Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

3D Supramolecular self-assembly of [60]fullerene hexaadducts decorated with triarylamine molecules

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1. Synthesis

General Methods

All reactions were performed under an atmosphere of argon unless otherwise indicated. All *reagents and solvents* were purchased at the highest commercial quality and used without further purification unless otherwise noted. Dry solvents were obtained using a double column SolvTech purification system. Water was deionized by using a milli-gradient system (Millipore, Molsheim, France). Yields refer to purified spectroscopically (^{1}H NMR) homogeneous materials. *Thin Layer Chromatographies* were performed with TLC silica on aluminium foils (Silica Gel/UV_{254}, Aldrich). In most cases, irradiation using a *Bioblock VL-4C* UV-Lamp (6 W, 254 nm and/or 365 nm) as well as *p*-anisaldehyde and Ce-molybdate stainings were used for visualization. *Preparative Adsorption Flash Column Chromatographies* were performed using silica gel (60 Å, 230–400 mesh, 40–63 μm, Sigma-Aldrich)). *^{1}H NMR spectra* were recorded on a *Bruker Avance 400* spectrometer at 400 MHz and ^{13}C spectra at 100 MHz. The spectra were internally referenced to the residual proton solvent signal. For ^{1}H NMR assignments, the chemical shifts are given in ppm. Coupling constants *J* are listed in Hz. The following notation is used for the ^{1}H NMR spectral splitting patterns: singlet (s), doublet (d), triplet (t), multiplet (m), broad (br). *Ultra Performance Liquid Chromatographies coupled to Mass Spectroscopy* (UPLC-MS) were carried out on a *Waters Acquity UPLC-SQD* apparatus equipped with a PDA detector (190-500 nm, 80Hz), using a reverse phase column (Waters, BEH C18 1.7 μm, 2.1mm x 50 mm), and the MassLynx 4.1 – XP software and a gradient (water-acetonitrile + 0.1% TFA) as eluent. *ESI-MS* mass spectra were recorded on a Waters SQD spectrometer.

Bis(4-nitrophenyl)amine is commercially available from TCI Europe.

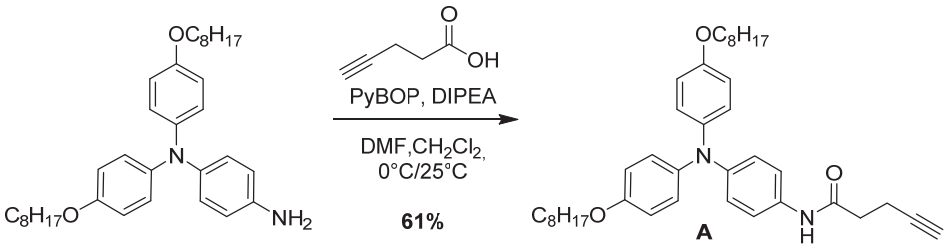
N,N'-bis(4-(octyloxy)phenyl)benzene-1,4-diamine was synthesized according to procedures from the literature.[1]

T_h-symmetrical C_{60} hexakis-adduct bearing 12 peripheral azide groups (**1**) was synthesized according to procedures from the literature.[2]

[1] E. Moulin, F. Niess, M. Maaloum, E. Buhler, I. Nyrkova and N. Giuseppone, *Angew. Chem. Int. Ed.*, 2010, **49**, 6974–6978.
[2] J. Iehl, R. Pereira de Freitas, B. Delavaux-Nicot and J.-F. Nierengarten, *Chem. Commun*., 2008, 2450-2452.

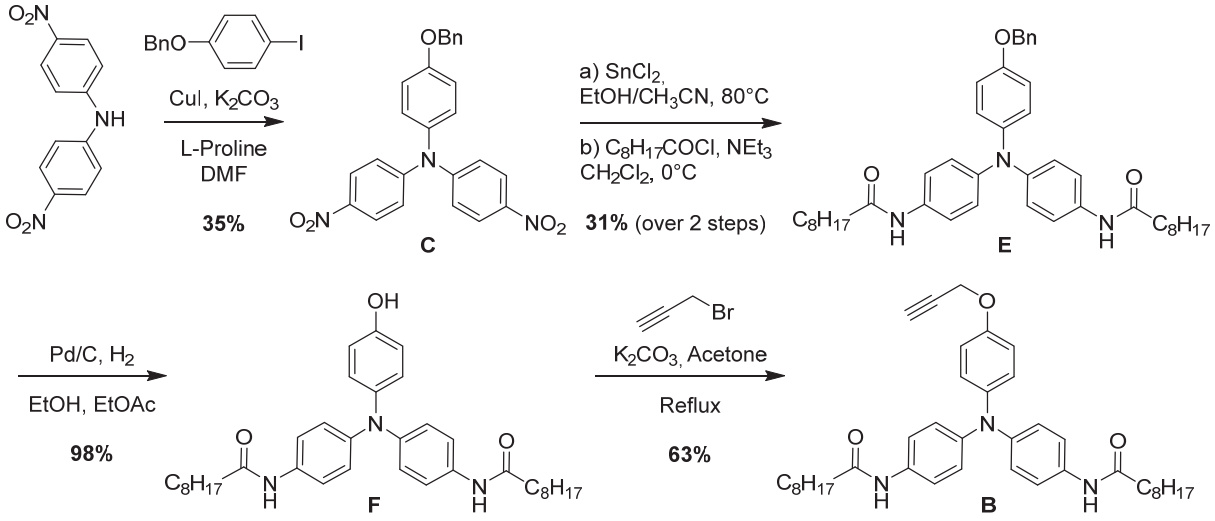
*Synthetic Routes for compounds **A** and **B***

Compound **A** was synthesized in one step from *N,N'*-bis(4-(octyloxy)phenyl)benzene-1,4-diamine[1] according to Scheme S1.



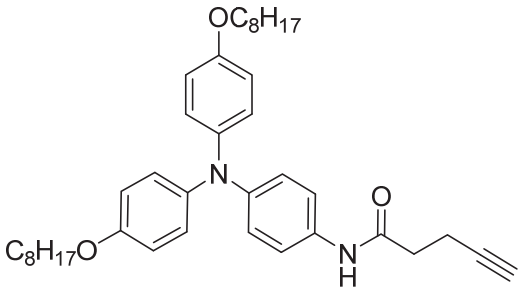
Scheme S1. Synthetic pathway for compound **A**.

Compound **B** was synthesized in five steps from commercially available bis-(4-nitrophenyl)aniline and 1-(benzyloxy)-4-iodobenzene according to Scheme S2.



Scheme S2. Synthetic pathway for compound **B**.

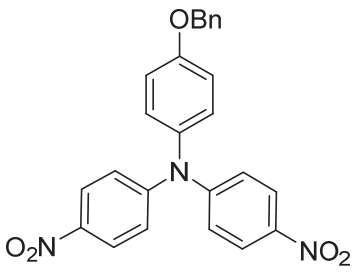
Synthetic Procedures



A

4-pentynoic acid (380 mg, 3.87 mmol) and *N,N′*-bis(4-(octyloxy)phenyl)benzene-1,4-diamine (2.0 g, 3.87 mmol) were dissolved in a 1:1 mixture of dry DMF and dichloromethane (54 mL). The solution was cooled to 0°C and PyBOP (2.1 g, 4.07 mmol) and diisopropylethylamine (3.4 mL, 19.35 mmol) were sequentially added slowly. The reaction mixture was stirred vigorously for 2 days and then diluted with ethyl acetate (15 mL). The organic phase was washed with sat. $NaHCO_3$ (2 × 10 mL) and brine (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Further purification by column chromatography (SiO_2, cyclohexane/Et_2O: 1/1 → pure Et_2O) afforded compound **A** (1.4 g, 61 %) as a white solid.

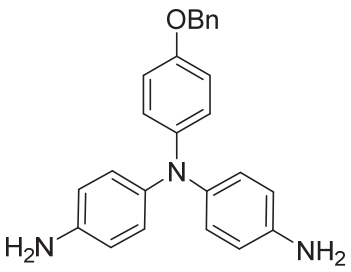
^{1}H NMR (CD_3OD, 400 MHz, 25°C): δ = 7.32 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 9.2 Hz, 4H), 6.81 (d, *J* = 9.2 Hz, 2H), 6.78 (d, *J* = 9.2 Hz, 4H), 3.90 (t, *J* = 6.4 Hz, 4H), 2.54 - 2.52 (m, 4H), 2.26 (t, *J* = 2.2 Hz, 1H), 1.77 - 1.70 (m, 4H), 1.47 - 1.40 (m, 4H), 1.35 - 1.30 (m, 16H), 0.90 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (CD_3OD, 100 MHz, 25°C): δ = 172.00, 156.64, 146.87, 142.56, 133.03, 127.01, 122.86, 122.45, 116.51, 83.56, 70.32, 69.42, 36.71, 33.00, 30.49, 30.48, 30.39, 27.18, 23.67, 15.65, 14.45; ESI-MS: *m/z* calcd for $C_{39}H_{52}N_2O_3$: 596.40 $[M]^+$, found 596.71.



