Electronic Supplementary Material (ESI) for Soft Matter.

SUPPORTING INFORMATION

FOR

The influence of substituents on gelation and stacking order of oligoaramid - based supramolecular networks

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MATERIALS

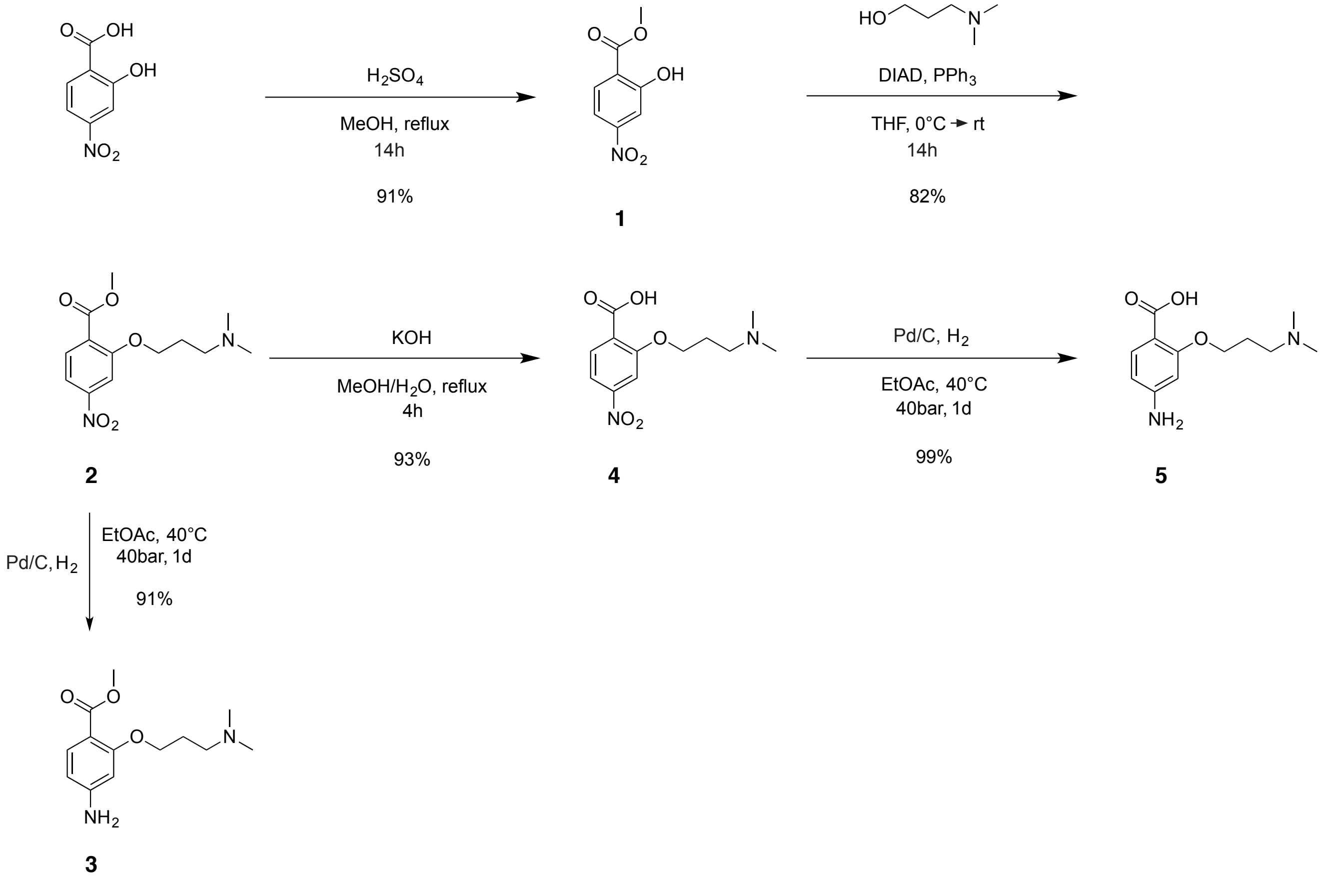
All commercially available reagents and solvents of analytical grade were purchased from Sigma Aldrich, Acros, Fluka, Fisher Scientific, Honeywell or Fluorochem and used without further purification, unless otherwise specified. Solvents of technical grade were purified by distillation, if necessary. Deuterated solvents such as Methanol-d_4, DMSO-d_6, Chloroform-d and D_2O were purchased from Cambridge Isotope Laboratories. Dry NMP over molecular sieves (4 Å) was purchased from Acros. For manual or automated column chromatography silica gel (technical grade, pore size 60 Å, 230 - 400 mesh, 40-63 µm particle size) was used.

TECHNIQUES

Standard ^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded either on a Bruker Avance III 300 spectrometer at 300 MHz (^{1}H) and 75 MHz (^{13}C) or a Bruker DPX 400 spectrometer at 400 MHz (^{1}H) and 100 MHz (^{13}C). All NMR signals were referenced internally to residual solvent signals. Electron spray ionization mass spectra (ESI-MS) were recorded on a Bruker-Ion Trap MS esquire HCT mass spectrometer. High resolution mass spectrometry (HRMS) was performed by means of a Bruker FTMS 4.7 T BioAPEX II ESI-MS. RP-HPLC analysis was performed on a HP 1090 Liquid Chromatograph (Hewlett Packard) using a PerfectSil column (MZ Analysentechnik, Mainz, Germany, 250 x 4.0 mm; 120 ODS - 2.5 µm). Samples were dissolved in ACN and eluted with an acetonitrile/water gradient buffered with 0.1 % TFA starting from 10% acetonitrile rising to 100 % over a period of 40 min. UV signals were detected at 254 nm. Analytical thin layer chromatography was performed on TLC plates from Merck (Kieselgel F-254 pre-coated aluminum sheets) and visualized under UV-light at 254 nm or stained with ninhydrin, $KMnO_4$ or a Silica gel/iodo mixture. Automated column chromatography was realized with an Biotage Isolera One system.

SYNTHESIS

Synthesis hydrophilic building block



Scheme S1. Synthesis pathway for the hydrophilic building block.

Methyl 2-hydroxy-4-nitrobenzoate (1)

4-nitrosalicylic acid (34.67 g, 0.189 mol) was dissolved in methanol (250 mL) and concentrated sulfuric acid (41.6 mL) and heated to reflux for 14 h. Methanol was removed under reduced pressure. The residue was dissolved in saturated $NaHCO_3$ (until slightly basic pH) and extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over magnesium sulfate and evaporated under reduced pressure. After column chromatography (10% ethyl acetate in hexane) the product was obtained as a yellow solid (33.8 g, 0.172 mol) in 90.7% yield. ^{1}H NMR (400 MHz, DMSO-*d₆*) δ (ppm) 3.89 (s, 3 H) 7.68 - 7.73 (m, 1 H) 7.73 - 7.75 (m, 1 H) 7.92 (d, J=8.93 Hz, 1 H) 10.96 (br. s., 1 H); ^{13}C NMR (101 MHz, DMSO- *d₆*) δ ppm 52.68 (s, 1 C) 111.89 (s, 1 C) 113.44 (s, 1 C) 121.20 (s, 1 C) 131.84 (s, 1 C) 150.66 (s, 1 C) 158.73 (s, 1 C) 166.55 (s, 1 C); HR-MS (ESI$^-$): m/z calculated for $[C_8H_6NO_5]^-$: 196.02515, mass found: 196.02502.

Methyl 2-(3-(dimethylamino)propoxy)-4-nitrobenzoate (2)

From hexane recrystallized triphenyl phospine (17.30 g, 0.066 mol) was dissolved in dry THF (140 mL) and cooled to 0°C over an ice bath. Diisopropyl azodicarboxylate (DIAD) (13.34 g, 0.066 mol) was added dropwise under inert atmosphere until a yellow, milky suspension occurred. After stirring for 15 min methyl 2-hydroxy-4-nitrobenzoate (compound 1, 10.0 g, 0.051 mol) dissolved in 40 mL dry tetrahydrofuran and 3-(dimethylamino)-propan-1-ol (6.28 g, 0.061 mol) were added. The reaction mixture was allowed to warm to room temperature and stirred for 14 h under inert atmosphere. After THF was reduced, the residue resolved in 0.1 M HCl and extracted three times with ethyl acetate. The aqueous phase was then basified to pH 10 with saturated $NaHCO_3$ solution and extracted three times with dichloromethane. The combined organic layers were dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue purified with automated column chromatography (10% methanol in dichloromethane) to yield the product as yellow viscous oil, which solidifies eventually (11.7 g, 0.042 mol) in 81.7% yield. ^{1}H NMR (400 MHz, DMSO- *d₆*) δ ppm 1.87 (quin, J=6.54 Hz, 2 H) 2.17 (s, 6 H) 2.41 (t, J=7.03 Hz, 2 H) 3.85 (s, 3 H) 4.21 (t, J=6.17 Hz, 2 H) 7.82 - 7.90 (m, 3 H); ^{13}C NMR (101 MHz, DMSO- *d₆*) δ ppm 26.30 (s, 1 C) 45.04 (s, 2 C) 52.44 (s, 1 C) 55.20 (s, 1 C) 67.34 (s, 1 C) 108.12 (s, 1 C) 114.99 (s, 1 C) 126.47 (s, 1 C) 131.32 (s, 1 C) 150.21 (s, 1 C) 157.55 (s, 1 C) 165.17 (s, 1 C); HR-MS (ESI$^+$): m/z calculated for $[C_{13}H_{19}N_2O_5]^+$: 283.12885, mass found: 283.12901.

Methyl 4-amino-2-(3-(dimethylamino)propoxy)benzoate (3)

Methyl 2-(3-(dimethylamino)propoxy)-4-nitrobenzoate (compound 2, 3.4 g, 0.0121 mol) was dissolved in ethyl acetate (40 mL) and 10% palladium on activated charcoal (0.34 g) was added. The reaction was placed in a hydrogen reactor and stirred at 40°C and 40 bar for 48 hours. After the reaction was complete, the solution was filtered over celite and washed with ethyl acetate. The solvent was removed under reduced pressure to give the product as a yellow solid (2.8 g, 0.011 mol) in 91% yield without further purification. ^{1}H NMR (400 MHz, DMSO- *d*$_6$) δ ppm 1.83 (quin, J=6.63 Hz, 2 H) 2.15 (s, 6 H) 2.42 (t, J=7.03 Hz, 2 H) 3.66 (s, 3 H) 3.91 (t, J=6.24 Hz, 2 H) 5.87 (s, 2 H) 6.12 (d, J=8.56 Hz, 1 H) 6.18 (s, 1 H) 7.48 (d, J=8.56 Hz, 1 H); ^{13}C NMR (101 MHz, DMSO- *d*$_6$) δ ppm 26.72 (s, 1 C) 45.12 (s, 2 C) 50.66 (s, 1 C) 55.62 (s, 1 C) 65.89 (s, 1 C) 97.23 (s, 1 C) 105.46 (s, 1 C) 105.55 (s, 1 C) 133.38 (s, 1 C) 154.51 (s, 1 C) 160.72 (s, 1 C) 165.55 (s, 1 C); HR-MS (ESI$^+$): m/z calculated for $[C_{13}H_{21}N2O_3]^+$: 253.15467, mass found: 253.15499.

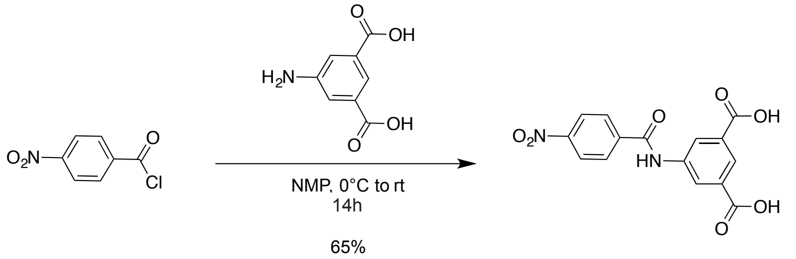
2-(3-(dimethylamino)propoxy)-4-nitrobenzoic acid (4)

Methyl 2-(3-(dimethylamino)propoxy)-4-nitrobenzoate (compound 2, 3.61 g, 0.0128 mol) and potassium hydroxide (0.67 g, 0.0128 mol) were dissolved in a 1:1 mixture of methanol and water (30 mL) and heated to reflux at 85°C. After the reaction was completed (followed with HPLC, 4 h) the reaction was allowed to cool to room temperature. Methanol was removed and the aqueous residue was neutralized to pH 7 with concentrated HCl. The solvent was evaporated and the residue resolved with acetonitrile to precipitate salts and solubilize the product. Salt was filtered off and acetonitrile was removed from the filtrate under reduced pressure to give the product as beige solid (3.19 g, 0.0119 mol) in 93% yield. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ ppm 2.16 (dt, J=10.64, 5.32 Hz, 2 H) 2.74 (s, 6 H) 3.20 - 3.29 (m, 2 H) 4.26 (t, J=5.38 Hz, 2 H) 7.72 (s, 1 H) 7.77 (s, 2 H); ^{13}C NMR (101 MHz, METHANOL-*d*$_4$) δ ppm 24.58 (s, 1 C) 44.18 (s, 2 C) 58.88 (s, 1 C) 69.85 (s, 1 C) 108.24 (s, 1 C) 117.11 (s, 1 C) 132.15 (s, 1 C) 135.78 (s, 1 C) 150.48 (s, 1 C) 157.69 (s, 1 C) 173.07 (s, 1 C); HR-MS (ESI$^+$): m/z calculated for $[C_{12}H_{17}N_2O_5]^+$: 269.11320, mass found: 269.11324.

4-amino-2-(3-(dimethylamino)propoxy)benzoic acid (5)

Compound 4 (2.2 g, 0.0082 mol) was dissolved in methanol/ ethyl acetate (1:3, 40 mL) and 10% palladium on activated charcoal (0.22 g) was added. The reaction was placed in a hydrogen reactor and stirred at 50°C and 40 bar for 24 h. After the reaction was complete, the solution was filtered over celite and washed with methanol. The solvent was removed under reduced pressure to give the product without further purification as beige solid (1.93 g, 0.00812 mol) in 99% yield. ^{1}H NMR (400 MHz, DMSO- *d*$_6$) δ ppm 1.90 (quin, J=6.36 Hz, 2 H) 2.25 (s, 6 H) 2.55 (t, J=6.66 Hz, 2 H) 3.98 (t, J=6.11 Hz, 2 H) 5.81 (br. s., 2 H) 6.14 (dd, J=8.56, 1.96 Hz, 1 H) 6.19 (d, J=1.96 Hz, 1 H) 7.51 (d, J=8.44 Hz, 1 H); ^{13}C NMR (101 MHz, METHANOL-*d*$_4$) δ ppm 24.63 (s, 1 C) 44.10 (s, 2 C) 59.01 (s, 1 C) 68.81 (s, 1 C) 99.29 (s, 1 C) 108.10 (s, 1 C) 116.34 (s, 1 C) 134.75 (s, 1 C) 153.30 (s, 1 C) 160.16 (s, 1 C) 175.45 (s, 1 C); HR-MS (ESI$^+$): m/z calculated for $[C_{12}H_{19}N_2O_3]^+$: 239.13902, mass found: 239.13923.

Synthesis of hydrophobic dimer



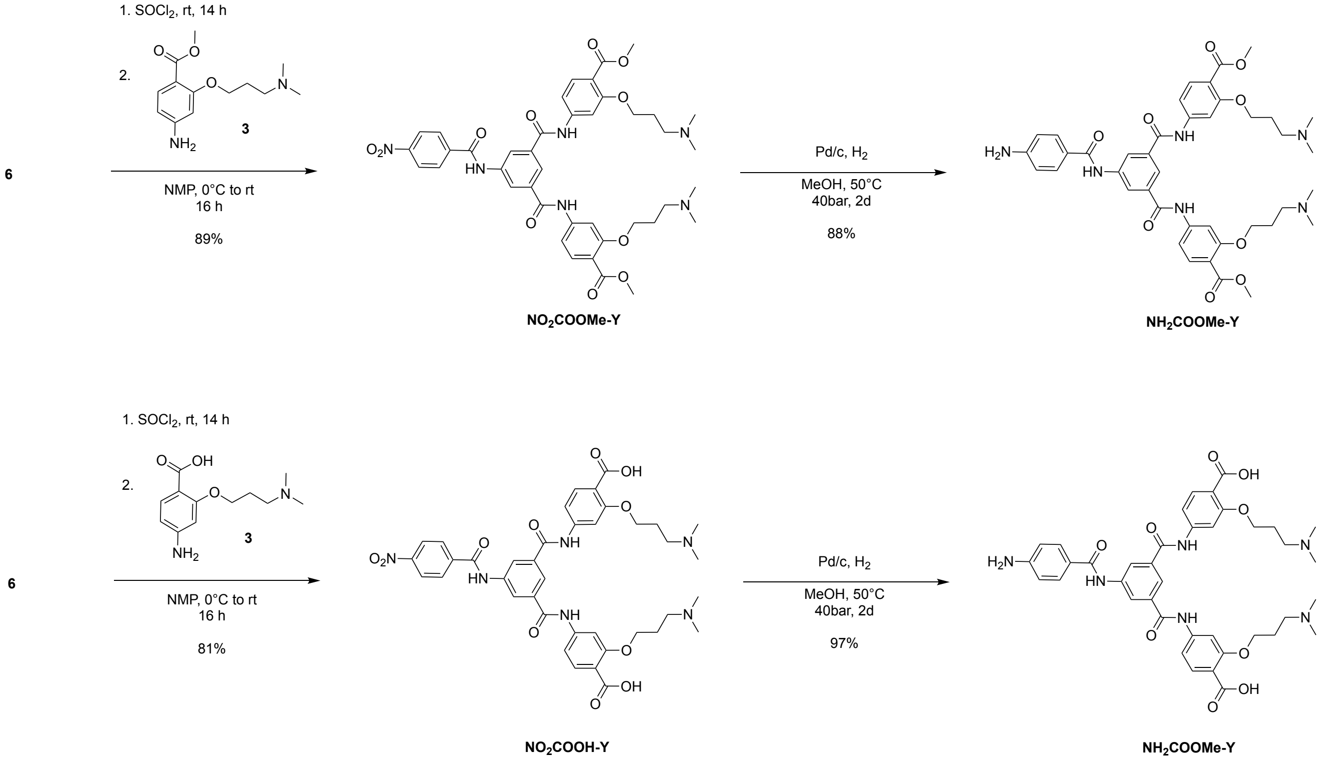
6

Scheme S2. Synthesis pathway for the hydrophobic linker **6**.

5-(4-nitrobenzamido)isophthalic acid (6)

4-nitrobenzoyl chloride (4.92 g, 0.0265 mol) and 5-aminoisophthalic acid (4 g, 0.0221 mol) were placed in a round bottom flask equipped with a stir bar and dried under Schlenk conditions for 2h. After purging with argon, dry NMP (60 mL) was added. The solution was stirred for 14 h under inert atmosphere. The reaction resulted in a turbid solution, which was purred into water and filtered and washed with water to remove NMP. The residue was resolved in a minimum amount of methanol, precipitated in dichloromethane and filtered. After drying, the product was obtained as a white solid (4.75 g, 0.0144 mol) in 65% yield. ^{1}H NMR (400 MHz, DMSO- *d*$_6$) δ (ppm) = 8.17 - 8.29 (m, 3 H) 8.38 (d, J=8.93 Hz, 2 H) 8.67 (d, J=1.47 Hz, 2 H) 10.88 (s, 1 H) 13.30 (br. s., 2 H); ^{13}C NMR (101 MHz, DMSO- *d*$_6$) δ (ppm) 123.59 (s, 2 C) 124.81 (s, 2 C) 125.39 (s, 1 C) 129.30 (s, 2 C) 131.74 (s, 2 C) 139.41 (s, 1 C) 139.93 (s, 1 C) 149.34 (s, 1 C) 164.14 (s, 1 C) 166.41 (s, 2 C); HR-MS (ESI$^-$): m/z calculated for $[C_{15}H_9N_2O_7]^-$: 329.04152, mass found: 329.04175.

Synthesis of oligomers



Scheme S3. Synthesis pathway for the four different potential gelators.

Dimethyl 4,4′-((5-(4-nitrobenzamido)isophthaloyl)bis(azanediyl))bis(2-(3-(dimethylamino)propoxy)benzoate) (NO$_2$COOMe-Y)

All solid compounds were dried under Schlenk conditions prior to use. Dimer 6 (0.6 g, 0.0018 mol) was dissolved in dry NMP (10 mL). Thionyl chloride (0.52 g, 0.0043 mol) was added and the reaction was stirred at room temperature for 14 h. After excess of thionyl chloride was removed via Schlenk vacuum and amino compound 3 (1 g, 0.0043 mol) dissolved in dry NMP (7 mL) was added dropwise over an ice bath. The reaction was allowed to warm to room temperature and stirred for 14 h. After the reaction mixture was precipitated in acetone, filtered and the residue resuspended in acetone for three consecutive times to yield the product in 89% yield as a yellow solid (1.28 g, 0.0016 mol). ^{1}H NMR (400 MHz, DMSO- d_6) δ ppm 2.23 (quin, J=6.45 Hz, 4 H) 2.84 (d, J=4.28 Hz, 12 H) 3.34 (br. s., 4 H) 3.82 (s, 6 H) 4.18 (t, J=5.75 Hz, 4 H) 7.72 - 7.78 (m, 2 H) 7.81 (d, J=8.68 Hz, 2 H) 7.99 (d, J=1.59 Hz, 2 H) 8.28 (m, J=9.05 Hz, 2 H) 8.40 (m, J=8.93 Hz, 2 H) 8.62 (d, J=1.22 Hz, 2 H) 8.83 (s, 1 H) 11.05 (s, 1 H) 11.17 (s, 2 H); ^{13}C NMR (101 MHz, DMSO- d_6) δ ppm 23.49 (s, 2 C) 42.40 (s, 4 C) 51.74 (s, 2 C) 54.72 (s, 2 C) 66.10 (s, 2 C) 104.86 (s, 2 C) 111.81 (s, 1 C) 113.94 (s, 2 C) 123.38 (s, 1 C) 123.60 (s, 3 C) 129.36 (s, 3 C) 132.09 (s, 2 C) 134.79 (s, 2 C) 139.47 (s, 1 C) 139.94 (s, 2 C) 144.58 (s, 2 C) 149.34 (s, 1 C) 158.43 (s, 2 C) 164.20 (s, 1 C) 165.05 (s, 2 C) 165.54 (s, 2 C); HR-MS (ESI$^+$): m/z calculated for $[C_{41}H_{47}N_6O_{11}]^+$: 799.32973, mass found: 799.32922.

Dimethyl 4,4′-((5-(4-aminobenzamido)isophthaloyl)bis(azanediyl))bis(2-(3-(dimethylamino)propoxy)benzoate) (NH$_2$COOMe-Y)

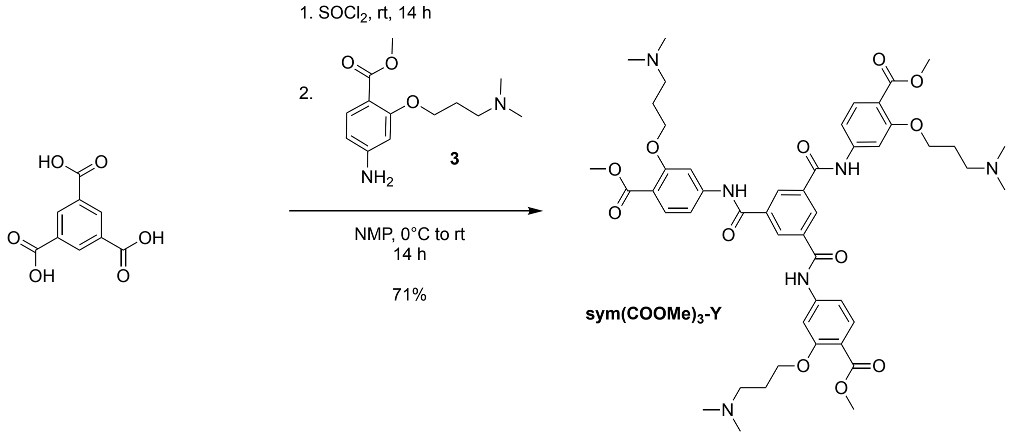
Compound NO$_2$COOMe-Y (1.53 g, 0.0019mol) was dissolved in methanol (50 mL) and 10% palladium on activated charcoal (0.15 g) was added. The reaction was placed in a hydrogen reactor and stirred at 50_C and 40 bar for 48 h. After the reaction was complete, the solution was filtered over celite and washed with methanol. The solvent was removed under reduced pressure to give the product without further purification as a beige solid (1.29 g, 0.0017 mol) in 88% yield. ^{1}H NMR (400 MHz, DMSO- d_6) δ ppm 2.17 - 2.28 (quin, 4 H) 2.83 (d, J=4.77 Hz, 12 H) 3.28 - 3.34 (m, 4 H) 3.82 (s, 6 H) 4.18 (t, J=5.69 Hz, 4 H) 5.90 (br. s., 2 H) 6.64 (d, J=8.68 Hz, 2 H) 7.72 - 7.85 (m, 6 H) 7.99 (d, J=1.59 Hz, 2 H) 8.59 (d, J=1.22 Hz, 2 H) 8.70 (s, 1 H) 10.22 (s, 1 H) 11.11 (s, 2 H); ^{13}C NMR (101 MHz, DMSO- d_6) δ ppm 23.50 (s, 2 C) 42.35 (s, 4 C) 51.74 (s, 2 C) 54.67 (s, 2 C) 66.07 (s, 2 C) 104.84 (s, 2 C) 111.77 (s, 2 C) 112.74 (s, 2 C) 113.88 (s, 3 C) 122.98 (s, 2 C) 129.55 (s, 3 C) 132.10 (s, 2 C) 134.61 (s, 2 C) 140.54 (s, 2 C) 144.66 (s, 2 C) 158.44 (s, 2 C) 165.35 (s, 2 C) 165.52 (s, 1 C) 165.55 (s, 3 C); HR-MS (ESI$^+$) m/z calculated for [C41H49N6O9]$^+$: 769.35555, mass found: 769.35510.

