7.36-7.42 (m, 2 H), 7.49 (d, 1 H, J = 7.9), 7.87 (d, 2 H, J = 8.8). Elemental analysis: for $C_{24}H_{34}N_2O_2$ (382.55) calculated: 75.35% C, 8.96% H, 7.32% N; found: 75.26% C, 8.88% H, 7.19% N.

***(E)-4-((3-(Dodecyloxy)phenyl)diazenyl)phenyl 4-dodecyloxybenzoate* (A/0/1)**

Compound **A/0/1** was prepared as above by the general procedure of acylation. Reaction of **2** (180 mg; 0.47 mmol) with the acid chloride prepared freshly from acid **3** (259 mg; 0.85 mmol), DMAP (61 mg; 0.5 mmol) in dry toluene (20 mL) afforded after the standard work-up

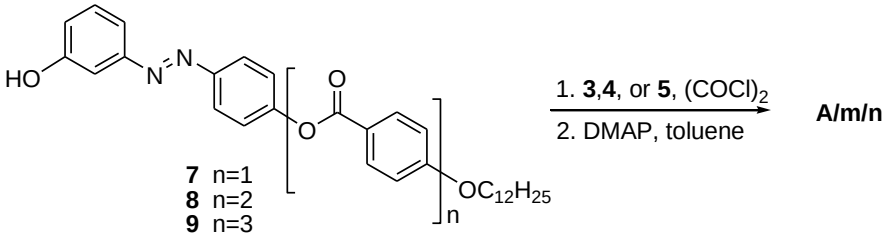
the crude product, which was purified by column chromatography (toluene). 292 mg (93%) of **A/0/1** was isolated. ^{1}H NMR ($CDCl_3$): 0.88 (t, 6 H, J = 6.0, 2 × CH_3), 1.27-1.49 (m, 36 H, 2 × $(CH_2)_9$), 1.83 (m, 4 H, 2 × $\underline{CH_2}CH_2O$), 4.05 (t, 4 H, J = 6.6, 2 × CH_2O), 6.98 (d, 2 H, J = 9.1), 7.04 (dd, 1 H, ^3J = 8.1, ^4J = 2.4), 7.37 (d, 2 H, J = 8.8), 7.42 (dd, 1 H, J = 7.9), 7.44 (d, 1 H, ^4J = 2.2), 7.54 (d, 1 H, J = 7.9), 8.00 (d, 2 H, J = 8.8), 8.16 (d, 2 H, J = 8.8). Elemental analysis: for $C_{43}H_{62}N_2O_4$ (670.98) calculated: 76.97% C, 9.31% H, 4.17% N; found: 76.84% C, 9.20% H, 4.08% N.

(E)-4-((4-((3-(dodecyloxy)phenyl)diazenyl)phenoxy)carbonyl)phenyl 4-(dodecyloxy)-benzoate **(A/0/2)** was obtained in the same way. Yield 84%. ^{1}H NMR ($CDCl_3$): 0.88 (t, 6 H, J = 6.4, 2 × CH_3), 1.27-1.49 (m, 36 H, 2 × $(CH_2)_9$), 1.83 (m, 4 H, 2 × $\underline{CH_2}CH_2O$), 4.05 (t, 4 H, J = 6.4, 2 × CH_2O), 6.99 (d, 2 H, J = 9.1), 7.04 (dd, 1 H, ^3J = 8.2, ^4J = 2.6), 7.39 (d, 4 H, J = 9.1), 7.42 (dd, 1 H, J = 7.9), 7.45 (d, 1 H, ^4J = 2.2), 7.55 (d, 1 H, J = 8.5), 8.02 (d, 2 H, J = 9.1), 8.16 (d, 2 H, J = 9.1), 8.30 (d, 2 H, J = 8.8). Elemental analysis: for $C_{50}H_{66}N_2O_6$ (791.09) calculated: 75.91% C, 8.41% H, 3.54% N; found: 75.66% C, 8.40% H, 3.39% N.

(E)-4-((-4-((4-((3-(dodecyloxy)phenyl)diazenyl)phenoxy)carbonyl)phenoxy)carbonyl)phenyl 4-(dodecyloxy)benzoate **(A/0/3)**. Yield 65%. ^{1}H NMR ($CDCl_3$): 0.88 (t, 6 H, J = 6.4, 2 × CH_3), 1.27-1.49 (m, 36 H, 2 × $(CH_2)_9$), 1.83 (m, 4 H, 2 × $\underline{CH_2}CH_2O$), 4.05 (t, 4 H, J = 6.4, 2 × CH_2O), 6.99 (d, 2 H, J = 9.1), 7.04 (dd, 1 H, ^3J = 8.2, ^4J = 2.6), 7.39 (d, 4 H, J = 9.1), 7.42 (dd, 1 H, J = 7.9), 7.45 (d, 1 H, ^4J = 2.2), 7.55 (d, 1 H, J = 8.5), 8.01 (d, 4 H, J = 9.1), 8.16 (d, 4 H, J = 9.1), 8.30 (d, 2 H, J = 8.8). Elemental analysis: for $C_{57}H_{70}N_2O_8$ (911.20) calculated: 75.14% C, 7.74% H, 3.07% N; found: 75.02% C, 7.60% H, 3.03% N.

