Supramolecular Control over the Structural Organization of a Second-Order NLO-active Organogelator

Fatima Aparicio,[a] Lara Faour,[a] Denis Gindre,[a] David Canevet,*[,a] Marc Sallé*[,a]

[a] Laboratoire MOLTECH-Anjou, Université d'Angers, UMR CNRS 6200, 2 bd Lavoisier, 49045 Angers Cedex, France.

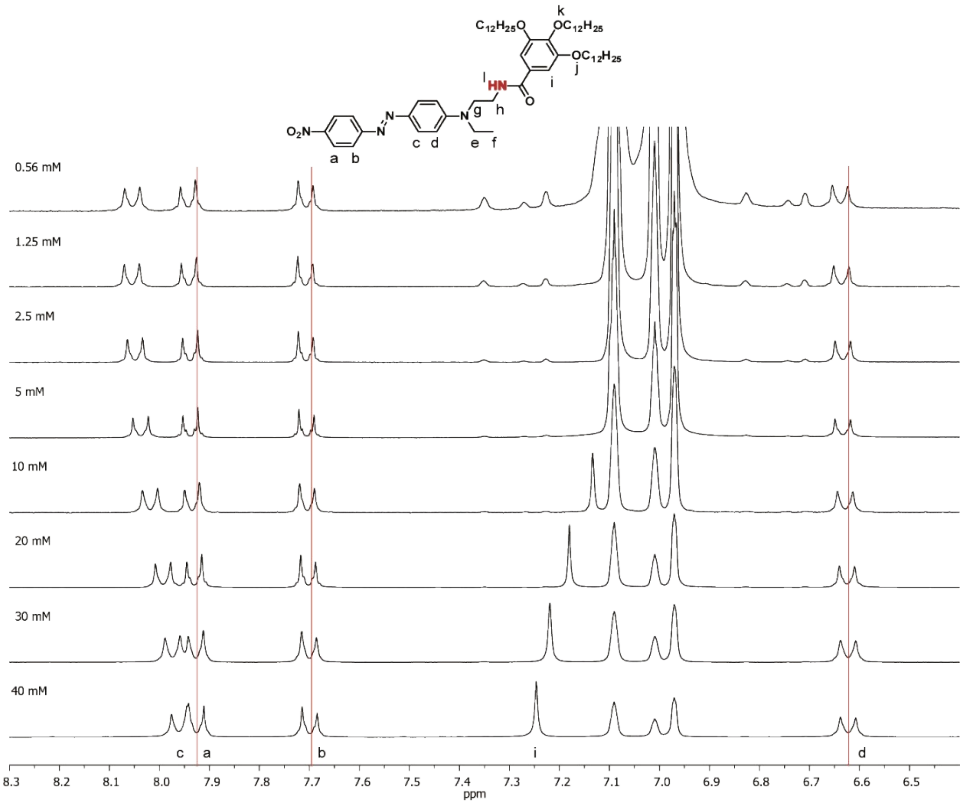


Figure S1. Aromatic region of ^{1}H NMR spectra (300 MHz, 298 K) of **1** at different concentrations in toluene-D_8.

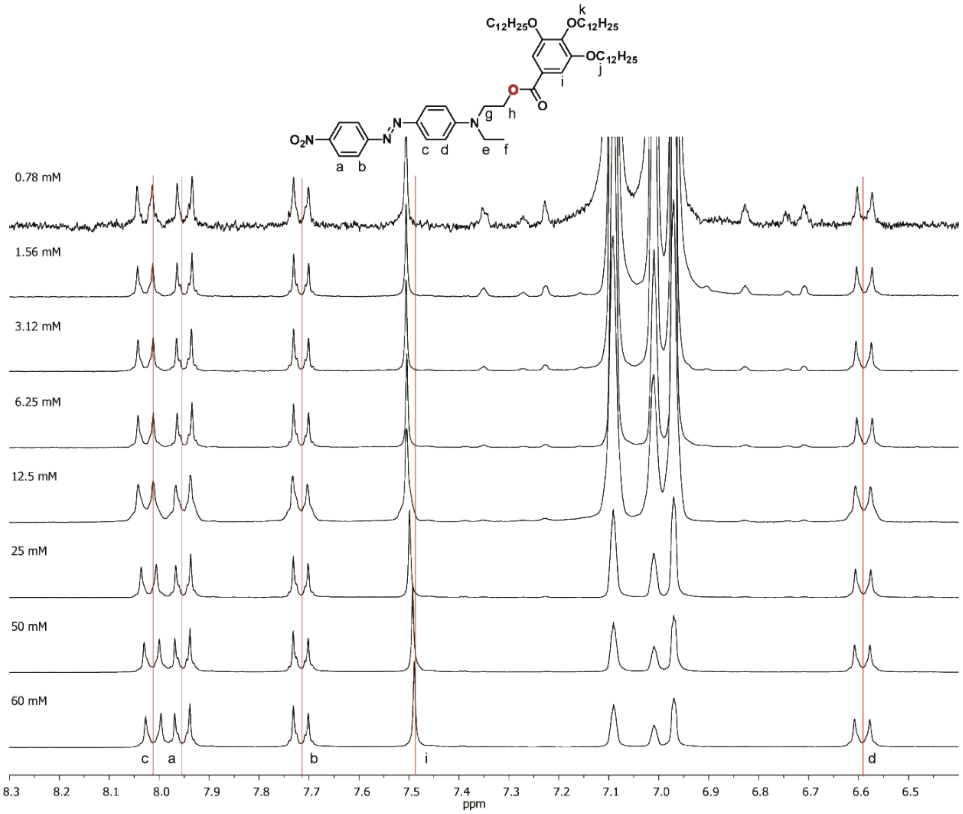


Figure S2. Aromatic region of ^{1}H NMR spectra (300 MHz, 298 K) of **2** at different concentrations in toluene-D_8.

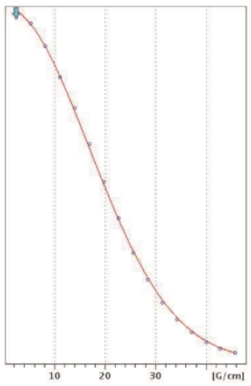
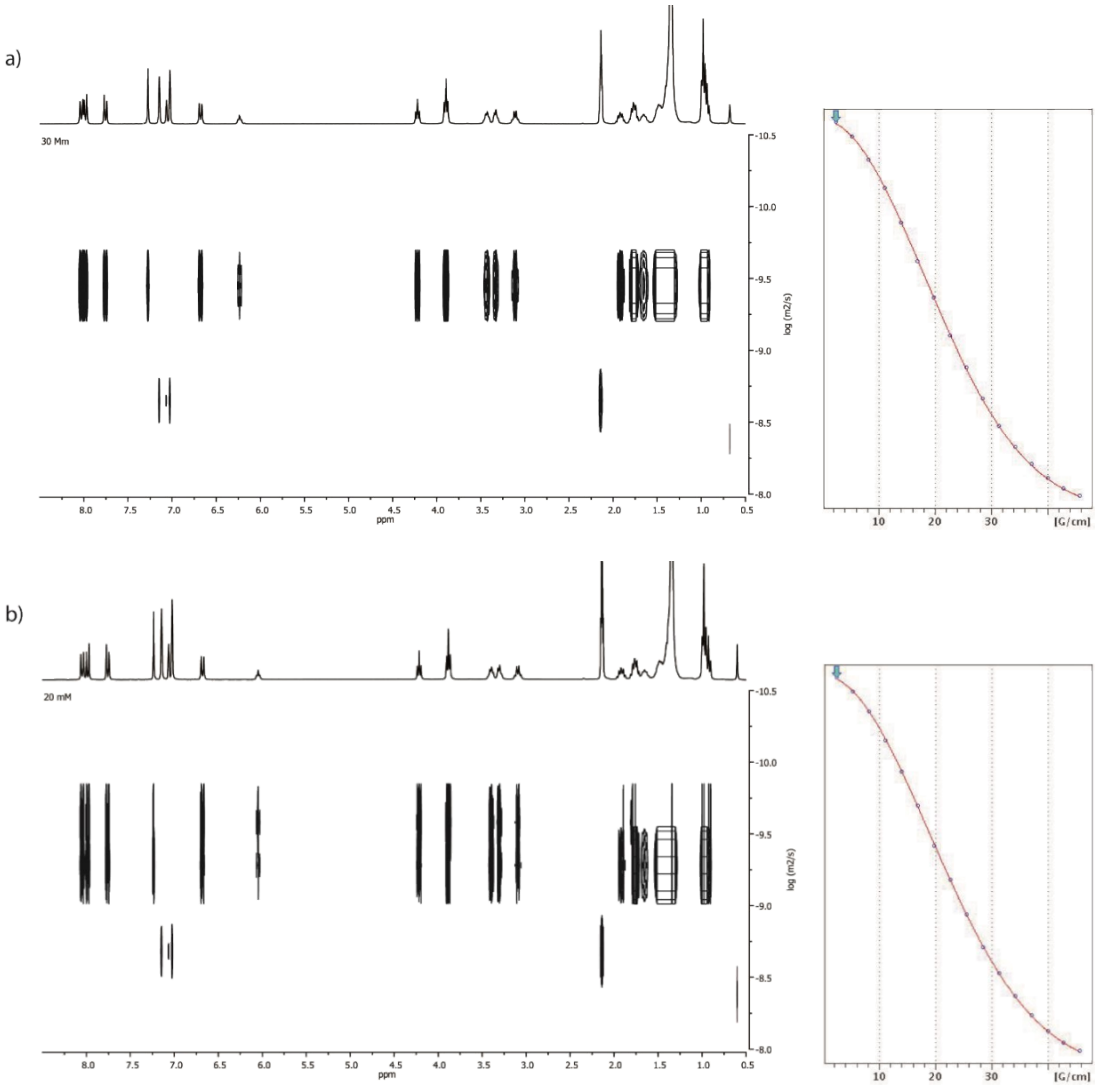


Figure S3. T1/T2 relaxation curve of the ^{1}H NMR signal at 7.78 ppm of compound **1** at 40 mM in toluene-D_8.