4,4'-((5-(4-Nitrobenzamido)isophthaloyl)bis(azanediyl))bis(2-(3-(dimethylamino)propoxy)benzoic acid) (NO_2COOH-Y)

All solid compounds were dried under Schlenk conditions prior to use. Dimer 6 (0.63 g, 0.0018 mol) was dissolved in dry NMP (10 mL). Thionyl chloride (0.55 g, 0.0046 mol) was added and the reaction was stirred at room temperature over night. After, excess of thionyl chloride was removed via Schlenk vacuum and amino compound 5 (1 g, 0.0042 mol) dissolved in dry NMP (7 mL) was added dropwise over an ice bath. The reaction was allowed to warm to room temperature and stirred for 14 h. After the reaction mixture was precipitated in acetone, filtered and the residue resuspended three times to yield the product in 81% yield as a yellow solid (1.12 g, 0.00015 mol). ^{1}H NMR (400 MHz, DMSO- *d_6*) δ ppm 2.25 (quin, J=6.11 Hz, 4 H) 2.85 (s, 12 H) 3.35 - 3.39 (m, 4 H) 4.21 (t, J=5.69 Hz, 4 H) 7.74 - 7.79 (m, 2 H) 7.84 (d, J=8.56 Hz, 2 H) 8.01 (d, J=1.59 Hz, 2 H) 8.29 (d, J=8.93 Hz, 2 H) 8.41 (d, J=8.93 Hz, 2 H) 8.64 (d, J=1.22 Hz, 2 H) 8.89 (s, 1 H) 11.06 (s, 1 H) 11.20 (s, 2 H) 12.74 (br. s., 2 H); ^{13}C NMR (101 MHz, DMSO- *d_6*) δ ppm 23.26 (s, 2 C) 42.59 (s, 4 C) 55.23 (s, 2 C) 66.62 (s, 2 C) 104.79 (s, 2 C) 111.82 (s, 1 C) 114.58 (s, 2 C) 123.41 (s, 1 C) 123.60 (s, 3 C) 129.38 (s, 3 C) 132.43 (s, 2 C) 134.77 (s, 2 C) 139.49 (s, 1 C) 139.95 (s, 2 C) 144.46 (s, 2 C) 149.34 (s, 1 C) 158.51 (s, 2 C) 164.20 (s, 1 C) 165.01 (s, 2 C) 166.96 (s, 2 C); HR-MS (ESI$^+$) m/z calculated for [$C_{39}H_{43}N_6O_{11}$]$^+$: 771.29843, mass found: 771.9863.

4,4'-((5-(4-Aminobenzamido)isophthaloyl)bis(azanediyl))bis(2-(3-(dimethylamino)propoxy)benzoic acid) (NH_2COOH-Y)

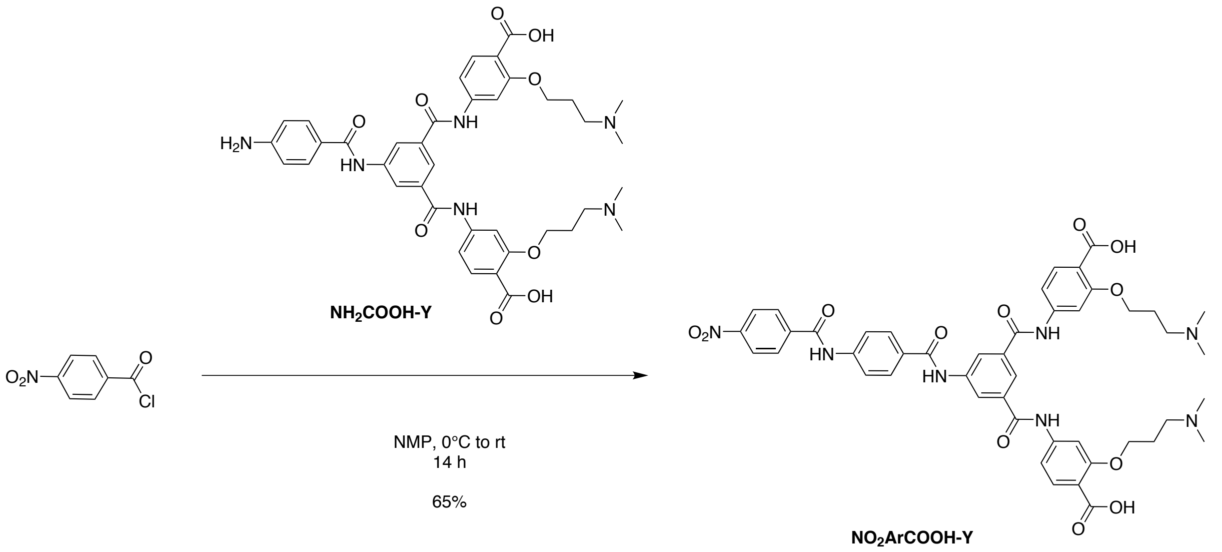
Compound NO_2COOH-Y (1.17 g, 0.00152 mol) was dissolved in methanol (50 mL) and 10% palladium on activated charcol (0.12 g) was added. The reaction was placed in a hydrogen reactor and stirred at 50_C and 40 bar for 48h. After the reaction was complete, the solution was filtered over celite and washed with methanol. The solvent was removed under reduced pressure to give the product without further purification as a beige solid (1.09 g, 0.00147 mol) in 97% yield. ^{1}H NMR (400 MHz, DMSO- *d_6*) δ ppm 2.25 (quin, J=6.02 Hz, 4 H) 2.85 (s, 12 H) 3.32 - 3.40 (m, 4 H) 4.21 (t, J=5.62 Hz, 4 H) 5.86 (br. s., 2 H) 6.63 (d, J=8.68 Hz, 2 H) 7.73 - 7.87 (m, 6 H) 7.97 - 8.03 (m, 2 H) 8.56 - 8.64 (m, 2 H) 8.72 (s, 1 H) 10.22 (s, 1 H) 11.12 (s, 2 H) 12.73 (br. s., 2 H); ^{13}C NMR (101 MHz, DMSO- *d_6*) δ ppm 23.27 (s, 2 C) 42.58 (s, 4 C) 55.20 (s, 2 C) 66.60 (s, 2 C) 104.76 (s, 2 C) 111.78 (s, 1 C) 112.55 (s, 2 C) 114.54 (s, 2 C) 120.33 (s, 2 C) 122.96 (s, 1 C) 129.55 (s, 2 C) 132.42 (s, 2 C) 134.61 (s, 2 C) 140.55 (s, 1 C) 144.52 (s, 2 C) 152.48 (s, 2 C) 158.51 (s, 2 C) 165.32 (s, 2 C) 165.53 (s, 2 C) 166.96 (s, 2 C); HR-MS (ESI$^+$) m/z calculated for [$C_{39}H_{45}N_6O_9$]$^+$: 741.32425, mass found: 741.32355.



Scheme S4. Synthesis pathway for the symmetric analogue **sym(COOMe)-Y**.

Trimethyl 4,4',4''-((benzene-1,3,5-tricarbonyl)tris(azanediyl))tris- (2-(3-(dimethylamino)propoxy)benzoate) (sym(COOMe)$_3$-Y)

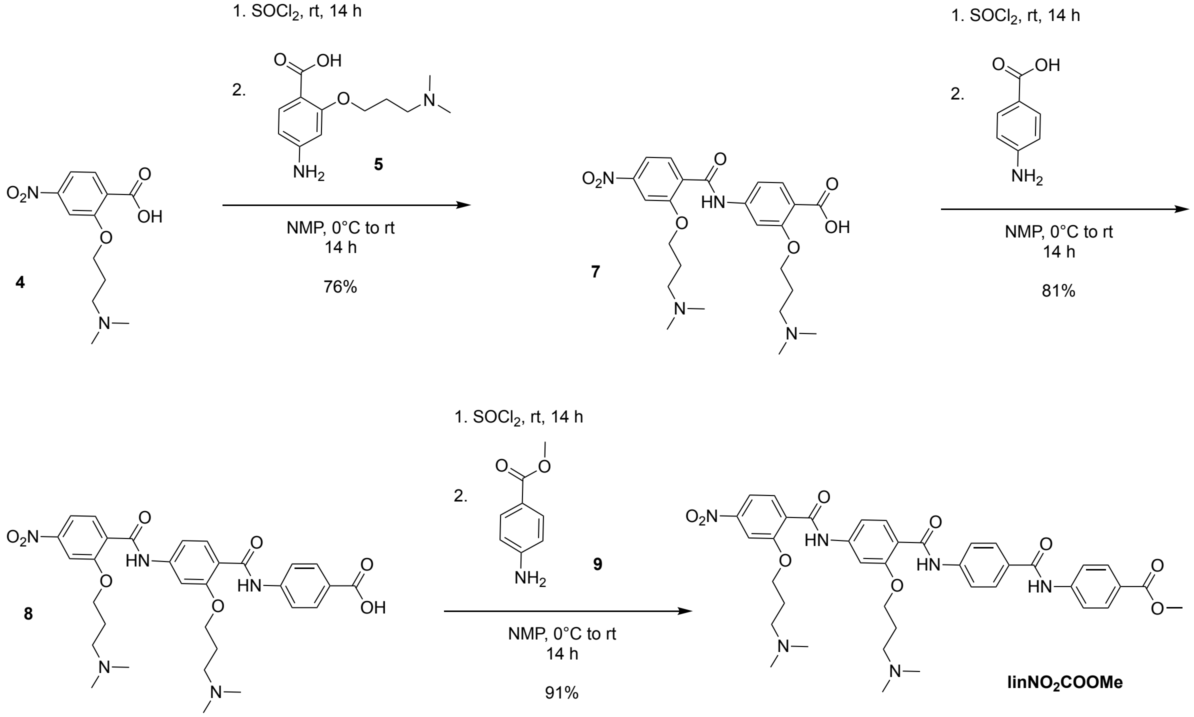
All solid compounds were dried under Schlenk conditions prior to use. Trimesic acid (0.1 g, 0.476 mmol) was dissolved in dry NMP (5 mL). Thionyl chloride (0.2 g, 1.43 mmol) was added and the reaction was stirred at room temperature for 14 h. After, excess of thionyl chloride was removed via Schlenk vacuum, amino compound 3 (0.431 g, 1.43 mmol) dissolved in dry NMP (2 mL) was added dropwise over an ice bath. The reaction was allowed to warm to room temperature and stirred for 14 h. After the reaction mixture was precipitated in acetone, filtered and the residue resuspended three times to yield the product in 65% yield as a brown solid (0.28 g, 0.309 mmol). ^{1}H NMR (400 MHz, DMSO- *d_6*) δ ppm 2.19 - 2.27 (m, 6 H) 2.84 (d, J=4.89 Hz, 18 H) 3.32 (d, J=5.62 Hz, 6 H) 3.83 (s, 9 H) 4.14 - 4.21 (m, 6 H) 7.72 (dd, J=8.68, 1.71 Hz, 3 H) 7.82 (d, J=8.68 Hz, 3 H) 7.97 (d, J=1.71 Hz, 3 H) 8.94 (s, 3 H) 11.25 (s, 3 H); ^{13}C NMR (101 MHz, DMSO- *d_6*) δ ppm 23.52 (s, 1 C) 42.29 (s, 1 C) 51.76 (s, 1 C) 54.56 (s, 1 C) 66.02 (s, 1 C) 104.91 (s, 1 C) 111.83 (s, 1 C) 114.17 (s, 1 C) 130.54 (s, 1 C) 132.12 (s, 1 C) 134.67 (s, 1 C) 144.44 (s, 1 C) 158.41 (s, 1 C) 164.62 (s, 1 C) 165.54 (s, 1 C); HR-MS (ESI$^+$) m/z calculated for [$C_{48}H_{61}N_6O_{12}$]$^+$: 913.43420, mass found: 913.43407.



Scheme S5. Synthesis pathway for **NO_2ArCOOH-Y** with extended hydrophobic part.

4,4'-((5-(4-(4-Nitrobenzamido)benzamido)isophthaloyl)bis(azanediyl))-bis(2-(3-(dimethylamino)propoxy)benzoic acid) (NO_2ArCOOH-Y)

4-nitrobenzoyl chloride (0.2 g, 1.08 mmol) and NH_2COOH-Y (0.4 g, 0.54 mmol) were placed in a round bottom flask equipped with a stir bar. All solid compounds were dried under Schlenk conditions for 2 h. After purging with argon, dry NMP (60 mL) was added. The solution was stirred for 14 h under inert atmosphere. Subsequently, the solution was purred into acetone to precipitate the product. The compound was filtered off and resuspended in acetone three times to remove NMP. After drying the product was obtained as a yellow solid (0.31 g, 0.349 mmol) in 65% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 2.24 (quin, J=5.93 Hz, 4 H) 2.84 (s, 12 H) 3.36 (t, J=6.72 Hz, 4 H) 4.20 (t, J=5.56 Hz, 4 H) 7.74 (dd, J=8.62, 1.53 Hz, 2 H) 7.84 (d, J=8.56 Hz, 2 H) 7.93 - 8.03 (m, 4 H) 8.06 - 8.15 (m, 2 H) 8.25 (d, J=8.93 Hz, 2 H) 8.39 (d, J=8.80 Hz, 2 H) 8.57 - 8.69 (m, 2 H) 8.77 (s, 1 H) 10.66 (s, 1 H) 10.93 (s, 1 H) 11.13 (s, 2 H); ^{13}C NMR (101 MHz, DMSO- d_6) δ (ppm) 23.28 (s, 2 C) 42.64 (s, 4 C) 55.29 (s, 2 C) 66.66 (s, 2 C) 104.75 (s, 2 C) 111.82 (s, 1 C) 114.65 (s, 2 C) 119.72 (s, 2 C) 123.22 (s, 1 C) 123.57 (s, 3 C) 128.71 (s, 2 C) 129.39 (s, 2 C) 129.48 (s, 3 C) 132.46 (s, 2 C) 134.77 (s, 2 C) 140.00 (s, 1 C) 140.22 (s, 1 C) 142.04 (s, 2 C) 144.45 (s, 2 C) 149.30 (s, 1 C) 158.52 (s, 2 C) 164.27 (s, 1 C) 165.20 (s, 2 C) 167.01 (s, 2 C); HR-MS (ESI): not possible due to solubility problems.



Scheme S6. Synthesis pathway for the linear amphiphilic oligomer **linNO_2COOMe**.

2-(3-(Dimethylamino)propoxy)-4-(2-(3-(dimethylamino)propoxy)-4-nitrobenzamido)benzoic acid (7)

All solid compounds were dried under Schlenk conditions prior to use. Compound 4 (0.4 g, 1.49 mmol) was dissolved in dry NMP (7 mL). Thionyl chloride (0.2 g, 1.64 mmol) was added drop-wise and the reaction was stirred at room temperature for 14 h. After, excess of thionyl chloride was removed via Schlenk vacuum and amino compound 5 (0.36 g, 1.49 mmol) dissolved in dry NMP (5 mL) was added slowly over an ice bath. The reaction was allowed to warm to room temperature and stirred for 14 h. After, the reaction mixture was precipitated in ethyl acetate, filtered and the residue resuspended in ethyl acetate for three consecutive times to yield the product in 76% yield as a yellow solid (0.55 g, 1.13 mmol). The product was used without further purification for the next step.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ ppm 2.15 - 2.23 (m, 4 H) 2.66 (s, 6 H) 2.82 (s, 6 H) 3.12 - 3.19 (m, 2 H) 3.23 - 3.31 (m, 2 H) 4.16 (t, *J*=5.62 Hz, 2 H) 4.33 (t, *J*=5.99 Hz, 2 H) 7.38 (dd, *J*=8.56 Hz, 1 H) 7.68 - 7.84 (m, 3 H) 7.88 - 7.9 (m, 2 H) 10.82 (s, 1 H) 12.68 (s, 1 H); ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ ppm 23.33 (s, 1 C) 23.39 (s, 1 C) 41.94 (s, 2 C) 42.51 (s, 2 C) 53.65 (s, 1 C) 54.99 (s, 1 C) 66.26 (s, 1 C) 66.43 (s, 1 C) 103.98 (s, 1 C) 107.78 (s, 1 C) 111.15 (s, 1 C) 114.91 (s, 1 C) 115.78 (s, 1 C) 130.21 (s, 1 C) 131.86 (s, 1 C) 132.69 (s, 1 C) 143.71 (s, 1 C) 149.39 (s, 1 C) 155.75 (s, 1 C) 158.73 (s, 1 C) 164.06 (s, 1 C) 166.79 (s, 1 C); HR-MS (ESI$^+$) m/z calculated for $[C_{24}H_{33}N_4O_7]^+$: 489.23438, mass found: 489.23362.

4-(2-(3-(Dimethylamino)propoxy)-4-(2-(3-(dimethylamino)propoxy)-4-nitrobenzamido)benzamido)benzoic acid (8)

All solid compounds were dried under Schlenk conditions prior to use. Compound 7 (0.1 g, 0.2 mmol) was dissolved in dry NMP (3 mL). Thionyl chloride (0.16 g, 1.37 mmol) was added drop-wise and the reaction was stirred at room temperature for 14 h. After, excess of thionyl chloride was removed via Schlenk vacuum and 4-aminobenzoic acid (0.042 g, 0.31 mmol) dissolved in dry NMP (3 mL) was added slowly over an ice bath. The reaction was allowed to warm to room temperature and stirred for 14 h. After, the reaction mixture was precipitated in acetone, filtered and resuspended for three consecutive times in acetone to yield the product in 81% yield as a brownish solid (0.1 g, 0.164 mmol). The product was used without further purification for the next step. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ ppm 1.86 - 1.96 (m, 2 H) 2.21 - 2.28 (m, 2 H) 2.69 - 2.75 (m, 12 H) 3.13 - 3.22 (m, 2 H) 3.22 - 3.28 (m, 2 H) 4.21 (t, *J*=5.56 Hz, 2 H) 4.34 (t, *J*=5.93 Hz, 2 H) 7.38 (d, *J*=8.44 Hz, 1 H) 7.69 (d, *J*=8.31 Hz, 1 H) 7.76 - 7.84 (m, 2 H) 7.87 - 8.03 (m, 6 H) 10.39 (s, 1 H) 10.79 (s, 1 H) 12.65 (s, 1 H)

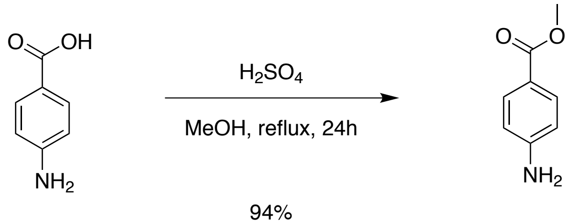
HR-MS (ESI): not possible due to solubility problems.

Methyl 4-(4-(2-(3-(dimethylamino)propoxy)-4-(2-(3-(dimethylamino)propoxy)-4-nitrobenzamido)benzamido)benzamido) benzoate (linNO$_2$COOMe)

All solid compounds were dried under Schlenk conditions prior to use. Compound 8 (0.1 g, 0.17 mmol) was dissolved in dry NMP (3 mL). Thionyl chloride (0.32 g, 2.74 mmol) was added drop-wise and the reaction was stirred at room temperature for 14 h. After, excess of thionyl chloride was removed via Schlenk vacuum and methyl 4-aminobenzoic acid (compound 9, 0.15 g, 0.99 mmol) dissolved in dry NMP (3 mL) was added slowly over an ice bath. The reaction was allowed to warm to room temperature and stirred for 14h. After, the reaction mixture was precipitated in acetone, filtered and resuspended in acetone for three consecutive times to yield the product in 91% yield as a brown solid (0.11 g, 0.15 mmol).

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ ppm 1.86 - 1.96 (m, 2 H) 2.21 - 2.28 (m, 2 H) 2.68 - 2.76 (m, 12 H) 3.12 - 3.23 (m, 2 H) 3.22 - 3.27 (m, 2 H) 3.84 (s, 3 H) 4.20 (t, *J*=5.56 Hz, 2 H) 4.33 (t, *J*=5.93 Hz, 2 H) 7.38 (dd, *J*=8.44 Hz, 1 H) 7.46 (d, *J*=8.31 Hz, 1 H) 7.81 (d, J=8.2 Hz, 2 H) 7.85 - 8.05 (m, 10 H) 10.30 (s, 1 H) 10.47 (s, 1 H) 10.76 (s, 1 H)

HR-MS (ESI): not possible due to solubility problems.

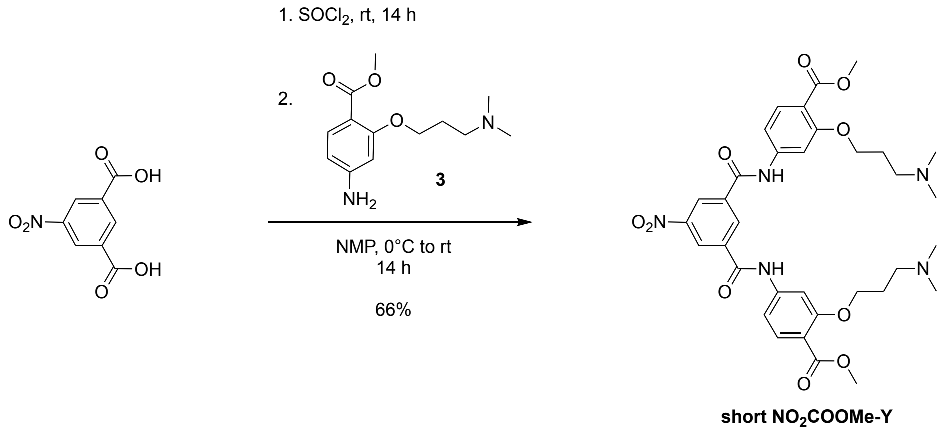


9

Scheme S7. Synthesis of methyl 4-aminobenzoate **9**.

Methyl 4-aminobenzoate (9)

To a solution of 4-aminobenzoic acid (30 g, 0.219 mol) in methanol (500 mL), H_2SO_4 (64.36 g, 0.656 mol) was added drop-wise. The reaction mixture was stirred at 80°C for 24 h under argon atmosphere. After the reaction mixture was cooled to room temperature and neutralized with a saturated $NaHCO_3$ solution until no further gas evolution was observed. The solid was filtered and washed with methanol. The filtrate was concentrated under reduced pressure. The crude product was diluted with water and the aqueous layer was extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over MgSO4 and filtered. Solvent was removed under reduced pressure to afford the product as a white solid in 94% yield. The product was used for the next step without further purification. ^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ (ppm) 3.86 (s, 3 H) 4.07 (br. s., 2 H) 6.60 - 6.68 (m, 2 H) 7.82 - 7.89 (m, 2 H); ^{13}C NMR (101 MHz, CHLOROFORM-*d*) δ (ppm) 51.56 (s, 1 C) 113.76 (s, 2 C) 119.71 (s, 1 C) 131.57 (s, 2 C) 150.79 (s, 1 C) 167.13 (s, 1 C); HR-MS (ESI$^+$): m/z calculated for $[C_8H_9NO_2Na]^+$: 174.05255, mass found: 174.05227.



Scheme S8. Synthesis of short NO2COOMe-Y with reduced hydrophobic part.

