Five-Fold Symmetric Penta-substituted Corannulene with Gelation Properties and Liquid Crystalline Phase

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1. General notes

Microwave reactions were carried out in a dedicated CEM Discovery microwave oven. The microwave power was limited by temperature control once the desired temperature was reached. All reagents and solvents were reagent grade and were used without further purification unless otherwise specified. Flash chromatographic purification was performed using silica gel Merck 60 (particle size 0.040–0.063 mm); the eluting solvent for each purification was determined by thin layer chromatography

(TLC). Analytical thin-layer chromatography was performed using Merck TLC silica gel 60 F254. Solvents for chromatography were technical grade and freshly distilled before use. ^{1}H NMR spectra were recorded on a Bruker AV2-500 (500MHz) and Bruker AV2-400 (400 MHz) spectrometers. Solvent for NMR spectroscopy were purchased from ARMAR chemicals, degassed with nitrogen and dried over molecular sieves. Chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak: $CDCl_3$ = 7.26 ppm. Multiplicities are given as: s (singlet), br (broad), d (doublet), t (triplet), q (quadruplet), m (multiplet). ^{1}H-decoupled ^{13}C NMR spectra were obtained on Bruker AV2-500 (125 MHz) and Bruker AV2-400 (100MHz) spectrometers. ^{13}C NMR chemical shifts are reported relative to the solvent residual peak: $CDCl_3$ =77.23 ppm. HR-ESI-MS: Finnigan Mat 900 MS. IR: Perkin Elmer Spectrum One (FT-IR). UV/Vis measurements were carried out on an Agilent 8453 UV/Vis spectrophotometer using a 1 mm path quartz cuvette. Emission spectra were recorded on an Edinburgh Instruments FLS920 spectrometer with excitation at 299 nm. Polarized Optical Microscopy (POM) images were taken on a Leica DM LB optical microscope equipped with a Linkam CSS450 hot stage. Small and Wide Angle X-ray Scattering (SAXS and WAXS) experiments were performed on a Rigaku MicroMax-002+ microfocused beam (4 kW, 45 kV, 0.88 mA) with the wavelength $\lambda_{\mathrm{Cu\text{-}K\alpha}}$= 0.15419 nm. The 2D scattering patterns were collected by a Fujifilm BAS-MS 2025 imaging plate system (15.2 x 15.2 cm^2, 50 µm resolution) with an effective scattering vector range of q= 1 nm^{-1} - 25 nm^{-1}. Differential Scanning Calorimetry (DSC) was performed on a DSC 2920 from TA Instruments equipped with a RCS cooling. The compounds were encapsulated in 40 µL crucibles and measured under nitrogen atmosphere in a temperature range from T=-10 to 150 °C with a heating and cooling rate of 2 K·min^{-1}. Molecular Models were created from ChemBio 3D Ultra 12. Transmission electron microscopy (TEM) was carried out using aJeol JEM-3200FSC field emission cryo electron microscope operating at 300 kV voltage. The images were taken in bright field mode using zero loss energy filtering (omega type) with the slit width of 20 eV. Micrographs were recorded using a GatanUltrascan 4000 CCD camera. The specimen temperature was maintained at -187 °C during imaging. Thin sections (~70 nm) were cut at -80 °C by Leica Ultracut UTC ultramicrotome using a 25o Diatome diamond knife. The sections were collected on 300 mesh lacey carbon grids. The samples were imaged without any staining.

2. Synthetic details

2.1 *Sym*-Penta-2-(1,2,3-triazole-1-(*N*-(2-ethyl)octadec-9-enamide)-4-ethyl)-corannulene (2). A mixture of *sym*-penta-(1-butyn-4-yl)-corannulene[S1] (**6**, 25 mg, 49.0μmol), *N*-(2-azidoethyl)octadec-9-enamide[S2] (132 mg, 0.38mmol) and copper nanoparticles (25 mg, 0.39mmol) in DMF (2.5 mL) in a microwave vessel was heated at 60 °C in a microwave reactor for 2 hours. The mixture was then filtrated over celite and the solvent was evaporated. The product was purified by column chromatography on silica gel eluted with a DCM:MeOH 93:7. The solvent was evaporated to yield a yellow wax (89 mg, 80%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.47 (s br, 10H), 6.87 (s, 5H), 5.28 (m, 10H), 4.44 (s, 10H), 3.69 (s br, 10H), 3.40 (s br, 10H), 3.16 (s br, 10H), 2.11 (t, J= 7.5 Hz, 10H), 1.95 (m, 20H), 1.54 (s br, 10H), 1.23 (s, 100H), 0.85 (t, J= 7.0 Hz, 15H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 174.13, 139.94, 134.67, 130.07, 129.73, 129.65, 122.82, 49.65, 31.98, 29.84, 29.81, 29.60, 29.40, 29.26, 27.30, 27.26, 25.78, 22.76, 14.20. IR (KBr): ν cm^{-1} 3298, 2925, 2854, 1649, 1547, 1456, 1374, 1217, 1145, 1052, 874, 722. UV ($CHCl_3$) λ_{max}, nm: 232, 264, 299. HRMS (ESI) m/z: found 1164.3731 (M + 2Na); calc ($C_{140}H_{220}N_{20}Na_2O_5$) 1154.3696.

2.2 *N*-(2-azidoethyl)heptanamide. Oxalyl chloride (1.5 mL, 17.5 mmol) was added dropwise to a solution of heptanoic acid (652 mg, 5.0 mmol) in dry DCM (2 mL) and DMF (3 drops) and stirred at 0 °C under inert atmosphere. After 3.5 h, the solvent and the oxalylchoride were evaporated and the residue was dissolved in dry DCM (5 mL); this solution was then slowly added to a mixture of 2-azidoethanamine (550 mg, 6.4 mmol) in dry TEA (1.5 mL) and dry DCM (15 mL); the reaction mixture was stirred at room temperature for 24 h under inert atmosphere. The solvent was evaporated and the product was purified by column chromatography on silica gel eluted with a DCM:MeOH 97:3. The solvent was evaporated to yield a colorless solid (880 mg, 89%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.84 (s br, 1H), 3.42 (m, 4H), 2.18 (t, J = 7.2 Hz, 2H), 1.62 (m, 2H), 1.31 (m, 6H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$):

δ173.61, 51.12, 39.00, 36.80, 31.64, 29.06, 25.71, 22.61, 14.13. HRMS (ESI) m/z: found 221.1370 (M + Na); calc ($C_9H_{18}N_4NaO$) 221.1373.