C

A mixture of Bis-(4-nitrophenyl)aniline (500 mg, 1.93 mmol), 1-(benzyloxy)-4-iodobenzene (719 mg, 2.31 mmol) K_2CO_3 (640 mg, 4.63 mmol), CuI (44.1 mg, 0.23 mmol) and L-Proline (53.3 mg, 0.46 mmol) were suspended in dry DMF (7 mL). The reaction mixture was then heated up to 135 °C for 7 days and then diluted with ethyl acetate (15 mL) and filtrated over silica gel. Purification by column chromatography (SiO_2, pure cyclohexane → cyclohexane/EtOAc: 1/1) and concentration under reduced pressure afforded compound **C** (257 mg, 35 %) as a yellow solid.

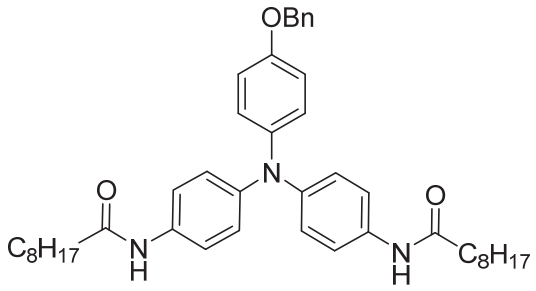
R_f = 0.53 (SiO_2, cyclohexane/ethyl acetate: 90/10); ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C): δ = 8.11 (d, *J* = 9.2 Hz, 4H), 7.50 - 7.34 (m, 5H), 7.11 (d, *J* = 9.2 Hz, 4H), 7.08 (d, *J* = 9.2 Hz, 2H), 7.02 (d, *J* = 9.2 Hz, 2H), 5.08 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, 25°C): δ = 157.84, 151.87, 142.44, 137.53, 136.35, 128.88, 128.69, 128.24, 127.50, 125.45, 121.71, 116.68, 70.41; ESI-MS: *m/z* calcd for $C_{25}H_{19}N_3O_5$: 441.13 $[M+H]^+$, found 441.33.



D

A solution of compound **C** (1.32 g, 0.58 mmol) and $SnCl_2 \cdot 2H_2O$ (7.61 g, 39.3 mmol) in CH_3CN (15.8 mL) and absolute EtOH (13.1 mL) was stirred overnight at reflux. After that time, the solution was cooled down to room temperature and diluted with EtOAc (100 mL). The organic phase was washed with NaOH 3M (2 × 100 mL), sat. Na_2CO_3 (2 × 100 mL) and brine (2 × 100 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The resulting olive-green product (607 mg, 53%) was not very stable to air but clean enough to be used as such in the next step.

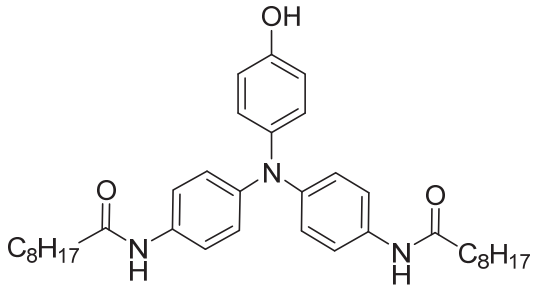
^{1}H NMR ($CDCl_3$, 400 MHz, 25°C): δ = 8.13 (d, *J* = 9.2 Hz, 4H), 7.47 - 7.36 (m, 5H), 7.13 (d, *J* = 9.6 Hz, 4H), 7.11 (d, *J* = 9.2 Hz, 2H), 7.04 (d, *J* = 9.2 Hz, 2H), 5.10 (s, 2H); ESI-MS: *m/z* calcd for $C_{25}H_{23}N_3O$: 381.18 $[M]^+$, found 381.31.



E

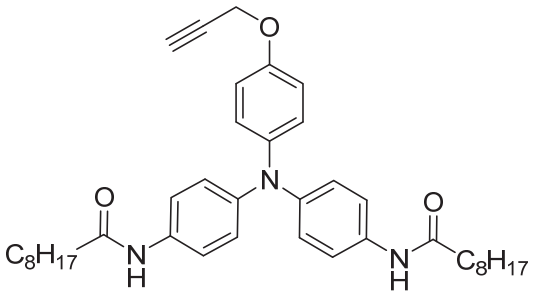
A solution of compound **D** (607 mg, 1.59 mmol) in dry dichloromethane (20 mL) was cooled down to 0°C and triethylamine (617 µL, 4.40 mmol) and nonanoyl chloride (485 µL, 2.69 mmol) were then sequentially added dropwise. The reaction mixture was heated overnight at 60°C and, after cooling down to room temperature, diluted with CH_2Cl_2 (80 mL). The organic phase was then washed with 3M NaOH (2 × 50 mL), brine (2 × 50 mL) and dried over anhydrous Na_2SO_4. Concentration under reduced pressure afforded compound **E** (623 mg, 59%) as a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz, 25°C): δ = 7.45 - 7.35 (m, 5H), 7.33 (d, *J* = 9.2 Hz, 4H), 7.09 (s, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 4H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.02 (s, 2H), 2.32 (t, *J* = 7.4 Hz, 4H), 1.75 - 1.67 (m, 4H), 1.36 - 1.21 (m, 20H), 0.88 (t, *J* = 7.0 Hz, 6H); ^{1}H NMR (CD_3COCD_3, 400 MHz, 25°C): δ = 9.00 (s, 2H), 7.54 (d, *J* = 8.8 Hz, 4H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.42 - 7.37 (m, 2H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.01 - 6.95 (m, 4H), 6.91 (d, *J* = 8.8 Hz, 4H), 5.09 (s, 2H), 2.33 (t, *J* = 7.4 Hz, 4H), 1.67 (tt, *J* = 7.6, 7.0 Hz, 4H), 1.38 - 1.28 (m, 20H), 0.88 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (CD_3COCD_3, 100 MHz, 25°C): δ = 171.63, 155.94, 144.61, 142.26, 138.52, 135.20, 129.29, 128.62, 128.46, 126.82, 124.13, 121.13, 116.55, 70.77, 37.70, 34.20, 32.60, 30.14, 29.96, 26.38, 23.31, 14.36; ESI-MS: *m/z* calcd for $C_{43}H_{55}N_3O_3$: 662.43 $[M+H]^+$, found 662.70.



F

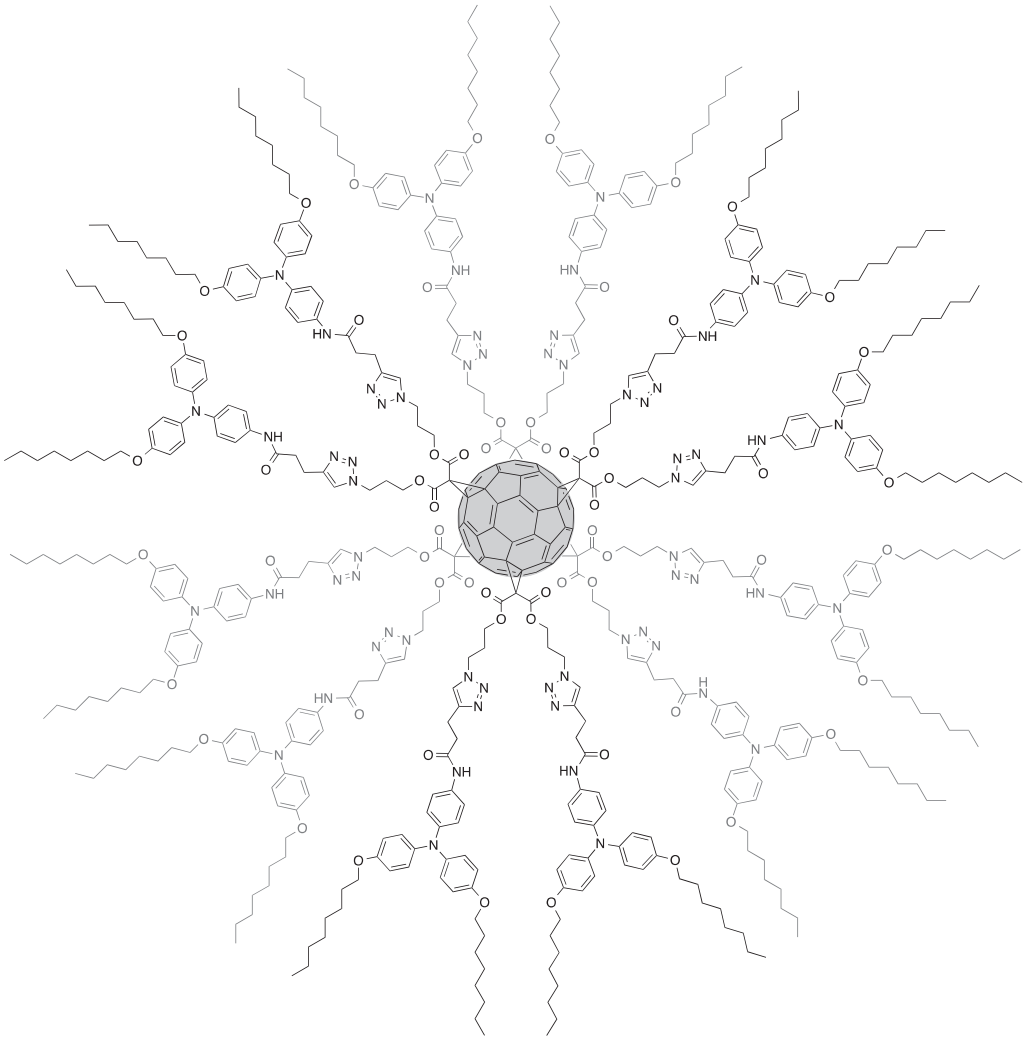
In a typical experimental setup, compound **E** (623 mg, 0.94 mmol) was dissolved in a 1:1 mixture of EtOH/EtOAc (74 mL), leading to a 0.01M concentration. A H-Cube continuous flow reactor was used for the hydrogenation. The flow rate was set with the HPLC pump to 1 mL/min. The hydrogen pressure was set to 40 bars, the temperature to 80°C and a cartridge containing 10% Pd/C was used. After the reaction, the sample was collected and evaporated to give compound **F** (527 mg, 98%), which was pure enough to be used as such in the next step. ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C): δ = 7.44 (s, 2H), 4H hidden by $CHCl_3$ signal, 6.88 (d, *J* = 8.0 Hz, 4H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 8.0 Hz, 2H), 2.34 (t, *J* = 7.6 Hz, 4H), 1.73 - 1.67 (m, 4H), 1.37 - 1.20 (m, 20H), 0.87 (t, *J* = 6.8 Hz, 6H); ^{1}H NMR (CD_3OD, 400 MHz, 25°C): δ = 7.36 (d, *J* = 9.2 Hz, 4H), 6.91 (d, *J* = 8.8 Hz, 6H), 6.74 (d, *J* = 8.4 Hz, 2H), 2.34 (t, *J* = 7.4 Hz, 4H), 1.69 (tt, *J* = 7.2, 7.2 Hz, 4H), 1.40 - 1.24 (m, 20H), 0.90 (t, *J* = 6.8 Hz, 6H); ^{1}H NMR (CD_3COCD_3, 400 MHz, 25°C): δ = 8.99 (s, 2H), 8.23 (s, 1H), 7.52 (d, *J* = 8.8 Hz, 4H), 6.92 (d, *J* = 9.2 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 4H), 6.79 (d, *J* = 9.2 Hz, 2H), 2.33 (t, *J* = 7.4 Hz, 4H), 1.67 (tt, *J* = 7.2, 7.2 Hz, 4H), 1.38 - 1.23 (m, 20H), 0.87 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (CD_3COCD_3, 100 MHz, 25°C): δ = 171.59, 154.73, 144.84, 140.82, 134.85, 127.66, 123.66, 121.07, 117.01, 37.69, 32.59, 30.59, 30.13, 29.96, 26.38, 23.31, 14.35; ESI-MS: *m/z* calcd for $C_{36}H_{49}N_3O_3$: 571.38 $[M]^+$, found 571.70.