Dimethyl 4,4'-((5-nitroisophthaloyl)bis(azanediyl))bis(2-(3-(dimethylamino)propoxy)benzoate) (short NO_2COOMe-Y)

All solid compounds were dried under Schlenk conditions prior to use. 5-nitroisophthalic acid (0.1 g, 0.47 mmol) was dissolved in dry NMP (5 mL). Thionyl chloride (0.16 g, 1.37 mmol) was added drop-wise and the reaction was stirred at room temperature for 14 h. After, excess of thionyl chloride was removed via Schlenk vacuum and amino compound 3 (0.318 g, 1.13 mmol) was added slowly over an ice bath. The reaction was allowed to warm to room temperature and stirred for 14h. After the reaction mixture was precipitated in acetonitrile, filtered and the residue resuspended three times to yield the product in 66% yield as a yellow solid (0.16 g, 0.24 mmol). ^{1}H NMR (400 MHz, DMSO-*d₆*) δ ppm 2.19 - 2.30 (m, 4 H) 2.83 (d, J=4.77 Hz, 12 H) 3.28 - 3.34 (m, 4 H) 3.82 (s, 6 H) 4.17 (t, J=5.75 Hz, 4 H) 7.71 (dd, J=8.62, 1.77 Hz, 2 H) 7.81 (d, J=8.68 Hz, 2 H) 7.94 (d, J=1.71 Hz, 2 H) 8.90 (d, J=1.47 Hz, 2 H) 9.43 (s, 1 H) 11.37 (s, 2 H); ^{13}C NMR (101 MHz, DMSO-*d₆*) δ ppm 23.50 (s, 2 C) 42.31 (s, 4 C) 51.76 (s, 2 C) 54.58 (s, 2 C) 66.04 (s, 2 C) 105.01 (s, 2 C) 111.95 (s, 2 C) 114.42 (s, 2 C) 125.77 (s, 2 C) 132.10 (s, 2 C) 132.68 (s, 1 C) 135.73 (s, 2 C) 144.05 (s, 2 C) 148.08 (s, 1 C) 158.37 (s, 2 C) 163.14 (s, 2 C) 165.48 (s, 2 C); HR-MS (ESI$^+$) m/z calculated for $[C_{34}H_{42}N_5O_{10}]^+$: 680.29262, mass found: 680.29074.

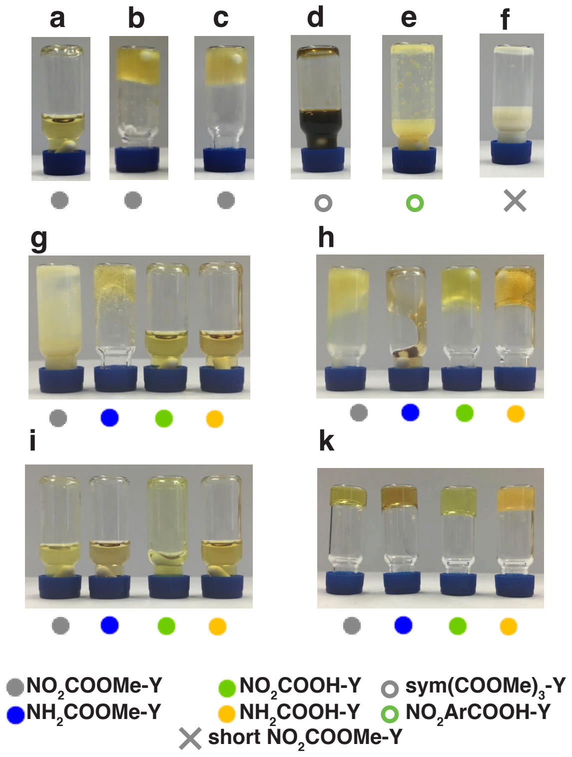


Figure S1. Photographs of gelation experiments of indicated compounds under different conditions: (a) in $H_2O_{millipore}$, (b) in 0.038 M $NaCl_{aq}$, (c) in 0.1 M $NaCl_{aq}$, (d-f) in 0.01 M $NaCl_{aq}$, (g) in 0.1 M $NaOH_{aq}$, (h) in 0.1 M HCl_{aq}, (i) in pure methanol and (k) in methanol/acetonitrile (5:2, v/v).

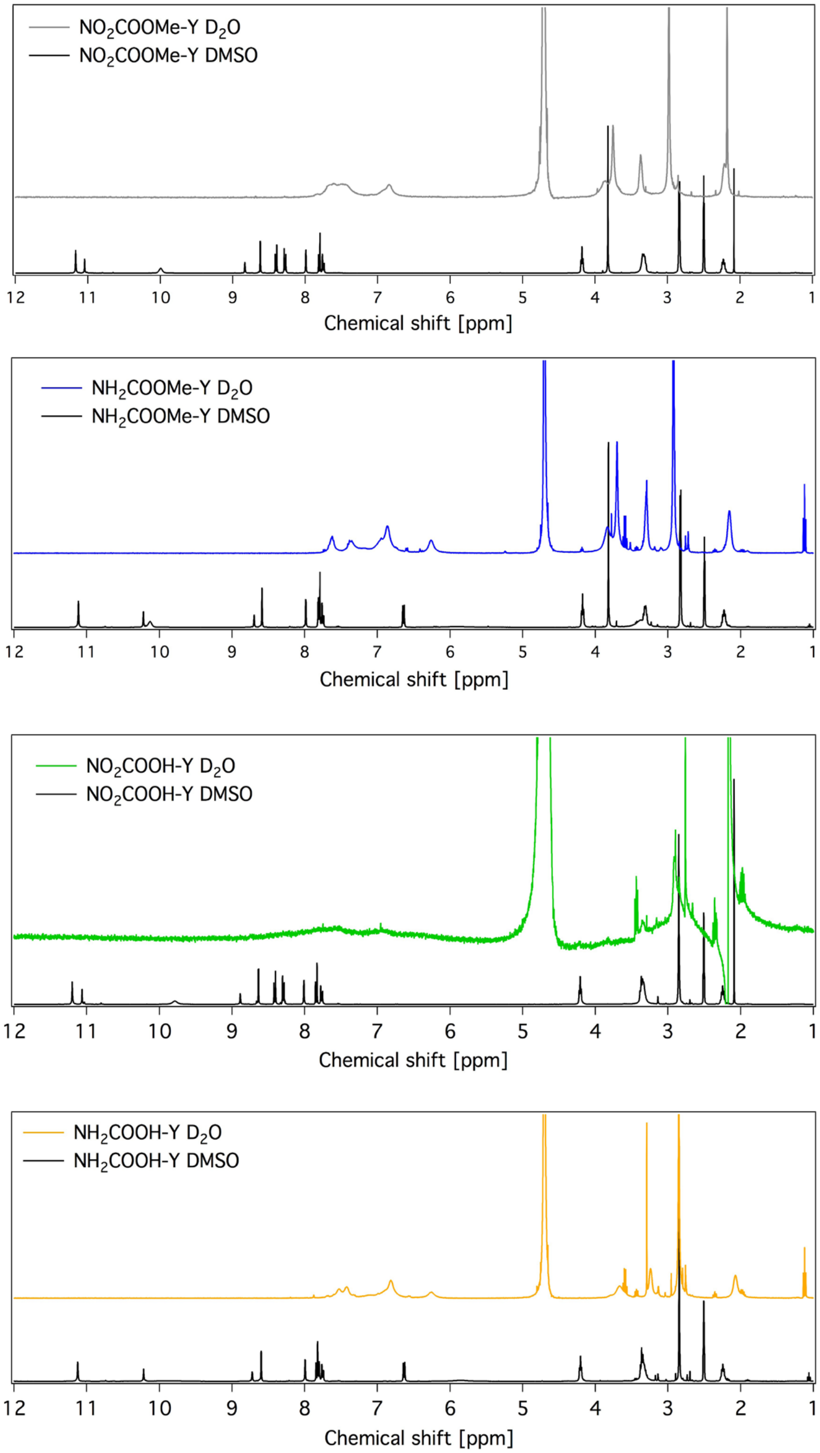


Figure S2. ^{1}H NMR spectra (400 MHz, DMSO-*d*$_6$ and D_2O) of compounds in D_2O and DMSO showing aromatic stacking.

Rheology data

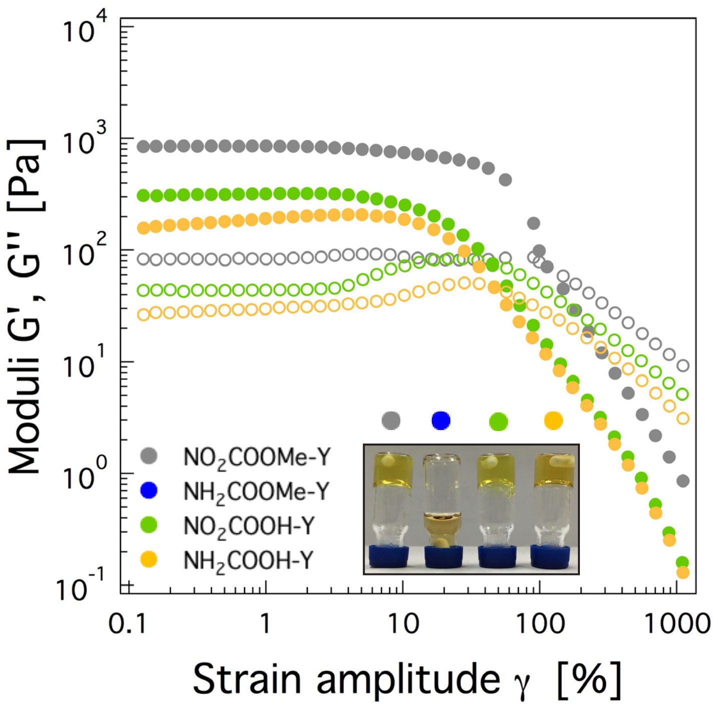


Figure S3. Rheological data derived from oscillatory strain sweep experiments at constant frequencies of 1 Hz at 25°C for gels prepared from 10 mM NaCl$_{aq}$. All gels with a final gelator concentration of 3 wt%.

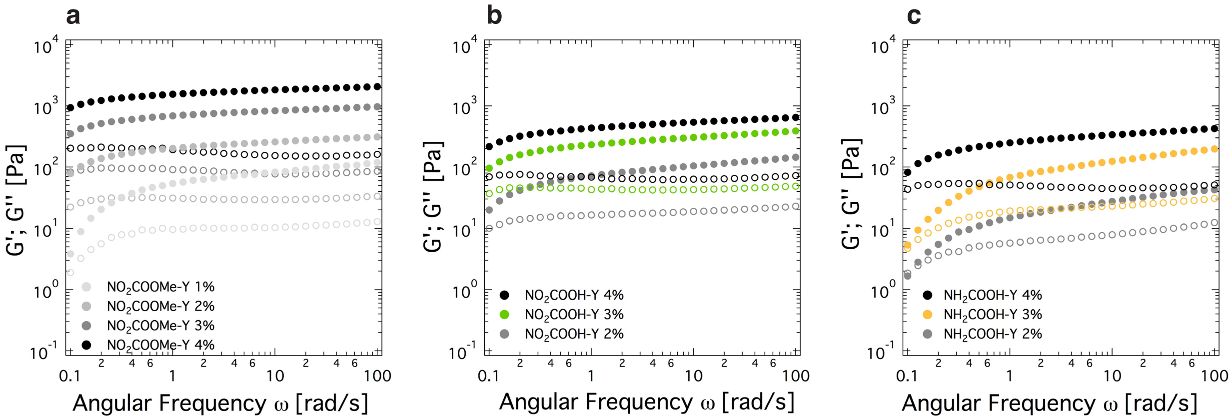


Figure S4. Concentration dependence of rheological data derived from oscillatory frequency sweep experiments at constant strain of 1% and 25°C (within linear viscoelastic range) for gels prepared from (a) **NO$_2$COOMe-Y**, (b) **NO$_2$COOH-Y** and (c) **NH$_2$COOH-Y**. All gels prepared from 10 mM NaCl$_{aq}$ solutions, concentrations in wt%. Filled circles: storage modulus G', open circles: loss modulus G''.

Table S1 Gel strength derived from rheological frequency sweep experiments. G' and G'' reported at frequencies of 1 Hz and constant strain of 1%, which gives representative moduli within the linear viscoelastic range of (a) **NO$_2$COOMe-Y**, (b) **NH$_2$COOMe-Y**, (c) **NO$_2$COOH-Y** and (d) **NH$_2$COOH-Y** under different gelation conditions and constant temperatures of 25°C.

#	Conditions	G‘ (a) [Pa]	G“ (a) [Pa]	G‘ (b) [Pa]	G“ (b) [Pa]	G‘ (c) [Pa]	G“ (c) [Pa]	G‘ (d) [Pa]	G“ (d) [Pa]
0	4% in 10 mM $NaCl_{aq}$	1775	160	N/A	N/A	521	63	322	46
1	3% in 10mM $NaCl_{aq}$	808	80	N/A	N/A	291	43	114	22
2	3% in 38 mM $NaCl_{aq}$	313	36	N/A	N/A	452	47	321	40
3	2% in 10 mM $NaCl_{aq}$	248	29	N/A	N/A	98	18	25	7
4	1% in 10 mM $NaCl_{aq}$	76	10	N/A	N/A	N/A	N/A	N/A	N/A
5	$H_2O_{millipore}$	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

Table S2 Gel strength derived from rheological amplitude sweep experiments. Ratios G'/G'' reported at frequencies of 1 Hz and at a constant strain of 1%, which gives representative moduli within the linear viscoelastic range of (a) **NO_2COOMe-Y**, (b) **NH_2COOMe-Y**, (c) **NO_2COOH-Y** and (d) **NH_2COOH-Y** under different gelation conditions and constant temperatures of 25°C. Criteria for solid-like gel: G’/G’’>1.

#	Conditions	G‘ /G”(a) [Pa]	G‘/G” (b) [Pa]	G‘/G” (c) [Pa]	G‘G/” (d) [Pa]
0	4% in 10 mM $NaCl_{aq}$	11.1	N/A	8.3	7.0
1	3% in 10mM $NaCl_{aq}$	10.1	N/A	6.8	5.2
2	3% in 38 mM $NaCl_{aq}$	8.7	N/A	9.6	8.0
3	2% in 10 mM $NaCl_{aq}$	8.6	N/A	5.4	3.6
4	1% in 10 mM $NaCl_{aq}$	7.6	N/A	N/A	N/A
5	$H_2O_{millipore}$	N/A	N/A	N/A	N/A

SAXS data fitting

Table S3. SAXS data fitting with SasView[2] to flexible cylinder model.

Parameter	NO_2COOMe-Y	NH_2COOMe-Y	NO_2COOH-Y	NH_2COOH-Y
scale	1	2.09	1	0.85
background	1.0 x 10^{-4} cm^{-1}	1.2 x 10^{-4} cm^{-1}	1.0 x 10^{-5} cm^{-1}	4.4 x 10^{-5} cm^{-1}
length	500 nm	4.4 nm	20 nm	10 nm
radius	1.9 nm	1.1 nm	2.0 nm	2.1 nm
sld	41.75 x 10^{-6} nm^{-2}	2.34 x 10^{-6} nm^{-2}	-1.5 x 10^{-6} nm^{-2}	41.6 x 10^{-6} nm^{-2}
sld-solvent	39.143 x 10^{-6} nm^{-2}	0.99 x 10^{-6} nm^{-2}	0.8 x 10^{-6} nm^{-2}	39.3 x 10^{-6} nm^{-2}
Polydispersity	off	off	off	off

UV-vis spectra

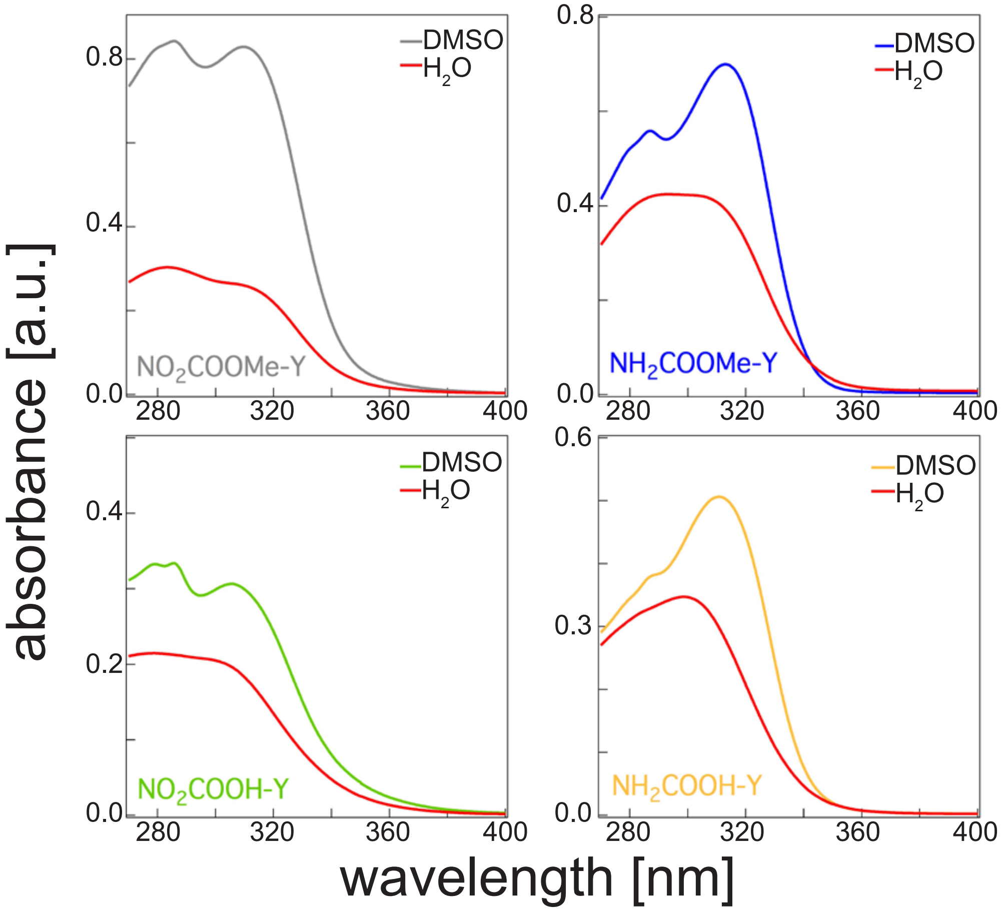


Figure S5. Solvent dependent UV-vis spectra of potential gelator compounds at 25 °C and c = 10 µM.

TEM images

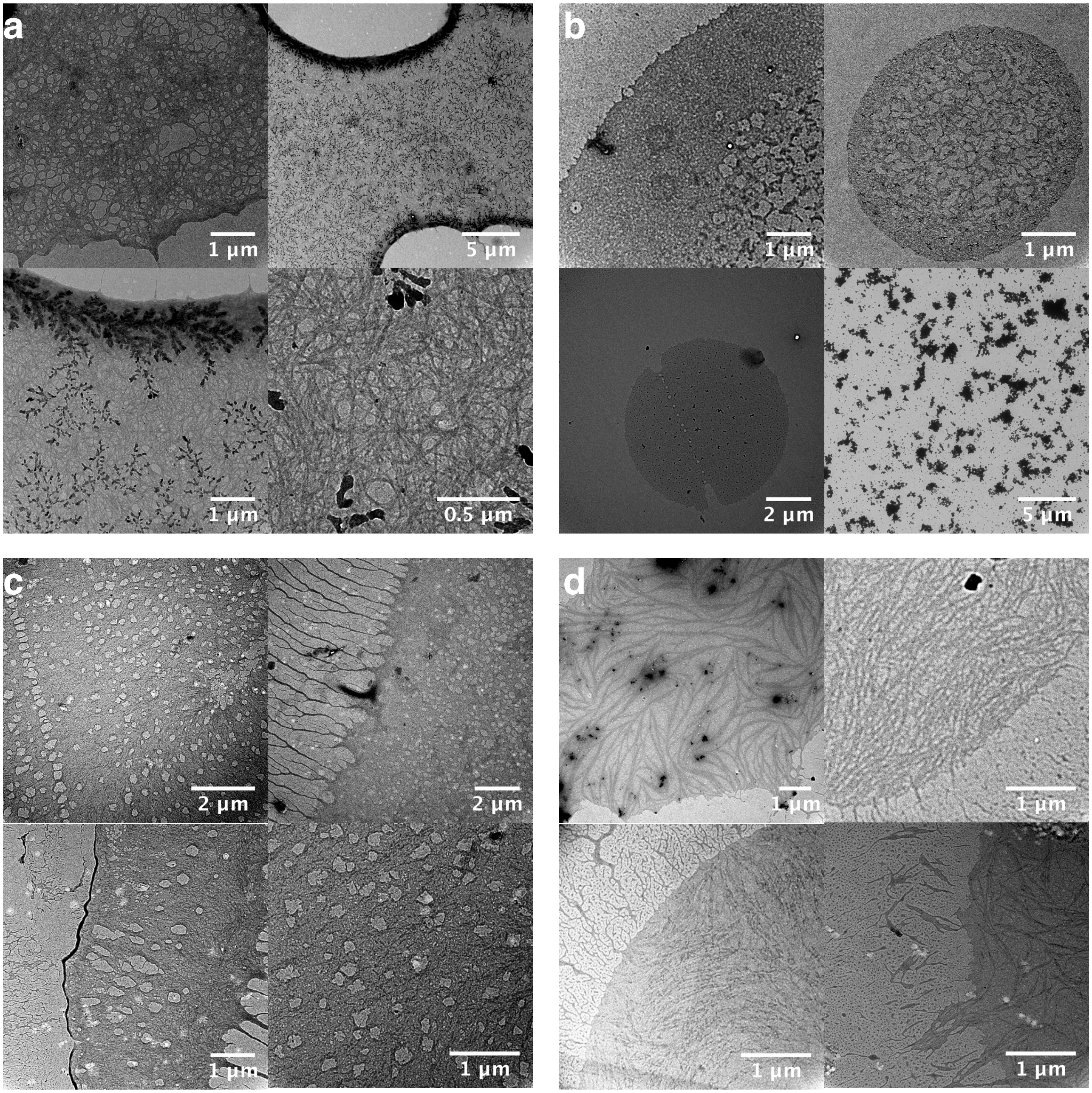


Figure S6. TEM micrographs of (a) **NO_2COOMe-Y**, (b) **NH_2COOMe-Y**, (c) **NO_2COOH-Y** and (d) **NH_2COOH-Y**. All gel samples prepared from 2.5 mg/mL in 10 mM $NaCl_{aq}$.

