Supplementary Material (ESI) for Soft Matter

Towards a general organogelator: combining a versatile scaffold and an efficient linking process

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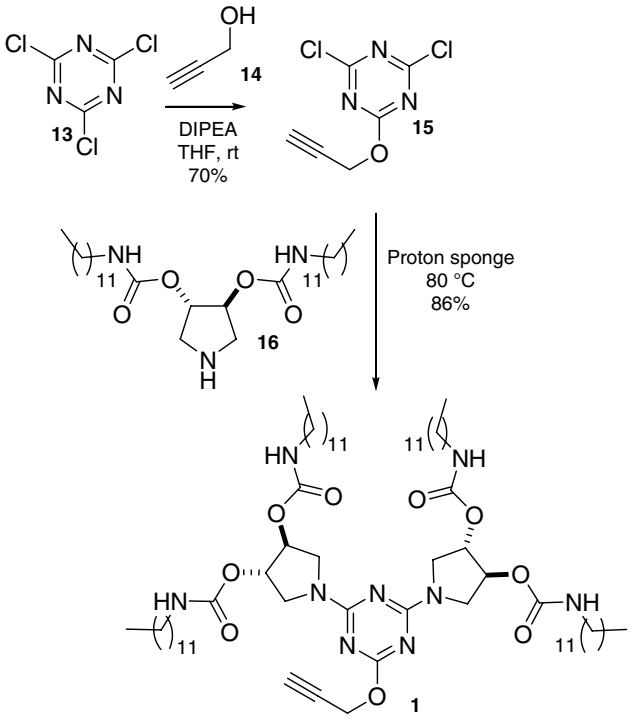
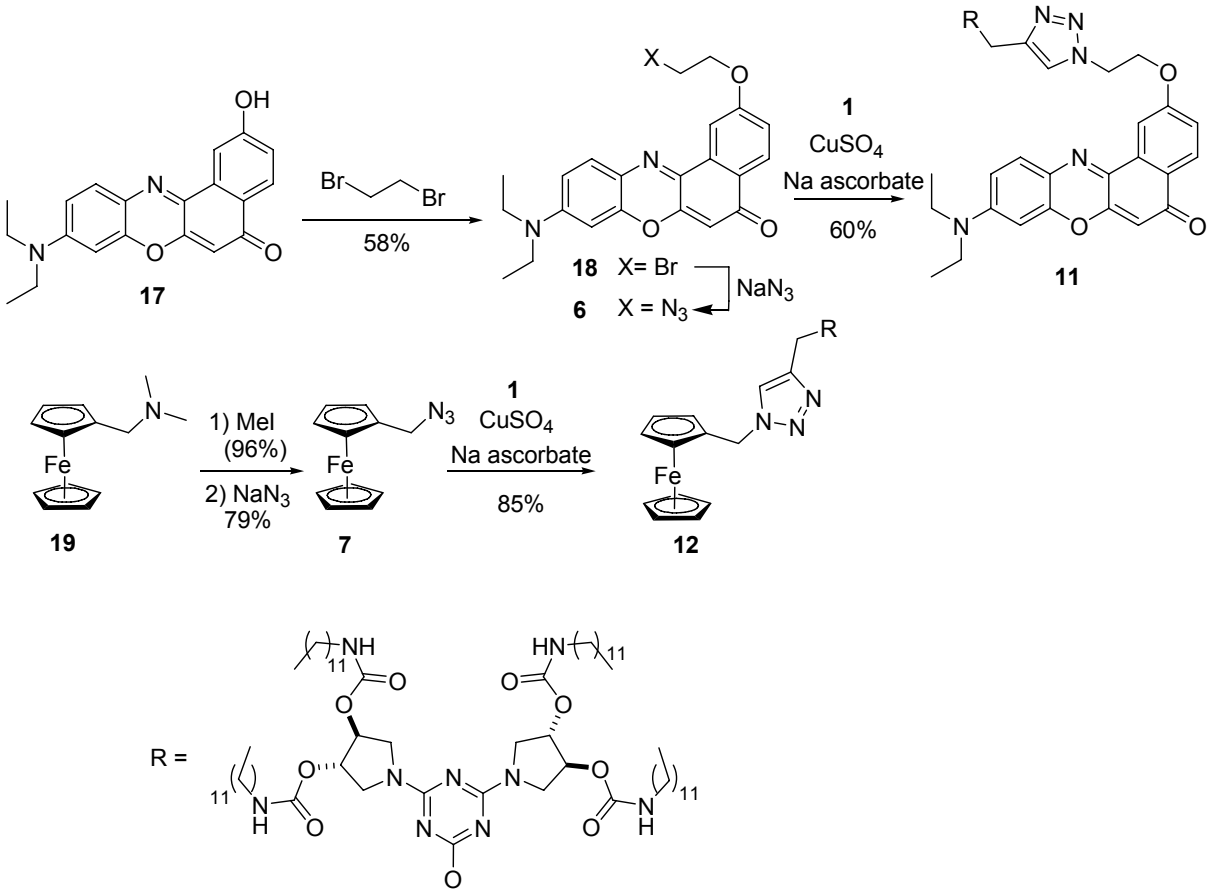
Supplementary Material



