Effect of Regioisomerism on the Self-assembly and Photophysical Behavior of 1,3,4-Thiadiazole-based Polycatenars

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Materials and methods

Commercially available chemicals were used without any purification; solvents were dried following the standard procedures. Chromatography was performed using either silica gel (60-120 and 100-200) or neutral aluminiun oxide. For thin layer chromatography, aluminium sheets pre-coated with silica gel were employed. IR spectra were recorded on a Perkin Elmer IR spectrometer at normal temperature by using KBr pellet. The spectral positions are given in wave number (cm⁻¹) unit. NMR spectra were recorded using Varian Mercury 400 MHz (at 298K) or Bruker 600 MHz NMR spectrometer. For ¹H NMR spectra, the chemical shifts are reported in ppm relative to TMS as an internal standard. Coupling constants are given in Hz. Mass spectra were determined from MALDI-TOF mass spectrometer using acyano-4-hydroxycinnamic acid as a matrix or High Resolution Mass Spectrometer. The mesogenic compounds were investigated for their liquid crystalline behavior (birefringence and fluidity) by employing a polarizing optical microscope (Nikon Eclipse LV100POL) equipped with a programmable hot stage (Mettler Toledo FP90). Clean glass slides and coverslips were employed for the polarizing optical microscopic observations. The transition temperatures and associated enthalpy changes were determined by differential scanning calorimeter (Mettler Toledo DSC1) under nitrogen atmosphere. Peak temperatures obtained in DSC corresponding to transitions were in agreement with the polarizing optical microscopic observations. The transition temperatures obtained from calorimetric measurements of the first heating and cooling cycles at a rate of 5 °C/min are tabulated. In the cases where the DSC signatures are not observed for the phase transitions, the transition temperatures have been taken from microscopic observations. Temperature dependent X-ray diffraction studies were carried on unaligned powder samples in Lindemann capillaries (1mm diameter) held in programmable hot stage and irradiated with CuKa radiation ($\lambda = 1.5418$ Å). The samples were filled in the capillary tube in their isotropic state and their both ends were flame sealed. The apparatus essentially consisted of a high resolution powder X-ray diffractometer (Xenocs) equipped with a focusing elliptical mirror and a high resolution fast detector. Thermogravimetric analysis (TGA) was performed using thermogravimetric analyzer (Mettler Toledo, model TG/SDTA 851 e) under a nitrogen flow at a heating rate of 10 °C/min. UV-Vis spectra were obtained by using Perkin-Elmer Lambda 750, UV/VIS/NIR

spectrometer. Fluorescence emission spectra in solution state were recorded with Horiba Fluoromax-4 fluorescence spectrophotometer or Perkin Elmer LS 50B spectrometer. Cyclic Voltammetry studies were carried out using a Versa Stat 3 (Princeton Applied Research) Electrochemical workstation.

(i) Experimental Section

Procedure for the synthesis of ethyl 3,4,5-tridecyloxy benzoate (**6a**)¹

A mixture of ethyl gallate (15.1 mmol, 1equiv.), anhyd K_2CO_3 (99.9 mmol, 6.6 equiv.), *n*-bromodecane (48.4 mmol, 3.2 equiv.) were taken in dry DMF (20 ml) and heated at 80 °C for 17 h under nitrogen atmosphere. Then the reaction mixture was poured into ice-water and extracted with CH₂Cl₂. The combined extract was washed with water and brine. Dried over anhyd Na₂SO₄ and concentrated. The crude product was purified by column chromatography on neutral alumina. Elution with hexanes followed by 5-10% ethylacetate-hexanes yielded the desired product.