2.3 *Sym*-Penta-2-(1,2,3-triazole-1-(*N*-(2-ethyl)heptanamide)-4-ethyl)-corannulene (3). A mixture of *sym*-penta-(1-butyn-4-yl)-corannulene[S1] (**6**, 10.6 mg, 20.8μmol), *N*-(2-azidoethyl)heptanamide (220 mg, 1.11mmol) and copper nanoparticles (10.1 mg, 0.16mmol) in DMF (1 mL) in a microwave vessel was heated at 60 °C in a microwave reactor for 2 hours. The mixture was then filtrated over celite and the solvent was evaporated. The product was purified by column chromatography on silica gel eluted with a DCM:MeOH 90:10. The solvent was evaporated to yield a yellow powder (19 mg, 61%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.48 (s, 5H), 7.43 (s, 5H), 6.71 (t br, J = 5.0 Hz, 5H), 4.43 (t br, J = 5.0 Hz, 10H), 3,68 (m, 10H), 3.42 (m, 10H), 3.19 (t br, J = 5.0 Hz, 10H), 2.08 (t, J = 5.0 Hz, 10H), 1.51 (t br, J= 5.0 Hz, 10H), 1.21 (m, 30H), 0.81 (t, J= 10.0 Hz, 15H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 174.19, 140.02, 134.69, 129.71, 122.95, 122.59, 49.64, 39.63, 36.56, 33.00, 31.62, 29.06, 28.02, 25.74, 22.61, 14.14. IR (KBr): ν cm^{-1} 3294, 3072, 2927, 2856, 2102, 1657, 1548, 1455, 1368, 1217, 1143, 1052, 723. UV ($CHCl_3$) λ_{max}, nm: 257, 264, 299. HRMS (ESI) m/z: found 1154.3731 (M + 2Na); calc ($C_{140}H_{220}N_{20}Na_2O_5$) 1154.3696.

2.4 *N*-(2-azidoethyl)stearamide. Oxalyl chloride (1.52 g, 12.0 mmol) was added dropwise toa solution of stearic acid (1.06 g, 3.7 mmol) in dry DCM (20 mL) and DMF (5 drops) and stirred at 0 °C under inert atmosphere. After 3.5 h, the solvent and the oxalylchoride were evaporated and the residue was dissolved in dry DCM (15 mL); this solution was then slowly added to a mixture of 2-azidoethanamine (410 mg, 4.7 mmol) in dry TEA (1.1 mL) and dry DCM (15 mL); the reaction mixture was stirred at room temperature for 18 h under inert atmosphere. The solvent was evaporated and the product was recrystallized from MeOH to yield a colorless solid (754 mg, 58%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.69 (s br, 1H), 3.43 (m, 4H), 2.19 (t, J = 7.5 Hz, 2H), 1.62 (m, 2H), 1.56 (s, 2H), 1.25 (m, 26H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C-NMR

(125MHz, $CDCl_3$): δ 173.54, 51.21, 36.88, 32.88, 29.85, 29.83, 29.81, 29.76, 29.63, 29.51, 29.49, 29.43, 25.78, 22.85, 14.27. HRMS (ESI) m/z: found 375.30906 (M + Na); calc ($C_{20}H_{40}N_4NaO$) 375.30943.

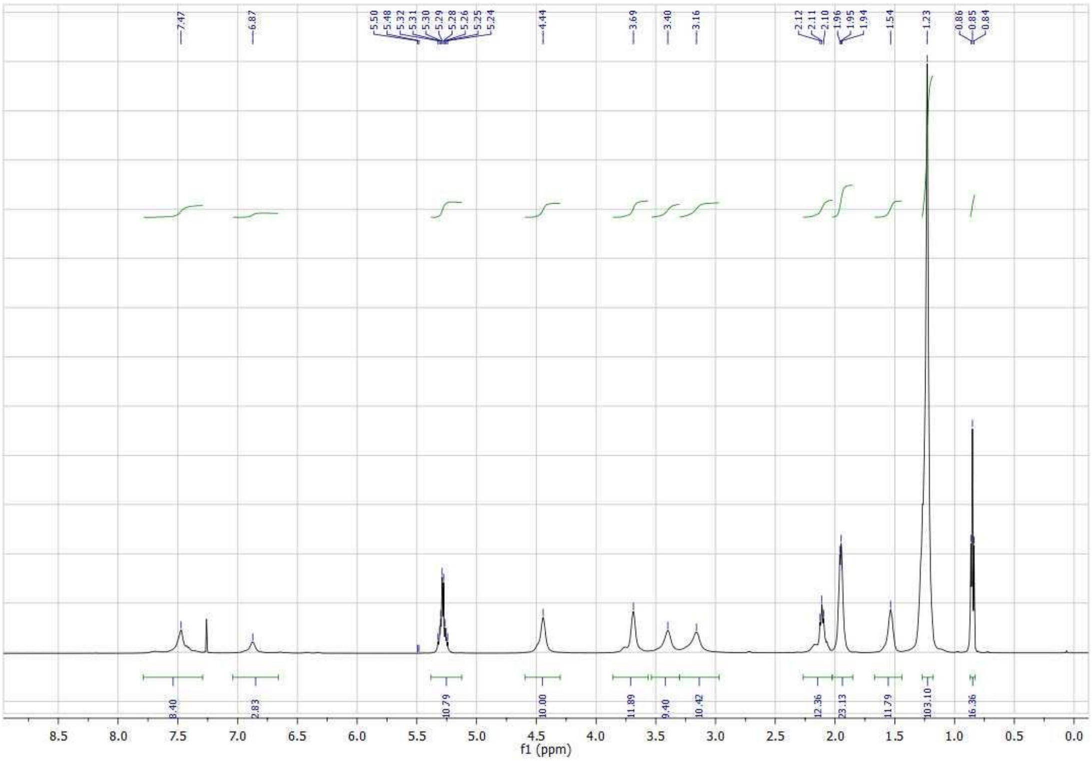
2.5 *Sym*-Penta-2-(1,2,3-triazole-1-(*N*-(2-ethyl)stearamide)-4-ethyl)-corannulene (4). A mixture of *sym*-penta-(1-butyn-4-yl)-corannulene[S1] (**6**, 29.8 mg, 58.4μmol), *N*-(2-azidoethyl)stearamide (164 mg, 0.47mmol) and copper nanoparticles (33.0 mg, 0.52mmol) in DMF (5 mL) in a microwave vessel was heated at 60 °C in a microwave reactor for 2 hours. The mixture was then filtrated over celite and the solvent was evaporated. The product was purified by column chromatography on silica gel eluted with a DCM:MeOH 93:7. The solvent was evaporated to yield a yellow powder (64 mg, 48%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.51 (s, 5H), 6.71 (s br, 2H), 4.47 (s br, 5H), 3.68 (s br, 10H), 3,44 (s br, 10H), 3.23 (s br, 10H), 2.10 (m, 10H), 1.53 (s br, 10H), 1.21 (m, 130H), 0.87 (t, J= 10.0 Hz, 15H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 174.30, 139.84, 134.75, 129.72, 123.11, 39.60, 36.63, 32.07, 29.85, 29.06, 29.80, 29.69, 29.55, 25.85, 22.83, 14.26. UV ($CHCl_3$) λ_{max}, nm: 256, 263, 300. HRMS (ESI) m/z: found 1159.4065 (M + 2Na); calc ($C_{140}H_{230}N_{20}Na_2O_5$) 1159.4086