Scheme 1. Synthesis of compound **1**



Scheme 2. Synthesis of compounds **11** and **12**

Experimental Section

General remarks: NMR experiment were recorded on a Varian Gemini 200 MHz or 400 MHz spectrometer. Chemical shift are denoted in δ units (ppm) relative to TMS both for ^{1}H-NMR and ^{13}C-NMR. All FT-IR spectra were recorded on a Perkin-Elmer FT-IR 881 spectrometer. Absorption frequencies are expressed in wave numbers ν (cm^{-1}) and s, m and w notation refer to signal intensity and mean respectively strong, medium and weak. Elemental Analysis were performed with a Perkin-Elmer 240 Analyzer. MS spectra are recorded with a EI technique or with an ESI one depending on product molecular weight. Polarimetric measurement were performed with a Jasco-DIP370 polarimeter. The reaction for which microwaves irradiation was used, were performed in a CEM discover apparatus (magnetic frequency 2450 MHz). All compound used, 2,4,6-thrichloro-1,3,5-triazine, *N*-ethyl-*N*,*N*-diisopropyl amine (DIPEA), triethyl amine (TEA), nile-red hydroxide, *N*,*N*-dimethylaminomethyl-ferrocene, 1,2-dibromoethane, 1-bromodecane, *N*,*N*-dimethyl formamide (DMF) on molecular sieves, benzyl bromide, 4-amino-biphenyl, sodium azide, iodomethane, were commercially available (Sigma-Aldrich, Fluka) and were used without further purification. Toluene was distilled from sodium, tetrahydrofuran, dichloromethane, diethyl ether and acetonitrile were distilled from calcium hydride, triethylamine and *N*-ethyl-*N*,*N*-diisopropyl amine were distilled from KOH prior to use. R_f values refer to silica TLC on aluminium 0.25 mm thick (Merck F254).

Differential Scanning Calorimetry measurements were performed with a TA Instrument DSC Q2000 apparatus. Steel pan were used. All reported results refer to scans with heating/cooling gradient of 1°C/min. All measurements were performed on weighted (balance sensibility 1/100mg) small amounts of freshly prepared gels transferred with a spatula in the steel pans, which were then sealed.

Secondary Electron Microscopy investigation. Sample were prepared from a xerogel. The sample were coated with a thin film of gold (15 nm). A Cambridge Instrument apparatus and the INCA software were used. Acceleration potential 25 kV, working distance 17 mm.

Atomic Force Microscopy Images. The samples for the AFM investigation were prepard by dropping 50 μL of gel (5-10mg/mL) on a fresly cleaved mica slide (Dumico, Rotterdam, The Netherlands) and directly mounted in the spin-coater(KW 4A Chemat Technology). Spinning has been carried out by two successive steps of 20s and 40s at 2000rpm and 3000rpm respectively. The obtained samples were dried under dry nitrogen flux and then

mounted to the sample holder of the microscope. AFM imaging were performed with a P47-PRO instrument (NT-MDT co. Zelenograd, Moscow, Russia).using a NSC 36 silicon tip (MikroMasch, Tallinn, Estonia) having a resonating frequency of 125 kHz. Semicontact mode was used in order to avoid deformation or damaging of the examined soft samples. All the images were processed using the WSXM 4.0 Nanotec software[1]

Gelation Experiments. In a typical gelation experiment a weighed amount of the organogelator under investigation and small amount of solvent (generally between 0.5 and 1.5 mL) were placed in a 2 mL close vial. Only if the organogelator is not soluble in the tested solvent gelation may occour. The vial was heated using a heating gun until the solvent started to reflux. The solution was allowed to cool at room temperature. Gelation was detected by ''test tube inversion''. Gelation request different times depending on the gelator , its concentration and the chosen solvents.

SAXS measurement. Small-Angle X-ray Scattering (SAXS) experiments were performed on the Hecus M. Braun X-ray System GMBH Graz. The X-ray beam was monochromated to 1.546 Å ($\lambda Cu_{k\alpha}$ anode) by a Seifert-Debye generator ID 303. The scattered X-rays were detected by a two-dimensional position sensitive detector with a sample-to-detector distance of 275 mm. This configuration allow values of the scattering vector q [$Å^{-1}$] in the range $0.009<q<0.64$. Here q is defined as $q=(4\pi/\lambda)\sin(\Theta/2)$. The resulting data were corrected for background subtraction, the beam stop presence and for the beam form (desmearing), which is not a spot but a 10 or 14 mm width beam, using an home-made program. Sample were prepared in glass capillaries of 2 mm diameter. The hot solution was introduced in the capillary, which was immediately sealed whit dual glue, and then allowed to cool and gel.
Acquisition times ranged from about 2400s to 3600s. When a temperature dependent behaviour was studied (experiments described in figure6) 15 minutes were used to equilibrate temperature between two consecutive measurements.