 $R_f = 0.58$ (10% EtOAc-hexanes); Low melting colorless solid; yield: 70%; IR (KBr pellet): v_{max} in cm⁻¹2920, 2850, 1710, 1597, 1516, 1466, 1424, 1347, 1213, 1103, 760, 613; ¹H NMR (CDCl₃, 400 MHz): δ 7.26 (s, 2H, Ar), 4.35-4.36 (m, 2H, COOCH₂), 4.01 (s, 6H, 3 × OCH₂), 1.27-1.81 (m, 48H, 24 × CH₂), 0.89 (bs, 12H, 4 × CH₃); ¹³C NMR (CDCl₃, 100 MHz): 166.67, 152.99, 145.31, 125.24, 108.19, 73.68, 69.37, 61.14, 32.12, 30.53, 29.93, 29.84, 29.79, 29.60, 29.56, 26.29, 22.89, 14.30; HRMS (ESI+) exact mass calculated for C₃₉H₇₁O₅ (M+1): 619.5302, Found: 619.5218

Procedure for the synthesis of ethyl 3,4,5-tri(dodecyloxy) benzoate (**6b**)²

A mixture of ethyl gallate (10.1 mmol, 1equiv.), anhyd K_2CO_3 (66.6 mmol, 6.6 equiv.), *n*-bromododecane (33.3 mmol, 3.3 equiv.) were taken in dry DMF (20 ml) and heated at 80 °C for 17 h under nitrogen atmosphere. Then the reaction mixture was poured into ice-water and extracted with CH₂Cl₂. The combined extract was washed with water and brine. Dried over anhyd Na₂SO₄ and concentrated. The crude product was purified by column chromatography on neutral alumina. Elution with hexanes followed by 5-10% ethylacetate-hexanes yielded the desired product.

 $R_f = 0.61(10\% \text{ EtOAc-hexanes})$; Low melting colorless solid; yield: 90%; IR (KBr pellet): v_{max} in cm⁻¹2924, 2853, 1716, 1590, 1504, 1465, 1432, 1333, 1222, 1119; ¹H

NMR (CDCl₃, 600 MHz): δ 7.25 (s, 2H, Ar), 4.35 (q, 2H, J = 6 Hz, COOCH₂), 4.01 (m, 6H, $3 \times \text{OCH}_2$), 1.23-1.83 (m, 60H, $30 \times \text{CH}_2$), 0.87-0.89 (m, 12H, $4 \times \text{CH}_3$); ¹³C NMR (CDCl₃, 150 MHz): 166.66, 153.01, 142.57, 125.26, 108.24, 73.68, 69.40, 61.14, 32.14, 30.54, 29.95, 29.92, 29.85, 29.79, 29.61, 29.54, 26.30, 22.90, 14.30; HRMS (ESI+) exact mass calculated for C₄₅H₈₃O₅ (M+1): 703.6235, Found: 703.6199.

Procedure for the synthesis of ethyl 3,4,5-tri(hexadecyloxy) benzoate $(6c)^3$

A mixture of ethyl gallate (10.1 mmol, 1equiv.), anhyd K_2CO_3 (66.6 mmol, 6.6 equiv.), *n*-bromohexadecane (33.3 mmol, 3.3 equiv.) were taken in dry DMF (20 ml) and heated at 80 °C for 17 h under nitrogen atmosphere. Then the reaction mixture was poured into ice-water and extracted with CH_2Cl_2 . The combined extract was washed with water and brine. Dried over anhyd Na_2SO_4 and concentrated. The crude product was purified by column chromatography on neutral alumina. Elution with hexanes followed by 2 - 5% ethylacetate-hexanes yielded the desired product.

 $R_f = 0.81(10\% \text{ EtOAc-hexanes});$ colorless solid, m.p.: 54-56 °C; yield: 85%; IR (KBr pellet): v_{max} in cm⁻¹ 2922, 2850, 1716, 1584, 1469, 1427, 1331, 1219, 1110; ¹H NMR (CDCl₃, 400 MHz): δ 7.25 (s, 2H, Ar), 4.35 (q, 2H, J = 7.2 Hz, COOCH₂), 4.01 (t, 6H, $3 \times \text{OCH}_2$), 1.25-1.82 (m, 84H, 42 × CH₂), 0.86-0.89 (m, 12H, 4 × CH₃); ¹³C NMR (CDCl₃, 100 MHz): 166.70, 153.04, 142.61, 125.28, 108.29, 73.72, 69.44, 61.17, 33.05, 32.16, 30.56, 29.94, 29.89, 29.87, 29.80, 29.63, 29.60, 29.57, 26.32, 26.29, 22.92, 14.63, 14.33. HRMS (ESI+) exact mass calculated for C₅₇H₁₀₇O₅ (M+1): 871.8113, Found: 871.8031.