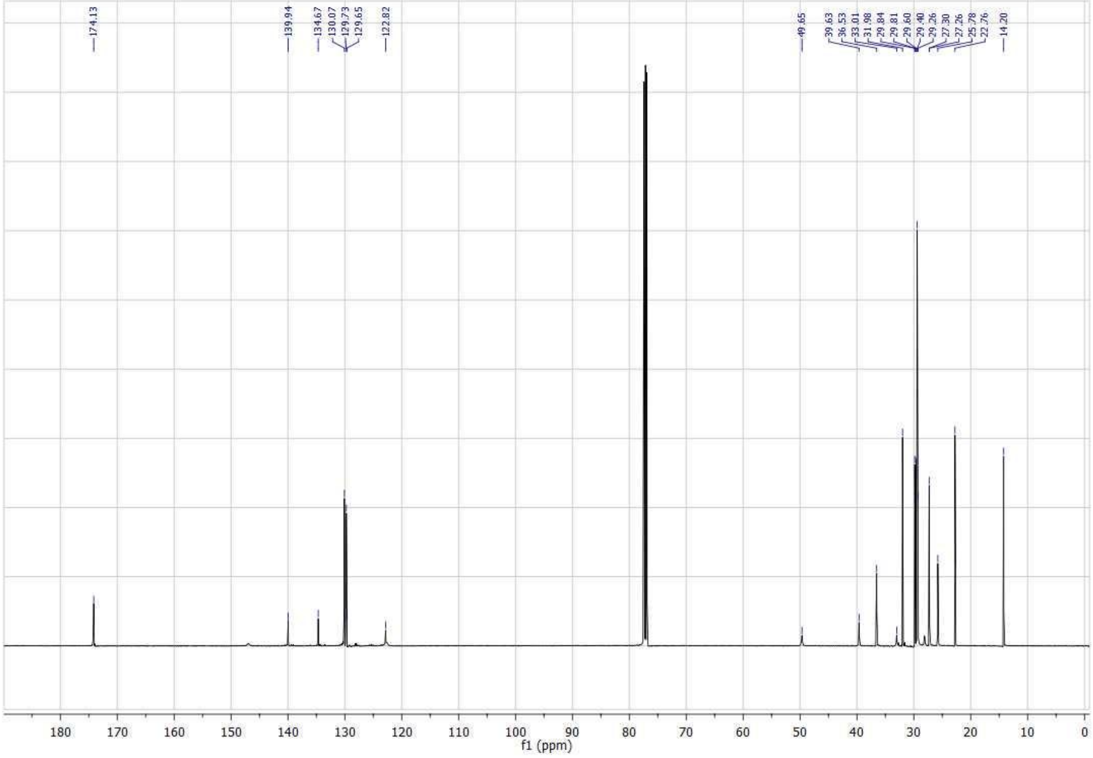
3. Characterization

3.1 *Sym*-Penta-2-(1,2,3-triazole-1-(*N*-(2-ethyl)octadec-9-enamide)-4-ethyl)-corannulene (2).