AFM images

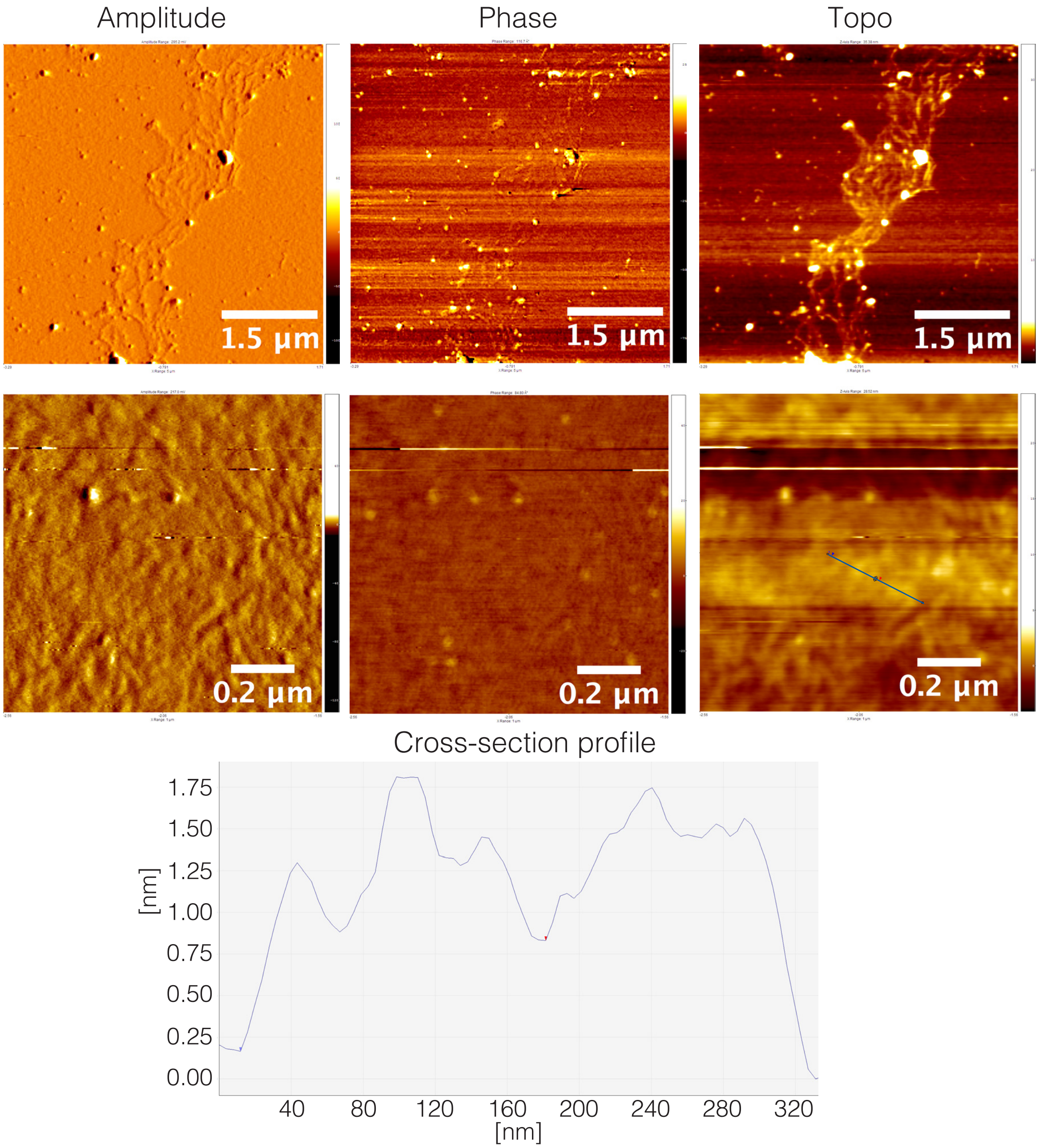
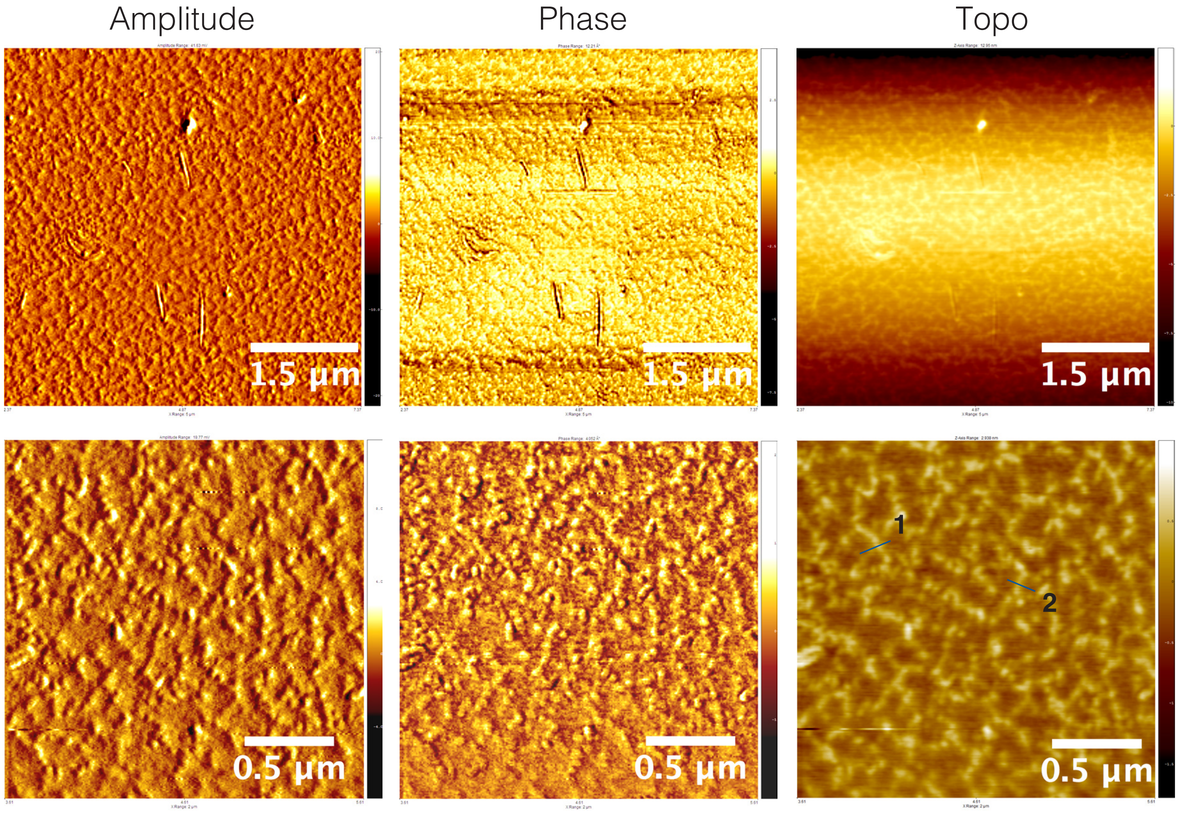


Figure S7. Amplitude-, phase-, and Z-axis-range AFM micrographs of **NO2COOMe-Y** and height-profile for cross-section indicated with blue line. Samples prepared from 2.5 x 10^{-2} mg/mL in 10 x 10^{-2} mM $NaCl_{aq}$ dilutions deposited on mica.



Cross-section profile

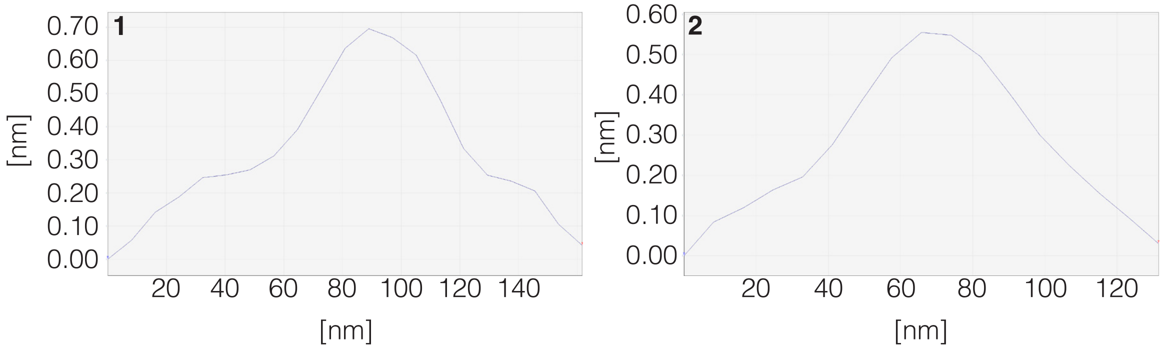


Figure S8. Amplitude-, phase-, and Z-axis-range AFM micrographs of **NH$_2$COOMe-Y** and height-profile for cross-section indicated with blue line. Samples prepared from 2.5 x 10^{-2} mg/mL in 10 x 10^{-2} mM NaCl$_{aq}$ dilutions deposited on mica.

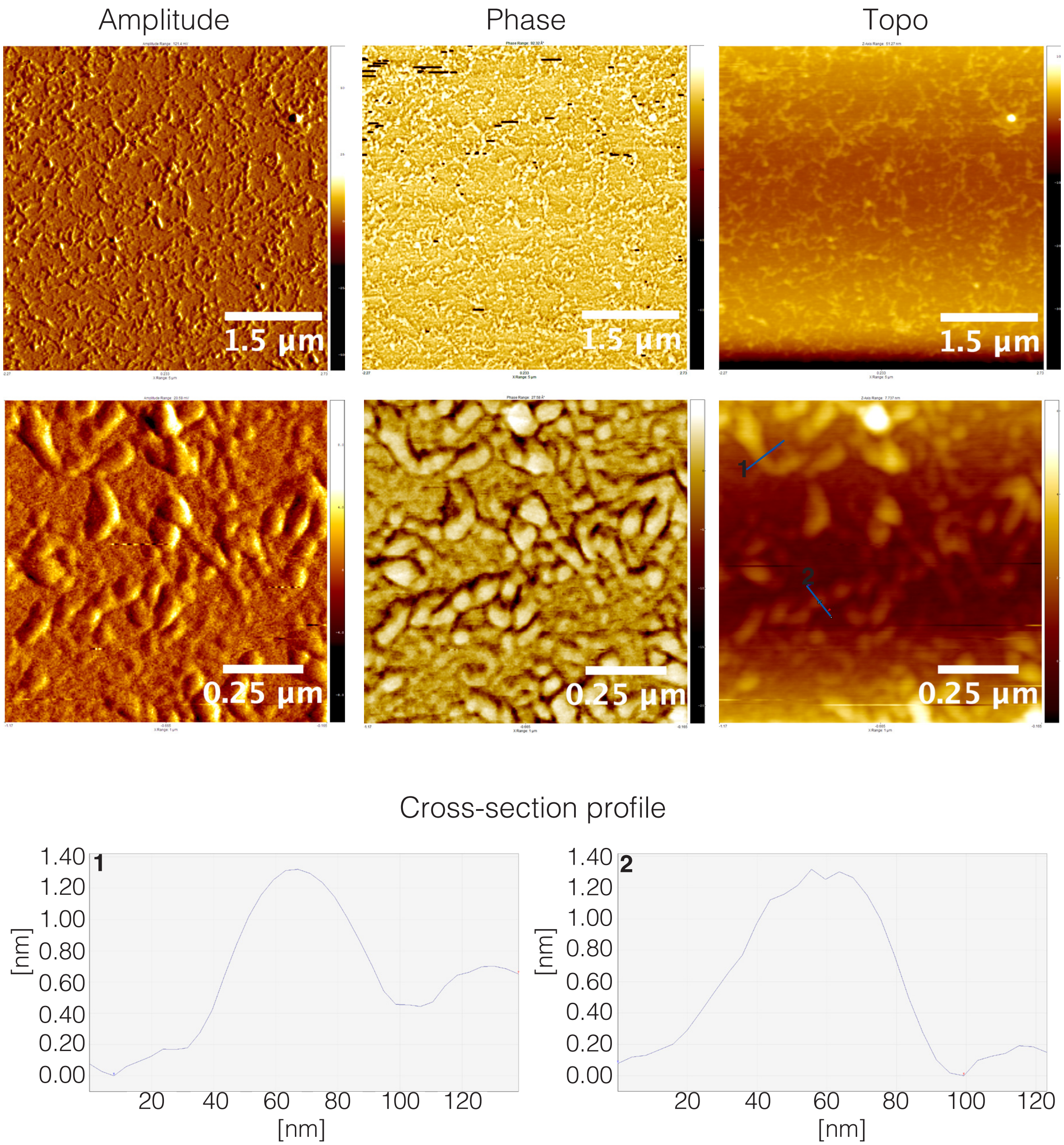


Figure S9. Amplitude-, phase-, and Z-axis-range AFM micrographs of **NO_2COOH-Y** and height-profile for cross-section indicated with blue line. Samples prepared from 2.5 x 10^{-2} mg/mL in 10 x 10^{-2} mM $NaCl_{aq}$ dilutions deposited on mica.

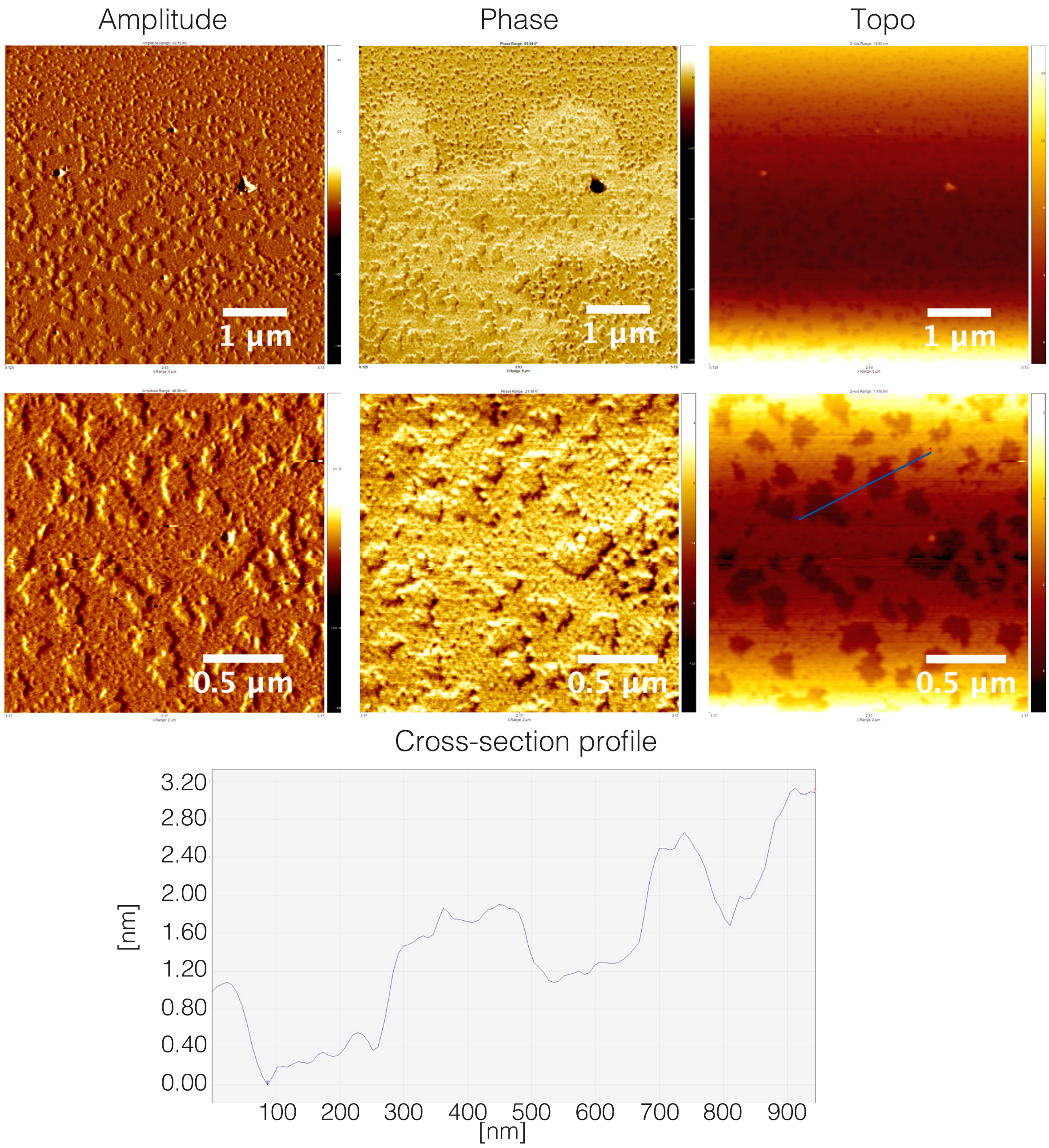


Figure S10. Amplitude-, phase-, and Z-axis-range AFM micrographs of **NH$_2$COOH-Y** and height-profile for cross-section indicated with blue line. Samples prepared from 2.5 x 10^{-2} mg/mL in 10 x 10^{-2} mM NaCl$_{aq}$ dilutions deposited on mica.

References -synthesis part

(1) pKa calculator https://epoch.uky.edu/ace/public/pKa.jsp (accessed Aug 12, 2017).
(2) SasView http://www.sasview.org (accessed Nov 3, 2017).

COMPUTATIONAL PARAMETERS

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S.1 Parameterization and atomic charges calculation

All the investigated monomers (**NO_2COOMe-Y**, **NH_2COOMe-Y**, **NO_2COOH-Y**, **NH_2COOH-Y**, **sym(COOMe)$_3$-Y**, **short NO_2COOMe-Y**, **NO_2ArCOOH-Y**) have been parameterized by means of the second generation General Amber Force Field (GAFF2), an improved version of the original GAFF[1], which proved to be a suitable choice for the description of self-assembling polymeric systems[2-4]. Atomic charges have been obtained according to the chosen force field by means of Restrained Electrostatic Potential (RESP) formalism[5,6], adopting a two-steps protocol. First of all, the structures have been optimized through density functional theory (DFT) calculations, at B3LYP/6-31G(d,p) level of theory *in vacuo*. The obtained geometries have been subsequently used to compute electrostatic potential (ESP) *in vacuo* at HF/6-31G* level of theory. In the first step, atomic charges have been fitted starting from electrostatic potential, imposing a proper value for the overall charge (+3 for **sym(COOMe)$_3$-Y**, +2 for **NO_2COOMe-Y**, **NH_2COOMe-Y** and **short NO_2COOMe-Y**, 0 for **NO_2COOH-Y**, **NH_2COOH-Y** and **NO_2ArCOOH-Y**); in the second phase, charge equivalence for chemically equivalent atoms has been imposed. All calculations have been carried out by means of Gaussian09 software[7]. Monomers structures are shown in Figure S1; atom names, atom types, atomic coordinates and atomic charges are summarized in Table S4-Table S10. TIP3P water model[8] has been chosen for the explicit solvent molecules, while the Na^+ and Cl^- parameters optimized for TIP3P water model have been taken from Joung and Cheatham works[9,10].

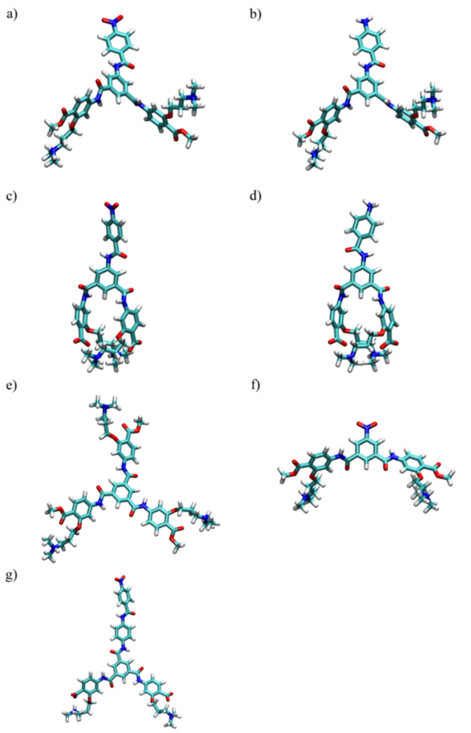

Figure S11. Optimized structures of **NO_2COOMe-Y** (a), **NH_2COOMe-Y** (b), **NO_2COOH-Y** (c), **NH_2COOH-Y** (d), **sym(COOMe)3-Y** (e), **short NO2COOMe-Y** (f) and **NO_2ArCOOH-Y** (g).

Table S4 Atom names, atom types, atomic coordinates and atomic charges for **NO_2COOMe-Y**.

Atom name	Atom type	X	Y	Z	Charge
C1	ca	-4.102	-0.322	3.043	-0.083673
C2	ca	-3.863	-0.342	1.662	0.020684
C3	ca	-4.775	-0.988	0.81	-0.163515
C4	ca	-5.915	-1.61	1.322	0.193116
C5	ca	-6.16	-1.617	2.713	-0.129522
C6	ca	-5.23	-0.961	3.534	-0.188568
N1	ns	-2.721	0.236	1.08	-0.36973
C7	c	-1.927	1.244	1.609	0.654992
O1	o	-2.13	1.771	2.691	-0.517572
O2	os	-6.823	-2.237	0.507	-0.320416
C8	c3	-6.861	-1.936	-0.871	0.096785
C9	c3	-8.207	-2.494	-1.351	-0.000334
C10	c3	-8.432	-2.256	-2.84	-0.128175
N2	nx	-9.842	-2.623	-3.285	-0.006054
C11	c3	-10.132	-4.098	-3.182	-0.325029
C12	c	-7.314	-2.241	3.429	0.771447
O3	os	-8.233	-2.831	2.632	-0.394718
C13	c3	-9.328	-3.436	3.347	-0.046132
C14	ca	-0.791	1.666	0.72	-0.212559
C15	ca	-0.455	3.019	0.717	-0.090956
C16	ca	0.57	3.504	-0.109	0.153924
C17	ca	1.275	2.606	-0.927	-0.090956
C18	ca	0.98	1.241	-0.866	-0.212559
C19	ca	-0.055	0.761	-0.056	-0.039596
N3	ns	0.823	4.883	-0.082	-0.449141
C20	c	1.879	5.569	-0.663	0.643203
O4	o	2.771	5.018	-1.292	-0.479208
C21	c	1.791	0.316	-1.735	0.654992
N4	ns	2.268	-0.804	-1.063	-0.36973
C22	ca	3.103	-1.81	-1.58	0.020684
C23	ca	3.877	-2.549	-0.669	-0.163515
C24	ca	4.715	-3.575	-1.109	0.193116
C25	ca	4.777	-3.905	-2.481	-0.129522
C26	ca	3.987	-3.151	-3.361	-0.188568
C27	ca	3.168	-2.112	-2.946	-0.083673
O5	os	5.488	-4.3	-0.237	-0.320416
C28	c3	5.765	-3.785	1.047	0.096785
C29	c3	6.946	-4.62	1.561	-0.000334
C30	c3	7.378	-4.186	2.957	-0.128175
N5	nx	8.682	-4.839	3.402	-0.006054
C31	c3	8.57	-6.332	3.568	-0.325029
C32	c	5.601	-4.976	-3.118	0.771447
O6	os	6.469	-5.602	-2.291	-0.394718
C33	c3	7.254	-6.627	-2.931	-0.046132
C34	ca	1.867	7.057	-0.448	-0.12112

C35	ca	0.699	7.794	-0.197	-0.100162
C36	ca	0.76	9.173	-0.017	-0.136726
C37	ca	2.001	9.799	-0.092	0.060846
C38	ca	3.174	9.097	-0.359	-0.136726
C39	ca	3.098	7.721	-0.544	-0.100162
N6	no	2.072	11.261	0.109	0.683115
O7	o	1.017	11.851	0.334	-0.41563
O8	o	3.179	11.787	0.039	-0.41563
O9	o	2.01	0.551	-2.91	-0.517572
O10	o	5.508	-5.257	-4.297	-0.566294
O11	o	-7.419	-2.221	4.64	-0.566294
C40	c3	-10.135	-2.108	-4.671	-0.325029
C41	c3	9.224	-4.192	4.65	-0.325029
H1	ha	-0.126	9.766	0.17	0.180403
H2	ha	4.114	9.631	-0.417	0.180403
H3	ha	3.986	7.141	-0.767	0.144384
H4	ha	-0.273	7.311	-0.179	0.144384
H5	hn	0.235	5.416	0.543	0.257362
H6	ha	-1.01	3.689	1.367	0.162604
H7	ha	-0.278	-0.302	-0.027	0.069137
H8	ha	2.058	2.964	-1.579	0.162604
H9	hn	2.17	-0.78	-0.058	0.306625
H10	ha	3.817	-2.308	0.388	0.09433
H11	ha	4.043	-3.41	-4.413	0.190162
H12	ha	2.598	-1.534	-3.658	0.161268
H13	hn	-2.565	0.025	0.104	0.306625
H14	ha	-4.58	-1	-0.258	0.09433
H15	ha	-5.429	-0.966	4.599	0.190162
H16	ha	-3.422	0.193	3.705	0.161268
H17	h1	-9.968	-3.877	2.582	0.092428
H18	h1	-8.964	-4.206	4.031	0.092428
H19	h1	-9.876	-2.687	3.922	0.092428
H20	h1	-6.803	-0.851	-1.039	0.067436
H21	h1	-6.028	-2.411	-1.412	0.067436
H22	hc	-8.228	-3.56	-1.106	0.053459
H23	hc	-8.993	-2.007	-0.76	0.053459
H24	hx	-8.309	-1.199	-3.092	0.121403
H25	hx	-7.754	-2.84	-3.469	0.121403
H26	hx	-11.161	-4.274	-3.497	0.177853
H27	hx	-9.444	-4.629	-3.841	0.177853
H28	hx	-9.998	-4.423	-2.153	0.177853
H29	hx	-11.166	-2.352	-4.929	0.177853
H30	hx	-9.99	-1.028	-4.687	0.177853
H31	hx	-9.451	-2.591	-5.37	0.177853
H32	h1	7.889	-7.04	-2.147	0.092428
H33	h1	6.61	-7.403	-3.35	0.092428
H34	h1	7.861	-6.204	-3.734	0.092428

H35	h1	6.035	-2.72	0.995	0.067436
H36	h1	4.899	-3.884	1.718	0.067436
H37	hc	6.645	-5.671	1.539	0.053459
H38	hc	7.77	-4.498	0.846	0.053459
H39	hx	7.56	-3.109	2.995	0.121403
H40	hx	6.638	-4.435	3.724	0.121403
H41	hx	9.543	-6.724	3.864	0.177853
H42	hx	7.832	-6.537	4.344	0.177853
H43	hx	8.262	-6.779	2.625	0.177853
H44	hx	10.178	-4.655	4.902	0.177853
H45	hx	9.361	-3.127	4.467	0.177853
H46	hx	8.508	-4.347	5.458	0.177853
H47	hn	-10.483	-2.145	-2.643	0.325736
H48	hn	9.362	-4.67	2.652	0.325736

Table S5. Atom names, atom types, atomic coordinates and atomic charges for **NH$_2$COOMe-Y**.