Procedure for the synthesis of 3,4,5-tri-*n*-decyloxy benzohydrazide $(5a)^{4,5}$

A mixture of ethyl 3,4,5-tri-*n*-decyloxybenzoate (10 mmol, 1equiv.), excess hydrazine hydrate (10 mL), *n*-butanol (20 mL) was refluxed for 40 h. Water (100 mL) was added and resulting precipitate was collected, dried under vacuum, and recrystallized from ethanol to yield pure **5a** as a colorless solid.

 $R_f = 0.45$ (20% EtOAc-hexanes); colorless solid, m.p.: 113-115 °C; yield: 80%; IR (KBr pellet): v_{max} in cm⁻¹ 3475, 2923, 2852, 1746, 1640, 1580, 1499, 1467, 1347, 1238, 1120, 1019, 826, 719, 523; ¹H NMR (CDCl₃, 400 MHz): δ 7.33 (br s, 1H, CONH), 6.92 (s, 2H, Ar), 3.99 (m, 8H, 1× NH₂, 3 × OCH₂), 1.27 – 1.80 (m, 48H, 24×CH₂), 0.88(bs, 9H, 3×CH₃); ¹³C NMR (CDCl₃, 100 MHz): 168.91, 153.37,

141.60, 127.61, 105.71, 73.70, 69.50, 32.10, 30.50, 29.91, 29.83, 29.77, 29.59, 29.53, 26.26, 22.87, 14.28. HRMS (ESI+) exact mass calculated for $C_{37}H_{69}N_2O_4$ (M+1): 605.5257, Found: 605.5171.

Procedure for the synthesis of 3,4,5-tri-*n*-dodecyloxy benzohydrazide $(5b)^{4,5}$

A mixture of ethyl 3,4,5-tri-*n*-dodecyloxybenzoate (9.7 mmol, 1equiv.), excess hydrazine hydrate (19.4 mL), *n*-butanol (20 mL) was refluxed for 40 h. Water (100 mL) was added and resulting precipitate was collected, dried under vacuum, and recrystallized from ethanol to yield pure **5b** as a colorless solid.

 $R_f = 0.46$ (20% EtOAc-hexanes); colorless solid, m.p.: 114-116°C; yield: 71%; IR (KBr pellet): v_{max} in cm⁻¹ 3244, 2923, 2851, 1646, 1581, 1500, 1467, 1237, 1122; ¹H NMR (CDCl₃, 400 MHz): δ 7.32 (br s, 1H, CONH), 6.92 (s, 2H, Ar), 3.99 (m, 8H, 1× NH₂, 3 × OCH₂), 1.26 – 1.83(m, 60H, 30×CH₂), 0.86-0.89(m, 9H, 3×CH₃); ¹³C NMR (CDCl₃, 100 MHz):168.96, 153.44, 141.69, 127.66, 105.71, 73.75, 69.57, 32.14, 30.52, 29.94, 29.91, 29.87, 29.85, 29.78, 29.60, 29.57, 29.54, 26.28, 22.90, 14.31. HRMS (ESI+) exact mass calculated for C₄₃H₈₁N₂O₄ (M+1): 689.6191, Found: 689.6189.

Procedure for the synthesis of 3,4,5-tri-*n*-hexadecyloxy benzhydrazide (5c)^{4,5}

A mixture of ethyl 3,4,5-tri-*n*-hexadecyloxybenzoate (9.2 mmol, 1equiv.), excess hydrazine hydrate (18.4 mL), *n*-butanol (20 mL) was refluxed for 40 h. Water (100 mL) was added and resulting precipitate was collected, dried under vacuum, and recrystallized from ethanol to yield pure **5c** as a colorless solid.