3.1.1 ^{1}H-NMR

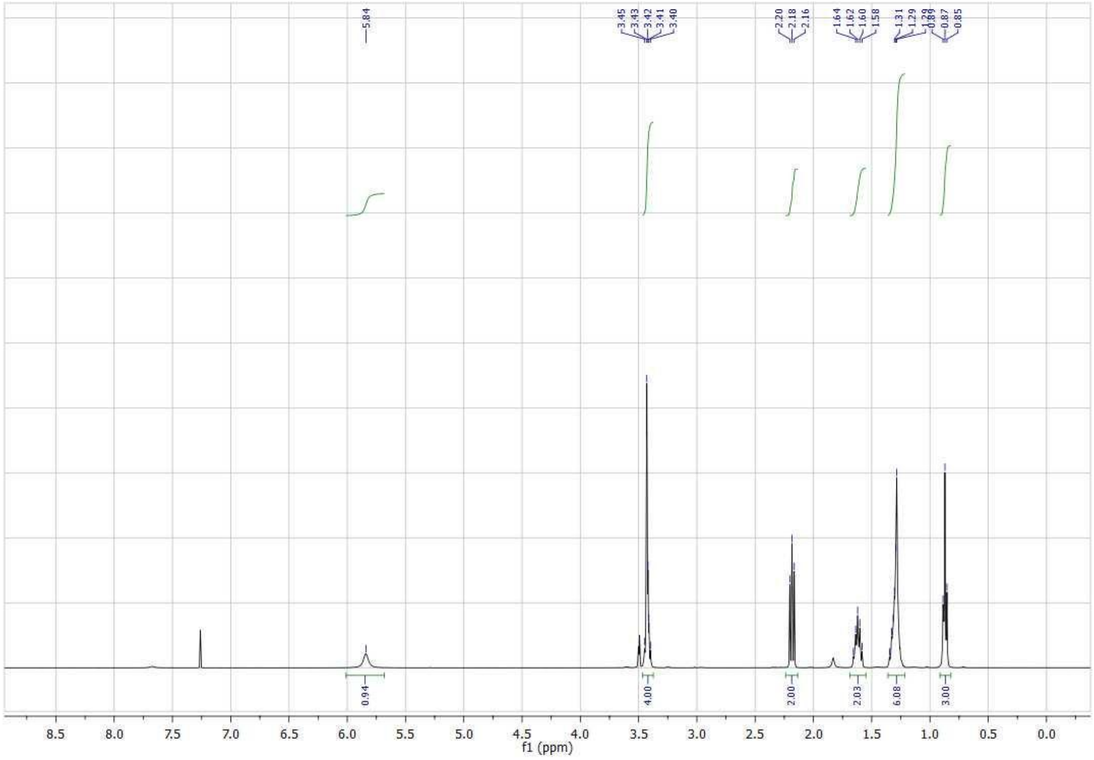


3.1.2 ^{13}C-NMR

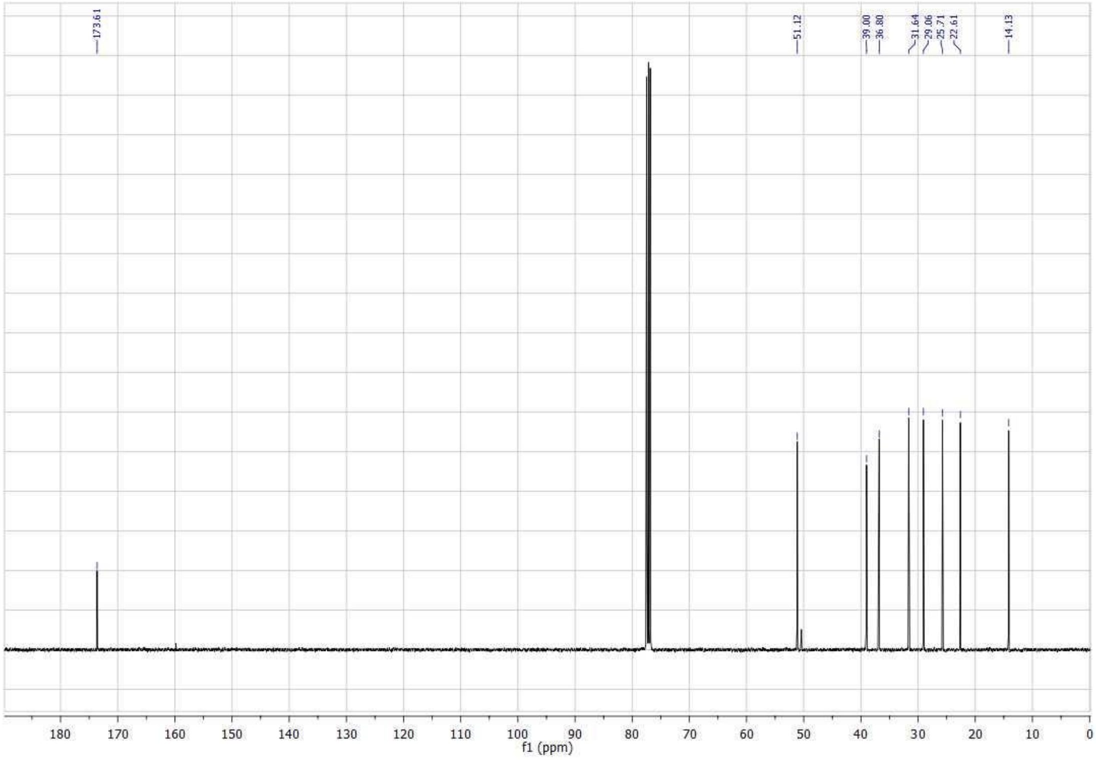


3.2 *N*-(2-azidoethyl)heptanamide.