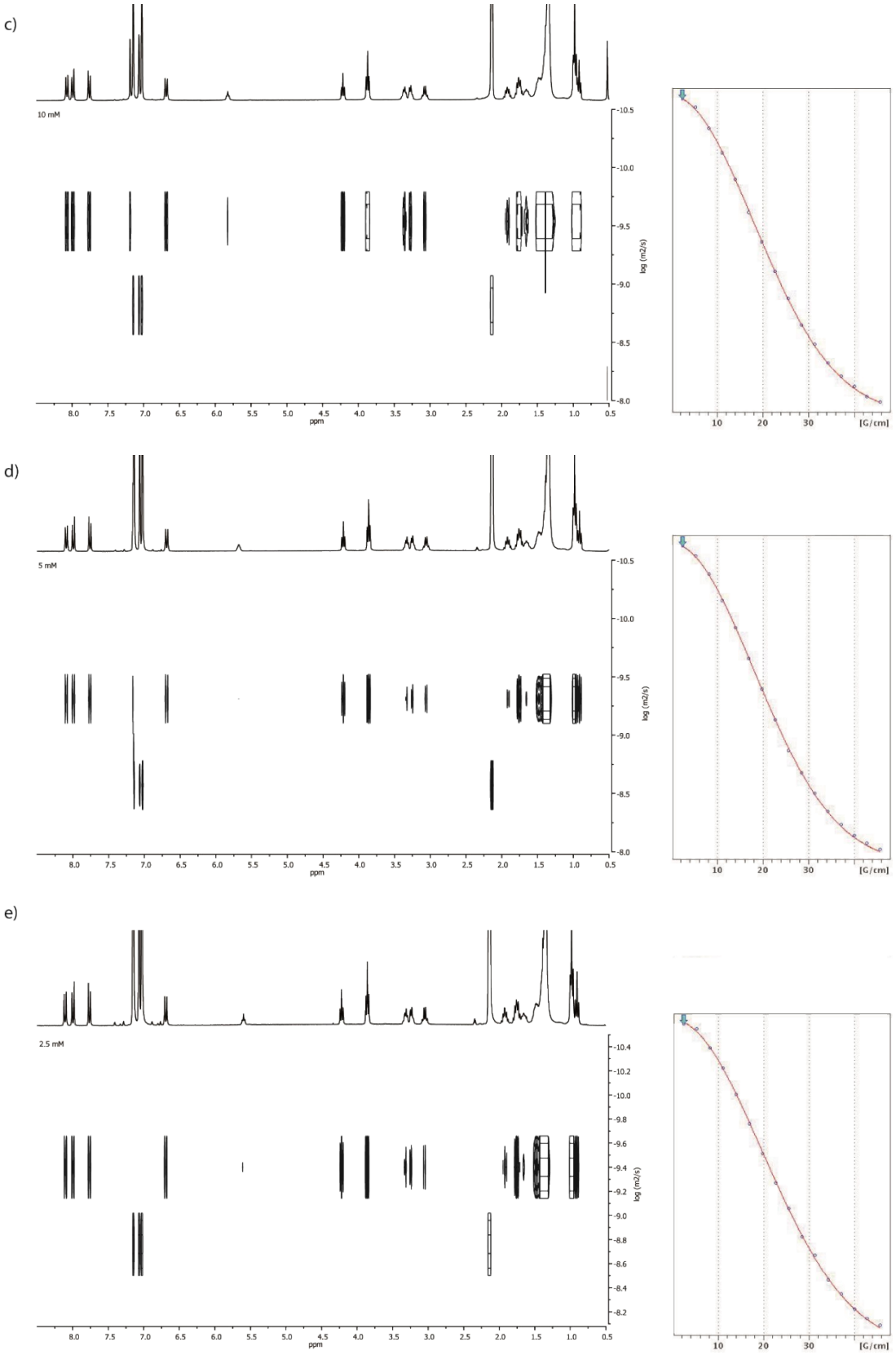
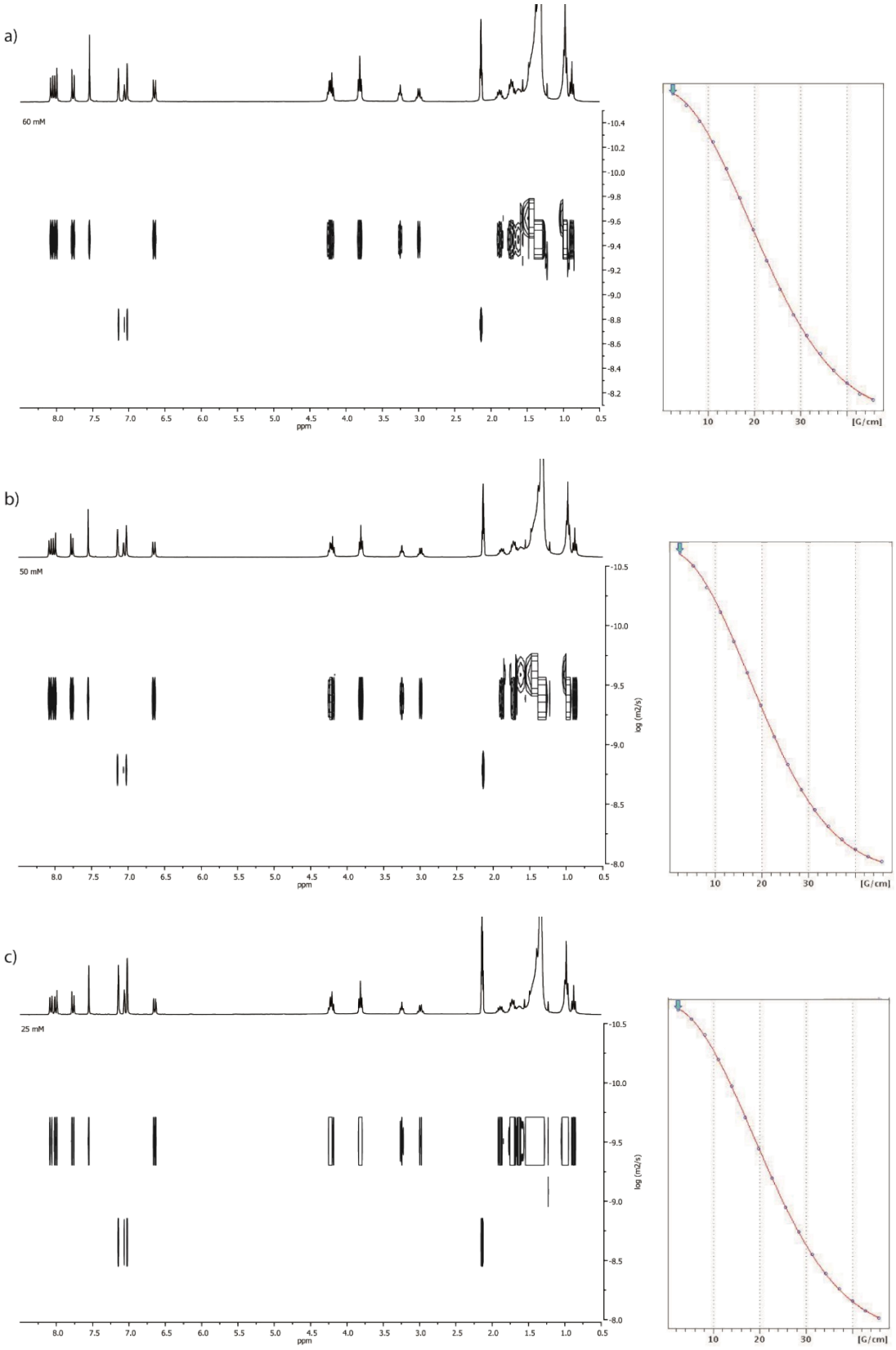


Figure S4. DOSY NMR spectra (300 MHz, 298 K) of **1** in toluene-D_8 and T1/T2 relaxation curves of the ^{1}H NMR signal at 7.78 ppm at 30 mM (a), 20 mM (b), 10 mM (c), 5 mM (d) and 2.5 mM (e).


a)
60 mM
b)
50 mM
c)
25 mM
ppm
log (m2/s)
[G/cm]