Synthesis of 2,4-Dichloro-6-prop-2-ynyloxy-[1,3,5]triazine (15):

A solution of 2,4,6-trichloro-[1,3,5]-triazine 1**3** (1.50 g, 8.13 mmol) in dry THF (8 mL) was added with *N*-ethyl-*N*,*N*-diisopropyl amine (1.45 g, 11.26 mmol, 1.9 mL, d= 0.755 g/cm^3). The resulting solution was stirred at r.t. under inert atmosphere for 5 min. Propargyl alcohol 1**4** (350 mg, 6.25 mmol, 0.36 mL, d= 0.963 g/cm^3) was added with a syringe and the yellow solution was stirred at r.t. for 30 h. The final suspension was then filtered and the solution concentrated to obtain a yellow thick oil. This crude was then purified on silica by flash column chromatography using, in a polarity gradient, Petroleum ether and Ethyl Acetate, to afford 1179 mg (92% yield) of compound **5** as a white solid (R_f= 0.65, Petroleum Ether/Ethyl

Acetate 6:1).

m.p. = 40-41°C; ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 5.09 (d, ^{4}J = 2.6 Hz, CH_2, 2H); 2.58 ppm (t, ^{4}J = 2.6Hz, CH, 1H); ^{13}C-NMR (50 MHz, $CDCl_3$): δ= 172.2 (*C*O, 1C), 169.9 (*C*Cl, 2C), 77.6 (*C*CH, 1C), 75.5 (C*C*H, 1C), 57.1 (*C*H_2O, 1C) ppm; IR (KBr): ν 3285 (w), 2139 (m, C≡C), 1350 (s), 1306 (s), 1256 (s), 1180 (s), 1048 (s), 969 (m), 933 (s) cm^{-1}; MS (70 eV): m/z(%): 404 (90.74), 335 (100), 200 (93.84), 190 (35.25), 149 (26.65), 69 (85.40), 57 (98.89), 55 (62.39); Elemen. Anal calcd for $C_6H_3N_3OCl_2$: C 35.32, H 1.48, N 20.60; found C 35.43 H 1.59, N 20.66.

Synthesis of Dodecyl-carbamic acid 1-[4-(3,4-bis-dodecylcarbamoyloxy-pyrrolidin-1-yl)-6-prop-2-ynyloxy-[1,3,5]triazin-2-yl]-4-dodecylcarbamoyloxy-pyrrolidin-3-yl ester (1):

A Sovirel tube containing a solution of compound **16**[4] (12.2 mg, 0.06 mmol, 1 eq) in dry Toluene (1 mL) was added with *N*,*N*,*N*′,*N*′-Tetramethylnaphtalene-1,8-diamine (30 mg, 0.14 mmol, 2.5 eq) and compound **15** (73 mg, 0.14 mmol, 2.5 eq).[4] The tube was sealed and stirred for 20 h at 80 °C. The mixture was concentrated under reduced pressure. The crude residue was then purified on silica by flash column chromatography using, in a polarity gradient, $CHCl_3$ and ethyl acetate and TEA (0.5 %), to afford 61 mg (86 % yield) of compound **1** like a white solid. (R_f= 0.60 $CHCl_3$/Ethyl Acetate 6:1 + 0.5% Triethyl amine, yellow spot at permanganate detection).

m.p. = 168-169°C; $[\alpha]_D^{20}$=−19.5° (*c* = 1, CH_2Cl_2); ^{1}H-NMR (200 MHz, $CDCl_3$): δ= 5.16 (bs, 4H, *H*CO), 4.91 (d, ^{4}J = 2.4 Hz, OC*H*$_2$, 2H), 4.71 (m, N*H*, 4H), 3.77 (bs, C*H*$_2$N, 8H), 3.15 (m, C*H*$_2$NCO, 8H), 2.4 (t, ^{4}J = 2.4Hz, CC*H*, 1H), 1.47 (bs, NCH_2CH_2, 8H), 1.25 (bs, C*H*$_2$, 72H), 0.87 ppm (t, C*H*$_3$, 12H); ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 164.3 (*C*), 154.8 (*C*O), 75.1 (H*C*O), 54.0 (O*C*H_2), 50.7 (H_2*C*N), 41.3 (*C*H_2NHCO), 32.1 (NH CH_2*C*H_2), 30.1, 29.8, 29.7, 29.5, 26.9, 22.8 (chain's *C*H_2), 14.3 ppm (*C*H_3) ppm; IR (KBr): ν 3333 (w, N-H), 2921 (s, C-H), 2850 (m), 1698 (s, CO), 1614 (w), 1587 (m), 1530 (m), 1484 (w), 1405 (w) cm^{-1}; MS (ESI MS): m/z %: 1204 (100) [M+Na^+], 1182 (4%) [M^+]; Elem. Anal. calcd for $C_{66}H_{119}N_9O_9$: C 67.02, H 10.14, N 10.66; found: C 67.33, H 10.40, N 11.02.