B

A solution of compound **F** (195 µL, 0.91 mmol), K_2CO_3 (378 mg, 2.74 mmol), and KI (30.3 mg, 0.18 mmol) in dry DMF (17.5 mL) was heated to 80 °C for 45 minutes. Propargyl bromide (80% solution in toluene, 195 µL, 2.19 mmol) was added dropwise over 30 min. The reaction mixture was then stirred at 80 °C for 2 days. After cooling down to room temperature, water (100 mL) was added, and the aqueous solution was extracted with diethylether (3 × 100 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and further purification by column chromatography (SiO_2, cyclohexane/ethyl acetate: 4/1) afforded compound **B** (351 mg, 63%) as a brown viscous liquid.

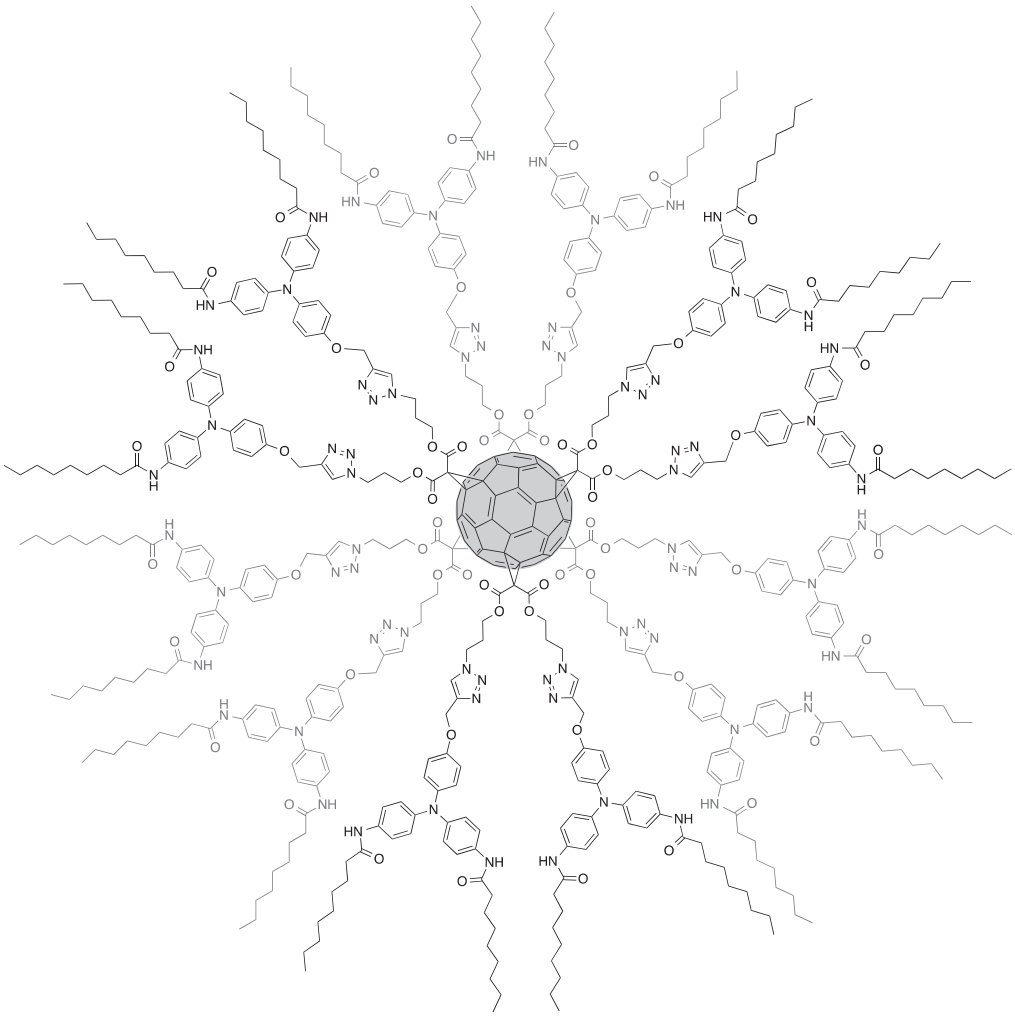
^{1}H NMR (CD_3COCD_3, 400 MHz, 25°C): δ = 8.99 (s, 1H), 7.55 (d, *J* = 8.8 Hz, 4H), 7.00 (d, *J* = 9.2 Hz, 2H), 6.94 (d, *J* = 9.2 Hz, 2H), 6.92 (d, *J* = 9.2 Hz, 4H), 4.75 (d, *J* = 2.4 Hz, 2H), 3.06 (t, *J* = 2.4 Hz, 1H), 2.33 (t, *J* = 7.4 Hz, 4H), 1.67 (tt, *J* = 7.6, 7.0 Hz, 4H), 1.35 - 1.27 (m, 20H), 0.88 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (CD_3COCD_3, 100 MHz, 25°C): δ = 171.74, 154.72, 144.62, 142.91, 135.39, 126.56, 124.36, 121.25, 116.77, 80.02, 76.96, 56.73, 37.79, 32.67, 30.20, 30.03, 26.46, 23.39, 14.42, 1C missing due to solvent peak; ESI-MS: : *m/z* calcd for $C_{39}H_{51}N_3O_3$: 609.39 $[M]^+$, found 609.70.



2A

A solution of **1** (70 mg, 0.03 mmol), **A** (251 mg, 0.42 mmol), $CuBr.(CH_3)_2S$ (3.7 mg, 0.018 mmol) in THF (2.0 mL) was stirred at 30°C in the dark. After 3 days, the reaction mixture was filtered through a plug of SiO_2 (THF) and concentrated. Column chromatography (SiO_2, PhMe/THF 100:3) followed by gel permeation chromatography (Biobeads SX-1, THF) provided compound **2A** (230 mg, 81%) as a brown-orange glassy product.

IR (neat): 1743cm^{-1} (C=O); UV/Vis (CH_2Cl_2): 310 nm (476000); ^{1}H-NMR (C_6D_6, 400 MHz, 25°C): δ = 7.76 (m, 12H), 7.04 (m, 96H), 6.81 (m, 48H), 4.90-2.50 (m, 120H), 1.66 (m, 48H), 1.38 (m, 48H), 1.25 (m, 190H), 0.90 (m, 72H); ^{13}C-NMR (C_6D_6, 100 MHz, 25°C): δ = 170.6, 163.5, 153.3, 146.9, 145.2, 141.4, 133.0, 126.0, 122.2, 121.5, 121.4, 115.4, 67.9, 63.7, 46.4, 40.5, 31.9, 29.5, 29.4, 26.2, 22.7, 21.7, 14.0. Elemental analysis calc. for $C_{582}H_{696}N_{60}O_{60}$: C 73.64, H 7.39, N 8.85; found: C 73.31, H 7.56, N 8.82.



2B

A solution of **1** (52 mg, 0.022 mmol), **B** (191 mg, 0.313 mmol), CuBr.$(CH_3)_2S$ (7.6 mg, 0.009 mmol) in THF (2.0 mL) was stirred at 30°C in the dark. After 3 days, the mixture reaction was concentrated. Column chromatography (SiO_2, THF) followed by gel permeation chromatography (Biobeads SX-1, THF) provided compound **2B** (192 mg, 91%) as a yellow-orange glassy product.