3.2.1 ^{1}H-NMR

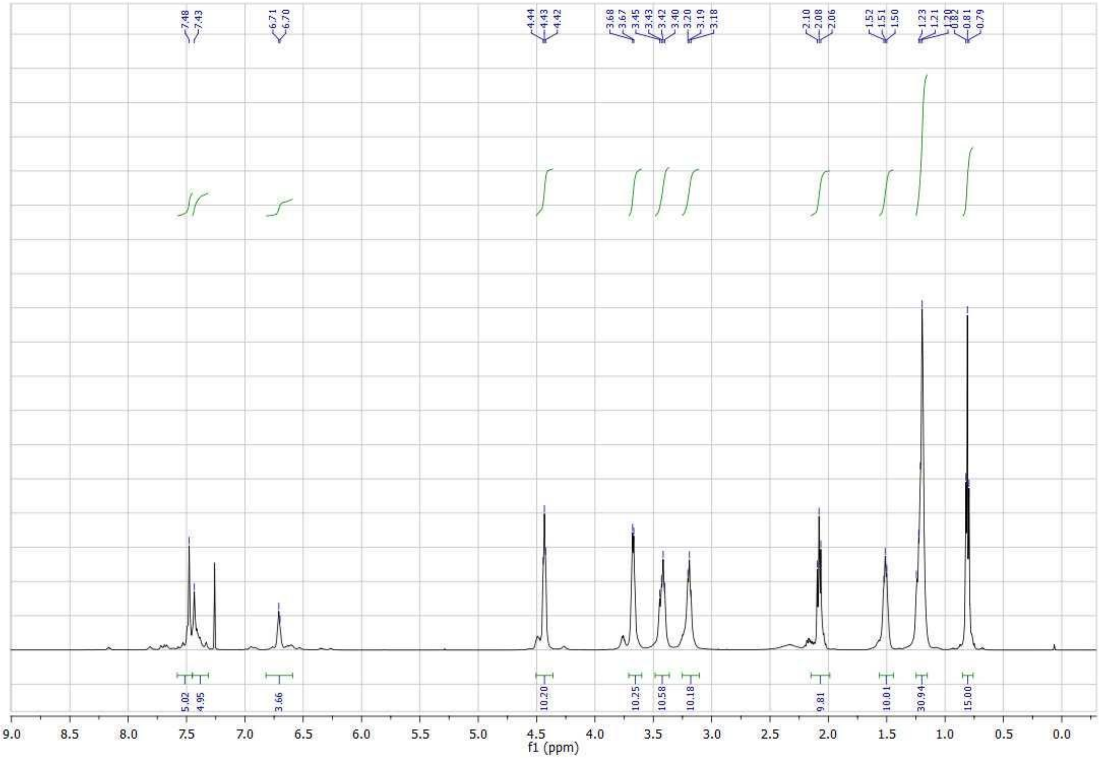


3.2.2 ^{13}C-NMR

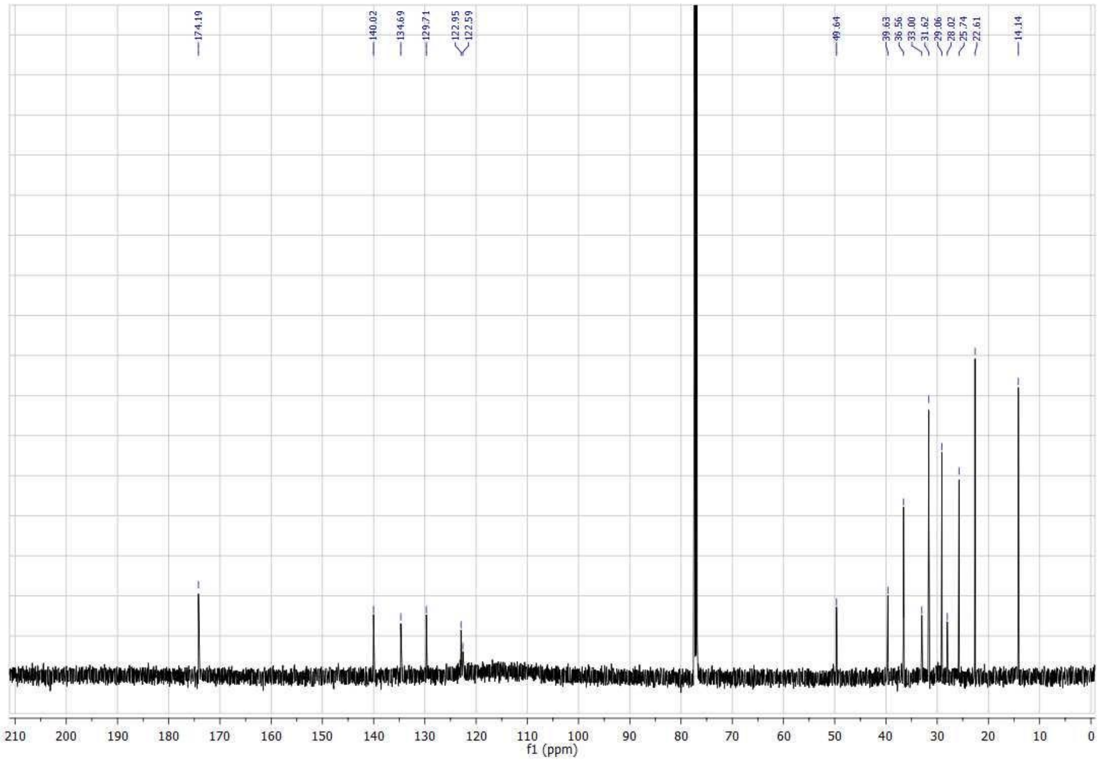


3.3 *Sym*-Penta-2-(1,2,3-triazole-1-(*N*-(2-ethyl)heptanamide)-4-ethyl)-corannulene (3).