Synthesis of 1-Azido-decane (3): [2] To a stirred solution of 1-Bromodecane (0.28 mL, 1.36 mmol) in DMF (3.0 mL) NaN_3 (132.62 mg, 2.04 mmol) was added. The reaction mixture was reacted for a few hours at 80 °C under nitrogen atmosphere. The precipitation of a white solid is observed. The mixture was diluted with water and then extracted with Petroleum Ether. The organic fraction is concentrated under reduced pressure to afford the product **3** as colourless oil in a quantitative yield.

^{1}H-NMR (200 MHz, $CDCl_3$): δ=3.24 (t, ^3J= 6.6Hz, CH_2N$_3$, 2H), 1.62 (m, $N_3CH_2CH_2$, 2H), 1.26 (bs, chain's CH_2, 14H), 0.87 (t, CH_3, 3H).

Synthesis of compound (8): In a microwaves reactor compound **3** (12.5 mg, 0.068 mmol) and compound **1** (20.1 mg, 0.017 mmol) were added with anhydrous tetrahydrofuran (1 mL), *N*-ethyl-*N*,*N*-diisopropyl amine (0.05 mmol, 9 µL, d= 0.755 g/cm^3) and finally with the catalyst $Cu(PPh_3)_3Br$ (6.3 mg, 0.007 mmol). The mixture was heated in a microwaves reactor using the following conditions: Power 300 W, T= 66 °C, temperature ramp 5 minutes, Hold 10 minutes. Two reaction cycles were carried out. After the first cycle further catalyst (6.3 mg, 0.007 mmol) was added. The mixture was concentrated and the crude residue was purified on silica by flash column chromatography ($CHCl_3$/Petroleum Ether 3/1) to afford 20.9 mg of product **8** as a waxy white solid (90% yield).

R_f=0.22 ($CHCl_3$); $[\alpha]_D^{20}$= 1.81 (c = 0.25, CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.60 (s, 1H, CC*H*), 5.47 (s, 2H, OCH_2), 5.15 (bs, 4H, C*H*OCO), 4.78 (bs, 4H, N*H*), 4.31 (pt, 2H, ^3J = 6.8 Hz, NCH_2), 3.78 (bs, 8H, *H*CN), 3.15-3.12 (m, 8H, NHCH_2), 1.42-1.12 (m, 96H, chain's CH_2), 0.86 ppm (m, 15H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 169.3 (*C*), 164.1 (*C*), 154.5 (*C*O), 143.3 (*C* triazole), 122.5 (*C*H triazole), 74.7 (H*C*O), 59.9 (CH_2O), 50.3 (NCH_2), 50.1 (NCH_2), 40.9 (NHCH_2), 31.6 (CH_2), 30.1 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 28.8 (CH_2), 26.5 (CH_2), 26.3 (CH_2), 22.4 (CH_2), 13.9 ppm (CH_3); IR (CH_2Cl_2): ν 3444 (w, NH), 3047 (w), 2927 (s, CH), 2846 (m), 1727 (m, CO), 1572 (m), 1516 (m), 1503 (m), 1403 (w), 1362 (w), 1314 cm^{-1} (w); MS (ESI MS): m/z (%):1388 (47) [M+Na$^+$], 1366 (100) [M$^+$]; Elem. Anal. for $C_{76}H_{140}N_{12}O_9$: C 66.82, H 10.33, N 10.33; found: C 66.51, H 10.67, N 10.05.

Synthesis of Azidomethyl-benzene (4):[3] A solution of benzyl-bromide (201.3 mg, 1.169 mmol, 0.14 mL, d= 1.438 g/mL) in dried *N*-*N*-dimethyl formamide (3 mL), was added with sodium azide (114.0 mg, 1.75 mmol). The mixture was stirred under nitrogen atmosphere and maintained at 80 °C for three hours. The mixture was hallowed to cool at r.t. and then the desired product is extracted with petroleum ether. The organic solution was concentrated under reduced pressure to afford 109.0 mg (70% yield) of product **4** as a colourless oil. ^{1}H-NMR (200 MHz, $CDCl_3$): δ= 7.37 (bs, 5H, aromatic C*H*), 4.35 ppm (s, 2H, CH_2).