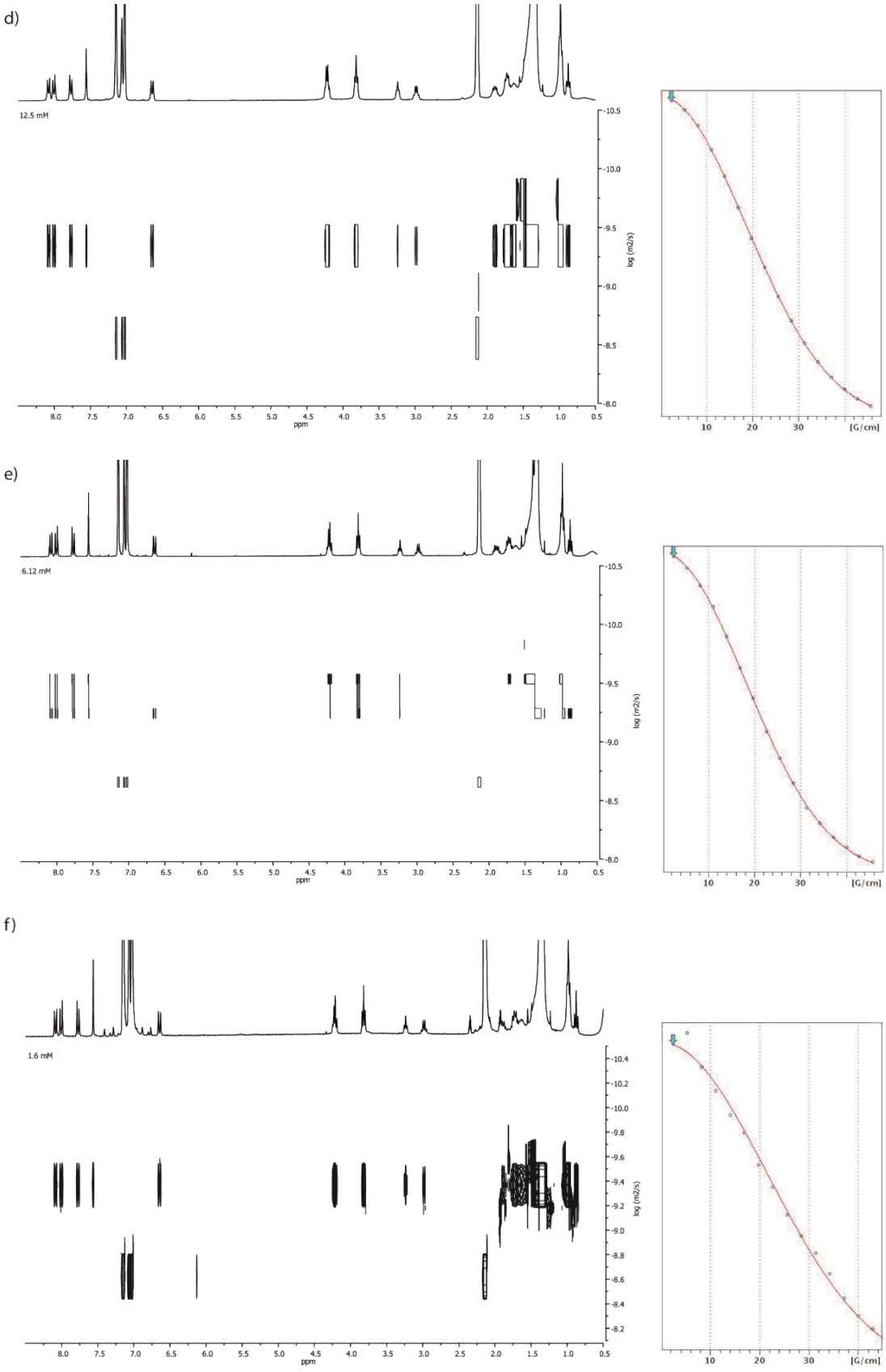


Figure S5. DOSY NMR spectra (300 MHz, 298 K) of **2** in toluene-D_8 and T1/T2 relaxation curves of the ^{1}H NMR signal at 7.79 ppm at 60 mM (a), 50 mM (b), 25 mM (c), 12.5 mM (d), 6.12 mM (e) and 1.60 mM (f).

Table S1. Critical gel concentrations (CGC, mg/mL) of compounds **1** and **2** in various solvents.

Solvent	Compound **1**	Compound **2**
Hexane	10	10
Chloroforme	§	§
Pentane	4	§
Cyclohexane	3.3	§
Toluene	45	§
Ethanol	1.5	6.6
Acetonitrile	1.5	6.6

§ No gelification could be observed

Table S2. Diffusion coefficients of **1** and **2** obtained from the relaxation curves showed in Figure S4 and S5.

[1] mM	**D** x10^{-10} m^{2}s^{-1}	**[2]** mM	**D** x10^{-10} m^{2}s^{-1}
40.0	4.30	60.0	4.69
30.0	4.30	50.0	4.71
20.0	4.63	25.0	4.76
10.0	4.78	12.5	5.02
5.0	5.10	6.1	5.09
2.5	5.12	1.6	5.08

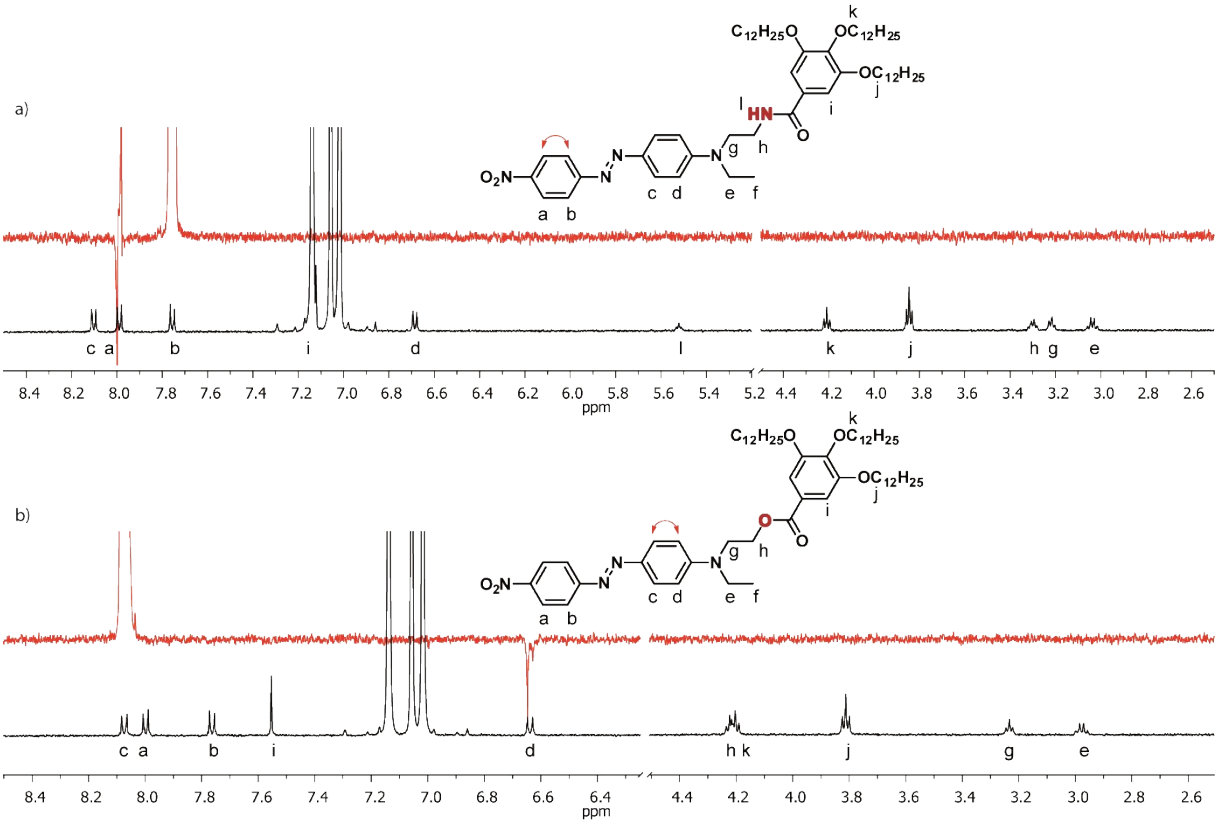


Figure S6. Partial ^{1}H NMR spectra (300 MHz, 298 K) (bottom) and NOE experiments of **1** (a) and **2** (b) in diluted conditions (1 mM, toluene-D_8), upon irradiating protons "b" and "c", respectively. Solid arrows represent the NOE contacts for intramolecular effects.

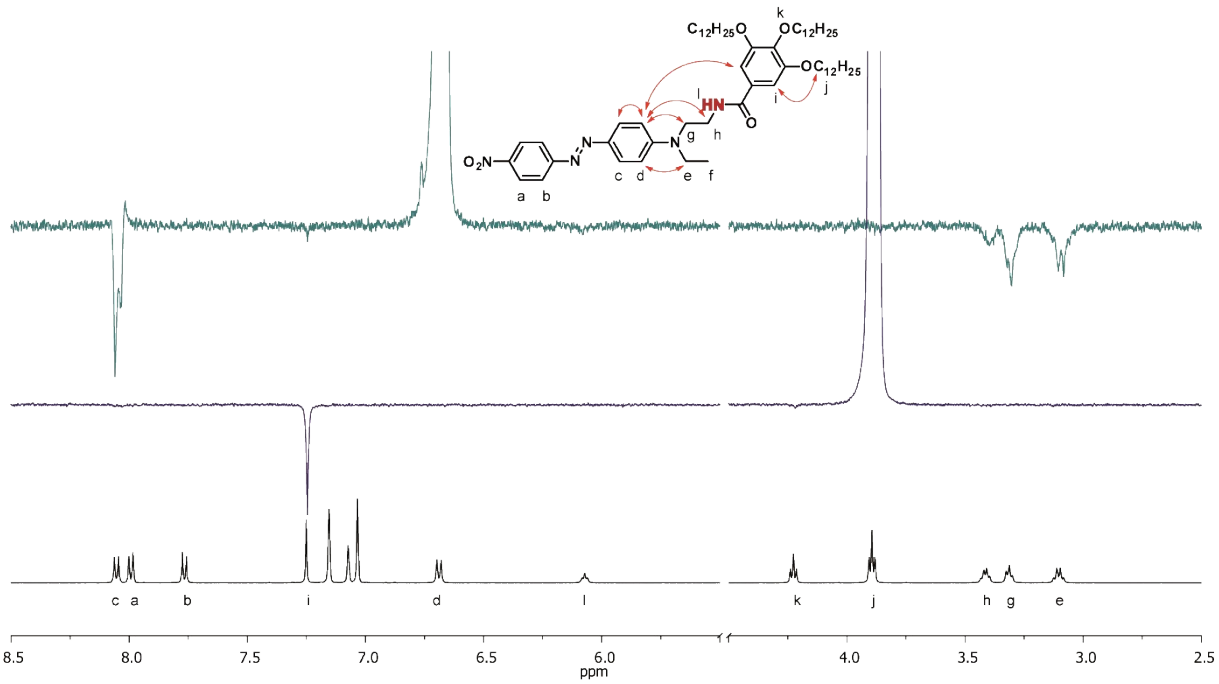


Figure S7. Partial ^{1}H NMR spectra (300 MHz, 298 K) (bottom) and NOE experiments of **1** in a concentrated solution (28 mM, toluene-D_8) upon irradiating protons "d" and "j" respectively. Solid arrows represent the NOE contacts for intramolecular effects.