 $R_f = 0.52$ (20% EtOAc-hexanes); colorless solid, m.p.: 102-104 °C; yield: 75%; IR (KBr pellet): v_{max} in cm⁻¹ 3449, 3248, 2922, 2851, 1635, 1580, 1466, 1428, 1239, 1122; ¹H NMR (CDCl₃, 600 MHz): δ 7.22 (br s, 1H, CONH), 6.92 (s, 2H, Ar), 4.07 (s, 2H, NH₂), 3.99 (m, 6H, 3 × OCH₂), 1.26 – 1.80 (m, 84H, 42×CH₂), 0.88 (m, 9H, 3×CH₃); ¹³C NMR (CDCl₃, 150 MHz):. HRMS (ESI+) exact mass calculated for C₅₅H₁₀₅N₂O₄ (M+1): 857.8069, Found: 857.8151.

Procedure for the synthesis of 1,3-bis(5-(3,4,5-tris(decyloxy)phenyl)-1,3,4-thiadiazol-2-yl)benzene (**2a**)^{4,5,6}

Isophthalic acid (1mmol) in 4.5 ml of thionyl chloride and DMF (catalytic amount) was heated under reflux for 4 h. The excess of thionyl chloride was removed by distillation, the crude product (Isophthaloyl dichloride) was dried *in vacuo* and used for the next reaction without further purification and characterization. The solution of Isophthaloyl dichloride (0.9 mmol, 1equiv.) in THF was added dropwise to a solution of 3,4,5-tri-*n*-decyloxy benzohydrazide (1.85 mmol, 2.05 equiv.) and triethylamine (1.8 mmol, 2 equiv.) in THF (20 mL). The reaction mixture was stirred at 55 °C for 12 h. After cooling, THF was evaporated and the residue was extracted with dichloromethane. The extract was washed with water and brine. Dried over Na₂SO₄ and concentrated. The resulting crude product (**3a**) was directly used for next reaction. The solution of crude product **3a** (0.4 mmol, 1equiv.) in dry toluene (8 mL) was added dropwise to a solution of Lawesson's reagent (1 mmol, 2.4 equiv.) at room temperature under Argon atmosphere and refluxed for 24 h. After removal of solvent *in vacuo*, the crude products were further purified through column chromatography on neutral alumina. Elution with 10-20% ethylacetate-hexanes yielded the desired product.

 $R_f = 0.3$ (20% EtOAc-hexanes); colorless solid, yield: 40%; IR (KBr pellet): v_{max} in cm⁻¹ 2924, 2853, 1589, 1512, 1187; ¹H NMR (CDCl₃, 600 MHz): ¹H NMR (CDCl₃, 400 MHz): δ 8.59 (s, 1H, Ar), 8.15 (d, 2H, *J* =6Hz, Ar), 7.64 (t, 1H, Ar), 7.23 (s, 4H, Ar), 4.08 (t, 8H, 4× OCH₂), 4.04 (t, 4H, 2× OCH₂), 1.24 – 1.88 (m, 96H, 48 × CH₂), 0.87 – 0.89 (m, 18H, 6 × CH₃); ¹³C NMR (CDCl₃, 100 MHz): 169.11, 166.77, 153.83, 141.38, 131.55, 130.29, 130.13, 127.29, 124.93, 106.81, 73.89, 69.65, 32.16, 32.14, 30.56, 29.95, 29.89, 29.86, 29.81, 29.63, 29.57, 26.31, 22.90, 14.32. HRMS (ESI+) exact mass calculated for C₈₂H₁₃₅N₄O₆S₂(M+1): 1335.9818, Found: 1335.9711.