IR (neat): 1744 cm^{-1} (C=O); UV/Vis (CH_2Cl_2): 316 nm (605000), 425 nm (sh, 17000); ^{1}H

NMR (DMSO-d_6, 400 MHz, 90°C): 9.34 (s, 24H), 8.00 (s, 12H), 7.40 (d, J = 8 Hz, 48H), 6.89 (s, 48H), 6.82 (d, J = 8 Hz, 48H), 5.03 (s, 24H), 4.34 (m, 48H), 2.25 (m, 72H), 1.59 (m, 48H), 1.26 (m, 240H), 0.85 (m, 72H); ^{13}C NMR (THF-d_8, 75 MHz, 25°C): 168.9 (br), 161.1 (br), 152.4 (br), 143.6 (br), 141.7 (br), 139.6 (br), 132.2 (br), 123.6 (br), 121.3 (br), 118.6 (br), 113.6 (br), 60.2 (br), 45.4 (br), 34.9, 30.0, 27.6, 27.5, 27.4, 23.8, 20.7, 11.7. Elemental analysis calc. for $C_{582}H_{696}N_{60}O_{60}$: C 72.45, H 7.15, N 10.45; found: C 72.16, H 7.44, N 10.09.

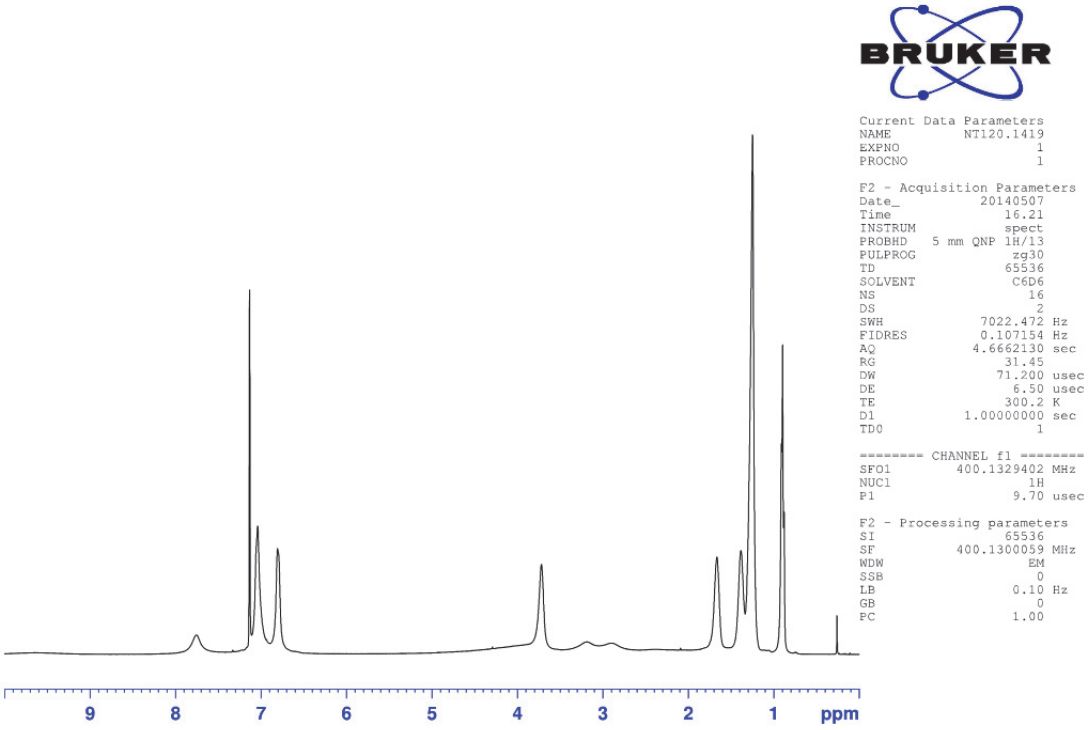


Figure S1A. ^{1}H NMR (C_6D_6, 400 MHz) spectrum of compound **2A**.

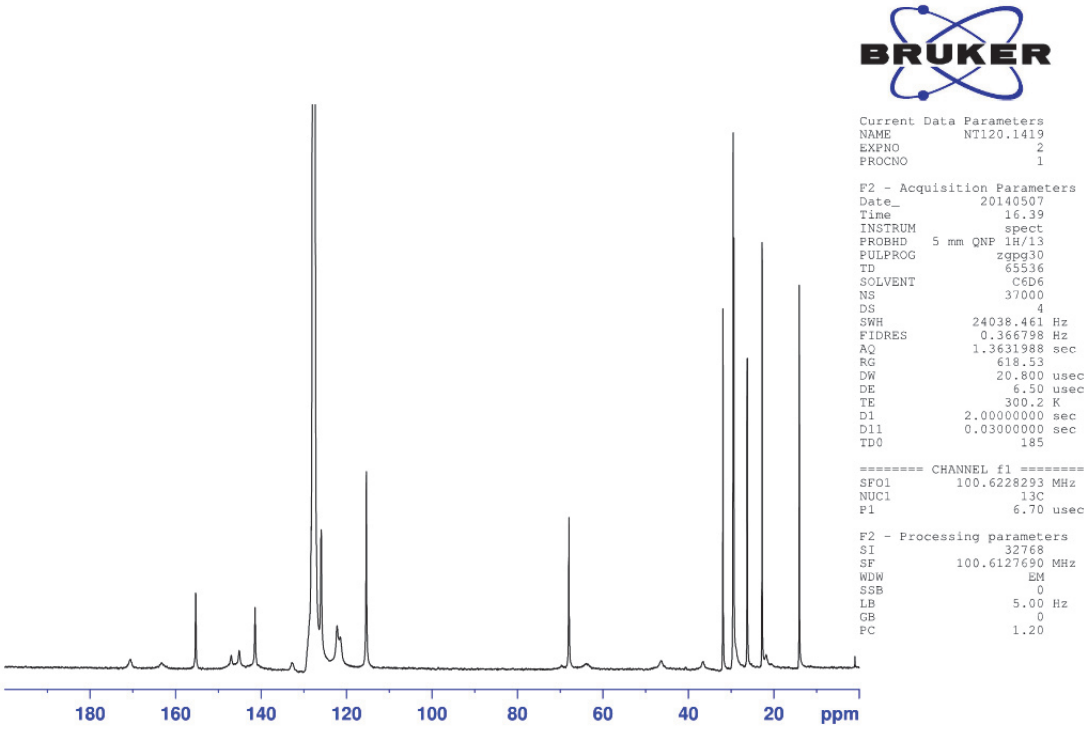


Figure S1B. ^{13}C NMR (C_6D_6, 100 MHz) spectrum of compound **2A**.

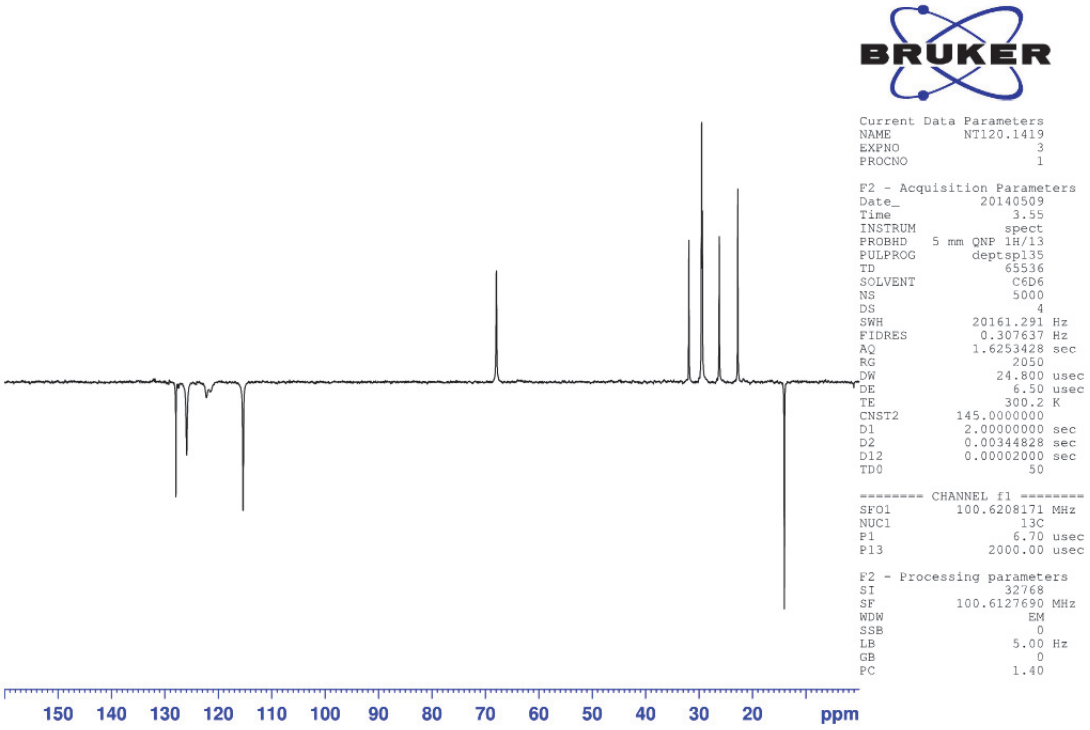


Figure S1C. DEPT (C_6D_6, 100 MHz) spectrum of compound **2A**.