3.3.1 ^{1}H-NMR

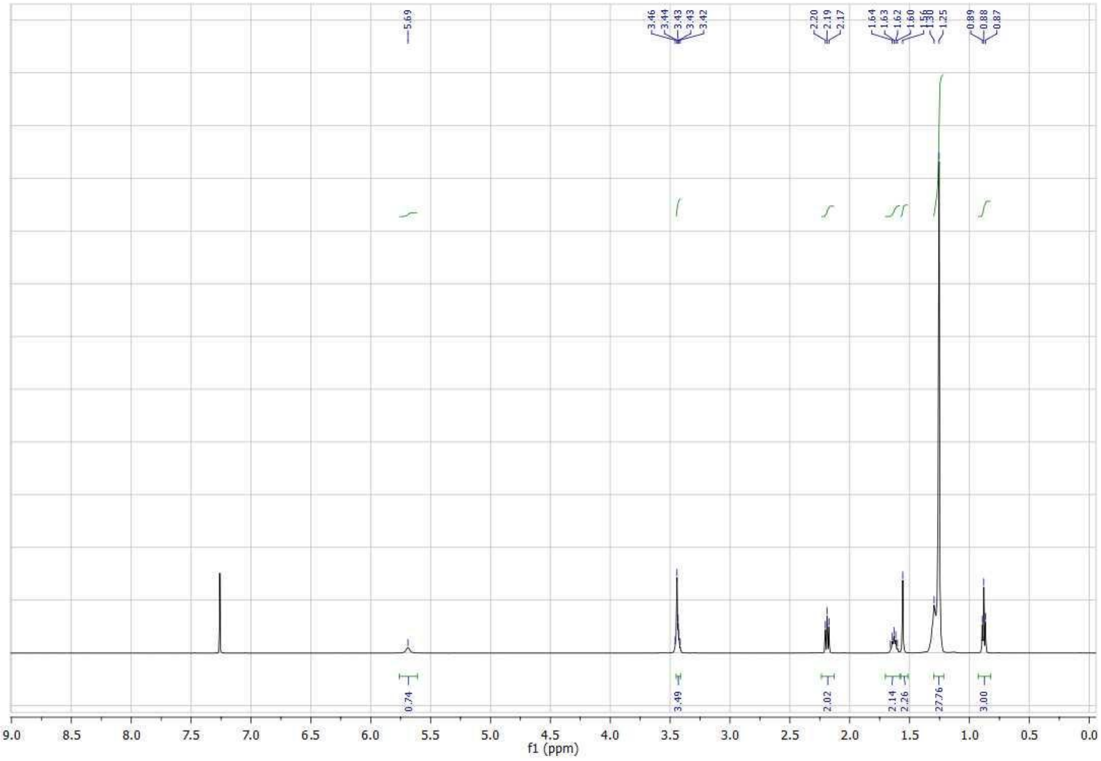


3.3.2 ^{13}C-NMR

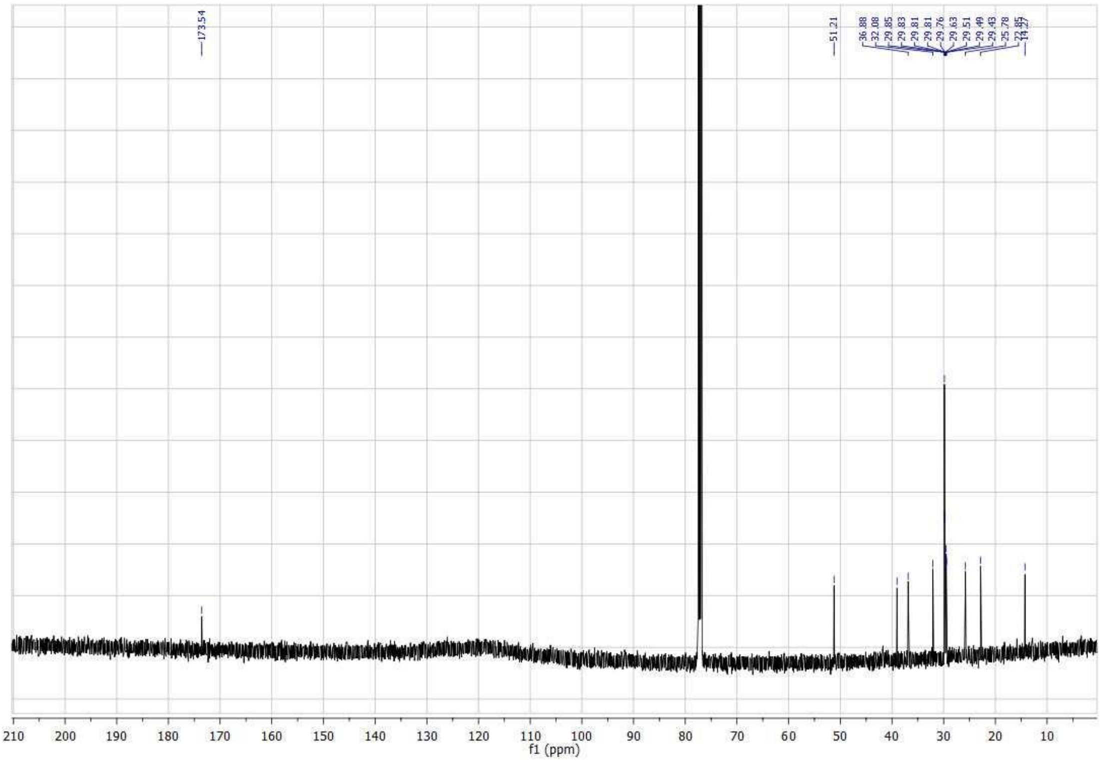


3.4 *N*-(2-azidoethyl)stearamide.