Procedure for the synthesis of 1,3-bis(5-(3,4,5-tris(dodecyloxy)phenyl)-1,3,4thiadiazol-2-yl)benzene (**2b**):

Isophthalic acid (0.9 mmol) in 4.2 ml of thionyl chloride and DMF (catalytic amount) was heated under reflux for 4 h. The excess of thionyl chloride was removed by distillation, the crude product (Isophthaloyl dichloride) was dried in vacuo and used for the next reaction without further purification and characterization. The solution of Isophthaloyl dichloride (0.8 mmol, 1equiv.) in THF was added dropwise

to a solution of solution of 3,4,5-tri-*n*-dodecyloxy benzhydrazide (1.6 mmol, 2.05 equiv.) and triethylamine (1.6 mmol, 2 equiv.) in THF (20 mL). The reaction mixture was stirred at 55 °C for 12 h. After cooling, THF was removed through distillation and the residue was extracted with dichloromethane. The extract was washed with water and brine. Dried over Na₂SO₄ and concentrated. The resulting crude product (**3b**) was directly used for next reaction. The solution of crude product **3b** (0.6 mmol, 1equiv.) in dry toluene (12 mL) was added dropwise to a solution of Lawesson's reagent (1.4 mmol, 2.4 equiv.) at room temperature under Argon atmosphere and refluxed for 24 h. Toluene was removed by distillation. After removal of solvent *in vacuo*, the crude products were further purified through column chromatography on neutral alumina. Elution with 10-20% ethylacetate-hexanes yielded the desired product.

 $R_f = 0.59$ (20% EtOAc-hexanes); colorless solid, yield: 45%; IR (KBr pellet): v_{max} in cm⁻¹ 2923, 2852, 1589, 1512, 1124; ¹H NMR (CDCl₃, 400 MHz): ¹H NMR (CDCl₃, 400 MHz): δ 8.58 (t, J = 1.6 Hz, 1H, Ar), 8.14 (dd, 2H, J = 6.4 Hz, J = 1.6 Hz, Ar), 7.63 (t, 1H, Ar), 7.22 (s, 4H, Ar), 4.02 – 4.09 (m, 12H, 6× OCH₂), 1.27 – 1.89 (m, 120H, 60 × CH₂), 0.86 – 0.89 (m, 18H, 6 × CH₃). ¹³C NMR (CDCl₃, 100 MHz): 169.10, 166.75, 153.81, 141.35, 131.53, 130.28, 130.11, 127.25, 124.93, 106.78, 77.88, 69.63, 32.14, 30.56, 29.92, 29.86, 29.80, 29.63, 29.58, 26.30, 22.91, 14.38. HRMS (ESI+) exact mass calculated for C₉₄H₁₅₉N₄O₆S₂(M+1): 1504.1696, Found: 1504.1878.

Procedure for the synthesis of 1,3-bis(5-(3,4,5-tris(hexadecyloxy)phenyl)-1,3,4thiadiazol-2-yl)benzene (2c):

Isophthalic acid (0.8 mmol) in 3.6 ml of thionyl chloride and DMF (catalytic amount) was heated under reflux for 4 h. The excess of thionyl chloride was removed by distillation, the crude product (Isophthaloyl dichloride) was dried in vacuo and used for the next reaction without further purification and characterization. The solution of Isophthaloyl dichloride (0.7 mmol, 1equiv.) in THF was added dropwise to a solution of solution of 3,4,5-tri-*n*-hexadecyloxy benzhydrazide (1.4 mmol, 2.05 equiv.) and triethylamine (2.1 mmol, 3 equiv.) in THF (20 mL). The reaction mixture was stirred at 55 °C for 12 h. After cooling, THF was removed through distillation and the residue was extracted with dichloromethane. The extract was washed with

water and brine. Dried over Na_2SO_4 and concentrated. The resulting crude product (4c) was directly used for next reaction. The solution of crude product 3c (0.5mmol, lequiv.) in dry toluene (8 mL) was added dropwise to a solution of Lawesson's reagent (1.2 mmoL, 2.4 equiv.) in toluene at room temperature under Argon atmosphere and refluxed for 24 h. After the reaction, toluene was evaporated under reduced pressure. After removal of solvent *in vacuo*, the crude product was further purified through column chromatography on neutral alumina. Elution with 10-20% ethylacetate-hexanes yielded the desired product.