Atom name	Atom type	X	Y	Z	Charge
C1	ca	2.838	8.162	-0.791	-0.117134
C2	ca	1.656	7.445	-0.533	-0.13719
C3	ca	0.516	8.17	-0.147	-0.117134
C4	ca	0.555	9.548	-0.002	-0.249345
C5	ca	1.749	10.261	-0.238	0.395767
C6	ca	2.891	9.537	-0.642	-0.249345
C7	c	1.701	5.972	-0.716	0.618576
O1	o	2.596	5.407	-1.335	-0.488844
N1	nv	1.809	11.621	-0.043	-0.887985
N2	ns	0.657	5.262	-0.115	-0.486885
C8	ca	0.438	3.883	-0.123	0.16978
C9	ca	-0.558	3.375	0.727	-0.076398
C10	ca	-0.857	2.014	0.752	-0.241066
C11	ca	-0.113	1.118	-0.027	-0.022248
C12	ca	0.89	1.62	-0.865	-0.241066
C13	ca	1.147	2.99	-0.948	-0.076398
C14	c	-1.971	1.571	1.657	0.659795
O2	o	-2.187	2.104	2.735	-0.517542
C15	c	1.708	0.702	-1.733	0.659795
O3	o	1.862	0.885	-2.927	-0.517542
N3	ns	-2.74	0.534	1.142	-0.355556
C16	ca	-3.872	-0.06	1.722	0.033244
C17	ca	-4.144	0.001	3.095	-0.08345
C18	ca	-5.267	-0.652	3.581	-0.198506
C19	ca	-6.159	-1.362	2.763	-0.115968
C20	ca	-5.879	-1.398	1.378	0.185442
C21	ca	-4.744	-0.763	0.872	-0.180825
O4	os	-6.755	-2.072	0.565	-0.311855
C22	c3	-6.697	-1.892	-0.832	0.078004
C23	c3	-7.992	-2.522	-1.362	-0.00318

C24	c3	-8.088	-2.425	-2.881	-0.113261
N4	nx	-9.454	-2.842	-3.413	-0.01369
C25	c3	-9.608	-2.489	-4.87	-0.321244
C26	c	-7.312	-1.994	3.472	0.762617
O5	o	-7.461	-1.918	4.676	-0.566041
C27	c3	-9.766	-4.297	-3.172	-0.321244
O6	os	-8.18	-2.659	2.677	-0.389099
C28	c3	-9.276	-3.269	3.384	-0.05193
N5	ns	2.279	-0.357	-1.031	-0.355556
C29	ca	3.159	-1.33	-1.53	0.033244
C30	ca	4.006	-1.976	-0.613	-0.180825
C31	ca	4.897	-2.964	-1.035	0.185442
C32	ca	4.941	-3.353	-2.392	-0.115968
C33	ca	4.078	-2.692	-3.279	-0.198506
C34	ca	3.204	-1.69	-2.884	-0.08345
O7	os	5.742	-3.594	-0.156	-0.311855
C35	c3	6.028	-2.992	1.088	0.078004
C36	c3	7.277	-3.72	1.603	-0.00318
C37	c3	7.731	-3.171	2.951	-0.113261
N6	nx	9.084	-3.721	3.386	-0.01369
C38	c3	9.636	-2.96	4.563	-0.321244
C39	c	5.817	-4.393	-3.008	0.762617
O8	o	5.713	-4.733	-4.171	-0.566041
C40	c3	9.061	-5.203	3.66	-0.321244
O9	os	6.746	-4.925	-2.181	-0.389099
C41	c3	7.58	-5.923	-2.799	-0.05193
H1	ha	-0.342	10.088	0.288	0.164044
H2	ha	3.819	10.068	-0.836	0.164044
H3	ha	3.714	7.61	-1.111	0.146051
H4	ha	-0.439	7.672	0.004	0.146051
H5	hn	0.074	5.785	0.521	0.273589
H6	ha	-1.121	4.038	1.378	0.152149
H7	ha	-0.302	0.05	0.022	0.055532
H8	ha	1.909	3.366	-1.615	0.152149
H9	hn	2.217	-0.286	-0.024	0.301306
H10	ha	3.961	-1.691	0.433	0.098207
H11	ha	4.12	-2.994	-4.319	0.19162
H12	ha	2.577	-1.182	-3.601	0.158065
H13	hn	-2.574	0.316	0.169	0.301306
H14	ha	-4.523	-0.802	-0.189	0.098207
H15	ha	-5.493	-0.625	4.641	0.19162
H16	ha	-3.495	0.557	3.754	0.158065
H17	h1	-9.874	-3.769	2.622	0.093012
H18	h1	-8.91	-3.991	4.117	0.093012
H19	h1	-9.87	-2.513	3.904	0.093012
H20	h1	-6.649	-0.824	-1.092	0.073025
H21	h1	-5.817	-2.388	-1.268	0.073025

H22	hc	-8.017	-3.561	-1.023	0.053965
H23	hc	-8.832	-2	-0.888	0.053965
H24	hx	-7.944	-1.395	-3.22	0.118541
H25	hx	-7.358	-3.059	-3.391	0.118541
H26	hx	-10.758	-4.511	-3.571	0.176862
H27	hx	-9.017	-4.899	-3.688	0.176862
H28	hx	-9.744	-4.5	-2.103	0.176862
H29	hx	-10.614	-2.757	-5.194	0.176862
H30	hx	-9.446	-1.419	-4.995	0.176862
H31	hx	-8.869	-3.051	-5.441	0.176862
H32	h1	8.259	-6.263	-2.016	0.093012
H33	h1	6.978	-6.755	-3.171	0.093012
H34	h1	8.141	-5.496	-3.634	0.093012
H35	h1	6.226	-1.917	0.968	0.073025
H36	h1	5.193	-3.108	1.795	0.073025
H37	hc	7.042	-4.787	1.66	0.053965
H38	hc	8.064	-3.596	0.85	0.053965
H39	hx	7.854	-2.085	2.91	0.118541
H40	hx	7.034	-3.407	3.76	0.118541
H41	hx	10.065	-5.522	3.94	0.176862
H42	hx	8.367	-5.389	4.48	0.176862
H43	hx	8.739	-5.732	2.765	0.176862
H44	hx	10.621	-3.357	4.811	0.176862
H45	hx	9.712	-1.905	4.3	0.176862
H46	hx	8.957	-3.09	5.407	0.176862
H47	hn	2.579	12.125	-0.456	0.394648
H48	hn	0.943	12.135	-0.003	0.394648
H49	hn	9.726	-3.571	2.6	0.325829
H50	hn	-10.149	-2.296	-2.893	0.325829

Table S6. Atom names, atom types, atomic coordinates and atomic charges for **NO$_2$COOH-Y**.

Atom name	Atom type	X	Y	Z	Charge
C1	ca	9.166	-0.869	1.43	-0.084945
C2	ca	8.382	-0.519	0.338	-0.148334
C3	ca	8.979	0	-0.805	-0.084945
C4	ca	10.349	0.186	-0.856	-0.133667
C5	ca	11.1	-0.148	0.253	0.019771
C6	ca	10.533	-0.676	1.399	-0.133667
C7	c	6.9	-0.765	0.446	0.707873
O1	o	6.474	-1.652	1.126	-0.50522
N1	no	12.546	0.056	0.209	0.745727
O2	o	13.174	-0.24	1.179	-0.442791
N2	ns	6.118	0.094	-0.268	-0.483585
C8	ca	4.708	0.122	-0.309	0.11713
C9	ca	4.102	1.342	-0.584	-0.109074
C10	ca	2.727	1.423	-0.715	-0.159243
C11	ca	1.955	0.293	-0.501	-0.048161

C12	ca	2.551	-0.915	-0.175	-0.159243
C13	ca	3.931	-1.019	-0.117	-0.109074
C14	c	2.011	2.732	-0.925	0.664922
O3	o	2.324	3.72	-0.336	-0.540001
C15	c	1.664	-2.115	0.052	0.664922
O4	o	1.897	-3.184	-0.426	-0.540001
N3	ns	0.939	2.645	-1.789	-0.475047
C16	ca	-0.386	3.039	-1.486	0.068037
C17	ca	-0.72	3.959	-0.504	-0.063195
C18	ca	-2.054	4.094	-0.151	-0.325233
C19	ca	-3.079	3.348	-0.725	0.066685
C20	ca	-2.722	2.508	-1.779	0.072516
C21	ca	-1.399	2.364	-2.156	-0.18245
O5	os	-3.642	1.787	-2.48	-0.277888
C22	c3	-3.843	0.478	-2.014	0.009799
C23	c3	-5.189	-0.003	-2.53	-0.053369
C24	c3	-5.379	-1.459	-2.129	-0.106687
N4	nx	-6.751	-1.984	-2.485	-0.067157
C25	c3	-6.733	-3.45	-2.784	-0.248207
C26	c	-4.462	3.407	-0.082	0.710112
O6	o	-4.692	4.388	0.628	-0.706751
C27	c3	-7.743	-1.679	-1.413	-0.248207
O7	o	-5.207	2.421	-0.24	-0.706751
N5	ns	0.573	-1.818	0.822	-0.475047
C28	ca	-0.715	-2.388	0.794	0.068037
C29	ca	-1.743	-1.588	1.273	-0.18245
C30	ca	-3.064	-1.987	1.186	0.072516
C31	ca	-3.408	-3.211	0.608	0.066685
C32	ca	-2.349	-4.011	0.183	-0.325233
C33	ca	-1.018	-3.638	0.273	-0.063195
O8	os	-3.976	-1.06	1.598	-0.277888
C34	c3	-4.653	-1.306	2.804	0.009799
C35	c3	-5.847	-0.367	2.851	-0.053369
C36	c3	-5.413	1.091	2.725	-0.106687
N6	nx	-6.559	2.047	2.952	-0.067157
C37	c3	-6.077	3.434	3.241	-0.248207
C38	c	-4.838	-3.65	0.27	0.710112
O9	o	-4.93	-4.603	-0.504	-0.706751
C39	c3	-7.522	2.067	1.809	-0.248207
O10	o	-5.775	-2.967	0.717	-0.706751
O11	o	13.01	0.506	-0.793	-0.442791
H1	ha	10.825	0.575	-1.732	0.171377
H2	ha	11.15	-0.93	2.236	0.171377
H3	ha	8.697	-1.293	2.297	0.136756
H4	ha	8.393	0.231	-1.675	0.136756
H5	hn	6.565	0.906	-0.629	0.268125
H6	ha	4.694	2.234	-0.694	0.169437

H7	ha	0.886	0.358	-0.575	0.132126
H8	ha	4.386	-1.962	0.099	0.169437
H9	hn	0.599	-0.921	1.25	0.287046
H10	ha	-1.539	-0.61	1.674	0.138768
H11	ha	-2.602	-4.951	-0.267	0.187993
H12	ha	-0.241	-4.281	-0.087	0.15385
H13	hn	0.962	1.827	-2.356	0.287046
H14	ha	-1.168	1.687	-2.96	0.138768
H15	ha	-2.326	4.778	0.629	0.187993
H16	ha	0.039	4.526	-0.005	0.15385
H17	h1	-3.041	-0.164	-2.374	0.072458
H18	h1	-3.843	0.463	-0.935	0.072458
H19	hc	-5.942	0.644	-2.099	0.068461
H20	hc	-5.221	0.107	-3.612	0.068461
H21	hx	-4.665	-2.097	-2.629	0.136907
H22	hx	-5.281	-1.601	-1.067	0.136907
H23	hx	-8.722	-1.984	-1.753	0.145659
H24	hx	-7.438	-2.225	-0.531	0.145659
H25	hx	-7.734	-0.615	-1.226	0.145659
H26	hx	-7.745	-3.764	-2.999	0.145659
H27	hx	-6.109	-3.609	-3.651	0.145659
H28	hx	-6.326	-3.979	-1.93	0.145659
H29	h1	-4.999	-2.325	2.843	0.072458
H30	h1	-3.978	-1.12	3.639	0.072458
H31	hc	-6.508	-0.654	2.045	0.068461
H32	hc	-6.37	-0.527	3.794	0.068461
H33	hx	-4.673	1.328	3.478	0.136907
H34	hx	-5.018	1.317	1.748	0.136907
H35	hx	-8.305	2.774	2.04	0.145659
H36	hx	-6.968	2.36	0.927	0.145659
H37	hx	-7.945	1.081	1.694	0.145659
H38	hx	-6.935	4.04	3.495	0.145659
H39	hx	-5.4	3.391	4.082	0.145659
H40	hx	-5.584	3.826	2.358	0.145659
H41	hn	-7.046	-1.509	-3.322	0.261034
H42	hn	-7.055	1.726	3.767	0.261034

Table S7. Atom names, atom types, atomic coordinates and atomic charges for **NH$_2$COOH-Y**.

Atom name	Atom type	X	Y	Z	Charge
C1	ca	-0.341	3.88	-0.205	-0.056284
C2	ca	0.094	2.964	-1.17	0.053482
C3	ca	-0.849	2.349	-2.005	-0.263581
C4	ca	-2.214	2.521	-1.788	0.18864
C5	ca	-2.681	3.341	-0.745	0.04442
C6	ca	-1.713	4.052	-0.02	-0.311082
N1	ns	1.429	2.506	-1.287	-0.366459
C7	c	2.426	2.571	-0.322	0.585069
O1	o	2.618	3.527	0.411	-0.525585
O2	os	-3.084	1.839	-2.622	-0.336689
C8	c3	-3.282	0.485	-2.227	0.022575
C9	c3	-4.633	0.016	-2.761	-0.00352
C10	c3	-4.793	-1.461	-2.421	-0.174952
N2	nx	-6.179	-2.01	-2.733	-0.09077
C11	c3	-7.18	-1.602	-1.684	-0.254286
C12	c	-4.122	3.357	-0.242	0.624594
O3	o	-4.792	2.285	-0.418	-0.665205
C13	ca	3.178	1.265	-0.193	-0.159681
C14	ca	2.396	0.116	-0.036	-0.021073
C15	ca	2.995	-1.132	0.163	-0.159681
C16	ca	4.385	-1.227	0.152	-0.114039
C17	ca	5.18	-0.074	0.019	0.128154
C18	ca	4.57	1.188	-0.13	-0.114039
N3	ns	6.572	-0.255	0.059	-0.441365
C19	c	7.577	0.678	-0.146	0.668013
O4	o	7.351	1.849	-0.435	-0.503003
C20	c	2.113	-2.35	0.288	0.585069
N4	ns	1.015	-2.121	1.094	-0.366459
C21	ca	-0.277	-2.691	1.042	0.053482
C22	ca	-0.673	-3.649	0.101	-0.056284
C23	ca	-2.03	-3.951	-0.008	-0.311082
C24	ca	-3.02	-3.34	0.776	0.04442
C25	ca	-2.578	-2.488	1.804	0.18864
C26	ca	-1.226	-2.171	1.933	-0.263581
C27	c	-4.472	-3.463	0.307	0.624594
O5	o	-5.212	-2.439	0.484	-0.665205
O6	os	-3.482	-1.985	2.711	-0.336689
C28	c3	-3.531	-0.573	2.867	0.022575
C29	c3	-4.987	-0.113	2.716	-0.00352
C30	c3	-5.018	1.401	2.552	-0.174952
N5	nx	-6.426	1.974	2.519	-0.09077
C31	c3	-7.173	1.552	1.282	-0.254286
C32	ca	8.968	0.152	-0.009	-0.199428
C33	ca	10	0.899	-0.599	-0.099533
C34	ca	11.321	0.488	-0.52	-0.205045

C35	ca	11.665	-0.69	0.173	0.304698
C36	ca	10.636	-1.429	0.787	-0.205045
C37	ca	9.315	-1.012	0.694	-0.099533
N6	nv	12.977	-1.132	0.212	-0.866692
O7	o	2.338	-3.396	-0.307	-0.525585
C38	c3	-6.399	3.477	2.628	-0.254286
O8	o	-4.77	-4.487	-0.351	-0.665205
C39	c3	-6.161	-3.51	-2.878	-0.254286
O9	o	-4.49	4.362	0.413	-0.665205
H1	ha	10.882	-2.329	1.345	0.153137
H2	ha	12.102	1.075	-0.996	0.153137
H3	ha	9.736	1.812	-1.121	0.136925
H4	ha	8.56	-1.591	1.22	0.136925
H5	hn	6.87	-1.216	0.133	0.248359
H6	ha	4.846	-2.205	0.258	0.165629
H7	ha	1.315	0.193	-0.076	0.120778
H8	ha	5.182	2.073	-0.223	0.165629
H9	hn	1.512	1.7	-1.892	0.252881
H10	ha	-0.53	1.68	-2.801	0.167654
H11	ha	-2.078	4.725	0.749	0.179049
H12	ha	0.382	4.398	0.411	0.145175
H13	hn	1.061	-1.265	1.628	0.252881
H14	ha	-0.911	-1.494	2.724	0.167654
H15	ha	-2.373	-4.649	-0.765	0.179049
H16	ha	0.062	-4.102	-0.552	0.145175
H17	h1	-3.131	-0.293	3.853	0.069114
H18	h1	-2.91	-0.086	2.105	0.069114
H19	hc	-5.37	-0.641	1.837	0.066415
H20	hc	-5.565	-0.439	3.592	0.066415
H21	hx	-4.514	1.907	3.381	0.151547
H22	hx	-4.573	1.705	1.601	0.151547
H23	hx	-8.166	2.004	1.315	0.147186
H24	hx	-6.574	1.911	0.432	0.147186
H25	hx	-7.252	0.465	1.278	0.147186
H26	hx	-7.43	3.838	2.616	0.147186
H27	hx	-5.925	3.742	3.575	0.147186
H28	hx	-5.819	3.876	1.776	0.147186
H29	h1	-2.465	-0.146	-2.614	0.069114
H30	h1	-3.297	0.417	-1.136	0.069114
H31	hc	-5.383	0.646	-2.273	0.066415
H32	hc	-4.683	0.187	-3.845	0.066415
H33	hx	-4.091	-2.074	-2.991	0.151547
H34	hx	-4.654	-1.652	-1.352	0.151547
H35	hx	-8.155	-2	-1.968	0.147186
H36	hx	-6.813	-2.022	-0.737	0.147186
H37	hx	-7.215	-0.514	-1.643	0.147186
H38	hx	-7.175	-3.841	-3.109	0.147186

H39	hx	-5.491	-3.764	-3.7	0.147186
H40	hx	-5.798	-3.947	-1.93	0.147186
H41	hn	13.691	-0.437	0.046	0.382208
H42	hn	13.214	-1.777	0.952	0.382208
H43	hn	-6.923	1.601	3.332	0.268275
H44	hn	-6.47	-1.607	-3.628	0.268275

Table S8. Atom names, atom types, atomic coordinates and atomic charges for **sym(COOMe)$_3$-Y**.

Atom name	Atom type	X	Y	Z	Charge
C1	ca	5.851	-1.548	-0.018	-0.181472
C2	ca	7.08	-2.197	-0.086	0.161725
C3	ca	7.14	-3.591	-0.329	-0.032758
C4	ca	5.916	-4.272	-0.469	-0.273979
C5	ca	4.686	-3.638	-0.386	-0.029605
C6	ca	4.646	-2.25	-0.171	0.041122
O1	os	8.197	-1.397	-0.002	-0.33738
C7	c	8.414	-4.335	-0.499	0.62369
H1	ha	5.94	-5.338	-0.658	0.184722
H2	ha	3.767	-4.194	-0.492	0.15484
N1	ns	3.456	-1.507	-0.108	-0.32927
H3	ha	5.858	-0.474	0.141	0.162547
O2	os	8.211	-5.557	-1.022	-0.318769
O3	o	9.537	-3.932	-0.213	-0.457634
C8	c3	9.374	-6.38	-1.214	-0.049041
H4	h1	9.002	-7.316	-1.627	0.090082
H5	h1	10.066	-5.905	-1.914	0.090082
H6	h1	9.881	-6.557	-0.263	0.090082
C9	c3	8.988	-1.487	1.187	0.027983
C10	c3	10.46	-1.306	0.772	0.013144
H7	h1	8.669	-0.707	1.89	0.078033
H8	h1	8.841	-2.46	1.663	0.078033
C11	c3	11.363	-2.207	1.605	-0.120441
H9	hc	10.497	-1.605	-0.275	0.052564
H10	hc	10.767	-0.256	0.85	0.052564
N2	nx	12.806	-2.237	1.11	-0.038899
H11	hx	11.413	-1.892	2.65	0.113799
H12	hx	11.013	-3.239	1.55	0.113799
C12	c3	13.684	-3.008	2.06	-0.226635
C13	c3	12.923	-2.774	-0.296	-0.226635
H13	hn	13.147	-1.271	1.098	0.311715
H14	hx	14.717	-2.952	1.716	0.146203
H15	hx	13.597	-2.574	3.056	0.146203
H16	hx	13.348	-4.045	2.072	0.146203
H17	hx	13.977	-2.929	-0.523	0.146203
H18	hx	12.367	-3.711	-0.35	0.146203
H19	hx	12.495	-2.055	-0.991	0.146203
H20	hn	3.579	-0.517	0.049	0.276326

C14	c	2.157	-1.965	-0.186	0.549723
C15	ca	1.081	-0.907	-0.152	-0.061542
O4	o	1.857	-3.149	-0.267	-0.504187
C16	ca	-0.219	-1.362	0.111	-0.104202
C17	ca	-1.294	-0.474	0.135	-0.061542
C18	ca	-1.061	0.892	-0.082	-0.104202
C19	ca	0.225	1.361	-0.35	-0.061542
C20	ca	1.29	0.45	-0.402	-0.104202
H21	ha	-0.334	-2.422	0.307	0.148654
C21	c	-2.721	-0.87	0.422	0.549723
H22	ha	-1.929	1.543	-0.057	0.148654
C22	c	0.57	2.8	-0.644	0.549723
H23	ha	2.26	0.854	-0.675	0.148654
O5	o	1.635	3.086	-1.176	-0.504187
N3	ns	-0.372	3.735	-0.264	-0.32927
H24	hn	-1.157	3.393	0.27	0.276326
C23	ca	-0.329	5.128	-0.431	0.041122
C24	ca	-1.377	5.875	0.129	-0.181472
C25	ca	-1.42	7.261	0.014	0.161725
C26	ca	-0.391	7.954	-0.671	-0.032758
C27	ca	0.642	7.179	-1.231	-0.273979
C28	ca	0.689	5.797	-1.132	-0.029605
H25	ha	-2.176	5.391	0.683	0.162547
O6	os	-2.446	7.897	0.673	-0.33738
C29	c	-0.334	9.434	-0.77	0.62369
H26	ha	1.44	7.69	-1.757	0.184722
H27	ha	1.501	5.238	-1.571	0.15484
O7	os	0.869	9.859	-1.191	-0.318769
O8	o	-1.245	10.216	-0.512	-0.457634
C30	c3	1.037	11.277	-1.353	-0.049041
H28	h1	2.05	11.408	-1.73	0.090082
H29	h1	0.311	11.672	-2.068	0.090082
H30	h1	0.921	11.788	-0.394	0.090082
C31	c3	-3.494	8.461	-0.125	0.027983
C32	c3	-3.97	9.742	0.588	0.013144
H31	h1	-3.119	8.691	-1.126	0.078033
H32	h1	-4.305	7.729	-0.22	0.078033
C33	c3	-4.278	10.838	-0.425	-0.120441
H33	hc	-4.83	9.531	1.231	0.052564
H34	hc	-3.131	10.043	1.216	0.052564
N4	nx	-4.394	12.235	0.186	-0.038899
H35	hx	-3.459	10.911	-1.142	0.113799
H36	hx	-5.217	10.669	-0.961	0.113799
H37	hn	-4.536	12.861	-0.612	0.311715
C34	c3	-5.59	12.405	1.081	-0.226635
C35	c3	-3.12	12.688	0.859	-0.226635
H38	hx	-5.647	13.446	1.399	0.146203

H39	hx	-6.489	12.132	0.528	0.146203
H40	hx	-5.473	11.759	1.95	0.146203
H41	hx	-3.157	13.773	0.967	0.146203
H42	hx	-3.057	12.223	1.841	0.146203
H43	hx	-2.271	12.376	0.251	0.146203
O9	o	-3.537	-0.034	0.788	-0.504187
N5	ns	-3.02	-2.204	0.228	-0.32927
H44	hn	-2.297	-2.771	-0.19	0.276326
C36	ca	-4.232	-2.869	0.471	0.041122
C37	ca	-4.311	-4.219	0.097	-0.181472
C38	ca	-5.462	-4.967	0.323	0.161725
C39	ca	-6.583	-4.378	0.959	-0.032758
C40	ca	-6.481	-3.02	1.313	-0.273979
C41	ca	-5.346	-2.26	1.074	-0.029605
H45	ha	-3.468	-4.722	-0.367	0.162547
O10	os	-5.396	-6.3	-0.013	-0.33738
C42	c	-7.811	-5.135	1.312	0.62369
H46	ha	-7.326	-2.553	1.802	0.184722
H47	ha	-5.307	-1.218	1.354	0.15484
O11	os	-8.581	-4.46	2.181	-0.318769
O12	o	-8.129	-6.241	0.886	-0.457634
C43	c3	-9.808	-5.092	2.586	-0.049041
H48	h1	-10.279	-4.394	3.276	0.090082
H49	h1	-10.453	-5.267	1.722	0.090082
H50	h1	-9.602	-6.041	3.086	0.090082
C44	c3	-6.158	-6.737	-1.14	0.027983
C45	c3	-6.574	-8.178	-0.84	0.013144
H51	h1	-7.049	-6.116	-1.264	0.078033
H52	h1	-5.544	-6.664	-2.048	0.078033
C46	c3	-7.619	-8.715	-1.821	-0.120441
H53	hc	-5.695	-8.831	-0.823	0.052564
H54	hc	-6.986	-8.14	0.171	0.052564
N6	nx	-8.559	-9.698	-1.128	-0.038899
H55	hx	-8.264	-7.927	-2.221	0.113799
H56	hx	-7.169	-9.249	-2.661	0.113799
C47	c3	-9.175	-10.677	-2.088	-0.226635
H57	hn	-7.984	-10.235	-0.471	0.311715
C48	c3	-9.616	-8.986	-0.317	-0.226635
H58	hx	-9.843	-11.341	-1.538	0.146203
H59	hx	-9.738	-10.119	-2.836	0.146203
H60	hx	-8.384	-11.254	-2.567	0.146203
H61	hx	-10.121	-9.718	0.313	0.146203
H62	hx	-9.155	-8.202	0.285	0.146203
H63	hx	-10.327	-8.545	-1.017	0.146203

Table S9. Atom names, atom types, atomic coordinates and atomic charges for **short NO_2COOMe-Y**.