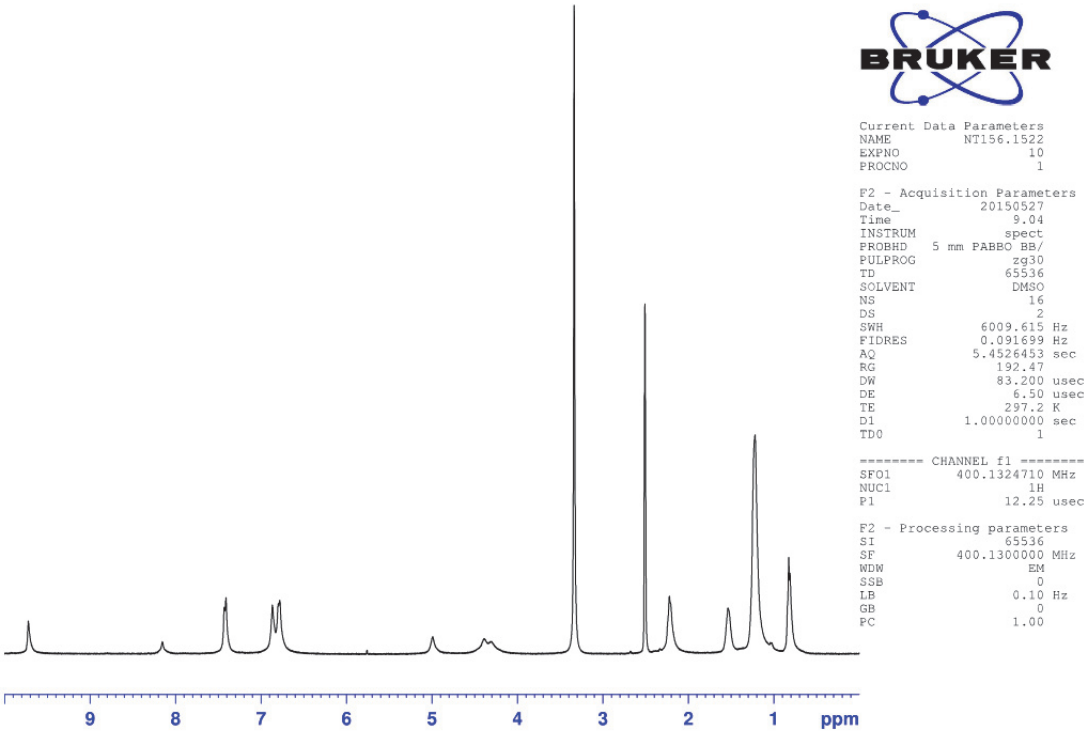


Figure S2A. ^{1}H NMR (DMSO-d_6, 400 MHz) spectrum of compound **2B**.

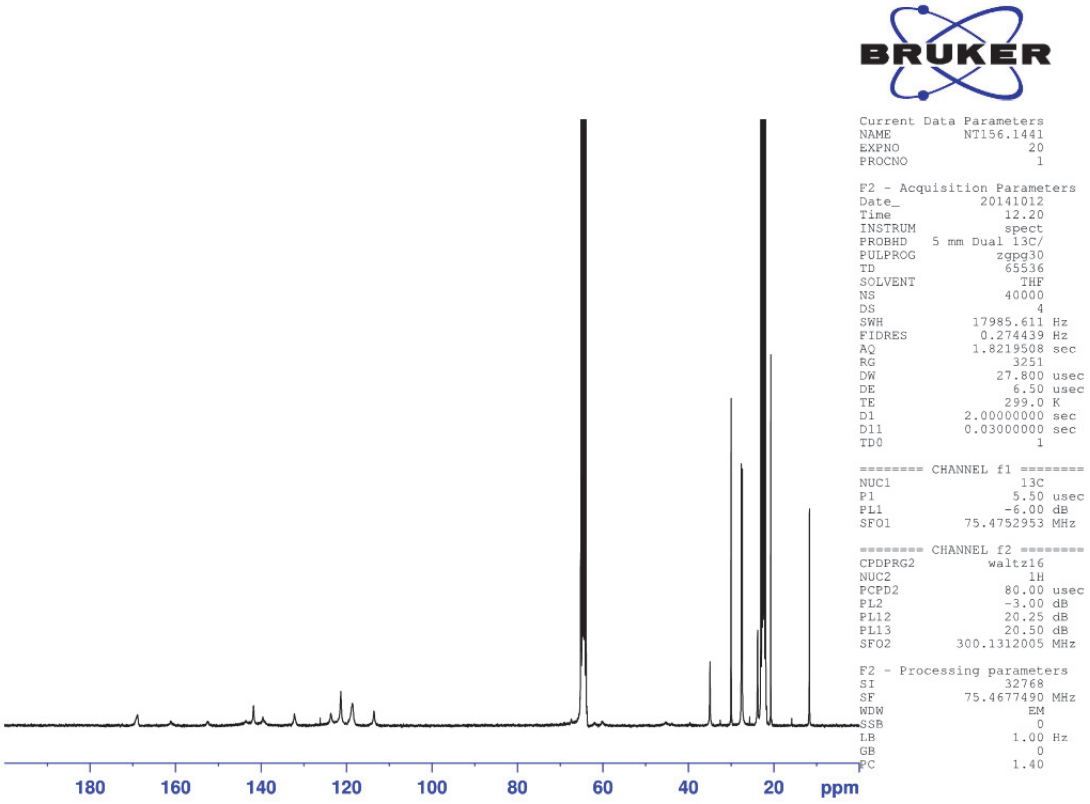


Figure S2B. ^{13}C NMR (THF-d_8, 100 MHz) spectrum of compound **2B**.

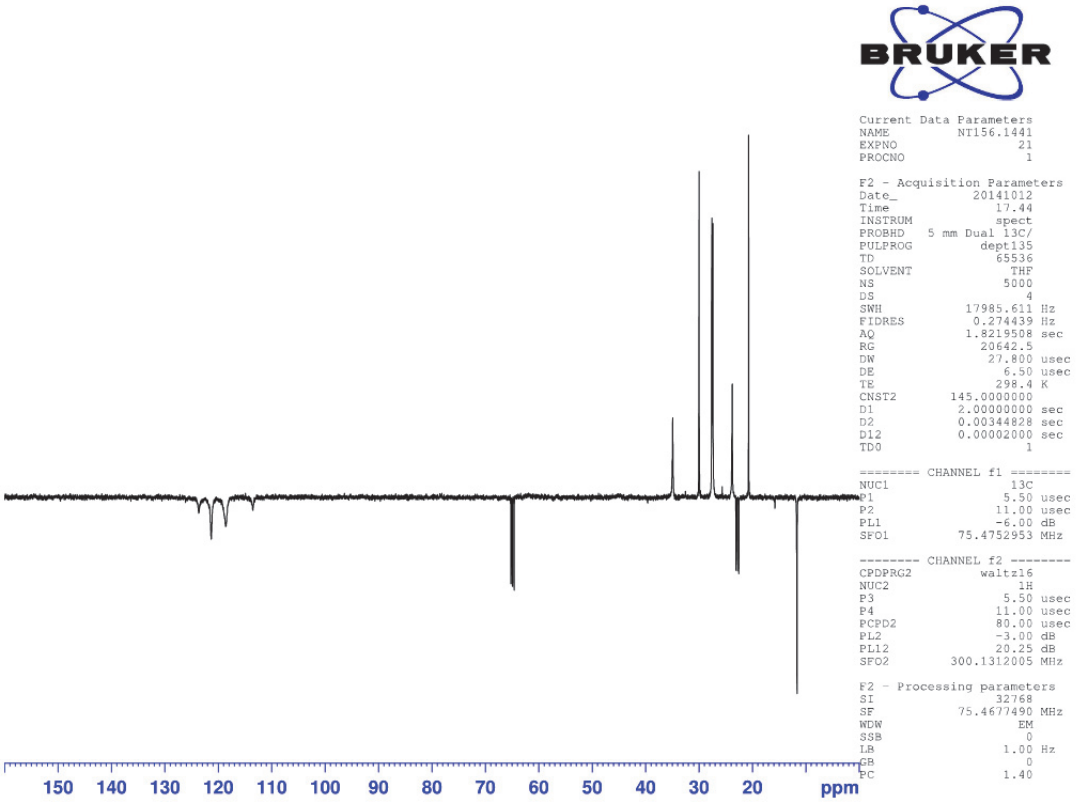


Figure S2C. DEPT (THF-d_8, 100 MHz) spectrum of compound **2B**.

2. Cyclic Voltammetry

All cyclic voltammograms were recorded with a three electrode setup on a PGSTAT101 potentiostat (Metrohm, Germany) under argon atmosphere at room temperature in 0.1 $NBu_4PF_6/C_2H_2Cl_4$. Spectroelectrochemistry was performed using a platinum wire mesh transmission with a silver wire pseudo electrode and platinum foil counter electrode. For spectroelectrochemistry, UV-Vis spectra were acquired on an Avaspec-2048 with an Avalight-DH-S-Bal light source and a Thorlabs GG420nm Glass longpass filter.