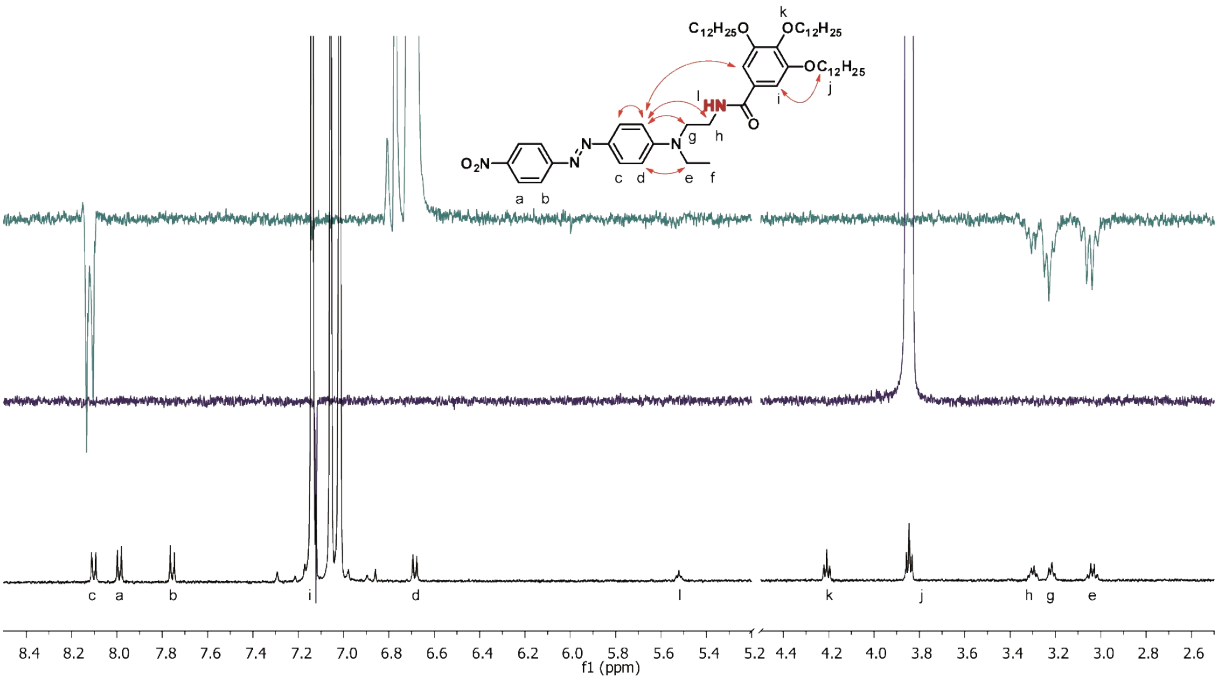


Figure S8. Partial ^{1}H NMR spectra (300 MHz, 298 K) (bottom) and NOE experiments of **1** at a diluted solution (1 mM, toluene-D_8) upon irradiating protons "d" and "j". Solid arrows represent the NOE contacts for intramolecular effects.

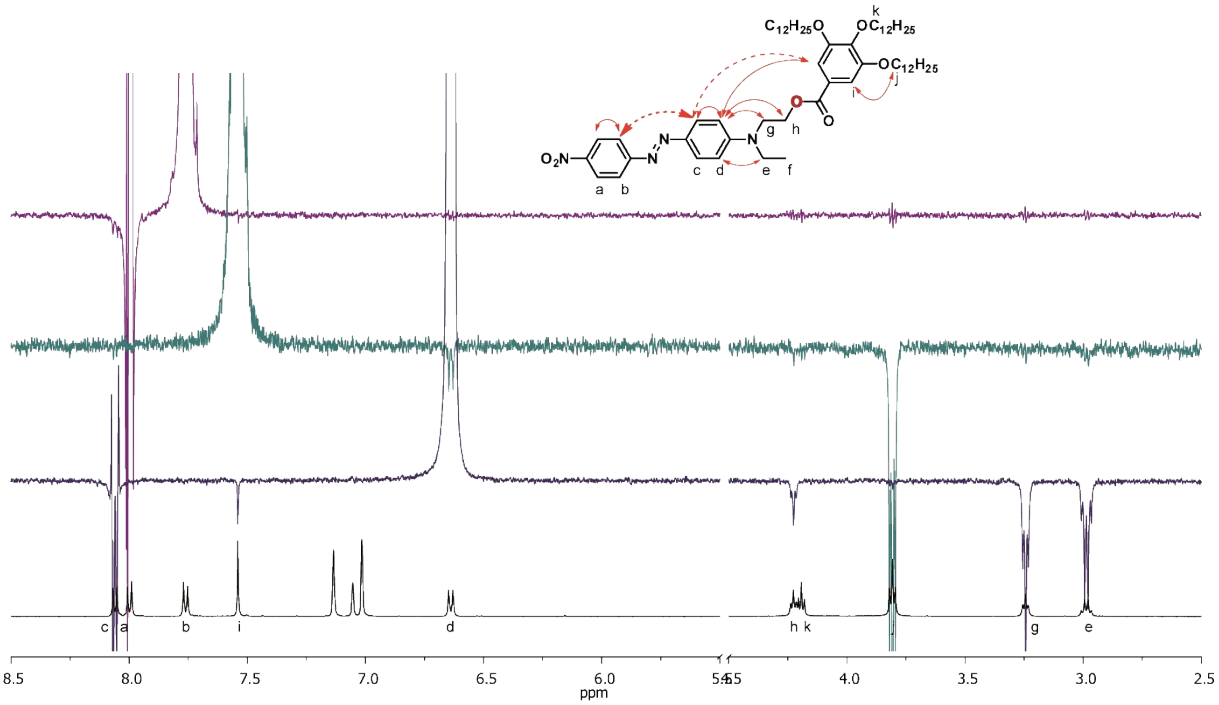


Figure S9. Partial ^{1}H NMR spectra (300 MHz, 298 K) (bottom) and NOE experiments of **2** in a concentrated solution (61 mM, toluene-D_8) upon irradiating protons "b" (top), "i" (middle) and "d" (bottom). Solid arrows represent the NOE contacts for intramolecular effects.

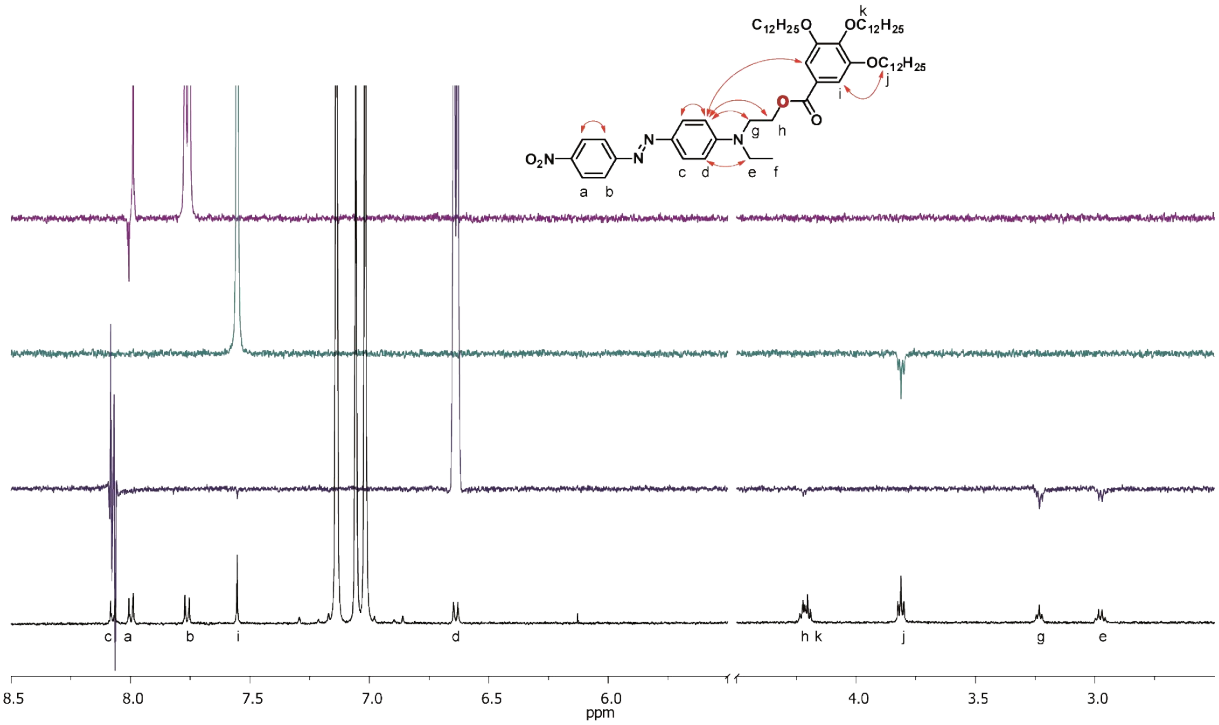


Figure S10. Partial ^{1}H NMR spectra (300 MHz, 298 K) (bottom) and NOE experiments of **2** in a diluted solution (1 mM, toluene-D_8) upon irradiating protons "b" (top), "i" (middle) and "d" (bottom). Solid arrows represent the NOE contacts for intramolecular effects.