 $R_f = 0.68$ (20% EtOAc-hexanes); colorless solid, yield: 44%; IR (KBr pellet): v_{max} in cm⁻¹ 2921, 2852, 1586, 1510, 1122; ¹H NMR (CDCl₃, 400 MHz): ¹H NMR (CDCl₃, 400 MHz): δ 8.60 (s, 1H, Ar), 8.15(d, 2H, *J* =8Hz, Ar), 7.64 (t, 1H, Ar), 7.23(s, 4H, Ar), 4.02 – 4.09 (m, 12H, 6 × OCH₂), 1.25 – 1.85 (m, 168H, 84 × CH₂), 0.86 – 0.89 (m, 18H, 6 × CH₃). ¹³C NMR (CDCl₃, 150 MHz): 169.11, 166.76, 153.83, 141.37, 131.55, 130.29, 130.12, 127.27, 124.93, 106.80, 73.89, 69.65, 32.15, 30.56, 29.94, 29.88, 29.81, 29.64, 29.59, 26.32, 22.91, 14.32. HRMS (ESI+) exact mass calculated for C₁₁₈H₂₀₇N₄O₆S₂(M+1): 1840.5452, Found: 1840.5558.

Procedure for the synthesis of 1,4-bis(5-(3,4,5-tris(decyloxy)phenyl)-1,3,4-thiadiazol-2-yl)benzene (1a):

Terephthalic acid (1.7mmol) in 8 ml of thionyl chloride and DMF (catalytic amount) was heated under reflux for 4 h. The excess of thionyl chloride was removed by distillation, the crude product (terepthaloyldichloride) was dried *in vacuo* and used for the next reaction without further purification and characterization. The terepthaloyldichloride (1.6 mmol, 1equiv.) was added dropwise to a solution of 3,4,5-tri-*n*-decyloxy benzhydrazide (3.3 mmol, 2.05 equiv.), triethylamine (3.2mmol, 2equiv.) in THF. The reaction mixture was stirred at 55 °C for 12 h. After cooling, THF was removed through distillation and the residue was extracted with dichloromethane. The extract was washed with water and brine. Dried over Na₂SO₄ and concentrated. The resulting crude product (**4a**) was directly used for next reaction. The solution of crude product **4a** (0.6mmol, 1equiv.) in toluene (12 mL) was added dropwise to a solution of Lawesson's reagent (1.4 mmoL, 2.4 equiv.) in toluene was evaporated under reduced pressure. After removal of solvent *in vacuo*, the crude product was further purified through

column chromatography on neutral alumina. Elution with 5-10% ethylacetate-hexanes yielded the desired product.

 $R_f = 0.38$ (20% EtOAc-hexanes); yellowish green solid, yield: 50%; IR (KBr pellet): v_{max} in cm⁻¹ 2922, 2851, 1583, 1510, 1127 ; ¹H NMR (CDCl₃, 400 MHz): δ 8.13 (s, 4H, Ar), 7.23 (s, 4H, Ar), 4.02 - 4.09(m, 12H, 6 × OCH₂), 1.28 – 1.87 (m, 96H, 48 × CH₂), 0.88 (m, 18H, 6 × CH₃). ¹³C NMR (CDCl₃, 100 MHz):168.91, 166.55, 153.70, 141.28, 132.44, 128.49, 124.79, 106.61, 73.75, 69.51, 32.08, 30.53, 29.91, 29.85, 29.82, 29.77, 29.60, 29.57, 29.53, 26.26, 22.84, 14.24. HRMS (ESI+) exact mass calculated for C₈₂H₁₃₅N₄O₆S₂(M+1): 1335.9818, Found: 1335.9850.