3.4.1 ^{1}H-NMR

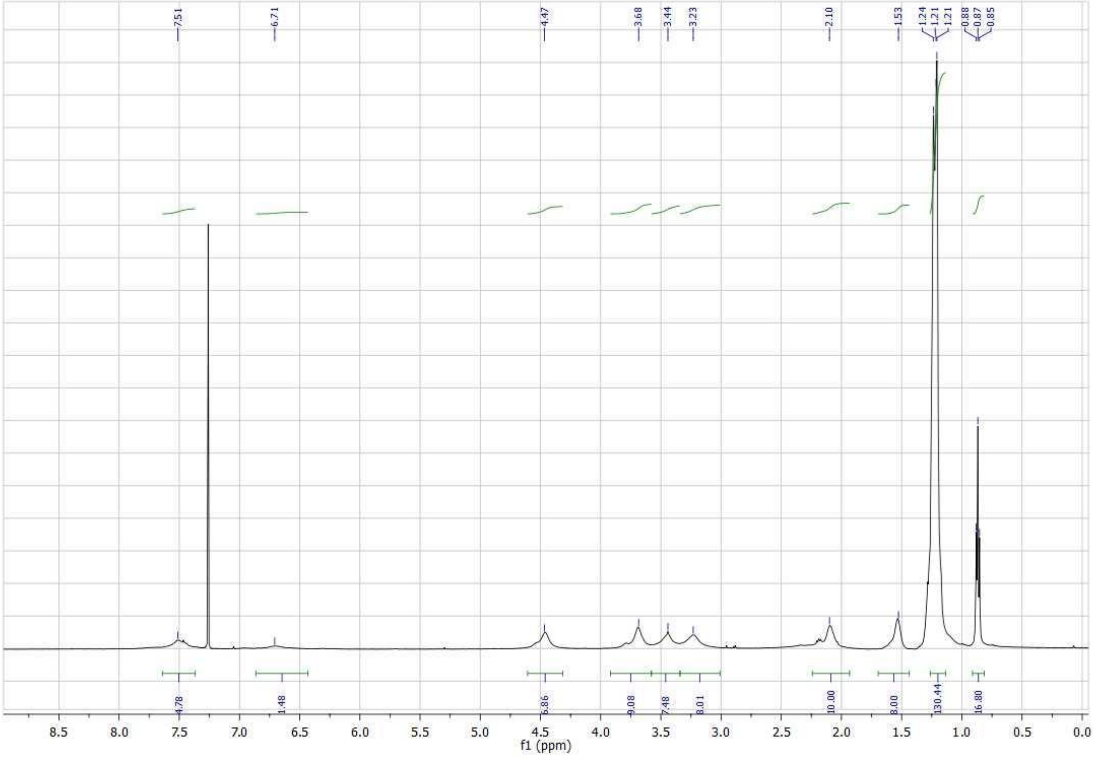


3.4.2 ^{13}C-NMR

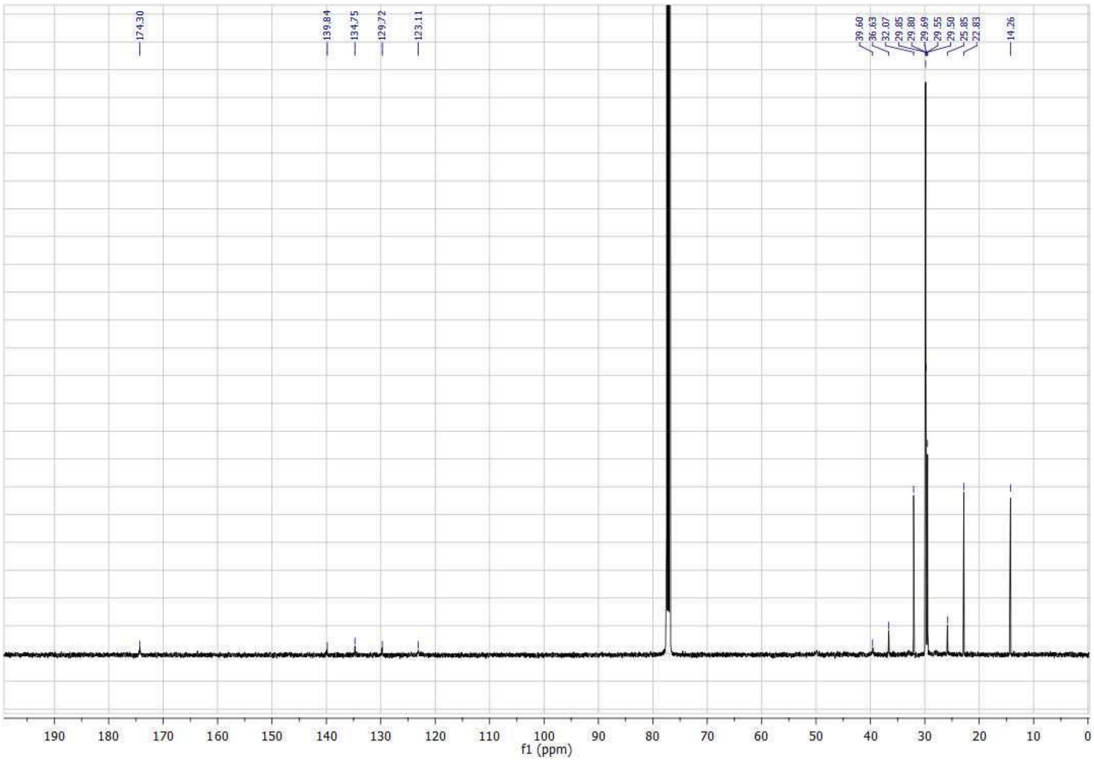


3.5 *Sym*-Penta-2-(1,2,3-triazole-1-(*N*-(2-ethyl)stearamide)-4-ethyl)-corannulene (4).

3.5.1 ^{1}H-NMR



3.5.2 ^{13}C-NMR



4. DSC and POM of 2 and 4

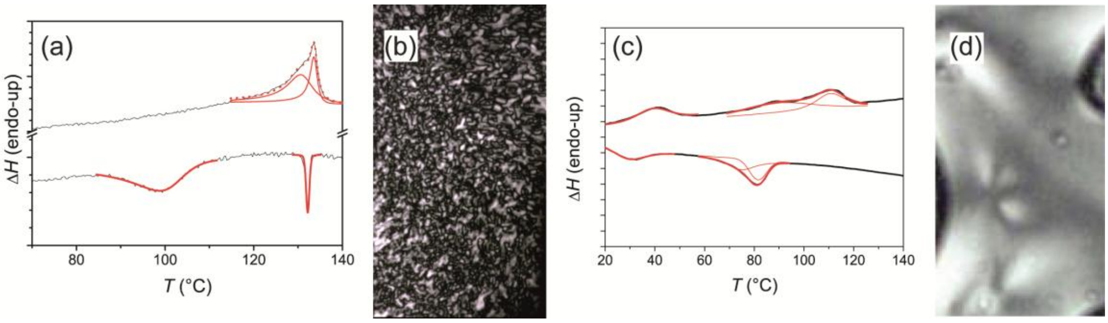


Figure S1: (a) DSC of compound **2** at 2 K min^{-1} and (b) polarized optical microscopy image of **2** at 20 °C. The birefringent phase proves the presence of a liquid-crystalline phase at room temperature.(c) DSC of compound **4** at 2 K min^{-1} and (d) POM image of **4** at 40 °Cafter melting, indicating a liquid-crystalline phase.

5. Gelation Test

In a typical gelation experiment a weighed amount of compound and 1 mL of the solvent mixture were placed in a vial, which was sealed and then heated until the compound dissolved. The solution was allowed to cool to room temperature. Gelation was considered to have occurred when a homogeneous substance was obtained, which exhibited no gravitational flow. The following abbreviations are used: gelation: G (minimum gelation concentration in mg compound per mL solvent); insoluble: I; soluble (solubility in mg mL^{-1}): S; viscous solution: VS.

Solvent	Compound 2	Compound 3	Compound 4
Heptane	I	I	I
Hexane	I	I	I
Cyclohexane	G (8)	I	G (10)
Methylcyclohexane	G (15)	I	S (> 40)
Benzene	VS	I	S (> 40)
Toluene	S (> 40)	I	S (> 40)
CCl_4	S (> 40)	I	S (> 40)
$CHCl_3$	S (> 40)	S (> 40)	S (> 40)
CH_2Cl_2	S (> 40)	S (> 40)	S (> 40)
THF	S (> 40)	S (> 40)	S (> 40)

Acetone	S (> 40)	S (> 40)	I
Ethyl Acetate	S (> 40)	I	I
Acetonitrile	I	I	I
Ethanol	S (> 40)	S (> 40)	S (> 40)
Isopropanol	S (> 40)	S (> 40)	S (> 40)
Water	I	I	I

Table S1. Gelation test for compounds **2**, **3** and **4** in common organic solvents.

Water : EtOH ratio	**Compound 2**	**Compound 3**	**Compound 4**
90:10	S (< 40)	S	S (< 40)
75:25	I	S	I
60:40	I	S (< 40)	I
50:50	I	I	I
25:75	I	I	I

Table S2. Gelation test for compounds **2**, **3** and **4** in water/ethanol solutions.

Water : IPA ratio	**Compound 2**	**Compound 3**	**Compound 4**
90:10	S (> 40)	S	S (< 40)
75:25	S (< 40)	S	S (< 40)
60:40	I	S	I
50:50	I	S (< 40)	I
25:75	I	I	I

Table S3. Gelation test for compounds **2**, **3** and **4** in water/isopropanol solutions.

5.1 FTIR analysis of compounds **2** and **4** in Cyclohexane.

	Compound 2		**Compound 4**	
Concentration (mg mL^{-1})	ν NH (cm^{-1})	ν CO (cm^{-1})	ν NH (cm^{-1})	ν CO (cm^{-1})
1.0	3298	1649	3316	1646
5.0	3297	1650	3314	1647
15.0 (gel)	3300	1652	3317	1646
20.0 (gel)	3298	1647	3314	1645

Table S4. FTIR ν values of NH and CO bonds for solutions and gel of **2** and **4** in cyclohexane.