Synthesis of compound 9: This compound was prepared and purified as described for compound **8**, starting from azidomethyl-benzene **4** and compound **1**, but using a molar ratio **4**/**1** of 1 : 1. Yield 76%. White wax.

R_f= 0.22 ($CHCl_3$); $[\alpha]_D^{20}$= - 6.19 (c = 0.21, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.54 (s, 1H, C*H* triazole), 7.38- 7.33 (m, 2H, aromatic C*H*), 7.26- 7.21 (m, 3H, aromatic C*H*), 5.49 (s, 2H, PhCH_2), 5.44 (m, 2H, OCH_2), 5.14 (bs, 4H, *H*CO), 4.79 (s, 4H, N*H*), 3.73 (m, 8H, *H*CN), 3.15 (m, 8H, NHCH_2), 1.47 (m, 8H, $NHCH_2CH_2$), 1.20 (m, 72 H, chain's CH_2), 0.87 ppm (t, 12H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 169.91 (C), 164.76 (C), 155.18 (C=O), 137.76 (C), 132.28(C), 129.42 (CH), 129.07 (CH), 128.49 (CH), 123.48 (CH), 75.36 (OCH), 60.52 (OCH_2), 54.55 (NCH_2), 50.93 (NCH_2), 50.67 (NCH_2), 41.53 ($NHCH_2$), 32.30 (CH_2), 30.22 (CH_2), 30.01 (CH_2), 29.73 (CH_2), 29.64 (CH_2), 27.15 (CH_2), 23.07 (CH_2), 14.51(CH_3); IR (CH_2Cl_2): ν 3446 (w), 3052 (s), 2929 (s), 2855 (m), 1723 (s), 1572 (s), 1517 (s), 1496 (s), 1454 (s) cm^{-1}; MS (ESI MS): m/z (%):1338 (35) [M+Na^+]; 1315 (100) [M^+], Elem. Anal. Calcd. for $C_{73}H_{126}N_{12}O_9$: C 62.67, N 11.90; H 8.99; found: C 62.45; N 11.74; H 8.68.

Synthesis of 4-Azido-biphenyl (5): [4] To a stirred solution of 4-Amino-biphenyl (200 mg, 1.18 mmol) in dry Acetonitrile (2 mL), tert-Butyl nitrite (0.21 mL, 1.77 mmol) and Azido-trimethylsilane (0.19 mL, 1.42 mmol) were added dropwise in about 10-15 minutes. During this time the solution had to be maintained at 0 °C in an ice bath. The reaction mixture was then allowed to cool and was stirred for further 2 hours. The reaction mixture was then extracted with Diethyl Ether and water; the organic phase was dried on anhydrous Sodium

sulfate and concentrated under reduced pressure to afford the desired product **9** (214 mg; 93% yield). R_f= 0.90 (Ethyl Acetate/ Petroleum Ether 1:5); ^{13}C-NMR (50 MHz, $CDCl_3$): δ= 139.82 (*C*), 138.85 (*C*), 137.65 (*C*), 128.64 (*C*H), 128.17 (*C*H), 127.15 (*C*H), 126.60 (*C*H), 119.15 ppm (*C*H); IR (KBr): $\tilde{\nu}$= 3034 (w, stretching CH), 2131-2100 (s, stretching N_3), 1596 (m), 1518 (m), 1486 cm^{-1} (s); elemental analysis calcd (%) for $C_{12}H_9N_3$: C 73.83, H 4.65, N 21.52; found: C 73.84, H 4.69, N 21.19.

Synthesis of compound 10: This compound was prepared and purified as described for compound **8**, starting from 4-Azido-biphenyl **5** and compound **1**, but using a molar ratio **5**/**1** 4:1. Yield 77%. Light Brown solid.

R_f = 0.12 ($CHCl_3$); $[\alpha]_D^{20}$= - 8.26 (c=0.12, CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$): δ= 8.12(s, 1H, Triazolic C*H*), 7.82÷7.39 (m, 9H, aromatics C*H*), 5.57 (s, 2H, OCH_2), 5.17 (s, 4H, *H*CO), 4.78 (bs, 4H, N*H*), 3.80 (pt, 8H, CH_2N pyrrolidine), 3.13 (m, 8H, NCH_2), 1.46 (m, 8H, NHCH$_2$CH_2); 1.15 (m, 72H, chain's CH_2), 0.88 ppm (m, 12H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 169.2 and 164.1 (Triazinic *C*), 154.5 (*C*O) 144.3, 141.4, 139.2, 135.7 (biphenyl *C*), 128.6, 128.3, 128.0, 126.7 (biphenyl *C*H), 120.9 (Triazolic *C*H), 74.7 (H*C*H), 59.8 (*C*H_2O), 50.3 and 50.1 (*C*H_2N pyrrolidine), 40.9 (NH*C*H_2), 31.6, 29.6, 29.4, 29.1, 29.0, 26.5 and 22.4 (Chain's *C*H_2), 13.9 ppm (*C*H_3); IR (CH_2Cl_2): ν 3445 (w, NH), 2928 (m, CH), 2855 (m, CH), 1726 (s, CO), 1572 (m), 1516 (m), 1456 cm^{-1}(w); MS (ESI MS): m/z (%): 1400 (49) [M + Na^+], 1378 (42) [M^+], 760 (100); Elem. Anal. Calcd. for $C_{78}H_{128}N_{12}O_3$: C 67.99, N 9.36, H 12.20; found: C 67.98, N 9.62, H 12.10.