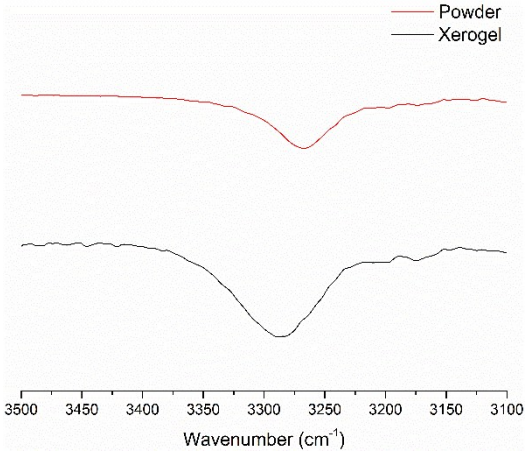


Figure S11. FTIR spectra of compound **1** (N-H region), recorded as a pure sample (xerogel prepared from a toluene solution) or diluted as mixed powder in KBr (**1** (6mg); KBr (150 mg)).

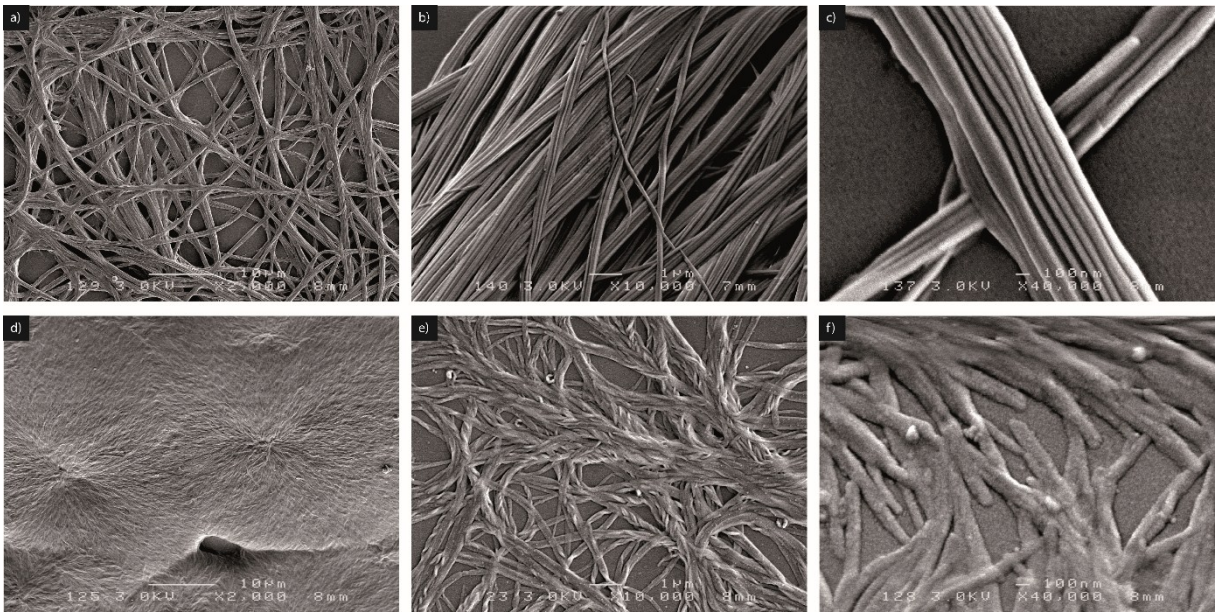


Figure S12. SEM images of the fibers formed by the self-assembly of compound **1** (a, b and c) and **2** (d, e and f) in toluene at the concentration corresponding to the largest assemblies (28 mM and 61 mM, respectively).

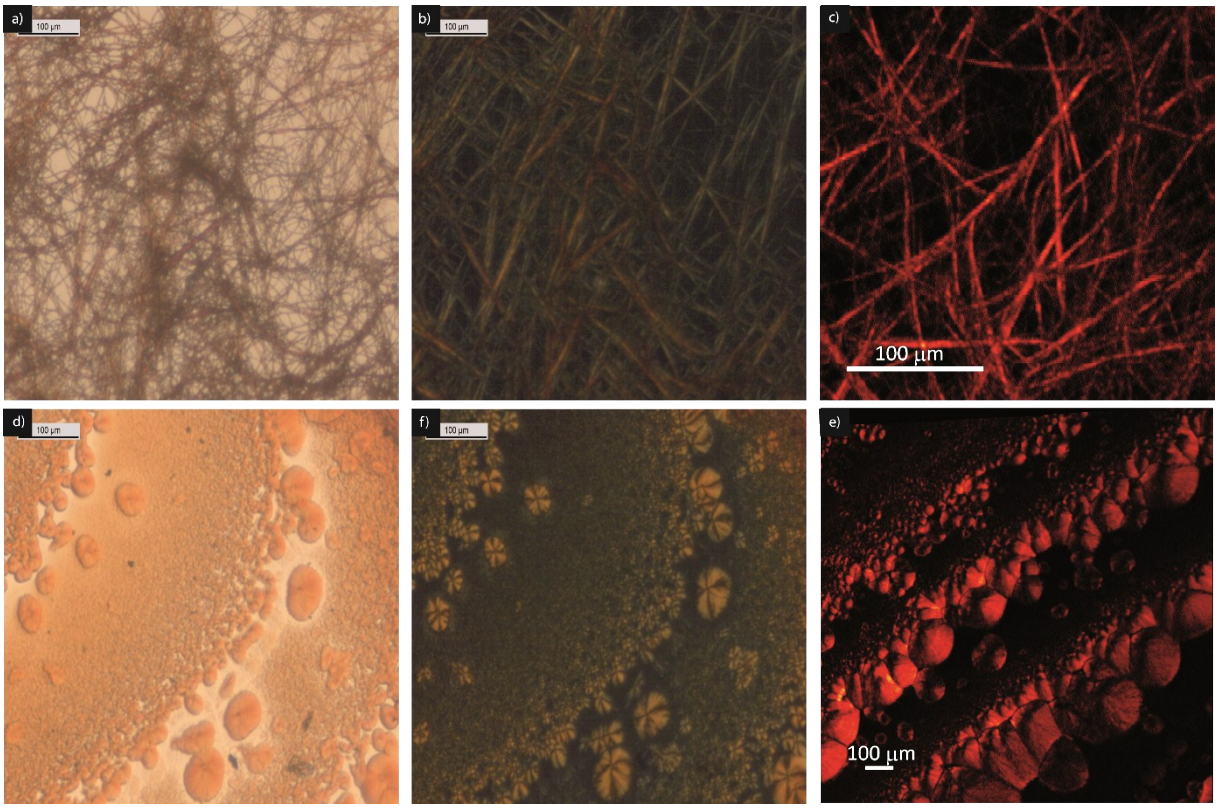


Figure S13. Optical microscopy with non-polarized (left), polarized (center) light and SHG (right) images of the samples prepared for SEM microscopy of compound **1** (a, b and c) and **2** (d, e and f) in toluene at the concentrations corresponding to the largest assemblies (28 mM and 61 mM, respectively).

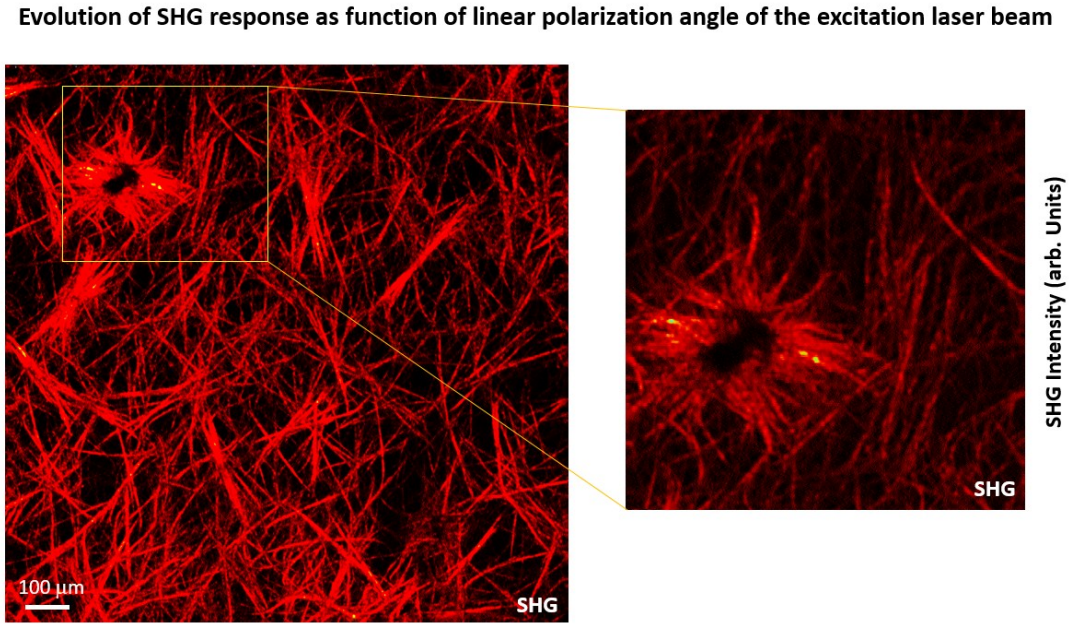


Figure S14. SHG micrograph (left) and zoom (right) of compound **1** in toluene. SHG is polarization dependent and consequently all objects cannot be SHG active simultaneously with the same intensity. The evolution of SHG response of the scanned area with the rotation of the polarization plane is shown in the **Movie S1**.