6. UV-vis and Fluorescence Spectra of Compound 2 and 4 in Cylcohexane.

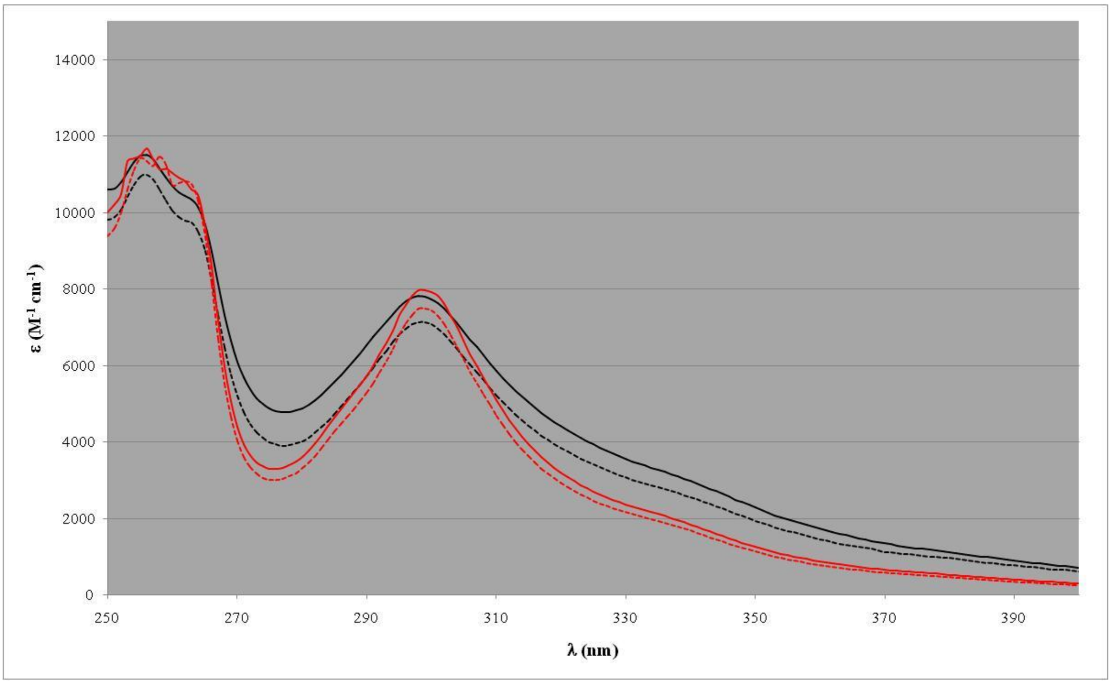


Figure S2: UV-vis spectra of **2**, 3.03x10^{-5} M (solid black) and 2.27x10^{-3} M (dashed black), and **4**, 3.15x10^{-5} M (solid red) and 1.98x10^{-3} M (dashed red), in cyclohexane.

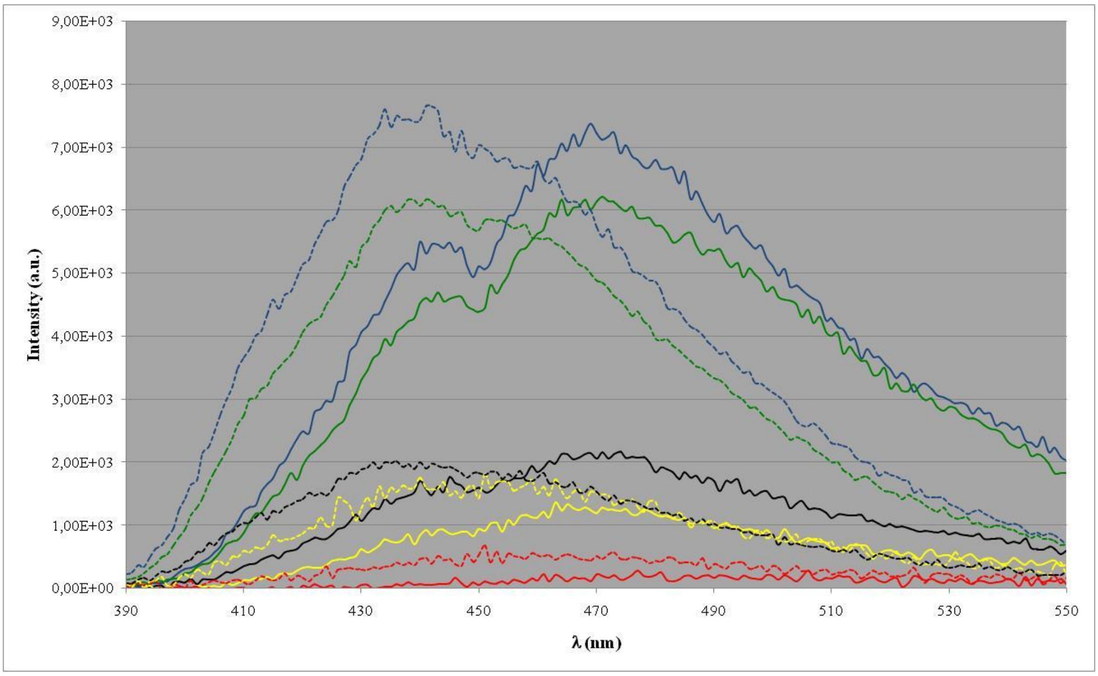


Figure S3: Emission spectra of **2**, 3.03x10^{-5} M (black), 9.08x10^{-4} M (blue), 4.54x10^{-4} M (green), 2.27x10^{-3} M (yellow), Gel 20 mg mL^{-1} (red), and **4**, 3.15x10^{-5} M (dashed black), 8.90x10^{-4} M (dashed blue), 4.11x10^{-4} M (dashed green), 1.98x10^{-3} M (dashed yellow), Gel 20 mg mL^{-1} (dashed red).

7. Literature References

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S2 Y. M. Osornio, P. Uebelhart, S. Bosshard, F. Konrad, J. S. Siegel, E. M. Landau, *J. Org. Chem.*, 2012, **77**, 10583.