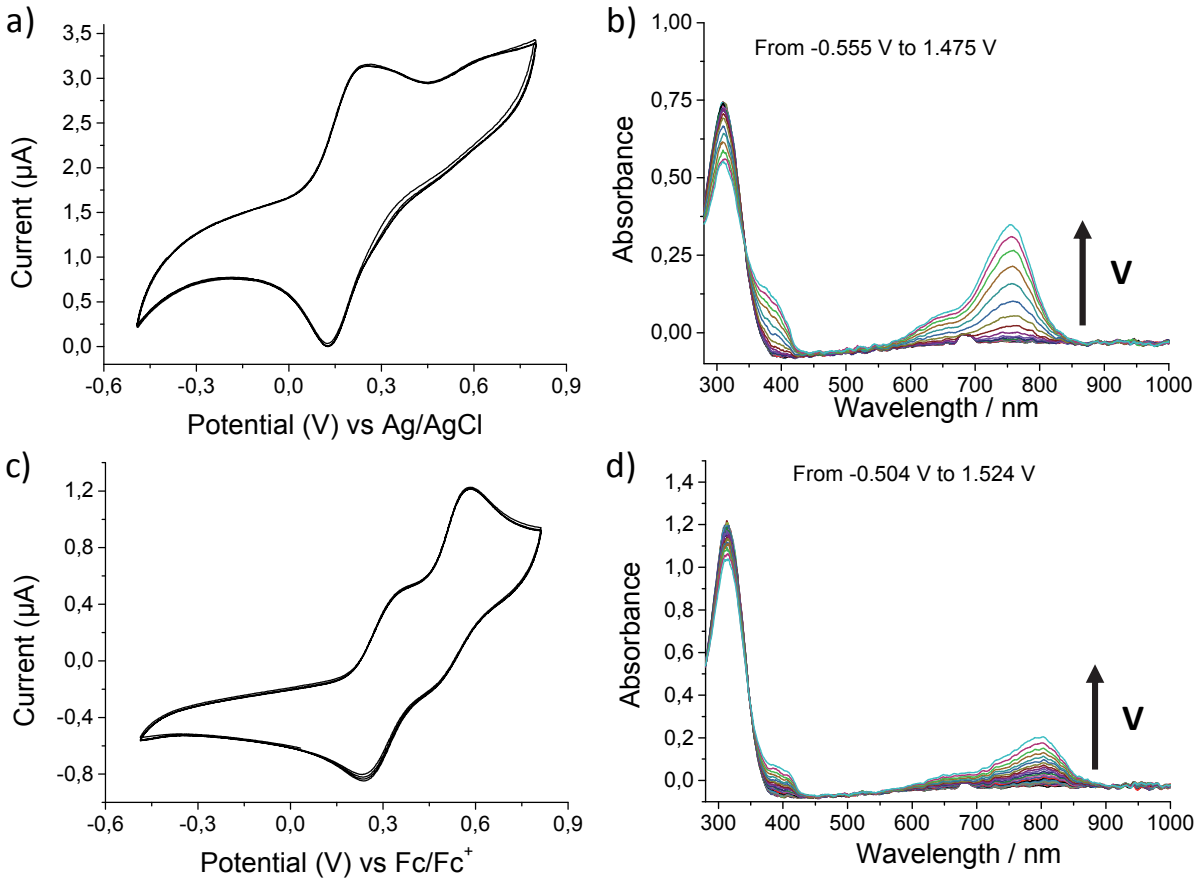


Figure S3. a) Cyclic voltammogram recorded at 50 mV/s and b) UV-Vis-NIR spectra recorded during oxidation from - 0.555 V to 1.475 V for a solution of compound **2A** (1.12 mg/mL) in 0.1M $NBu_4PF_6/C_2H_2Cl_4$; and c) cyclic voltammogram recorded at 50 mV/s and d) UV-Vis-NIR spectra recorded during oxidation from - 0.504 V to 1.524 V for a solution of compound **2B** (0.78 mg/mL) in 0.1M $NBu_4PF_6/C_2H_2Cl_4$

3. NMR Spectroscopy

^{1}H NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz before irradiation with white light and after different times of exposure to visible light.

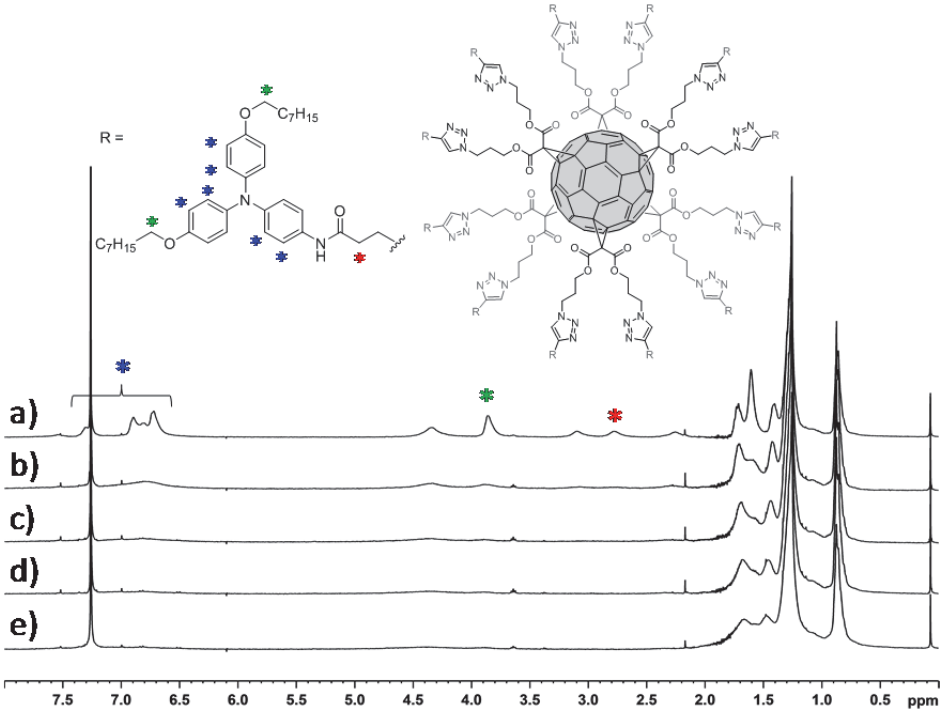


Figure S4. ^{1}H NMR spectra of compound **2A** obtained immediately after purification (a) and after b) 1 hour, c) 2 hours, d) 3 hours and e) 5 hours exposure to visible light.

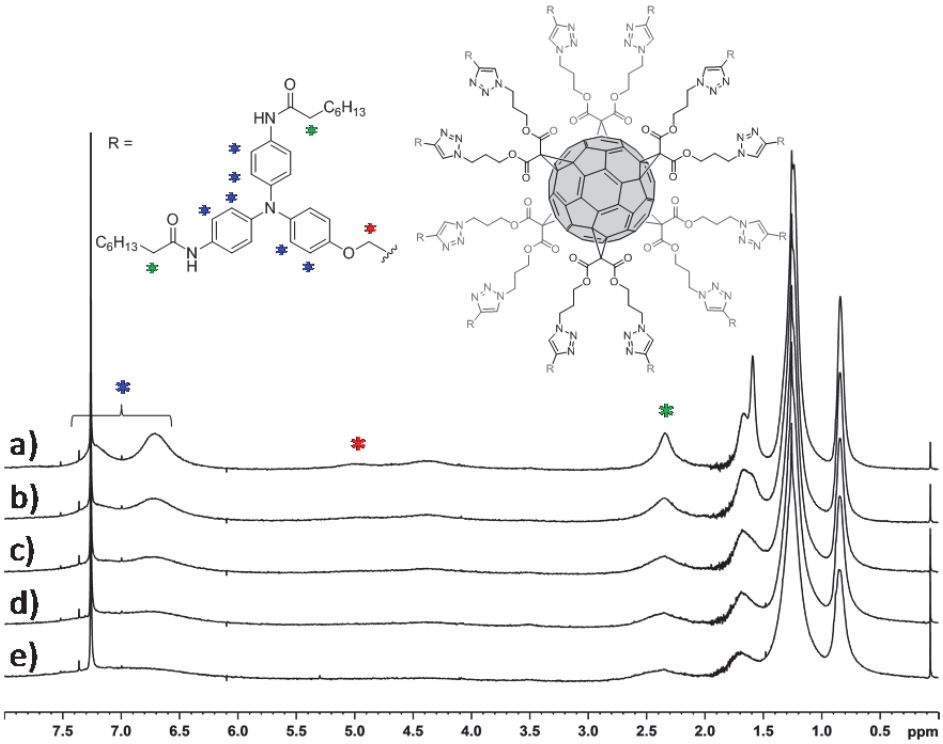


Figure S5. ^{1}H NMR spectra of compound **2B** obtained immediately after purification (a) and after b) 1.5 hours, c) 3 hours, d) 5 hours and e) 8 hours exposure to visible light.

4. Optical Spectroscopy

UV-Vis spectra were recorded using a Perkin Elmer - Lambda 25 apparatus with quartz glass cuvettes of 1 mm optical path under ambient conditions, unless otherwise stated.