Atom name	Atom type	X	Y	Z	Charge

C1	ca	0	1.268	0	-0.046885
C2	ca	-1.205	1.96	0.171	-0.119561
C3	ca	-1.206	3.359	0.168	-0.091749
C4	ca	0	4.029	0	0.027234
C5	ca	1.206	3.359	-0.168	-0.091749
C6	ca	1.205	1.96	-0.171	-0.119561
C7	c	-2.48	1.163	0.288	0.578639
H1	ha	-2.114	3.943	0.261	0.154664
N1	no	0	5.507	-0.001	0.663528
H2	ha	2.114	3.943	-0.261	0.154664
C8	c	2.48	1.163	-0.288	0.578639
H3	ha	0	0.184	0	0.168566
O1	o	1.08	6.069	-0.164	-0.399835
O2	o	-1.08	6.069	0.162	-0.399835
O3	o	2.627	0.107	0.315	-0.522828
N2	ns	3.427	1.729	-1.112	-0.287495
H4	hn	3.123	2.519	-1.664	0.271664
C9	ca	4.733	1.287	-1.392	0.005279
C10	ca	5.418	1.919	-2.439	-0.197868
C11	ca	6.713	1.531	-2.737	-0.133235
C12	ca	7.381	0.53	-2.017	-0.148531
C13	ca	6.681	-0.084	-0.954	0.155482
C14	ca	5.365	0.279	-0.651	-0.042549
H5	ha	4.938	2.703	-3.016	0.170106
H6	ha	7.257	2.003	-3.547	0.183489
C15	c	8.775	0.243	-2.475	0.783287
O4	os	7.337	-1.046	-0.233	-0.303507
H7	ha	4.807	-0.208	0.133	0.081095
O5	os	9.413	-0.731	-1.79	-0.39988
O6	o	9.294	0.839	-3.398	-0.567809
C16	c3	10.748	-1.003	-2.259	-0.038961
H8	h1	11.122	-1.807	-1.624	0.091437
H9	h1	10.734	-1.317	-3.305	0.091437
H10	h1	11.378	-0.116	-2.168	0.091437
C17	c3	6.762	-1.539	0.959	0.063717
C18	c3	7.869	-2.382	1.603	-0.015023
H11	h1	6.461	-0.717	1.623	0.084708
H12	h1	5.871	-2.15	0.752	0.084708
C19	c3	7.415	-2.997	2.923	-0.118246
H13	hc	8.169	-3.148	0.883	0.059343
H14	hc	8.734	-1.725	1.763	0.059343
N3	nx	8.561	-3.636	3.697	-0.015026
H15	hx	6.997	-2.236	3.588	0.121059
H16	hx	6.665	-3.782	2.787	0.121059
C20	c3	8.147	-3.994	5.101	-0.327982
C21	c3	9.166	-4.822	2.991	-0.327982
H17	hx	9.009	-4.397	5.633	0.179183

H18	hx	7.782	-3.098	5.603	0.179183
H19	hx	7.357	-4.744	5.047	0.179183
H20	hx	9.985	-5.209	3.598	0.179183
H21	hx	8.393	-5.583	2.875	0.179183
H22	hx	9.539	-4.511	2.017	0.179183
H23	hn	9.296	-2.924	3.769	0.324796
N4	ns	-3.427	1.729	1.112	-0.287495
O7	o	-2.627	0.107	-0.315	-0.522828
C22	ca	-4.733	1.287	1.392	0.005279
H24	hn	-3.123	2.519	1.664	0.271664
C23	ca	-5.418	1.919	2.439	-0.197868
C24	ca	-6.713	1.532	2.737	-0.133235
C25	ca	-7.381	0.53	2.017	-0.148531
C26	ca	-6.681	-0.084	0.954	0.155482
C27	ca	-5.365	0.279	0.651	-0.042549
H25	ha	-4.938	2.704	3.016	0.170106
H26	ha	-7.257	2.004	3.547	0.183489
C28	c	-8.775	0.243	2.475	0.783287
O8	os	-7.337	-1.046	0.233	-0.303507
H27	ha	-4.807	-0.208	-0.133	0.081095
O9	os	-9.414	-0.729	1.789	-0.39988
O10	o	-9.293	0.839	3.399	-0.567809
C29	c3	-10.749	-1.001	2.258	-0.038961
H28	h1	-11.124	-1.803	1.621	0.091437
H29	h1	-10.735	-1.316	3.303	0.091437
H30	h1	-11.379	-0.113	2.168	0.091437
C30	c3	-6.762	-1.54	-0.958	0.063717
C31	c3	-7.869	-2.383	-1.603	-0.015023
H31	h1	-6.461	-0.718	-1.623	0.084708
H32	h1	-5.871	-2.151	-0.751	0.084708
C32	c3	-7.414	-2.998	-2.922	-0.118246
H33	hc	-8.169	-3.148	-0.882	0.059343
H34	hc	-8.733	-1.726	-1.763	0.059343
N5	nx	-8.561	-3.637	-3.697	-0.015026
H35	hx	-6.997	-2.238	-3.587	0.121059
H36	hx	-6.665	-3.783	-2.785	0.121059
C33	c3	-8.147	-3.995	-5.1	-0.327982
C34	c3	-9.165	-4.823	-2.99	-0.327982
H37	hx	-9.009	-4.399	-5.631	0.179183
H38	hx	-7.782	-3.1	-5.602	0.179183
H39	hx	-7.357	-4.745	-5.046	0.179183
H40	hx	-9.985	-5.21	-3.596	0.179183
H41	hx	-8.393	-5.584	-2.874	0.179183
H42	hx	-9.539	-4.513	-2.016	0.179183
H43	hn	-9.295	-2.925	-3.768	0.324796

Table S10. Atom names, atom types, atomic coordinates and atomic charges for **NO$_2$ArCOOH-Y**.

Atom name	Atom type	X	Y	Z	Charge
C1	ca	12.091	0.13	0.984	-0.11662
C2	ca	11.697	-0.638	-0.122	-0.068159
C3	ca	12.675	-1.159	-0.982	-0.11662
C4	ca	14.022	-0.893	-0.767	-0.14074
C5	ca	14.381	-0.112	0.331	0.061593
C6	ca	13.436	0.399	1.217	-0.14074
C7	c	10.263	-0.99	-0.429	0.634817
O1	o	9.988	-2.001	-1.066	-0.50886
N1	no	15.807	0.175	0.569	0.668273
O2	o	16.621	-0.288	-0.228	-0.422719
N2	ns	9.333	-0.095	0.042	-0.457583
C8	ca	7.926	-0.146	-0.066	0.156594
C9	ca	7.229	-1.227	-0.626	-0.179541
C10	ca	5.84	-1.191	-0.674	-0.175357
C11	ca	5.113	-0.1	-0.177	0.101898
C12	ca	5.812	0.982	0.381	-0.175357
C13	ca	7.2	0.945	0.431	-0.179541
N3	ns	3.707	-0.16	-0.263	-0.34608
C14	c	2.783	0.774	0.133	0.536824
O3	o	3.075	1.87	0.605	-0.509136
C15	ca	1.341	0.382	-0.062	-0.062224
C16	ca	0.405	1.424	-0.036	-0.082713
C17	ca	-0.956	1.165	-0.207	-0.110088
C18	ca	-1.381	-0.155	-0.414	-0.057877
C19	ca	-0.467	-1.21	-0.407	-0.110088
C20	ca	0.895	-0.929	-0.235	-0.082713
C21	c	-2.028	2.225	-0.222	0.571762
O4	o	-3.133	1.993	-0.703	-0.507594
C22	c	-0.825	-2.666	-0.603	0.571762
O5	o	0.047	-3.477	-0.905	-0.507594
N4	ns	-1.676	3.422	0.353	-0.323014
C23	ca	-2.435	4.604	0.476	0.019894
C24	ca	-3.752	4.722	0.008	-0.140554
C25	ca	-4.417	5.937	0.161	0.109501
C26	ca	-3.798	7.042	0.769	0.024274
C27	ca	-2.508	6.89	1.279	-0.265193
C28	ca	-1.821	5.692	1.12	-0.1241
C29	c	-4.581	8.312	0.889	0.705426
O6	o	-5.037	8.718	-0.306	-0.692083
O7	os	-5.753	6.038	-0.175	-0.340476
C30	c3	-6.068	6.196	-1.569	0.148668
C31	c3	-7.552	6.545	-1.693	-0.035595
C32	c3	-7.972	8.025	-1.621	-0.048267
N5	nx	-7.684	8.778	-0.381	0.018759
C33	c3	-8.19	8.119	0.831	-0.076925
O8	o	-4.801	8.878	1.943	-0.692083

N6	ns	-2.14	-2.978	-0.4	-0.323014
C34	ca	-2.785	-4.234	-0.508	0.019894
C35	ca	-4.137	-4.282	-0.145	-0.140554
C36	ca	-4.856	-5.474	-0.215	0.109501
C37	ca	-4.249	-6.662	-0.667	0.024274
C38	ca	-2.903	-6.572	-1.049	-0.265193
C39	ca	-2.157	-5.4	-0.964	-0.1241
O9	os	-6.209	-5.383	0.088	-0.340476
C40	c3	-6.621	-5.883	1.36	0.148668
C41	c3	-7.934	-6.679	1.167	-0.035595
C42	c3	-7.868	-8.022	1.887	-0.048267
N7	nx	-8.778	-9.098	1.283	0.018759
C43	c3	-10.232	-8.826	1.497	-0.076925
C44	c	-4.941	-8.025	-0.82	0.705426
O10	o	-4.567	-8.741	-1.756	-0.692083
C45	c3	-8.462	-9.42	-0.166	-0.076925
O11	o	-5.83	-8.301	0.061	-0.692083
C46	c3	-8.219	10.141	-0.494	-0.076925
O12	o	16.094	0.861	1.549	-0.422719
H1	ha	7.729	1.79	0.867	0.160872
H2	ha	5.266	1.832	0.763	0.167674
H3	ha	5.311	-2.037	-1.108	0.167674
H4	hn	3.346	-0.983	-0.723	0.258591
H5	ha	0.798	2.427	0.094	0.128462
H6	ha	-2.439	-0.301	-0.605	0.123515
H7	ha	1.565	-1.783	-0.232	0.128462
H8	hn	-2.732	-2.233	-0.065	0.242971
H9	ha	-4.66	-3.386	0.181	0.141498
H10	ha	-2.45	-7.475	-1.444	0.194132
H11	ha	-1.116	-5.375	-1.253	0.14476
H12	h1	-5.844	-6.53	1.77	0.033219
H13	h1	-6.775	-5.034	2.042	0.033219
H14	hc	-8.806	-6.093	1.482	0.043163
H15	hc	-7.992	-6.843	0.091	0.043163
H16	hx	-6.86	-8.422	1.767	0.072811
H17	hx	-8.155	-7.96	2.942	0.072811
H18	hn	-8.548	-9.945	1.808	0.2558
H19	hx	-10.814	-9.66	1.102	0.083568
H20	hx	-10.424	-8.704	2.564	0.083568
H21	hx	-10.493	-7.912	0.966	0.083568
H22	hx	-8.865	-10.412	-0.375	0.083568
H23	hx	-8.958	-8.681	-0.794	0.083568
H24	hx	-7.365	-9.339	-0.295	0.083568
H25	hn	-0.77	3.458	0.795	0.242971
H26	ha	-0.807	5.595	1.498	0.14476
H27	ha	-4.25	3.873	-0.437	0.141498
H28	ha	-2.036	7.726	1.786	0.194132

H29	h1	-5.434	6.977	-2.001	0.033219
H30	h1	-5.868	5.25	-2.091	0.033219
H31	hc	-7.891	6.202	-2.679	0.043163
H32	hc	-8.106	5.942	-0.964	0.043163
H33	hx	-7.483	8.569	-2.438	0.072811
H34	hx	-9.058	8.063	-1.825	0.072811
H35	hx	-7.939	10.715	0.392	0.083568
H36	hx	-7.792	10.633	-1.373	0.083568
H37	hx	-9.317	10.152	-0.588	0.083568
H38	hx	-7.941	8.736	1.697	0.083568
H39	hx	-9.283	7.976	0.798	0.083568
H40	hx	-7.701	7.152	0.956	0.083568
H41	hn	9.695	0.759	0.441	0.258911
H42	ha	7.774	-2.072	-1.018	0.160872
H43	ha	12.354	-1.777	-1.813	0.145362
H44	ha	14.793	-1.276	-1.424	0.175431
H45	ha	13.764	0.983	2.068	0.175431
H46	ha	11.357	0.494	1.697	0.145362
H47	hn	-6.695	8.746	-0.191	0.2558

S.2 Molecular dynamics simulations protocol

Initial system configurations have been prepared by means of Packmol[11] software, while explicit water molecules and ions (added in order to assure electroneutrality and to take into account the presence of salt) have been added with the tleap module of AmberTools.

All molecular dynamics (MD) simulations have been performed by means of GROMACS software, version 5.0.2[12], according to the following protocol. First of all, energy minimization has been carried out in order to remove bad solute/solvent and solvent/solvent contacts, due to the random placements of explicit water molecules. Temperature has been subsequently raised to 300 K by means of 20 ps in NVT ensemble (a weak harmonic restraint has been here applied to the solute in order to avoid wild fluctuations), and the system has been equilibrated through 1 ns in NPT ensemble at 300 K and 1 atm. Finally, MD simulations have been performed in NPT ensemble, at 300 K and 1 atm. Average temperature and pressure have been kept equal to the desired values by means of velocity rescale algorithm[13] and Parrinello - Rahman barostat[14], respectively. In particular, isotropic pressure scaling has been employed for the simulations of free monomers in solution, while anisotropic pressure scaling has been chosen for the infinite fiber model.

Periodic boundary conditions have been here adopted. Long - range electrostatic interactions have been computed by means of Particle Mesh Ewald[15] method, adopting a cut - off equal to 1.2 nm; the same value has been used for Van der Waals interactions. All the covalent bonds involving hydrogen atoms have been restrained through LINCS algorithm[16]. Leap - frog algorithm has been used to propagate the dynamics, along with a time step equal to 2 fs. All performed simulations have been summarized in Table S11. Data have been collected every 20 ps.

Table S11. Summary of performed molecular dynamics simulations. [a]Average box size of the equilibrated system. For the infinite fiber model, this corresponds to the last 100 ns.

System	*Box size[a] [nm x nm x nm]*	*Number of monomers*	*Na+ ions*	*Cl- ions*	*Water molecules*	*Total number of atoms*	*Simulation time [ns]*
NO_2COOMe-Y *(monomer)*	*6.19 x 6.12 x 5.24*	*1*	*0*	*2*	*6511*	*19641*	*400*
NH_2COOMe-Y *(monomer)*	*6.19 x 6.03 x 5.24*	*1*	*0*	*2*	*6399*	*19305*	*400*
NO_2COOH-Y *(monomer)*	*6.21 x 6.11 x 5.03*	*1*	*0*	*0*	*6453*	*19457*	*400*
NH_2COOH-Y	*6.15 x 6.08 x 5.34*	*1*	*0*	*0*	*6382*	*19244*	*400*

(monomer)							
Sym(COOMe)$_3$-Y *(monomer)*	6.76 x 6.71 x 5.01	1	0	3	7443	22461	400
Short NO$_2$COOMe-Y *(monomer)*	6.57 x 5.52 x 5.49	1	0	2	6588	19858	400
NO$_2$ArCOOH-Y *(monomer)*	7.00 x 6.38 x 4.99	1	0	0	7330	22102	400
NO$_2$COOMe-Y *(dimer)*	6.12 x 5.39 x 6.12	2	0	4	6559	19893	40
NH$_2$COOMe-Y *(dimer)*	5.21 x 6.16 x 5.22	2	0	4	5407	16437	40
NO$_2$COOH-Y *(dimer)*	5.33 x 5.14 x 6.02	2	0	0	5341	16219	40
NH$_2$COOH-Y *(dimer)*	5.77 x 6.11 x 5.71	2	0	0	6568	19900	40
NO$_2$COOMe-Y *(minimum energy structure)*	5.32 x 4.90 x 5.11	2	0	4	4320	13176	100
NH$_2$COOMe-Y *(minimum energy structure)*	5.35 x 5.01 x 4.99	2	0	4	4347	13257	100
NO$_2$COOH-Y *(minimum energy structure)*	4.58 x 5.75 x 5.42	2	0	0	4629	14083	100
NH$_2$COOH-Y *(minimum energy structure)*	4.74 x 5.16 x 5.04	2	0	0	4008	12220	100
Sym(COOMe)$_3$-Y *(minimum energy structure)*	6.20 x 6.22 x 6.32	2	0	6	7934	24066	100
Short NO$_2$COOMe-Y *(minimum energy structure***)**	6.22 x 5.06 x 5.85	2	0	4	5997	18179	100
NO$_2$ArCOOH-Y *(minimum energy structure)*	6.65 x 6.54 x 7.05	2	0	0	10411	30206	100
NO$_2$COOMe-Y *(free monomers)*	11.13 x 11.13 x 11.13	30	8	68	44430	136456	400
NH$_2$COOMe-Y *(free monomers)*	11.13 x 11.13 x 11.13	30	8	68	44430	136456	400
NO$_2$COOH-Y *(free monomers)*	11.13 x 11.13 x 11.13	30	8	8	44430	136246	400
NH$_2$COOH-Y *(free monomers)*	11.13 x 11.13 x 11.13	30	8	8	44430	136246	400
NO$_2$COOMe-Y *(infinite fiber)*	7.71 x 7.66 x 18.94	54	0	108	36000	113832	600
NH$_2$COOMe-Y *(infinite fiber)*	8.62 x 7.70 x 17.27	54	0	108	36000	113832	600

NO$_2$COOH-Y *(infinite fiber)*	*7.84 x 8.94 x 16.26*	*54*	*0*	*0*	*36000*	*113292*	*800*
NH$_2$COOH-Y *(infinite fiber)*	*8.67 x 8.14 x 16.15*	*54*	*0*	*0*	*36000*	*113292*	*800*

The attainment of reasonable equilibrated structures of supramolecular chains has been verified by checking the box length along z direction, Van der Waals energy, Electrostatic energy and Solvation free energy of the polymer as a function of simulation time (computed by means of MMGBSA approach, vide infra), as reported in Figures S15 – S18.

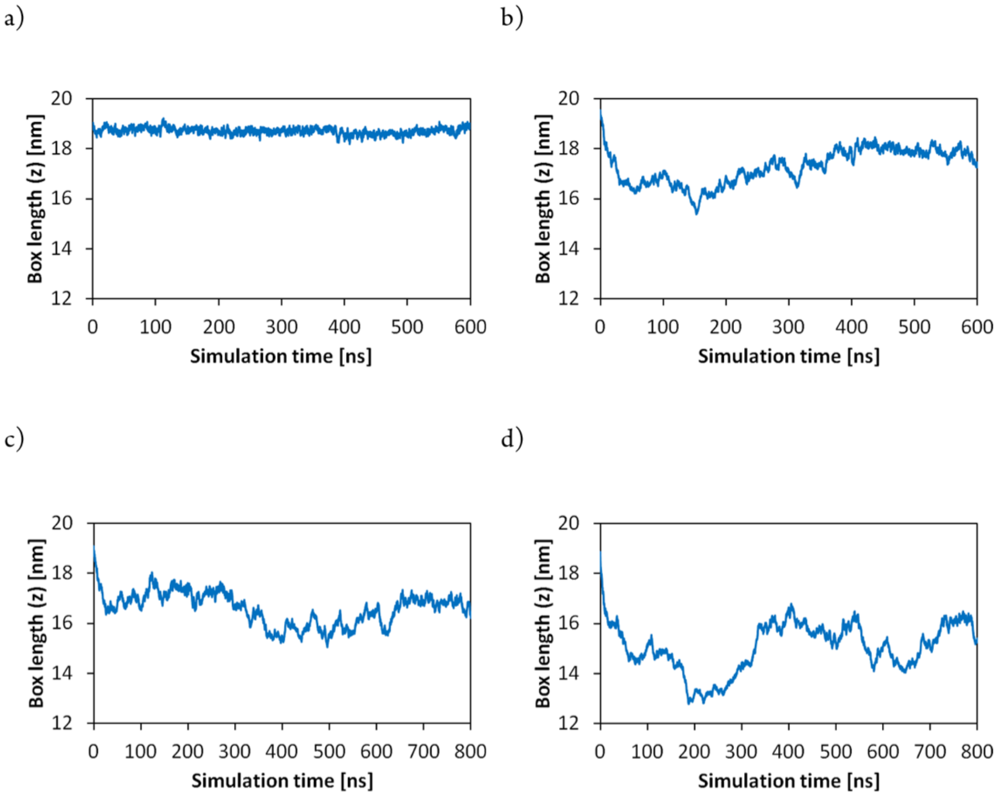

Figure S12. Box length along z direction as a function of simulation time for **NO$_2$COOMe-Y** (a), **NH$_2$COOMe-Y** (b), **NO$_2$COOH-Y** (c) and **NH$_2$COOH-Y** (d).

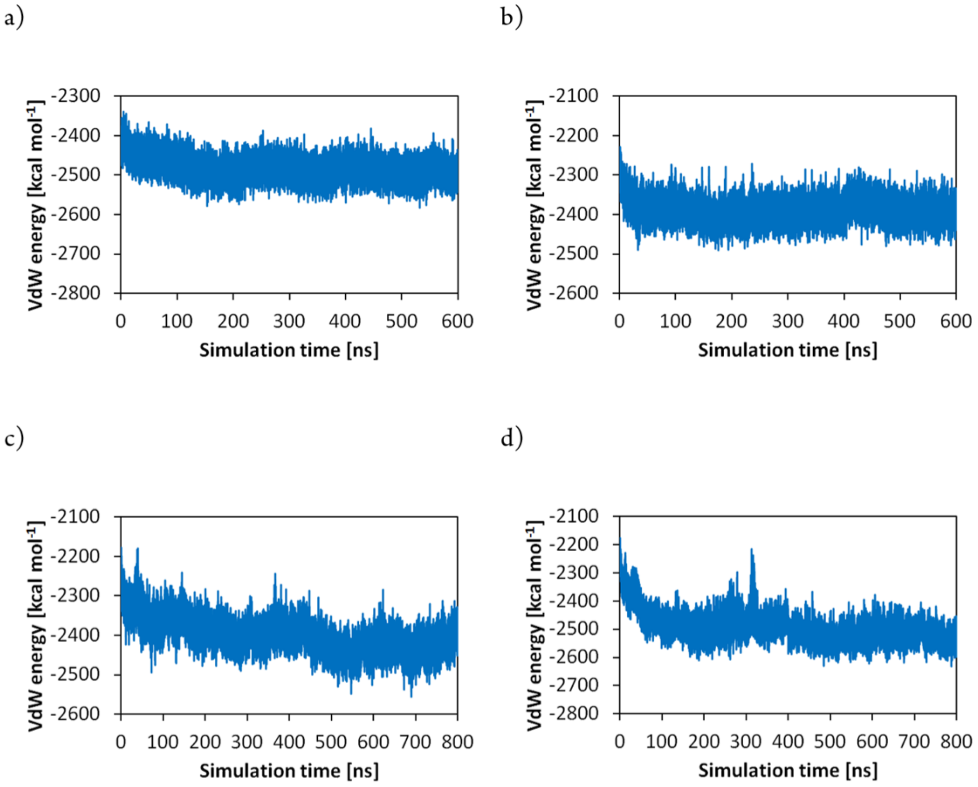

Figure S13. Van der Waals energy of the polymer as a function of simulation time for **NO$_2$COOMe-Y** (a), **NH$_2$COOMe-Y** (b), **NO$_2$COOH-Y** (c) and **NH$_2$COOH-Y** (d).