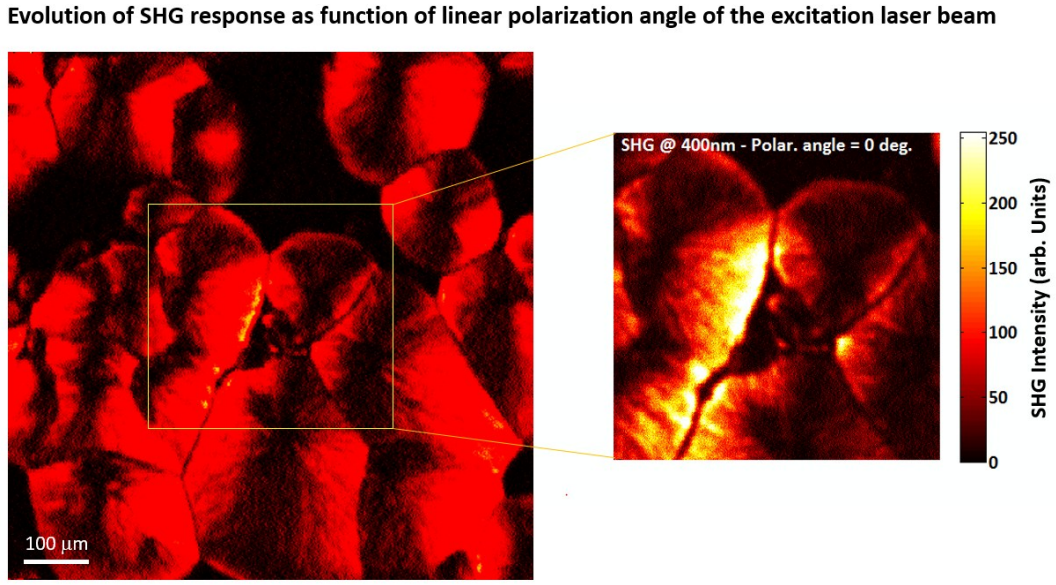


Figure S15. SHG micrograph (left) and zoom (right) of compound **2** in toluene. The evolution of SHG response of the scanned area with the rotation of the polarization plane is shown in the **Movie S2**.

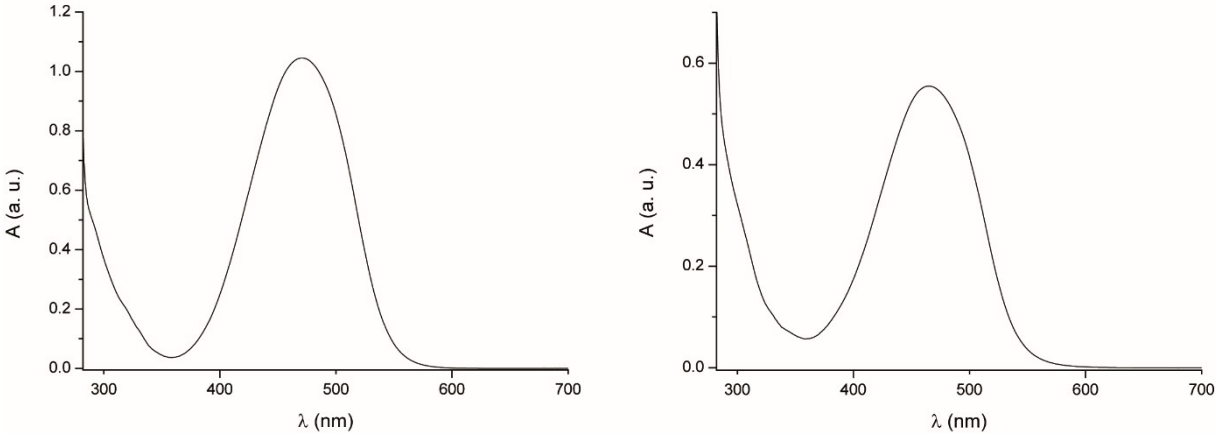


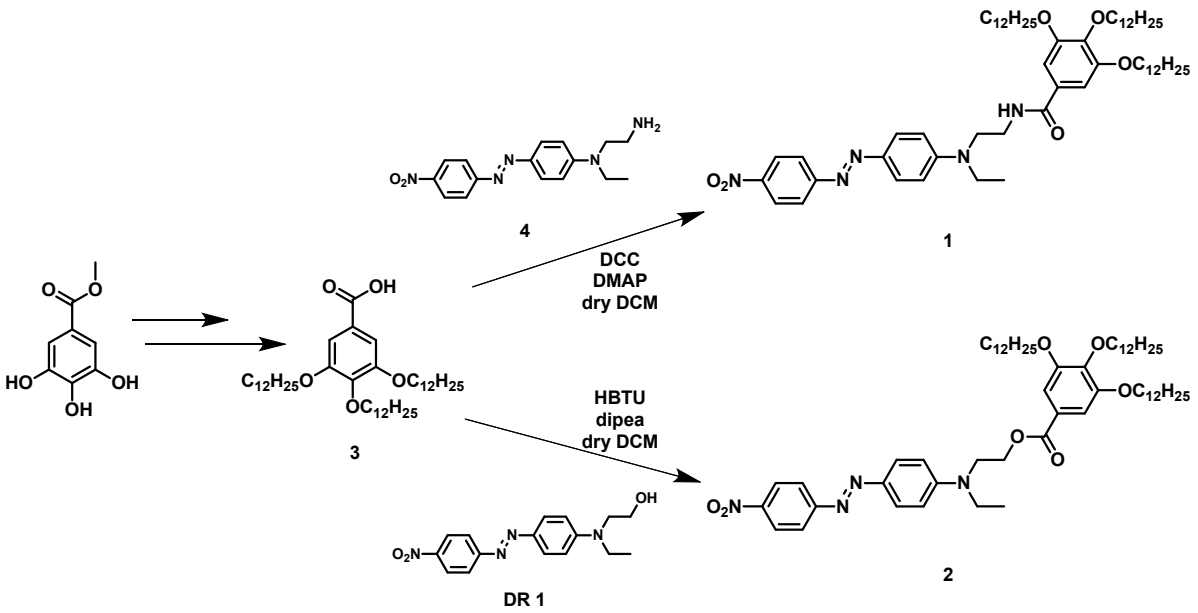
Figure S16. UV-visible absorption spectra of compound **1** (left) and compound **2** (right) at 2.5 x 10^{-4} M in toluene (l = 1 cm).

Experimental section

General.

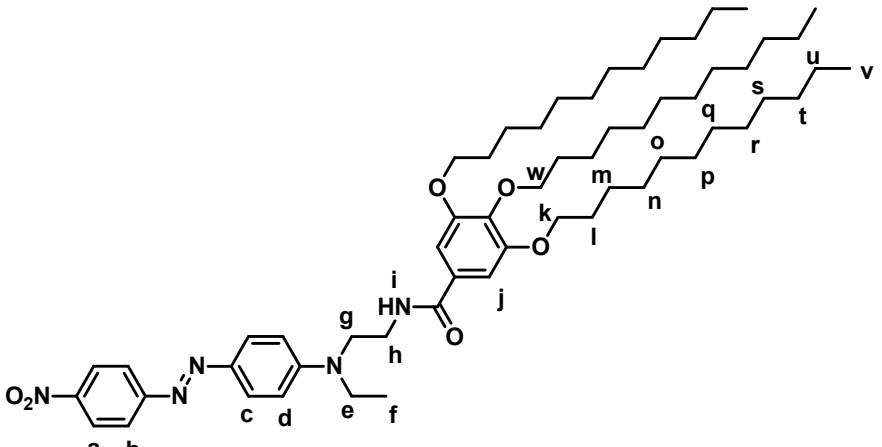
The starting materials were purchased and used without further purification. All solvents were dried according to standard procedures. All air-sensitive reactions were carried out under argon atmosphere. Thin-layer chromatography (TLC) was performed on aluminium plates coated with Merck Silica gel 60 F254. Developed plates were air-dried and scrutinized under a UV lamp. Silica gel 60 (35–70 mesh, SDS) was used for column chromatography. ^{1}H and ^{13}C NMR spectra were recorded using the deuterated solvent as an internal reference on a BRUKER Advance DRX 300 spectrometer. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. The mass spectra were recorded on a a Jeol JMS 700 (high resolution mass spectra (HRMS)) by electronic impact (EI). The infrared absorption spectra were recorded on an FTIR BRUKER VERTEX 70. SEM images were acquired by scanning electron microscopy (SEM) JEOL JSM 6301F operating at tensions of 3 kV. SHG measurements were performed with the setup described in A. B. Marco, F. Aparicio, L. Faour, K. Iliopoulos, Y. Morille, M. Allain, S. Franco, R. Andreu, B. Sahraoui, D. Gindre, D. Canevet and M. Salle, *J. Am. Chem. Soc.*, 2016. DOI: 10.1021/jacs.6b04554.