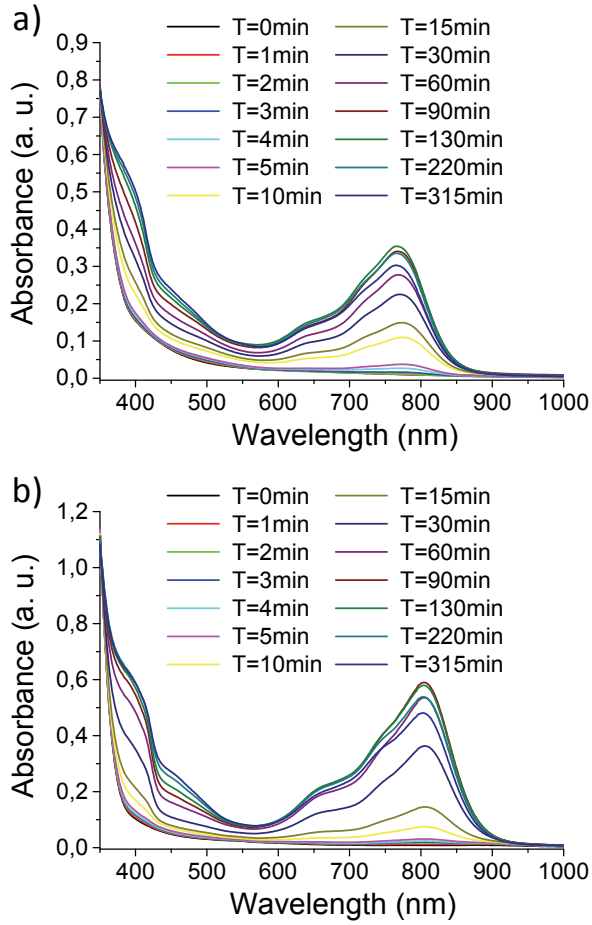


Figure S6 UV-Vis-NIR spectra obtained as a function of time of irradiation for an initial 0.1 mM solution of compounds **2A** (a) and **2B** (b) in chloroform.

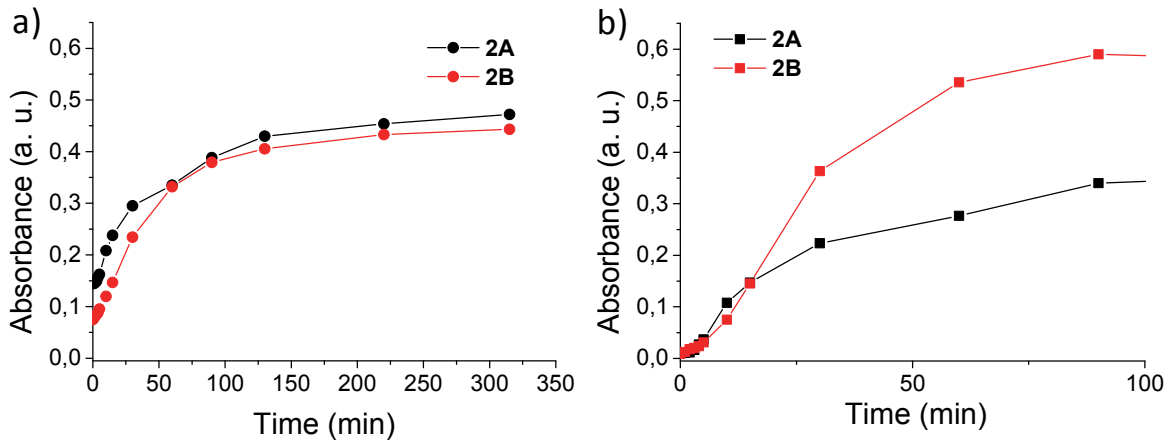


Figure S7. a) Irradiation kinetic experiment plotted from Vis absorption at λ = 405 nm (**2A**, black dot) or 420 nm (**2B**, red dot) for 0.1 mM solutions in chloroform; a) Irradiation kinetic experiment plotted from NIR absorption at λ ~ 765 nm (**2A**, black square) or 805 nm (**2B**, red square) for 0.1 mM solutions in chloroform.

5. Scattering Experiments

Dynamic Light Scattering Experiments:

In the dynamic light scattering experiments (DLS), the normalised time autocorrelation function, $g^{(2)}(q,t)$, is measured as a function of the scattering wave-vector, q, given by $q=(4\pi n/\lambda)\sin(\theta/2)$, where n is the refractive index of the solvent (1.44 for $CDCl_3$ at 20 °C), and θ is the scattering angle. The measurements used a 3D DLS spectrometer (LS Instruments, Fribourg, Swiss) equipped with a 25mW HeNe laser (JDS uniphase) operating at λ=632.8 nm, a two channel multiple tau correlator (1088 channels in autocorrelation), a variable-angle detection system, and a temperature-controlled index matching vat (LS Instruments). The scattering spectrum was measured using two single mode fibre detections and two high sensitivity APD detectors (Perkin Elmer, model SPCM-AQR-13-FC). Solutions were filtered before illumination through 0.2 μm PTFE Millipore filter into the cylindrical scattering cell.

The experimental signal is the normalised time autocorrelation function of the scattered intensity:

$$g^{(2)}(q,t)=\frac{\langle I(q,0)I(q,t)\rangle}{\langle I(q,0)\rangle^2} \qquad \text{(SI-1)}$$

The latter can be expressed in terms of the field autocorrelation function or equivalently in terms of the autocorrelation function of the concentration fluctuations, $g^{(1)}(q,t)$, through:

$$g^{(2)}(q,t)-1=\alpha+\beta\left|g^{(1)}(q,t)\right|^2 \qquad \text{(SI-2)}$$

Where α is the baseline (varying between 1×10^{-3} and 2×10^{-3} depending on the scattering angle and/or the system) and β the coherence factor, which in our experiments is varying between 0.8 and 0.9 depending on the samples and angles.

For diffusive processes with characteristic relaxation times inversely proportional to q^2 as in our experiments, the homodyne light scattering experiment yields $\left|g^{(1)}(q,t)\right| \approx \exp(-\Gamma t)$ where $\Gamma=Dq^2$ with D the mutual diffusion coefficient. However, our self-assemblies solutions are polydisperse as seen by the bimodal correlations functions displaying two characteristic decays well separated in time (see Figure S8a) and a distribution of Γ values must be considered. If $G(\Gamma)$ is the normalized distribution function for Γ, then

$$\left|g^{(1)}(q,t)\right| = \int_0^\infty G(\Gamma)\exp(-\Gamma t)\,d\Gamma \qquad \text{(SI-3)}$$

The distribution of decay rates $G(\Gamma)$ was determined using the CONTIN algorithm. The

Stokes-Einstein relation allows one to determine the hydrodynamic radius R_H of the scattered objects; R_H=kT/6πηD, if the temperature T and solvent viscosity η are known (here η=0.57 cP at 20 °C for $CDCl_3$).

X-ray Scattering Experiments:

X-ray scattering experiments were performed by using a diffractometer developed by Molecular Metrology (Elexience in France). It operates with a pinhole collimation of the X-ray beam and a two-dimensional gas-filled multiwire detector. A monochromatic (λ = 1.54 Å with Δλ/λ < 4%) and focused X-ray beam is obtained through a multilayer optic designed and fabricated by Osmic. The size of the incident beam on the sample was close to 600 µm. The sample to detector distance was set either at 0.70 m, allowing to explore scattering vectors ranging from q = 0.01 $Å^{-1}$ to 0.3 $Å^{-1}$ or at 1.35 m, allowing to explore scattering vectors ranging from q = 0.1 $Å^{-1}$ to 4 $Å^{-1}$. The magnitude of the scattering vector is defined by q=4πsin(θ/2)/λ, where λ and θ are the wavelength of the incident beam and the scattering angle, respectively. The q-resolution related to the beam size on the sample and the beam divergence was close to 0.005 $Å^{-1}$.

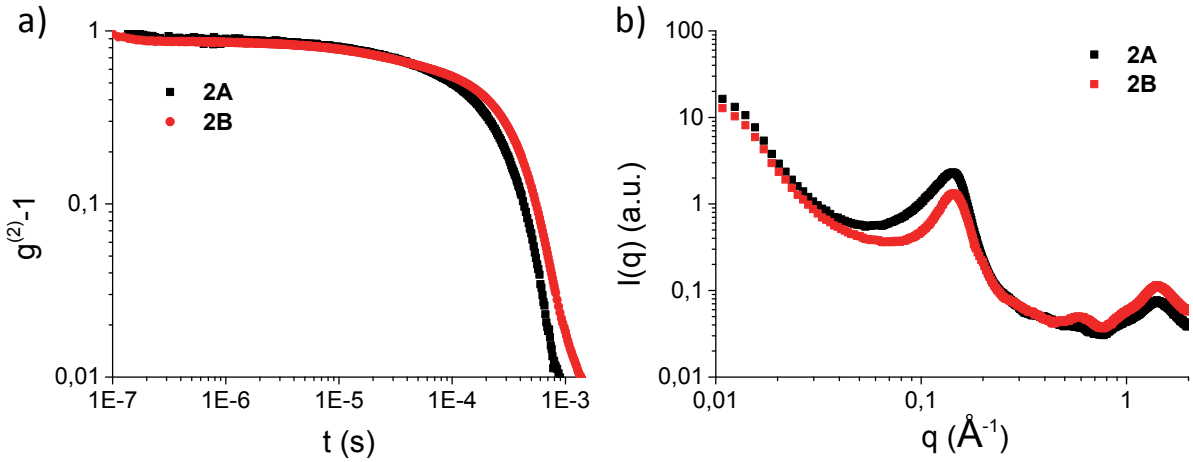


Figure S8: a) Time intensity autocorrelation function [($g^{(2)}$-1) at 90°)] for a chloroform solution of **2A** and **2B** irradiated with a 20W halogen lamp for 1 hour at C = 0.094 and 0.010 $g.cm^{-3}$, respectively; b) X-ray scattering curves of compounds **2A** and **2B** obtained from powders after evaporation of a chloroform solution irradiated for one hour with a 20W halogen lamp.

6. Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) images were obtained by scanning the samples using a Nanoscope 8 (Bruker) operated in Peak-Force tapping mode. Peak-Force AFM is based on Peak force tapping technology, during which the probe is oscillated in a similar fashion as it is in tapping mode, but at far below the resonance frequency. Each time the tip and the sample are brought together, a force curve is captured. These forces can be controlled at levels much lower than contact mode and even lower than tapping mode allowing operation on even the most delicate soft samples, as is the case here. Ultra-sharp silicon tip on nitride lever were used (Bruker, Scanasyst with spring constant of 0.4 N/m). During AFM imaging, the force was reduced in order to avoid dragging of molecules by the tip. All analyses of the images were conducted in integrated software.

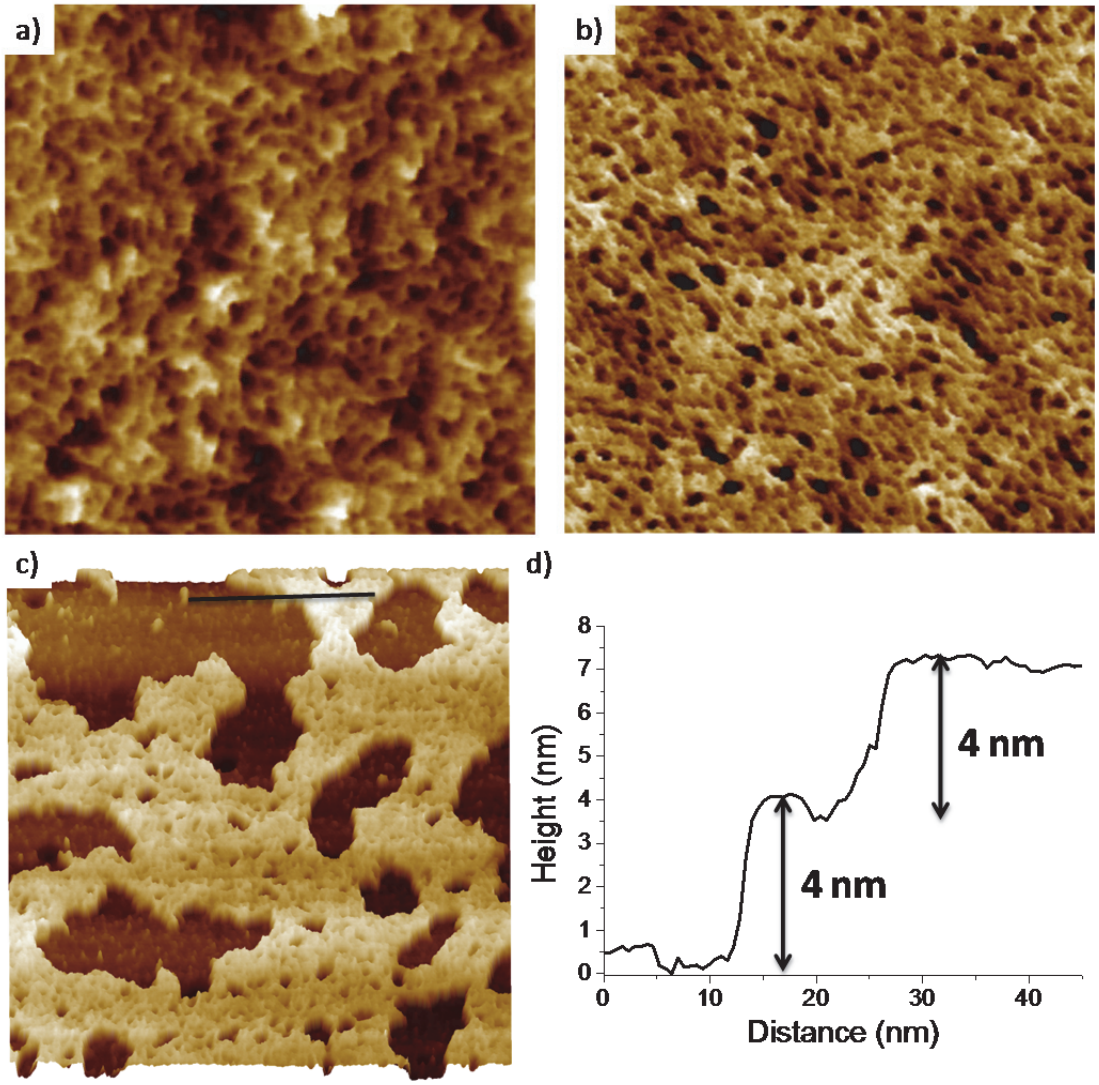


Figure S9. a-b) AFM images of 1 mM irradiated solutions of **2A** (a) and **2B** (b) in chloroform (surface scale 200 x 200 nm²); c) AFM image of a diluted solution of compound **2B** and d) height profile along the black line in image c) showing the presence of a bilayer with a 4 nm height for each layer.

7. Modelling

Modelling of compounds **2A** and **2B** was performed using MM2 minimization in ChemBio3D Ultra 14.0 software.

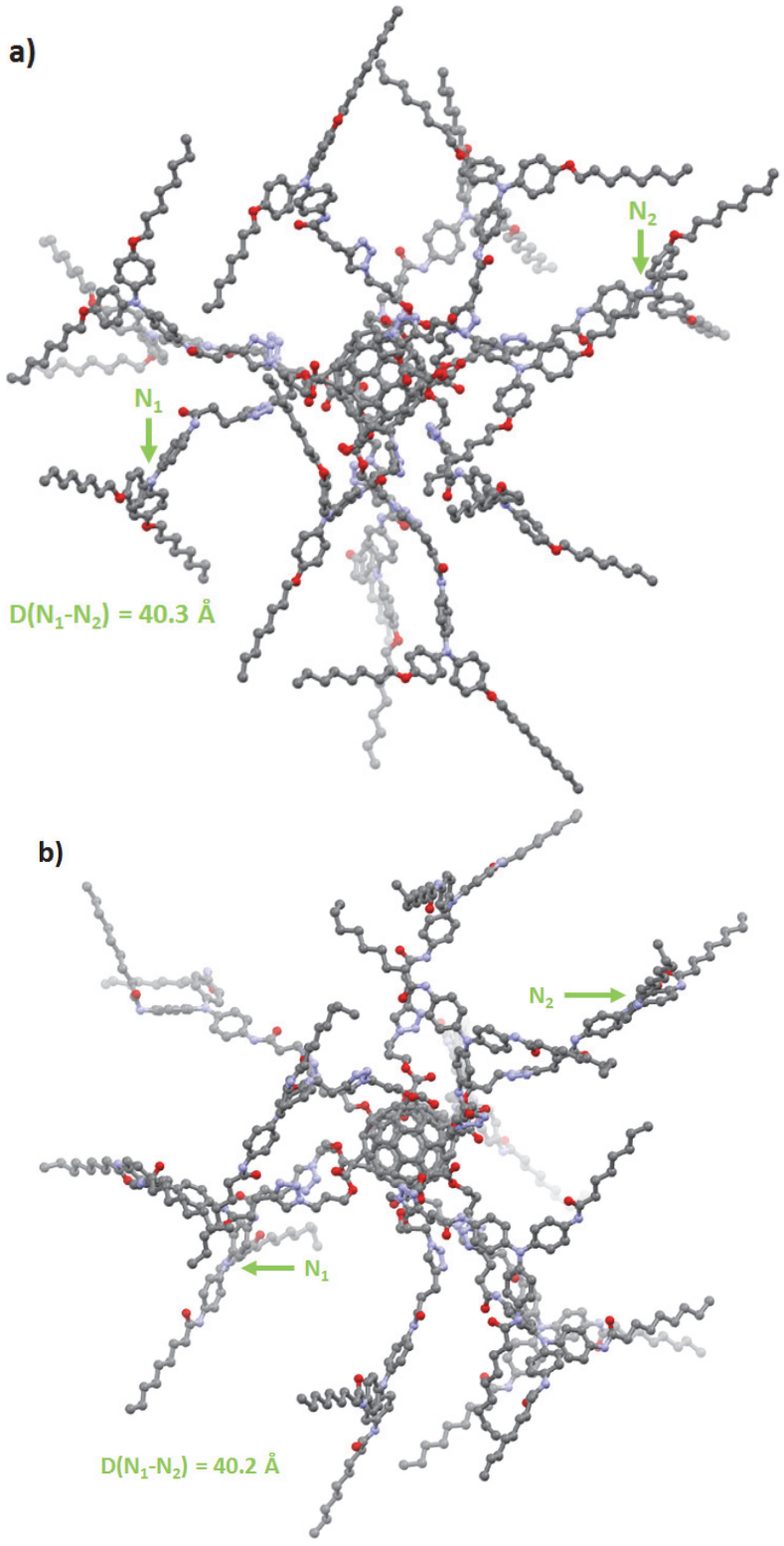


Figure S10. Molecular models of compounds a) **2A** and b) **2B**.
Arrows indicates the longest distance between central nitrogen atoms of the triarylamine unit.