Synthesis of 2-(2-Bromoethoxy)-9-diethylamino-5*H*-benzo[a]phenoxazin-5-one (18):[5] A stirred solution of Nile- Red Hydroxide **17** (300 mg, 0.90 mmol) in DMF (2 mL) was added with K_2CO_3 (2.5 mg, 0.018 mmol) and 1,2-Dibromoethane (1.74 g, 0.8 mL, 9.28 mmol). The reaction mixture was then stirred for 18 hours at 60 °C, under nitrogen atmosphere. The solution was concentrated under reduced pressure and the residue washed with water and extracted with CH_2Cl_2 (3 x 20 mL). The organic phase was dried on anhydrous Na_2SO_4 and concentrated to afford a dark solid. The crude material was then purified on silica gel by

flash column chromatography eluting with CH_2Cl_2 and $CHCl_3$ to afford 274 mg (69 % yield) of compound **18** as a dark purple solid.

Synthesis of 2-(2-Azido-ethoxy)-9-diethylamino-benzo[a]phenoxazin-5-one (6): A DMF (5 mL) solution of **18** (227 mg, 0.5 mmol) and NaN_3 (50.3 mg, 0.8 mmol) was heated at 80 °C for 24 h under stiring. Ice (10 mL) was added and the resulting suspension was filtrated. The collected solid was dried under reduced pressure. Then the reaction was stopped putting the reaction's flask in a ice bath and adding ice directly in the reaction flask, to allow product precipitation. The mixture was then filtered and washed with water; the solid was collected and dried to afford compound **6**. The remaining solution was extracted with diethyl ether (3 x 20 mL). The organic phase was dried with Na2SO4 and concentrated to afford a second portion of compound **6**. Altogether 164 mg (83% yield) of product **6** were obtained.
m.p. = 146-147 °C; ^{1}H-NMR (200 MHz, $CDCl_3$): δ= 8.24 (d, ^3J = 8.7 Hz, 1H, C*H* Nile-Red), 8.07 (d, ^4J = 2.6 Hz, 1H, CH Nile-Red), 7.60 (d, ^3J = 9.0 Hz, 1H, C*H* Nile-Red), 7.21 (dd, ^3J = 8.7 Hz, ^4J = 2.6 Hz, 1H, C*H* Nile-Red), 6.66 (dd, ^3J = 9.0 Hz, ^4J = 2.8 Hz, 1H, C*H* Nile-Red), 6.46 (d, ^4J = 2.8 Hz, 1H, C*H* Nile-Red), 6.31 (s, 1H, C*H* Nile-Red), 4.37 (t, ^3J = 5.0 Hz, 2H, OCH_2), 3. 70 (t, ^3J = 5.0 Hz, 2H, CH_2N_3), 3.46 (q, ^3J = 7.4 Hz, 4H, NCH_2), 1.26 ppm (t, ^3J = 7.4 Hz, 6H, NCH_2CH_3); ^{13}C-NMR (50 MHz, $CDCl_3$): δ= 174.61, 160.80, 152.09, 150.80, 146.89, 134.11, 131.11, 127.98, 124.76, 118.44, 109.65, 106.66, 105.48, 101.06, 96.49, 67.43, 50.41, 45.32, 12.93 ppm; 8.24 IR (KBr): ν 3068 (w), 2974 (m), 2930 (m) 2100 (s), 1580 (s), 1406 (s), 1345 (s); MS (70eV): m/z (%): 403 (17.10) [M^+], 375 (54.87) [M – 28$^+$], 360 (100) [M- N_3^+], 347 (28.36) [M- $CH_2N_3^+$], 319 (54.66); Elem. Anal. Calcd. for $C_{22}H_{21}N_5O_3$: C 62.19, H 5.25, N 17.36; found C 62.33, H 5.45, N 17.33.