1.5 Synthesis of non-symmetrical materials A/m/n

Materials **A/m/n** with different length of the arms were obtained by acylation of intermediates **7-9** with acid chlorides of acids **3-5** (Scheme S5).



Scheme S5 Synthesis of non-symmetrical materials **A/m/n**

General synthesis of non-symmetrical target materials A/m/n

To a solution of the intermediate phenol **7-9** (0.2 mmol) and DMAP (27 mg; 0.22 mmol) in dry toluene (25 mL), a solution of acid chloride in toluene (10 mL) prepared from acid **3-5** (0.4 mmol) was heated to 100 °C for 30 min, cooled to room temperature and decomposed with water (10 mL). After stirring for 10 min, the mixture was poured into 2% aq. hydrochloric acid (25 mL), the organic layer was separated and the aqueous layer extracted with chloroform (15 mL). The combined organic solution was washed with water (15 mL) and dried with anhydrous magnesium sulfate. The solvent was evaporated and the product was purified by column chromatography (toluene/triethylamine 99.85/0.15) and crystallisation.

(E)-4-((3-(4-(4-(Dodecyloxy)benzoyloxy)benzoyloxy)phenyl)diazenyl)phenyl 4-(dodecyloxy)-benzoate **(A/2/1)**. Yield 86%, crystallisation from cyclohexane. ^{1}H NMR ($CDCl_3$): 0.88 (t, 6 H, J = 6.7, 2 × CH_3), 1.27-1.48 (m, 36 H, 2 × $(CH_2)_9$), 1.83 (m, 4 H, 2 × $\underline{CH_2}CH_2O$), 4.05 (t, 4 H, J = 6.6, 2 × CH_2O), 6.99 (d, 4 H, J = 8.8), 7.35-7.41 (m, 5 H), 7.60 (dd, 1 H, J = 7.9), 7.81 (d, 1 H, ^4J = 1.9), 7.90 (d, 1 H, J = 7.9), 8.01 (d, 2 H, J = 8.8), 8.16 (d, 4 H, J = 8.8), 8.31 (d, 2 H, J = 8.8). Elemental analysis: for $C_{57}H_{70}N_2O_8$ (911.20) calculated: 75.14% C, 7.74% H, 3.07% N; found: 75.00% C, 7.80% H, 2.96% N.

(E)-4-((3-(4-(4-(4-(Dodecyloxy)benzoyloxy)benzoyloxy)benzoyloxy)phenyl)diazenyl)phenyl 4-(dodecyloxy)benzoate **(A/3/1)**. Yield 73%, crystallisation from cyclohexane**.** ^{1}H NMR ($CDCl_3$): 0.88 (t, 6 H, J = 6.7, 2 × CH_3), 1.27-1.49 (m, 36 H, 2 × $(CH_2)_9$), 1.83 (m, 4 H, 2 × $\underline{CH_2}CH_2O$), 4.06 (t, 4 H, J = 6.6, 2 × CH_2O), 6.99 (d, 4 H, J = 9.1), 7.35-7.43 (m, 7 H), 7.61 (dd, 1 H, ^3J = 8.2, ^4J = 7.9), 7.81 (d, 1 H, ^4J = 2.1), 7.90 (d, 1 H, J = 8.2), 8.02 (d, 2 H, J = 9.1), 8.16 (d, 4 H, J = 9.1), 8.31 (d, 2 H, J = 9.1), 8.34 (d, 2 H, J = 8.8). Elemental analysis: for $C_{64}H_{74}N_2O_{10}$ (1031.31) calculated: 74.54% C, 7.23% H, 2.72% N; found: 74.38% C, 7.20% H, 2.63% N.

(E)-3-((4-(4-(4-(Dodecyloxy)benzoyloxy)benzoyloxy)phenyl)diazenyl)phenyl 4-(dodecyloxy)-benzoate **(A/1/2).** Yield 92%, crystallisation from cyclohexane. ^{1}H NMR ($CDCl_3$): 0.88 (t, 6 H, J = 6.6, 2 × CH_3), 1.27-1.48 (m, 36 H, 2 × $(CH_2)_9$), 1.83 (m, 4 H, 2 × $\underline{CH_2}CH_2O$), 4.05 (t, 4 H, J = 6.6, 2 × CH_2O), 6.99 (d, 4 H, J = 9.1), 7.33-7.41 (m, 5 H), 7.59 (dd, 1 H, ^3J = 8.2, ^4J = 7.9), 7.79 (d, 1 H, ^4J = 2.1), 7.88 (d, 1 H, J = 7.3), 8.02 (d, 2 H, J = 8.8), 8.16 (d, 2 H, J = 8.8),

8.17 (d, 2 H, *J* = 8.8), 8.30 (d, 2 H, *J* = 8.8). Elemental analysis: for $C_{57}H_{70}N_2O_8$ (911.20) calculated: 75.14% C, 7.74% H, 3.07% N; found: 75.09% C, 7.82% H, 2.90% N.