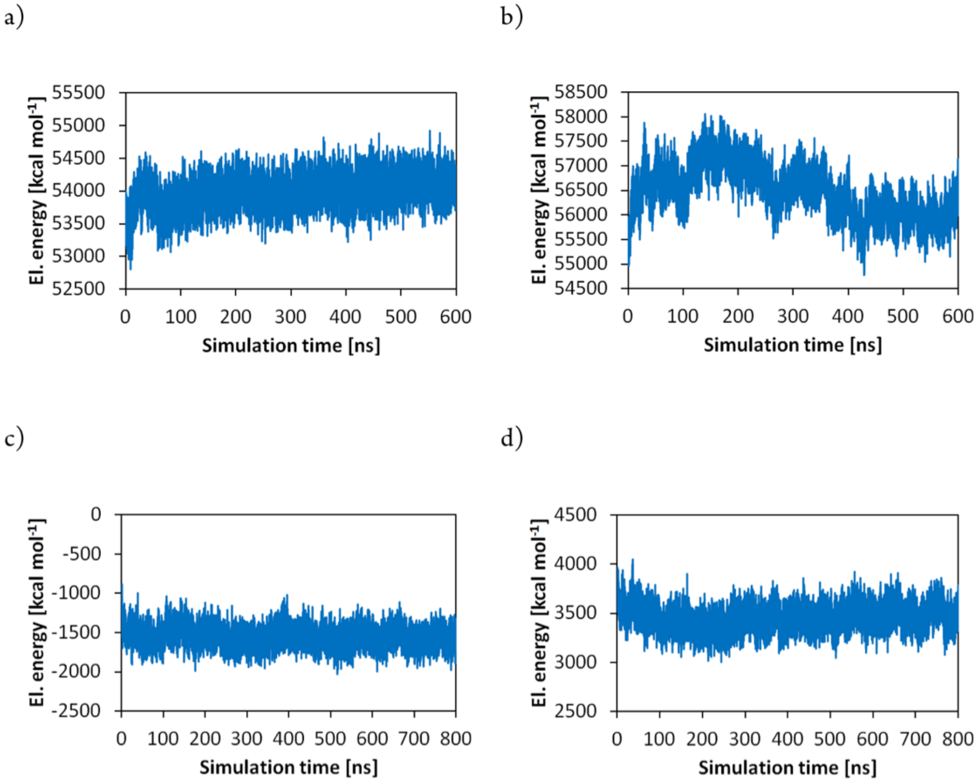

Figure S14. Electrostatic energy of the polymer as a function of simulation time for **NO$_2$COOMe-Y** (a), **NH$_2$COOMe-Y** (b), **NO$_2$COOH-Y** (c) and **NH$_2$COOH-Y** (d).

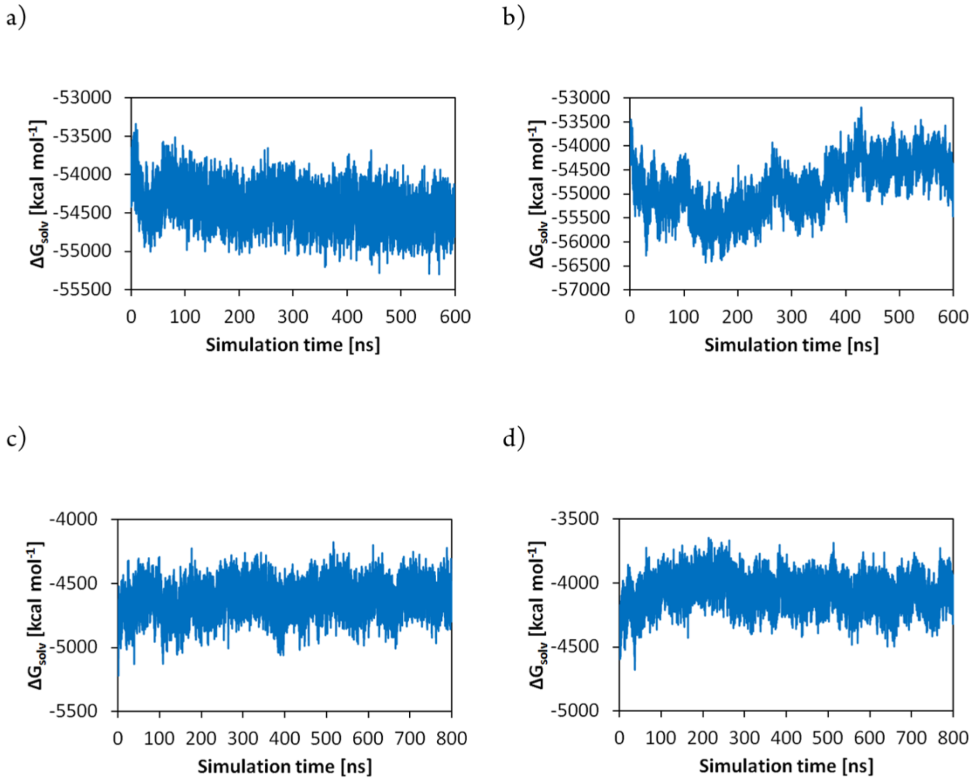

Figure S15. Solvation free energy of the polymer as a function of simulation time for **NO$_2$COOMe-Y** (a), **NH$_2$COOMe-**Y (b), **NO$_2$COOH-Y** (c) and **NH$_2$COOH-Y** (d).

S.3 Well - tempered metadynamics simulations

Metadynamics is an enhanced sampling method, which allows to reconstruct the free energy of a system as a function of few relevant conformational degrees of freedom (collective variables) and discouraging the sampling of conformations which have already been visited during the simulation. In this framework, well - tempered metadynamics[17,18] (WTMD) has been adopted, since it proved to be an efficient and flexible method in a wide range of applications, from drug/protein interactions[19] to supramolecular polymers[20]. In particular, WTMD simulations have been employed to properly investigate the self-assembling of two monomer units, according to the following protocol. For each considered compound, two monomers have been placed in a cubic box and solvated with explicit TIP3P water molecules; ions have been added in order to assure electroneutrality. Each system has been equilibrated according to the adopted simulation protocol (vide supra) and then 320 ns WTMD simulation in NVT ensemble at 300 K have been carried out.

Simulations have been performed by means of GROMACS 5.0.2 patched with PLUMED 2.1.0[21].

For all considered compounds, the number of contacts between the centers of mass of aromatic rings (representative of π - π stacking) and the Debye - Hückel interaction energy (representative of electrostatic interactions) have been chosen as suitable CV.

The number of contacts is computed through the following switching function:

$$\boldsymbol{s_{ij}(t)} = \frac{1-\left(\frac{r_{ij}(t)}{r_0}\right)^{n}}{1-\left(\frac{r_{ij}(t)}{r_0}\right)^{m}} \qquad \text{(S.1)}$$

where $r_{ij}(t)$ is the distance between the centers of mass of two aromatic rings at time t, r_0 is the reference distance for a contact (equal to 0.45 nm), n and m are exponential factors for the switching function (equal to 6 and 12, respectively). The number of contacts as a function of time $S_{\pi-\pi}(t)$ is given by:

$$\boldsymbol{S_{\pi-\pi}(t)} = \sum_{i=1}^{NR1}\sum_{j=1}^{NR2} s_{ij}(t) \qquad \text{(S.2)}$$

where NR1 and NR2 are the numbers of aromatic rings in the first and in the second monomer respectively.

Debye - Hückel interaction energy is expressed as follows:

$$\boldsymbol{E_{DH}(t)} = \frac{1}{4\pi\varepsilon_0\varepsilon_r}\sum_{i=1}^{NA1}\sum_{j=1}^{NA2} q_i q_j \frac{e^{-\kappa r_{ij}(t)}}{|r_{ij}(t)|} \qquad \text{(S.3)}$$

where ε_0 is vacuum permettivity, ε_r is the relative permettivity of the solvent (equal to 78 for water), q_i and q_j are the partial atomic charges of the i-th and the j-th atom respectively, $r_{ij}(t)$ is the distance between the i-th and the j-th atom as a function of time and ϰ is the Debye - Hückel parameter, computed assuming an ionic strength equal to 0.01 M and a temperature equal to 300 K; NA1 and NA2 are the number of atoms in the first and in the second monomer respectively.

Well - tempered metadynamics simulations have been performed adding bias every 500 steps (i.e., 1 ps), adopting an hill height equal to 0.5 kJ mol^{-1} and a bias factor equal to 10. Sigma values are equal to 0.1 and 0.2 for hydrophobic contacts and electrostatic interactions respectively. Input parameters have been chosen by monitoring the selected CV during 40 ns of unbiased MD simulations.

Convergence has been verified by checking the dimerization free energy value as a function of simulation time. Performed WTMD simulations are summarized in Table S12.

Free energy surfaces are represented in Figure S19; contour lines are plotted every 2 kcal mol^{-1}.

Table S12. Summary of performed well - tempered metadynamics simulations.

System	*Biased CV*	*Na+ ions*	*Cl- ions*	*Water molecules*	*Total number of atoms*	*Simulation time [ns]*
NO_2COOMe-Y	*Hydrophobic contacts* *Electrostatic interactions*	0	4	6559	19893	320
NH_2COOMe-Y	*Hydrophobic contacts* *Electrostatic interactions*	0	4	5407	16437	320
NO_2COOH-Y	*Hydrophobic contacts* *Electrostatic interactions*	0	0	5341	16219	320
NH_2COOH-Y	*Hydrophobic contacts* *Electrostatic interactions*	0	0	6568	19900	320
Sym$(COOMe)_3$-Y	*Hydrophobic contacts* *Electrostatic interactions*	0	6	7138	21678	320
Short NO_2COOMe-Y	*Hydrophobic contacts* *Electrostatic interactions*	0	4	6461	19571	320
$NO_2ArCOOH$-Y	*Hydrophobic contacts* *Electrostatic interactions*	0	0	8440	25544	320

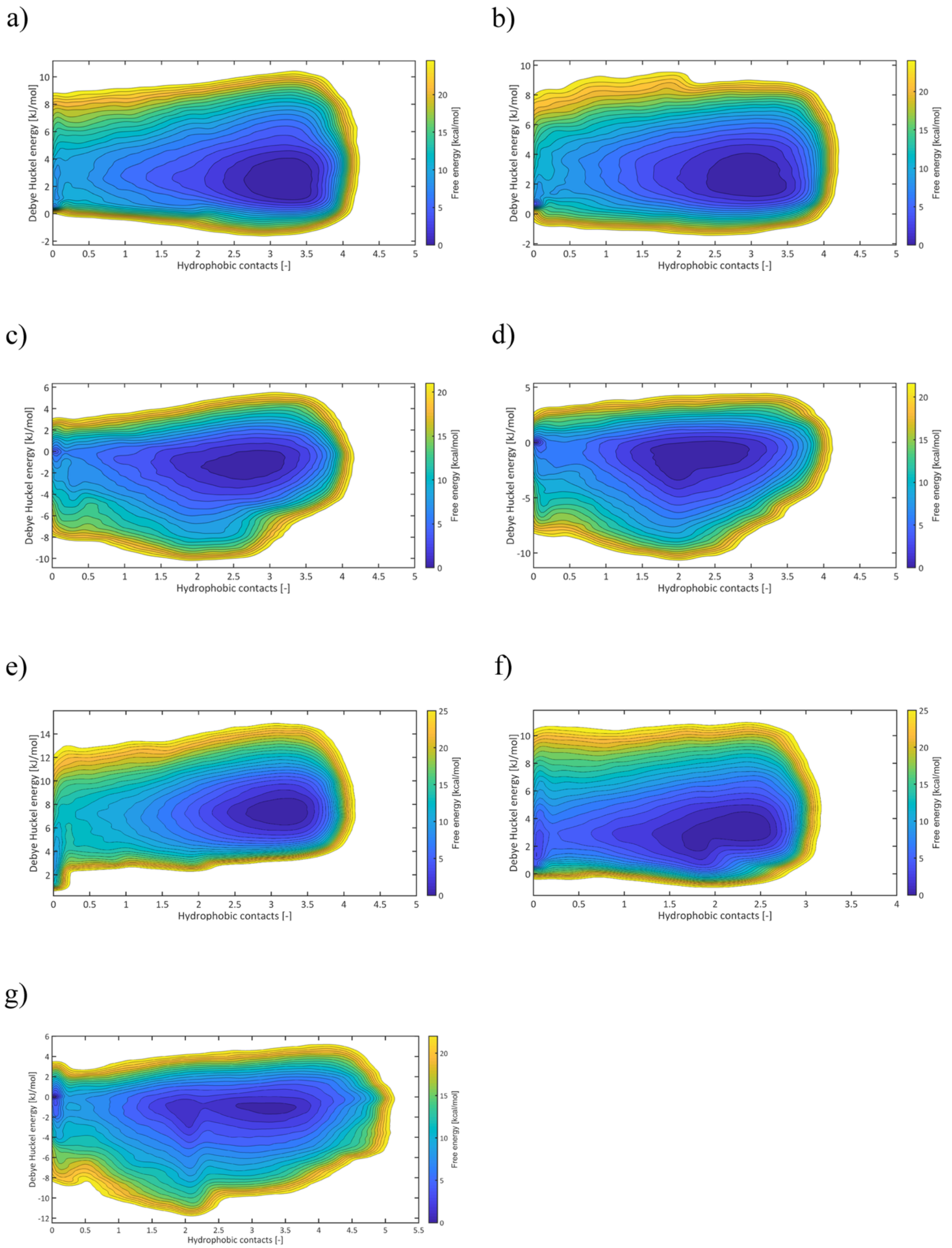

Figure S16. Free energy surfaces as a function of hydrophobic contacts and Debye - Hückel energy for **NO$_2$COOMe-Y** (a), **NH$_2$COOMe-Y** (b), **NO$_2$COOH-Y** (c), **NH$_2$COOH-Y** (d), **sym(COOMe)$_3$-Y** (e), **short NO$_2$COOMe-Y** (f) and **NO$_2$ArCOOH-Y** (g). Contour lines are plotted every 2 kcal mol^{-1}.

Convergence has been checked by computing free energy difference between bound and unbound state ΔF as a function of simulation time, as shown in Figure S20.

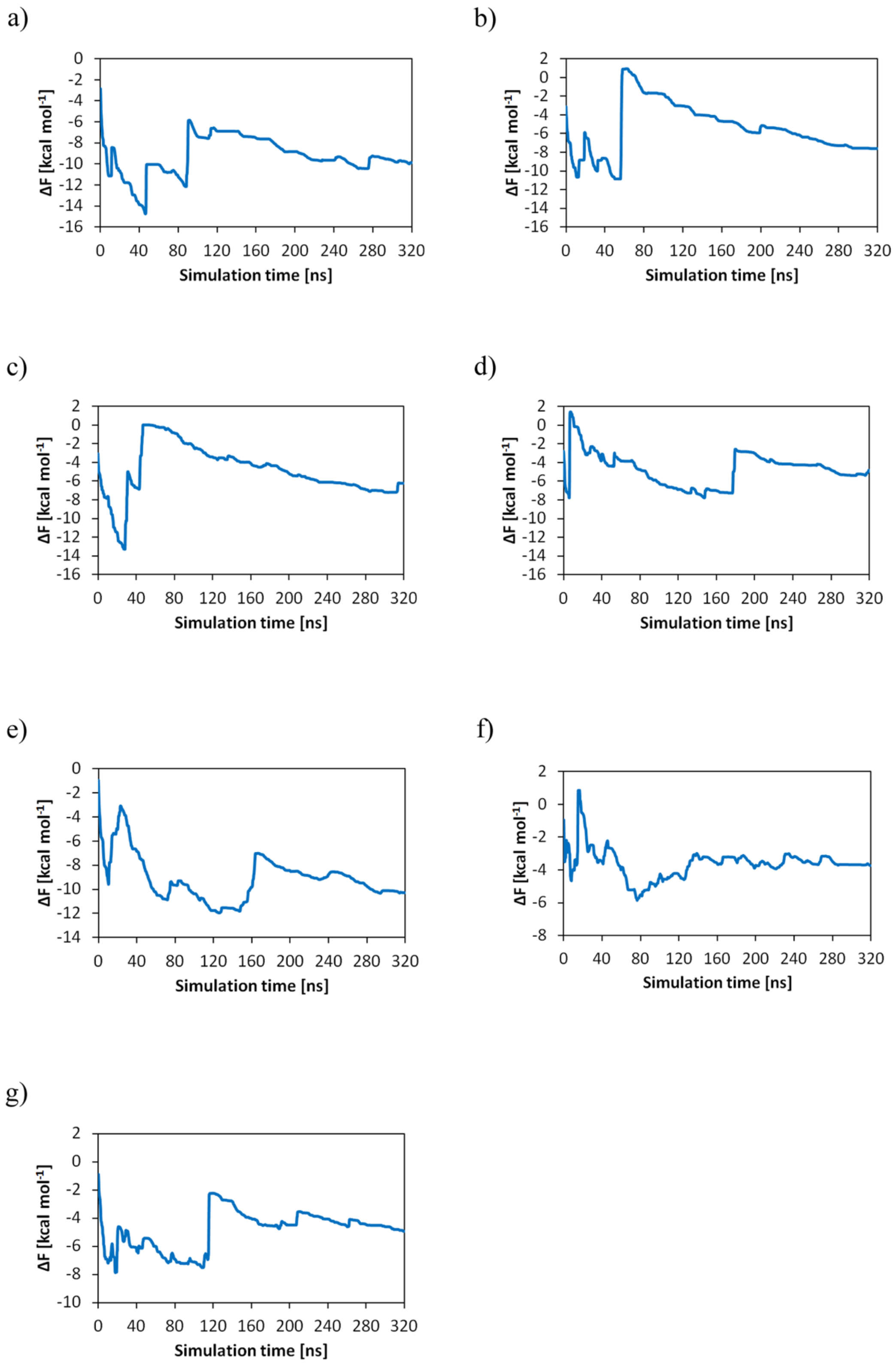

Figure S17. Free energy difference between bound and unbound state as a function of simulation time for **NO$_2$COOMe-Y** (a), **NH$_2$COOMe-Y** (b), **NO$_2$COOH-Y** (c), **NH$_2$COOH-Y** (d), **sym(COOMe)$_3$-Y** (e), **short NO$_2$COOMe-Y** (f) and **NO$_2$ArCOOH-Y** (g).

S.4 Molecular Mechanics Generalized Born Surface Area (MMGBSA) method

According to Molecular Mechanics Generalized Born Surface Area (MMGBSA), interaction energy values ΔE are the sum of two contributions:

$$\Delta \boldsymbol{E} = \Delta \boldsymbol{E}_{\boldsymbol{gas}} + \Delta \boldsymbol{G}_{\boldsymbol{sol}} \tag{S.4}$$

where ΔE_{gas} is the molecular mechanical (MM) gas - phase energy obtained through the force field and ΔG_{solv} is solvation free energy. Gas - phase energy is obtained as a sum of internal energy ΔE_{int} (which takes into account bond, angle and torsion terms), electrostatic and Van der Waals long - range interactions (ΔE_{elec} and ΔE_{VdW}, respectively):

$$\Delta \boldsymbol{E}_{\boldsymbol{gas}} = \Delta \boldsymbol{E}_{\boldsymbol{int}} + \Delta \boldsymbol{E}_{\boldsymbol{elec}} + \Delta \boldsymbol{E}_{\boldsymbol{VdW}} \tag{S.5}$$

Solvation free energy accounts for a polar (ΔG_{pol}) and a non - polar (ΔG_{np}) contribution. The first one is computed by means of generalized Born approach[22,23], while ΔG_{np} is obtained as a function of Solvent Accessible Surface Area (SASA):

$$\Delta \boldsymbol{G}_{\boldsymbol{solv}} = \Delta \boldsymbol{G}_{\boldsymbol{pol}} + \Delta \boldsymbol{G}_{\boldsymbol{np}} \tag{S.6}$$

$$\Delta \boldsymbol{G}_{\boldsymbol{np}} = \boldsymbol{a} \cdot \boldsymbol{SASA} + \boldsymbol{b} \tag{S.7}$$

where a is equal to 0.00542 kcal mol^{-1} Å^{-2} and b is equal to 0.92 kcal mol^{-1}.

The energy gain ΔE_{sf} related to the self-assembling of one monomer free in solution in a generic chain can be expressed as follows[3]:

$$\Delta \boldsymbol{E}_{\boldsymbol{sf}} = \boldsymbol{E}_{\boldsymbol{n}} - \boldsymbol{E}_{\boldsymbol{n-1}} - \boldsymbol{E}_{\boldsymbol{mon}} \tag{S.8}$$

where E_n and E_{n-1} are the energies of a chain composed by n and n-1 monomeric units respectively, and E_{mon} is the energy of a monomer free in solution. Assuming that the energy of a generic chain can be expressed as a function of the average energy of an assembled monomer $E_{assembled}$, eq. S.8 can be rewritten in a more convenient way:

$$\begin{aligned} \boldsymbol{\Delta E}_{\boldsymbol{sf}} &= \boldsymbol{nE}_{\boldsymbol{assembled}} - (\boldsymbol{n}-\boldsymbol{1})\boldsymbol{E}_{\boldsymbol{assembled}} - \boldsymbol{E}_{\boldsymbol{mon}} = \\ &= \boldsymbol{E}_{\boldsymbol{assembled}} - \boldsymbol{E}_{\boldsymbol{mon}} = \frac{\boldsymbol{E}_{\boldsymbol{n}}}{\boldsymbol{n}} - \boldsymbol{E}_{\boldsymbol{mon}} \end{aligned} \tag{S.9}$$

It is worth mentioning that, according to MMGBSA method, the energy gain also accounts for the solvation free energy (eq. S.4). Van der Waals, Electrostatic and Solvation contributions to the monomer self-assembling are shown in Figures S21 - S23. Energy gain after self – assembling as a function of simulation time is shown in Figure S24.

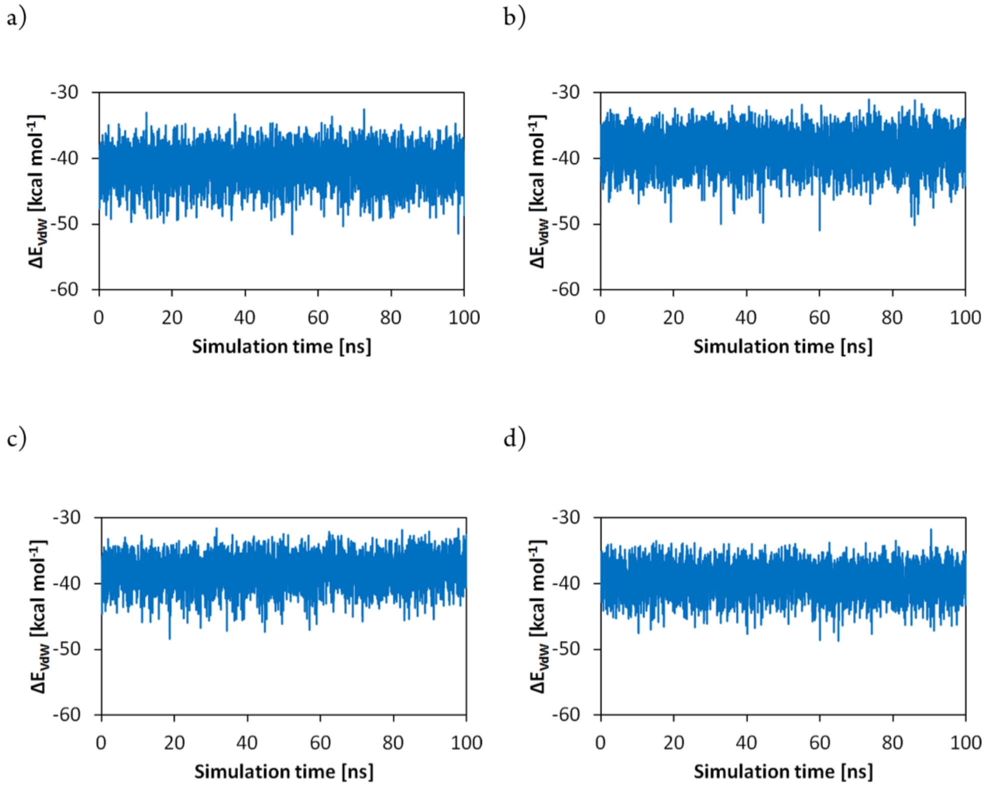

Figure S18. Van der Waals contribution for self-assembling a function of simulation time for **NO$_2$COOMe-Y** (a), **NH$_2$COOMe-Y** (b), **NO$_2$COOH-Y** (c) and **NH$_2$COOH-Y** (d).