Synthetic details and characterization



Disperse Red 1 (DR 1) was purchased from a commercial source. Compounds **3** and **4** were prepared by following reported procedures J. P. A. Custers, M. C. Hersmis, J. Meuldijk, J. A. J. M. Vekemans and L. A. Hulshof, *Org. Process Res. Dev.*, 2002, **6**, 645-651 and A. B. Marco, F. Aparicio, L. Faour, K. Iliopoulos, Y. Morille, M. Allain, S. Franco, R. Andreu, B. Sahraoui, D. Gindre, D. Canevet and M. Salle, *J. Am. Chem. Soc.*, 2016. DOI: 10.1021/jacs.6b04554, respectively and showed identical spectroscopic properties to those reported therein.

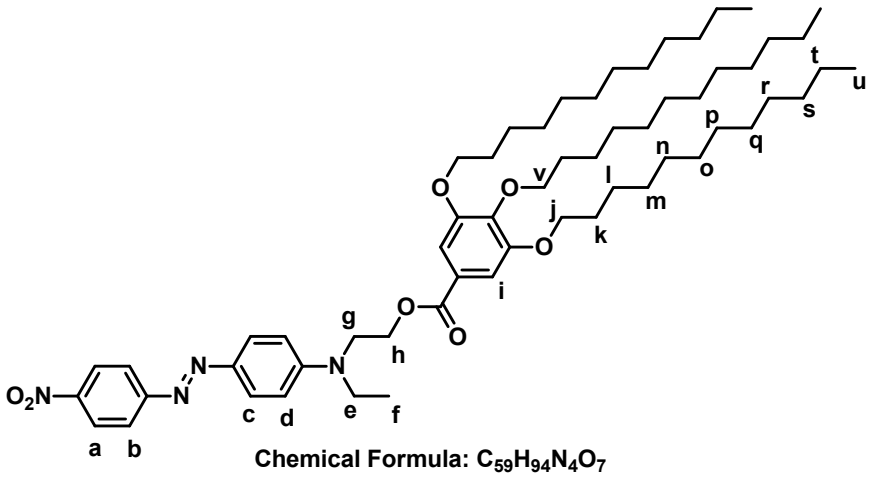
(*E*)-3,4,5-Tris(dodecyloxy)-*N*-(2-(ethyl(4-((4-nitrophenyl)diazenyl)phenyl)amino)ethyl)benzamide (1)



To a solution of carboxylic acid **3** (155 mg, 0.23 mmol, 1.2 eq.) in dry dichloromethane (5 mL) was added at 0°C and under inert atmosphere 4-dimethylaminopyridine (28 mg, 0.23 mmol, 1.2 eq.) and *N*-dimethylaminopropyl-*N*-ethylcarbodiimide hydrochloride (44 mg, 0.23 mmol, 1.2 eq.) After 30 minutes, amine **4** (60 mg, 0.19 mmol) was added and the mixture was slowly allowed to warm at room temperature and stirred for 60 hours. Target compound **1** was finally isolated by silica gel chromatography (eluent: 1) dichloromethane/petroleum ether: 2/1 to 1/0 and 2) dichloromethane/ethyl acetate: 95/5) with a 38% yield (70 mg). Mp 105°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.30 (2H, H_a, d, J = 8.98 Hz), 7.91 (2H, H_b, d, J = 8.98 Hz), 7.89 (2H, H_c,d, J =

9.03 Hz), 6.90 (2H, H_j, s), 6.87 (2H, H_d, d, *J* = 9.03 Hz), 6.33 (1H, H_i, br), 3.97 (3H, H_w, t, *J* = 6.52 Hz), 3.93 (6H, H_k, t, *J* = 6.48 Hz), 3.71 (4H, H_{g+h}, br), 3.55 (2H, H_e, q, *J* = 6.76 Hz), 1.74 (6H, H_l, m), 1.43 (6H, H_m, br), 1.25 (48H, H_{n-u},br), 0.88 (12H, H_{f+v}, t, *J* = 6.35 Hz); ^{13}C NMR($CDCl_3$, 75 MHz): δ 168.0, 156.8, 153.3, 151.6, 147.6, 143.9, 141.5, 129.0, 126.5, 124.8, 122.8, 111.6, 105.7, 73.6, 69.5, 49.2, 45.6, 38.3, 32.1, 30.4, 29.9, 29.8, 29.5, 26.2, 22.8, 14.3, 12.4; FT-IR (neat): $\bar{\upsilon}$ = 544, 664, 688, 719, 755, 820, 838, 858, 997, 1074, 1120, 1243, 1337, 1359, 1387, 1423, 1515, 1586, 1600, 2849, 2917, 3263 cm^{-1}.HRMS (ESI$^+$) calcd. for $C_{59}H_{96}N_5O_6$ $[M+H]^+$, 970.7360; found, 970.7372.

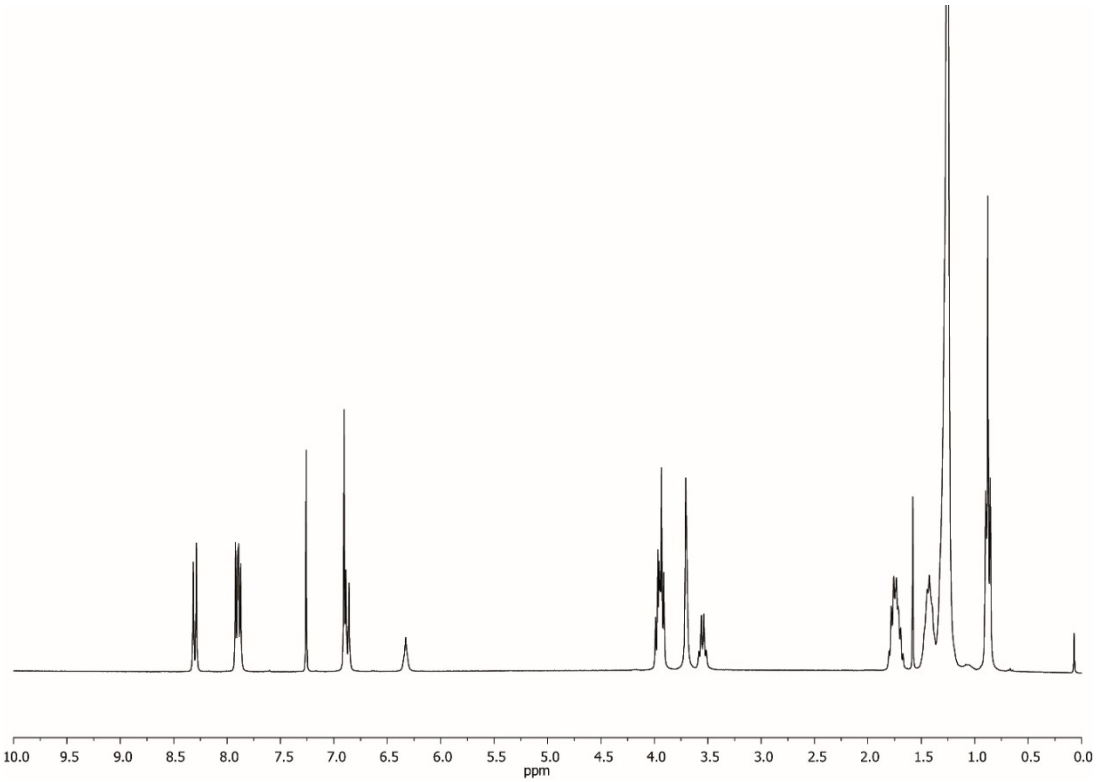
(*E*)-2-(Ethyl(4-((4-nitrophenyl)diazenyl)phenyl)amino)ethyl 3,4,5-tris(dodecyloxy)benzoate (2)



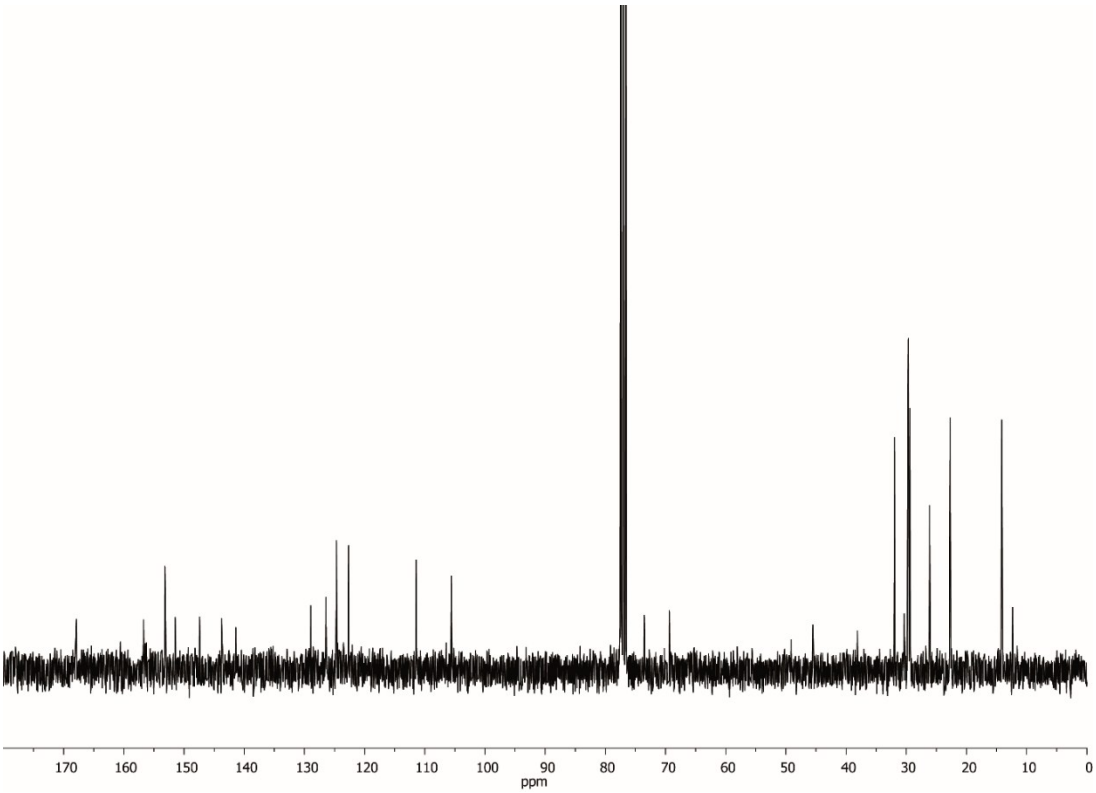
Chemical Formula: $C_{59}H_{94}N_4O_7$
Molecular Weight: 971.40