Synthesis of compound 11: A microwave flask was charged with **1** (100 mg, 0.08 mmol), Na ascorbate (1.6 mg, 0.008 mmol), **6**. (35.5 mg, 0.1 mmol) and $CuSO_4$ (6 μL of a 1 M solution, 0.004 mmol). A mixture H_2O/THF 1:1 (2.0 mL) was added to obtain a dark purple suspension. The reaction mixture was heated in a microwaves reactor (Power 100 W,

Temperature 120 °C, Ramp 10 minutes, Hold 10 minutes, cooling on). The resulting suspension was extracted with $CHCl_3$. The organic phase was dried with anhydrous Na_2SO_4 and concentrated. The crude residue was purified on silica by flash column chromatography eluting in polarity gradient with, $CHCl_3$ and MeOH to afford 76 mg (60% yield) of **11** as a dark purple waxy solid.

R_f=0.1 ($CHCl_3$); $[a]_D^{24}$= = +7.39° (c=0.084, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 8.13 (d, ^3J = 8.6 Hz, 1H, -CH Nile-Red), 7.94 (d, ^4J = 2.6 Hz, 1H, -CH Nile-Red), 7.63 (s, 1H, triazolic CH), 7.56 (d, ^3J = 9.4 Hz, 1H, CH Nile-Red) 7.02 (dd, ^3J = 8.6 Hz, ^4J = 2.6 Hz, 1H, -CH Nile-Red), 6.63 (dd, ^3J = 9.4 Hz, ^4J = 2.8 Hz, 1H, -CH Nile-Red), 6.42 (s, 1H, CH Nile-Red), 6.23 (s, 1H, -CH Nile-Red), 5.45 (AB system, 2H, OCH_2), 5.13 (bs, 4H, HCO), 5.00 (bs, 4H, NH), 4.81 (s, 2H, CH_2O Nile- triazole), 4.53 (s, 2H, NCH_2 triazole), 3.74 (s, 8H, H_2CN), 3.44 (q, 4H, NCH_2, ^3J = 7.2 Hz), 1.26- 1.21 (m, 82 H, nCH_2 e NCH_3 nilo), 0.85 (t, ^3J = 7.2 Hz, 3H, CH_3,); ^{13}C-NMR (50 MHz, $CDCl_3$): 169.5, 164.4, 160.1, 154.9, 152.0, 150.8, 146.8, 144.0, 139.3, 134.1, 126.3, 122.2, 115.8, 102.6, 101.0, 131.1, 127.9, 118.5, 109.7, 106.2, 105.2, 96.3 (CH Nile), 124.7 (CH triazole), 75.1 (HCO), 66.9 (NCH_2 triazole- Nile), 59.9 (OCH_2 triazine- triazole), 50.5 (OCH_2, Nile- triazole e HCN), 45.2 (NCH_2 Nile), 41.3 (NCH_2CH_3 Nile and CH_2), 32.1, 30.7, 30.0, 29.7, 29.5, 29.4, 26.9, 22.9, 14.9, 14.3, 12.8, 11.3 (nCH_2 chains and CH_3 Nile); IR ($CHCl_3$): ν 3458 (w), 2928 (m), 1732 (m), 1716 (m), 1598 (m), 1498 (m) 1451 (m) cm^{-1} (m); MS (ESI MS): m/z (%):1609 (60) [M + Na^+], 1586 (100) [M^+]; Elem. Anal. Calcd. for $C_{88}H_{140}N_{14}O_{12}$: C 66.64, H 8.90, N 12.36; found: C 66.64, H 8.80, N 12.42.

Synthesis of *N*,*N*- dimethylaminomethylferrocene methiodide (20):[6] This synthesis had previously been described, but not product characterization. *N*,*N*-dimethylaminomethyl ferrocene **14** (0.14 mL, 170 mg, 0.7 mmol, d=1.228 g/cm^3) was diluted with methanol (1 mL). The resulting solution was added with MeI (0.06 mL, 151 mg, 1.05 mmol, d=2.26 g/cm^3). The reaction mixture was stirred in a water bath (50 °C) for 5 minutes and then allowed to cool. Diethyl Ether was added (1 mL) and an orange solid precipitate. The solid was then collected and dried to afford 247 mg (96% yield) of **20** as an orange solid.

R_f= 0.23 (Ethyl Acetate/Methanol 2.5/1 + 0.5% Triethylamine); ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 4.90 (s, 2H, NCH_2), 4.57 (t, ^3J =2.0 Hz, 2H, substituted Cp ring), 4.34 (t, ^3J = 2.0 Hz, 2H,

substituted Cp ring), 4.31 (s, 5H, C*H* unsubstituted Cp ring), 3.31 ppm (s, 9H, CH_3); ^{13}C-NMR (50 MHz, $CDCl_3$): δ= 72.07 (superimposed *C* and *C*H), 72.36 (*C*H), 70.89 (*C*H), 69.78 (*C*H_2), 52.89 ppm (*C*H_3).