***(E)-4-((4-((3-(4-(4-(4-(Dodecyloxy)benzoyloxy)benzoyloxy)benzoyloxy)phenyl)diazenyl)-phenoxy)carbonyl)phenyl 4-(dodecyloxy)benzoate* (A/3/2)**. Yield 57%, crystallisation from chloroform/hexane. ^{1}H NMR ($CDCl_3$): 0.88 (t, 6 H, *J* = 6.7, 2 × CH_3), 1.27-1.48 (m, 36 H, 2 × $(CH_2)_9$), 1.83 (m, 4 H, 2 × $\underline{CH_2}CH_2O$), 4.06 (t, 4 H, *J* = 6.4, 2 × CH_2O), 6.99 (d, 4 H, *J* = 8.5), 7.37-7.44 (m, 9 H), 7.61 (dd, 1 H, *J* = 7.9), 7.82 (d, 1 H, ^4J = 2.2), 7.91 (d, 1 H, *J* = 8.8), 8.04 (d, 2 H, *J* = 8.8), 8.16 (d, 4 H, *J* = 8.8), 8.32 (m, 6 H). Elemental analysis: for $C_{71}H_{78}N_2O_{12}$ (1151.42) calculated: 74.06% C, 6.83% H, 2.43% N; found: 74.01% C, 6.90% H, 2.33% N.

(*E)-3-((4-(4-(4-(4-(4-(Dodecyloxy)benzoyloxy)benzoyloxy)benzoyloxy)benzoyloxy)-phenyl)diazenyl)phenyl 4-(dodecyloxy)benzoate* (A/1/3). Yield 79%, crystallisation from a toluene/acetone mixture. ^{1}H NMR ($CDCl_3$): 0.88 (t, 6 H, *J* = 6.7, 2 × CH_3), 1.27-1.48 (m, 36 H, 2 × $(CH_2)_9$), 1.83 (m, 4 H, 2 × $\underline{CH_2}CH_2O$), 4.06 (t, 4 H, *J* = 6.4, 2 × CH_2O), 6.99 (d, 4 H, *J* = 8.9), 7.35 (dd, 1 H, ^3J = 8.1, ^4J = 2.3), 7.39-7.43 (m, 6 H), 7.59 (dd, 1 H, *J* = 7.9), 7.79 (d, 1 H, ^4J = 2.1), 7.88 (d, 1 H, *J* = 8.8), 8.03 (d, 2 H, *J* = 9.1), 8.16 (d, 2 H, *J* = 9.1), 8.17 (d, 2 H, *J* = 9.1), 8.30 (d, 2 H, *J* = 8.5), 8.32 (d, 2 H, *J* = 8.8). Elemental analysis: for $C_{64}H_{74}N_2O_{10}$ (1031.31) calculated: 74.54% C, 7.23% H, 2.72% N; found: 74.44% C. 7.12% H, 2.66% N.

***((E)-4-((3-((4-(4-(4-(4-(Dodecyloxy)benzoyloxy)benzoyloxy)benzoyloxy)phenyl)diazenyl)-phenoxy)carbonyl)phenyl 4-(dodecyloxy)benzoate* (A/2/3).** Yield 48%, crystallisation from a dichloromethane/cyclohexane mixture. ^{1}H NMR ($CDCl_3$): 0.88 (t, 6 H, *J* = 6.7, 2 × CH_3), 1.27-1.48 (m, 36 H, 2 × $(CH_2)_9$), 1.83 (m, 4 H, 2 × $\underline{CH_2}CH_2O$), 4.06 (t, 4 H, *J* = 6.4, 2× CH_2O), 6.99 (d, 4 H, *J* = 8.8), 7.35-7.43 (m, 9 H), 7.61 (dd, 1 H, ^3J = 7.9, ^4J = 8.2), 7.82 (d, 1 H, ^4J = 2.1), 7.91 (d, 1 H, *J* = 8.5), 8.04 (d, 2 H, *J* = 8.8), 8.16 (d, 4 H, *J* = 9.1), 8.29-8.34 (m, 6 H). Elemental analysis: for $C_{71}H_{78}N_2O_{12}$ (1151.42) calculated: 74.06% C, 6.83% H, 2.43% N; found: 73.91% C, 6.80% H, 2.36% N.