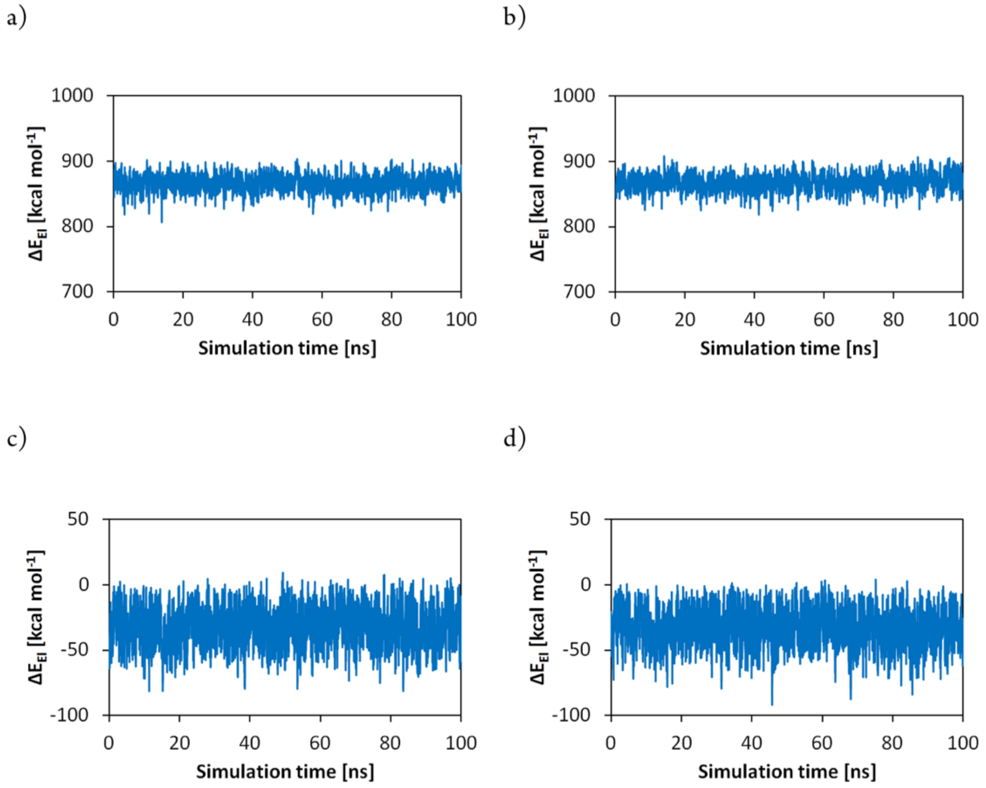

Figure S19. Electrostatic contribution for self-assembling a function of simulation time for **NO$_2$COOMe-Y** (a), **NH$_2$COOMe-Y** (b), **NO$_2$COOH-Y** (c) and **NH$_2$COOH-Y** (d).

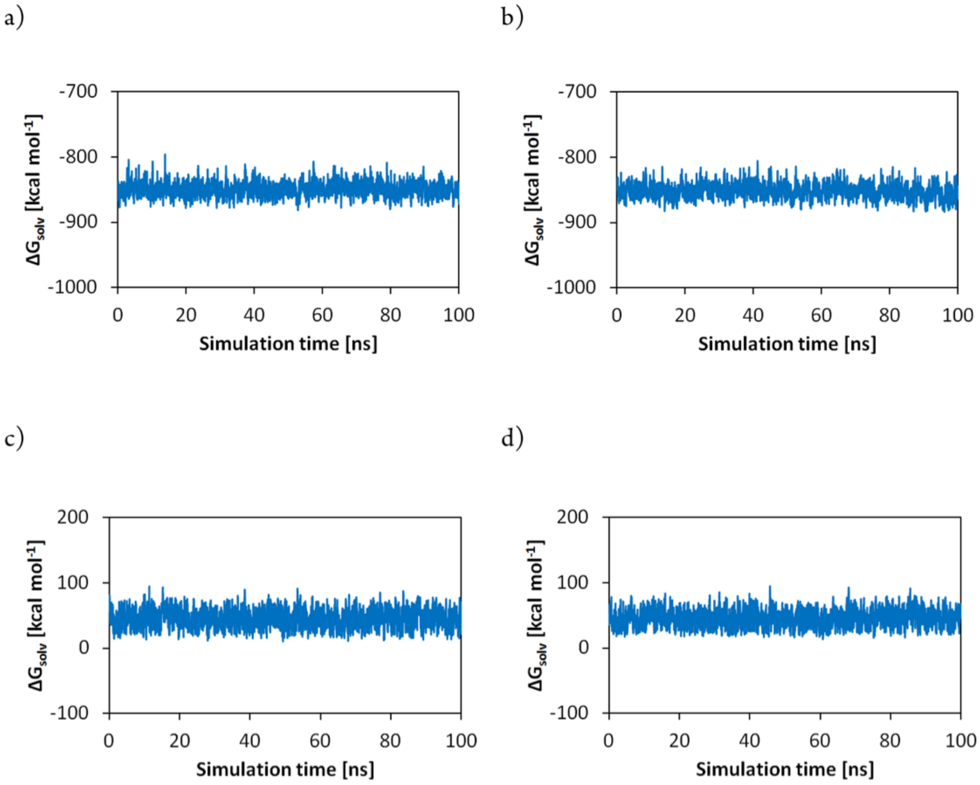

Figure S20. Solvation contribution for self-assembling a function of simulation time for **NO$_2$COOMe-Y** (a), **NH$_2$COOMe-Y** (b), **NO$_2$COOH-Y** (c) and **NH$_2$COOH-Y** (d).

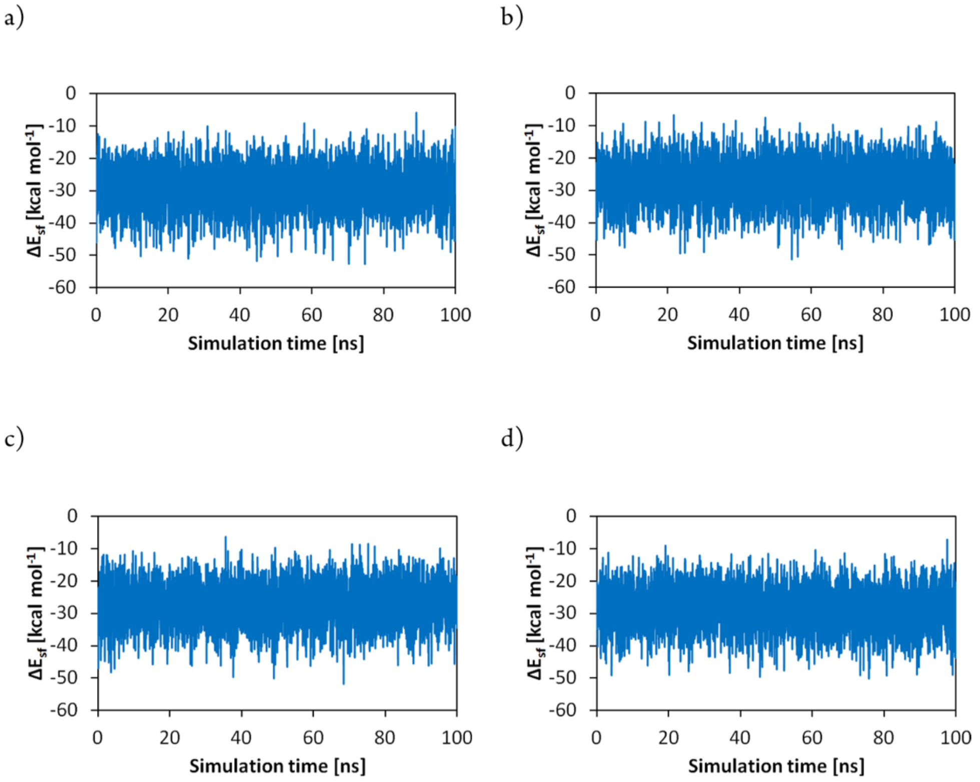

Figure S21. Energy gain for self-assembling a function of simulation time for **NO$_2$COOMe-Y** (a), **NH$_2$COOMe-Y** (b), **NO$_2$COOH-Y** (c) and **NH$_2$COOH-Y** (d).

S.5 Trajectories post-processing

Solvent Accessible Surface Area has been computed by means of LCPO algorithm[24] implemented in cpptraj[25]. Radial distribution functions have been obtained through radial algorithm implemented in cpptraj.

Electrostatic potential map have been obtained by means of Adaptive Poission Boltzmann Solver[26].

S.6 Supporting plots

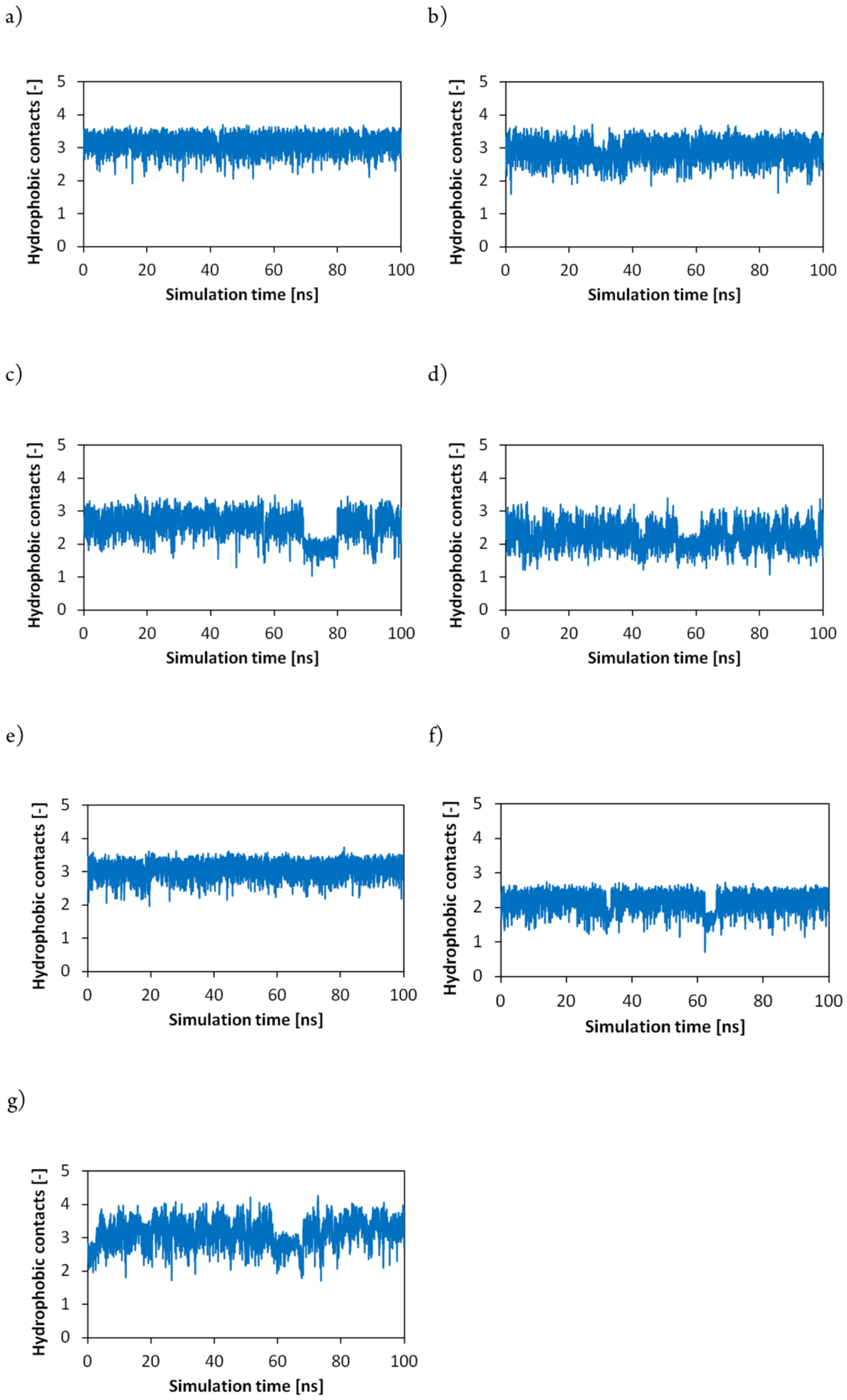

Figure S22. Hydrophobic contact of the dimer as function of simulation time for **NO$_2$COOMe-Y** (a), **NH$_2$COOMe-Y** (b), **NO$_2$COOH-**Y (c) **NH$_2$COOH-Y** (d), **sym(COOMe)$_3$-Y** (e), **short NO$_2$COOMe-Y** (f) and **NO$_2$ArCOOH-Y** (g).

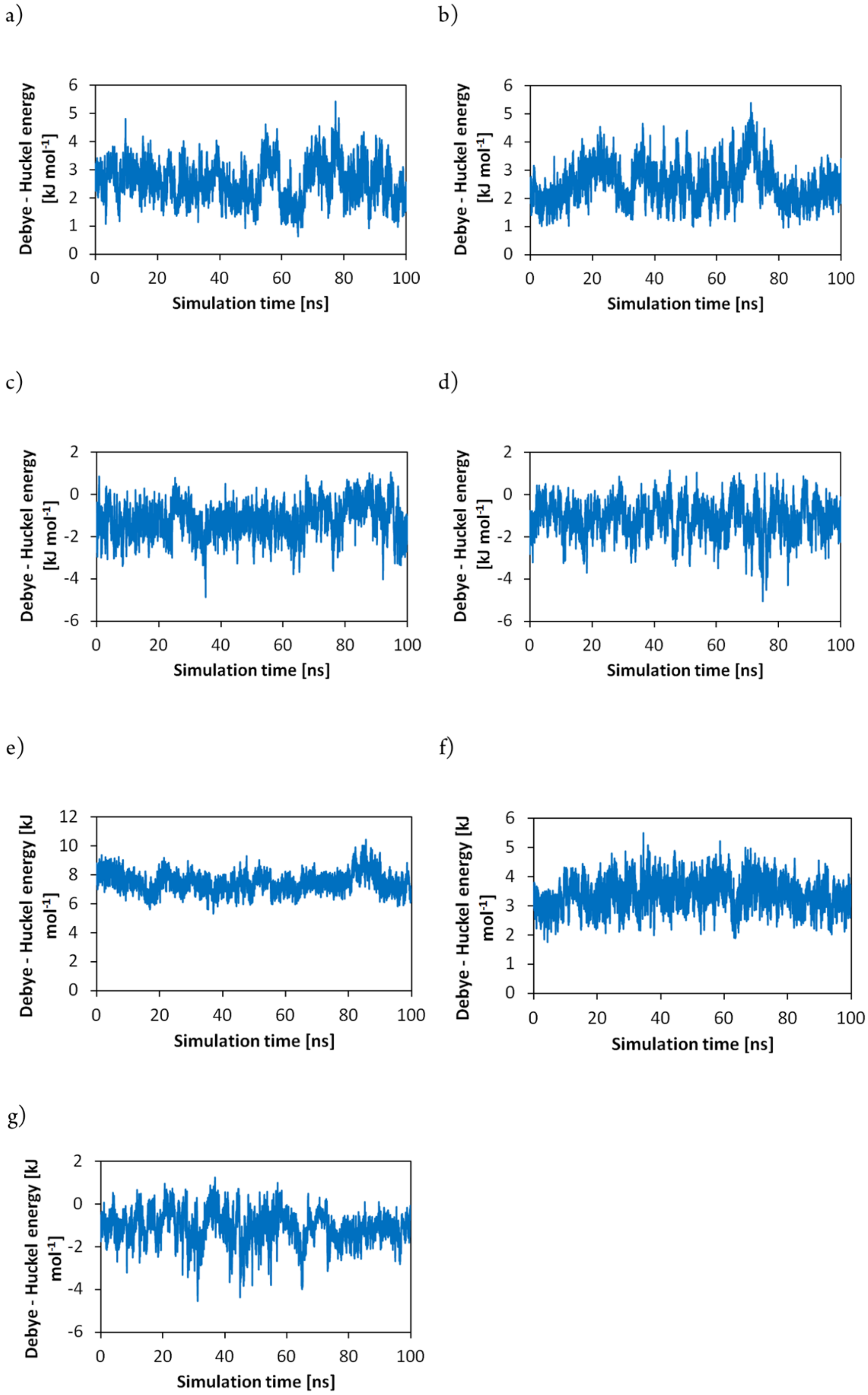

Figure S23. Debye - Hückel energy of the dimer as function of simulation time for **NO$_2$COOMe-Y** (a), **NH$_2$COOMe-**Y (b), **NO$_2$COOH-Y** (c) and **NH$_2$COOH-Y** (d), **sym(COOMe)$_3$-Y** (e), **short NO$_2$COOMe-Y** (f) and **NO$_2$ArCOOH-Y** (g).

.

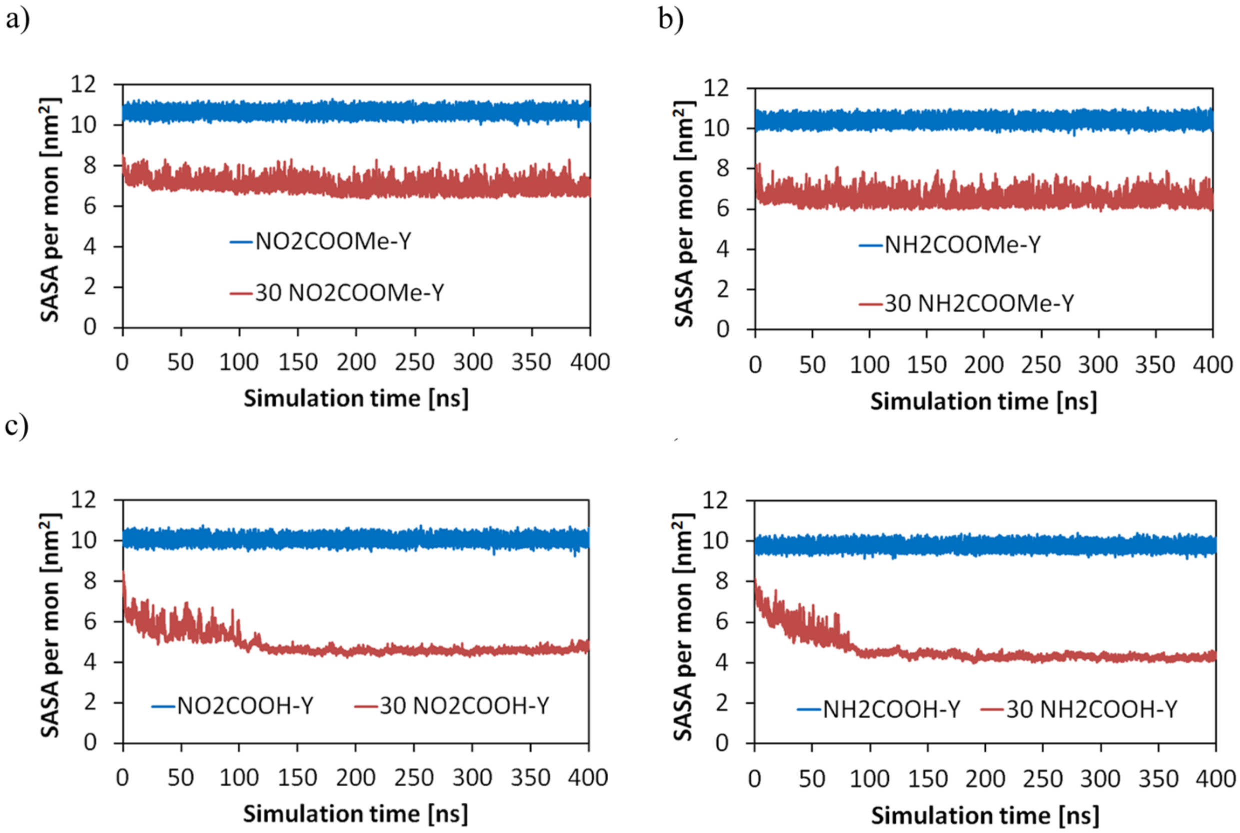

Figure S24. Solvent Accessible Surface Area as function of simulation time for **NO$_2$COOMe-Y** (a), **NH$_2$COOMe-**Y (b), **NO$_2$COOH-Y** (c) and **NH$_2$COOH-Y** (d). The value of a single monomer in solution is shown as reference.

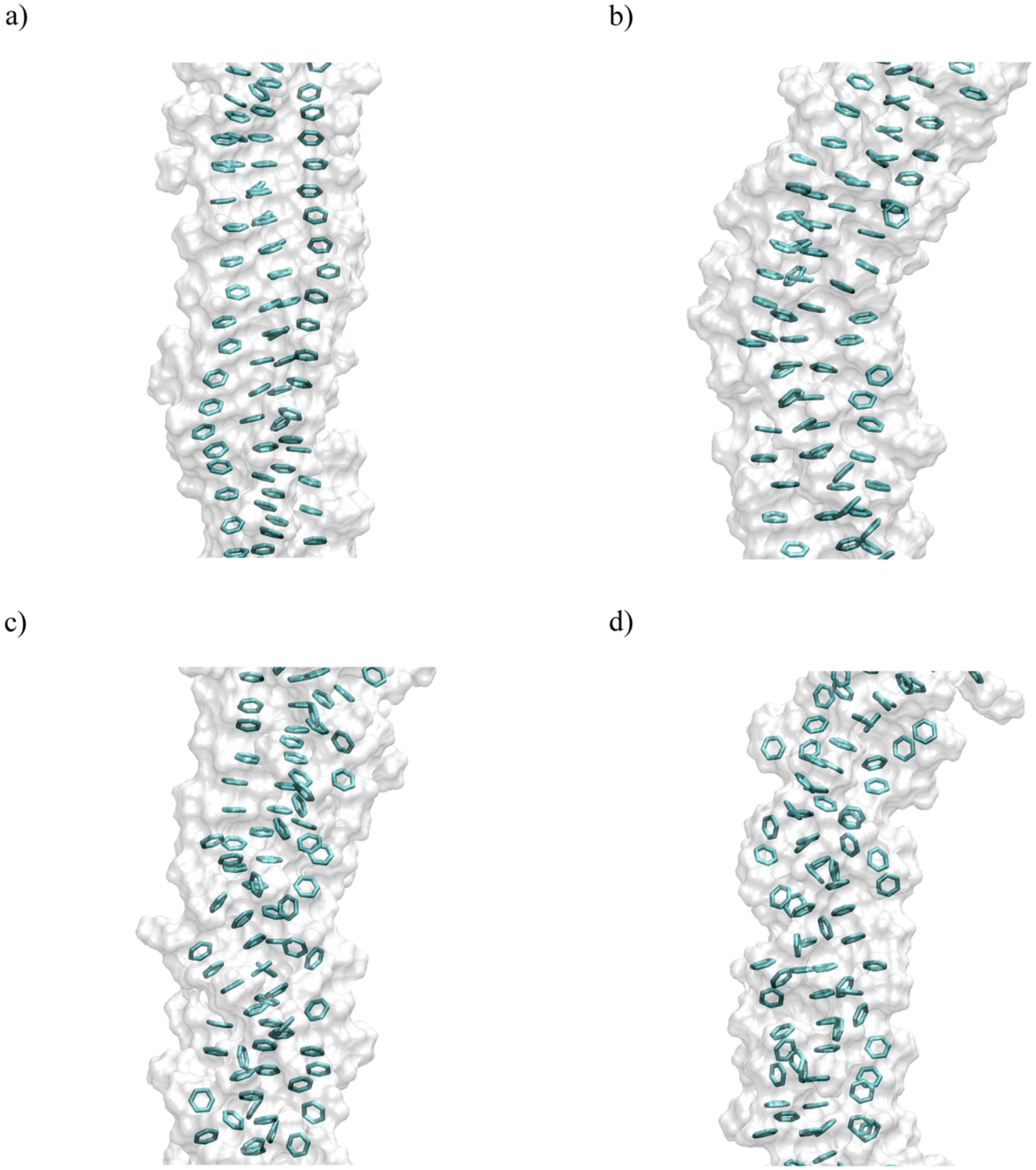

Figure S25. Equilibrated structures of **NO_2COOMe-Y** (a), **NH_2COOMe-**Y (b), **NO_2COOH-Y** (c) and **NH_2COOH-Y** (d) supramolecular chain. Aromatic rings are explicitly shown in green, while the stack is represented as a transparent white surface.

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