Synthesis of Azidomethyl ferrocene (7): A DMF solution (4.2 mL) of **20** (324 mg, 0.84 mmol), was added with NaN_3 (82.0 mg, 1.26 mmol). The reaction mixture was stirred overnight at 85 °C under nitrogen atmosphere. Addition of ice (10 mL) to the cooled mixture induced the precipitation of a red solid. The suspension was extracted with diethyl ether (3x15 mL). The organic phase was then dried on Na_2SO_4 and concentrated to afford 160 mg (79% yield) of compound **7** as an orange solid. No further purification was requested.
UV/Vis ($CHCl_3$): λ_{max} = 437 nm; R_f= 0.80 ($CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 4.24 (t, ^3J = 1.6 Hz, 2H, substituted Cp ring), 4.20 (t, ^3J = 1.6 Hz, 2H, substituted Cp ring), 4.17 (s, 5H, CH unsubstituted Cp ring), 4.12 ppm (s, 2H, CH_2); ^{13}C-NMR (50 MHz, $CDCl_3$): δ= 68.45 (superimposed *C* and *C*H), 68.34 (*C*H), 50.64 ppm (*C*H_2); IR (KBr): ν 3100-3081(w, aromatic CH stretching), 2930 (w, aliphatic CH stretching), 2098-2066 (s, N_3 stretching), 1725 cm^{-1}(m, CN stretching); MS (EI, 70 eV): m/z (%): 241(47.25) [M^+], 213 (50.00) [M – N_2^+], 149 (67.92) [$FeCpCH_2N^+$], 121 (80.64) [$CpFe^+$], 57 (36.29), 56 (100) [CH_2N_3+ or $^{56}Fe^+$]; Elem. Anal. Calcd. for $C_{11}H_{11}FeN_3$: C 54.80, H 4.60, N 17.43, Fe 23.17; found: C 55.12, H 4.68, N 17.08.

Synthesis of compound 12: A THF/H_2O 1:1 (8 mL) solution was added with **1** (100 mg, 0.09 mmol), **7** (24 mg, 0.10 mmol), $CuSO_4$ (0.8 mg, 0.0045 mmol) and Na ascorbate (3.6 mg, 0.018 mmol). The reaction mixture was the vigorously stirred under nitrogen atmosphere for 24 hours. After 12 hours further $CuSO_4$ (0.8 mg) and sodium-L-ascorbate (3.6 mg) were added. The reaction mixture was then extracted with $CHCl_3$ (3x15 ml); the organic phase was then dried on Na_2SO_4 and concentrated to afford a yellow waxy crude residue. This was then purified on silica by flash column chromatography eluting with $CHCl_3$ and Ethyl Acetate in polarity gradient to afford 109 mg (85 % yield) of compound **12** as a waxy yellow solid.
R_f= 0.50 ($CHCl_3$/Ethyl Acetate 5.1); $[\alpha]_D^{20}$= = -4.4° (c=0.25 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (s, Triazolic C*H*), 5.42 (q, ^2J = 13.2 Hz, 2H, OCH_2), 5.27 (s, 2H, NCH_2Cp), 5.15 (m, 4H, *H*CO), 4.73 (bs, 4H, N*H*), 4.25 (m, 2H, NCH_2CH), 4.20 (m, 2H, NCH_2CHCH), 4.17(s, 5H, C*H* Cp ring), 3.76 (m, 8H, NCH_2 pyrrolidine), 3.15 (dq, ^3J = 12.8, 6.8 Hz, 8H, chain NHCH_2), 1.48(m, 8H, $NHCH_2CH_2$) 1.25 (bs, 72H, chain's CH_2), 0.87 ppm (t, 12H, ^3J = 6.4 Hz, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ= 169.64 (*C*O), 164.45 (Triazinic N=*C*-O), 154.92 (Triazinic N=*C*-N), 143.62 (Triazolic *C*), 122.61 (Triazolic *C*H), 75.08 (*C*H, HCO), 69.24 (*C*, Cp), 69.10 (*C*H, substituted Cp ring), 69.02 (*C*H, unsubstituted Cp ring), 60.32 (*C*H_2, O*C*H_2), 50.72 (*C*H_2 pyrrolidine), 50.41 (*C*H_2 pyrrolidine), 50.18 (CH_2, N*C*H_2Cp), 41.29, (CH_2, NH*C*H_2), 32.08, (CH_2, $NHCH_2CH_2$), 29.98, 29.80, 29.53, 29.44 and 26.93

(*C*H_2,aliphatic chain), 22.87 (*C*H_2, CH_3*C*H_2), 14.34 ppm (*C*H_3); IR (KBr): ν = 3663 (m), 2933(s), 2854(m), 1792(s), 1590(m), 1531(s), 1500 cm^{-1} (m); MS (ESI MS): m/z (%):1446 (100) [M+Na^+], 1423 (2) [M+H^+]; Elem. Anal. Calcd. for $C_{77}H_{130}FeN_{12}O_9$: C 64.96, H 9.20, N 11.81; found: C 64.67, H 8.93, N, 11.51.

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