To a solution of **3** (0.5 g, 0.74 mmol) in dry dichloromethane (6 mL), *N*,*N*-diisopropylethylamine (0.26 mL, 1.48 mmol, 2 eq.) was added under argon atmosphere, and the mixture was stirred for 5 min. Then, O-(Benzotriazol-1-yl)-*N*,*N*,*N*′,*N*′-tetramethyluronium hexafluorophosphate (HBTU) (0.31, 0.81 mmol, 1.1 eq.) was added and the reaction mixture was stirred for 15 min. Then, Disperse Red 1 (0.27 g, 0.81 mmol, 1.1 eq.) was added portionwise and the mixture was stirred at room temperature for 16 h. The organic layer was washed with chlorhydric acid (1 M), sodium hydrogenocarbonate (1 M) and water and dried over magnesium sulfate. After evaporation of the solvent, the residue was purified by silica gel chromatography (eluent: petroleum ether:AcOEt 9:1) affording **2** as a red solid (0.30 g, 43%). Mp 69°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.33 (2H, H_a, d, *J* = 8.96 Hz), 7.93 (2H, H_b, d, *J* = 8.96 Hz), 7.91 (2H, H_c,d, *J* = 9.03 Hz), 7.03 (2H, H_i, s), 6.89 (2H, H_d, d, *J* = 9.03 Hz), 4.52 (2H, H_h, t, *J* = 6.09 Hz), 3.99 (2H, H_v, t, *J* = 6.55 Hz), 3.92 (4H, H_j, t, *J* = 6.38 Hz), 3.82 (2H, H_g, t, *J* = 6.21 Hz), 3.58 (2H, H_e, q, *J* = 7.18 Hz), 1.75 (6H, H_k, m), 1.43 (6H, H_l, br), 1.25 (48H, H_{m-t},br), 0.88 (12H, H_{f+u}, t, *J* = 6.26 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 166.6, 156.8, 152.9, 151.6, 147.6, 143.9, 142.7, 126.4, 124.8, 124.2, 122.8, 111.6, 108.1, 73.7, 69.3, 62.1, 48.8, 45.5, 32.1, 30.4, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 26.2, 22.8, 14.3, 12.4, 1.2; FT-IR (neat): $\bar{\upsilon}$ = 509, 540, 688, 721, 760, 798, 817, 858, 904, 1016, 1033, 1074, 1114, 1132, 1157, 1215, 1232, 1245, 1257, 1338, 1367, 1388, 1427, 1465, 1515, 1587, 1598, 1695, 1706, 2848, 2917 cm^{-1}. HRMS (ESI$^+$) calcd. for $C_{59}H_{95}N_4O_7$ $[M+H]^+$, 971.7200; found, 971.7213.

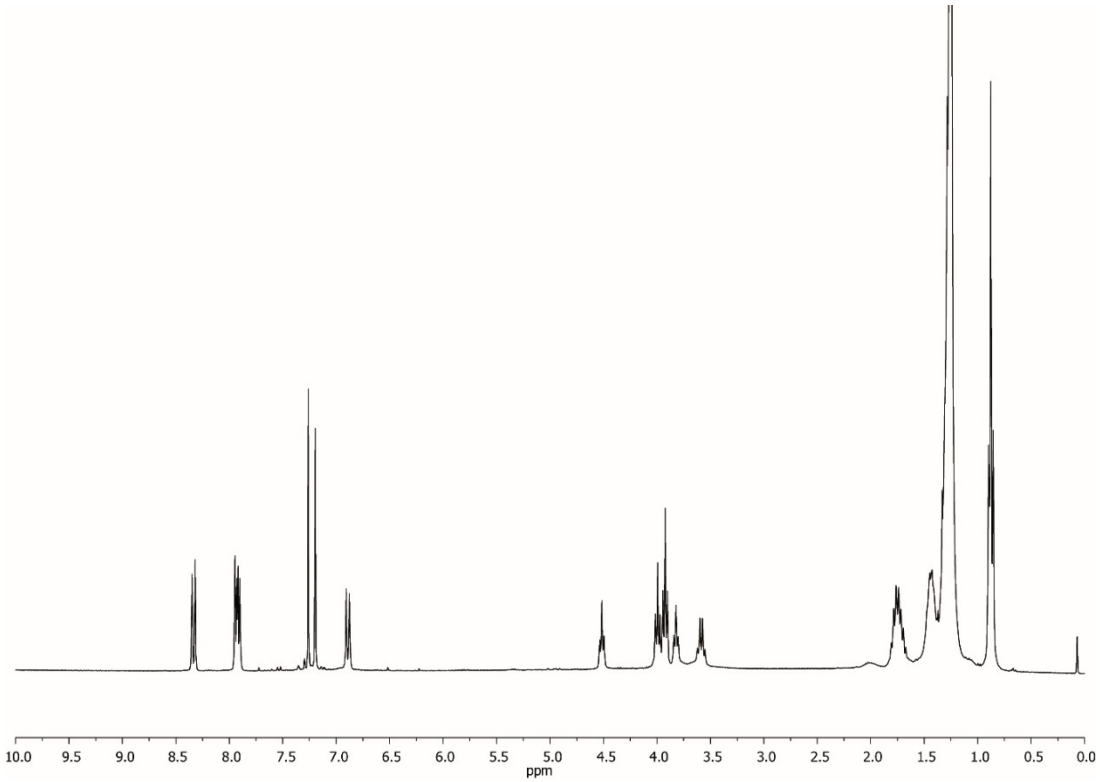
Collection of spectra



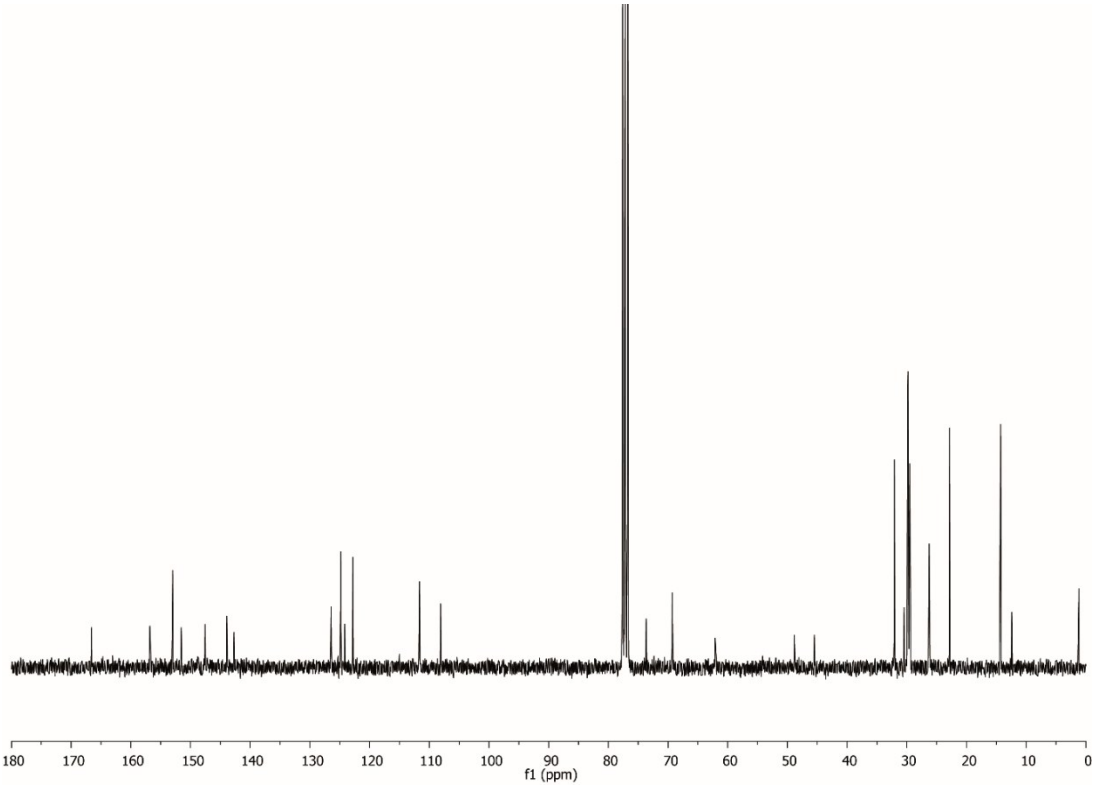
^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) of compound **1**.



^{13}C NMR ($CDCl_3$, 75 MHz, 298 K) of compound **1.**



^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) of compound **2**.



^{13}C NMR ($CDCl_3$, 75 MHz, 298 K) of compound **2.**