Procedure for the synthesis of 1,4-bis(5-(3,4,5-tris(dodecyloxy)phenyl)-1,3,4thiadiazol-2-yl)benzene (**1b**):

Terephthalic acid (0.9 mmol) in 4.1 ml of thionyl chloride and DMF (catalytic amount) was heated under reflux for 4 h. The excess of thionyl chloride was removed by distillation, the crude product (terepthaloyldichloride) was dried in vacuo and used for the next reaction without further purification and characterization. The terepthaloyldichloride (0.8 mmol, 1equiv.) was added dropwise to a solution of 3,4,5tri-*n*-dodecyloxy benzhydrazide (1.6 mmol, 2.05 equiv.), triethylamine (1.6mmol, 2equiv.) in THF. The reaction mixture was stirred at 55 °C for 12 h. After cooling, THF was removed through distillation and the residue was extracted with dichloromethane. The extract was washed with water and brine. Dried over Na₂SO₄ and concentrated. The resulting crude product (4b) was directly used for next reaction. The solution of crude product 4b (0.6mmol, 1equiv.) in dry toluene (12 mL) was added dropwise to a solution of Lawesson's reagent (1.4 mmoL, 2.4 equiv.) at room temperature under Argon atmosphere and refluxed for 24 h. After the reaction, toluene was evaporated under reduced pressure. After removal of solvent in vacuo, the crude product was further purified through column chromatography on neutral alumina. Elution with 5-10% ethylacetate-hexanes yielded the desired product.

 $R_f = 0.62$ (20% EtOAc-hexanes); yellowish green solid, yield: 55%; IR (KBr pellet): v_{max} in cm⁻¹ 2923, 2851, 1585, 1511, 1121 ; ¹H NMR (CDCl₃, 400 MHz): δ 8.11 (s, 4H, Ar), 7.21 (s, 4H, Ar), 4.02 - 4.08 (m, 12H, 6 × OCH₂), 1.27 – 1.88 (m, 120H, 60 × CH₂), 0.88 (m, 18H, 6 × CH₃). ¹³C NMR (CDCl₃, 100 MHz): 168.84, 166.49, 153.59, 141.15, 132.38, 128.43, 124.68, 106.54, 73.65, 69.41, 31.92, 30.34, 29.74, 29.70, 29.66, 29.64, 29.58, 29.41, 29.39, 29.37, 29.34, 26.09, 22.69, 14.10. HRMS (ESI+) exact mass calculated for $C_{94}H_{159}N_4O_6S_2(M+1)$:1504.1696, Found: 1504.1868.

Procedure for the synthesis of 1,4-bis(5-(3,4,5-tris(hexadecyloxy)phenyl)-1,3,4thiadiazol-2-yl)benzene (1c):

Terephthalic acid (0.8mmol) in 3.6 ml of thionyl chloride and DMF (catalytic amount) was heated under reflux for 4 h. The excess of thionyl chloride was removed by distillation, the crude product (terepthaloyl dichloride) was dried in vacuo and used for the next reaction without further purification and characterization. The terepthaloyldichloride (0.7 mmol, lequiv.) was added dropwise to a solution of 3,4,5tri-n-hexadecyloxy benzhydrazide (1.4 mmol, 2.05 equiv.), triethylamine (1.4 mmol, 2equiv.) in THF. The reaction mixture was stirred at 55 °C for 12 h. After cooling, THF was removed through distillation and the residue was extracted with dichloromethane. The extract was washed with water and brine. Dried over Na₂SO₄ and concentrated. The resulting crude product (4c) was directly used for next reaction. The solution of crude product 4c (0.2mmol, lequiv.) in dry toluene (4 mL) was added dropwise to a solution of Lawesson's reagent (0.5 mmoL, 2.4 equiv.) at room temperature under Argon atmosphere and refluxed for 24h. After the reaction, toluene was evaporated under reduced pressure. After removal of solvent in vacuo, the crude product was further purified through column chromatography on neutral alumina. Elution with 5-10% ethylacetate-hexanes yielded the desired product.

 $R_f = 0.69$ (20% EtOAc-hexanes); yellowish green solid, yield: 56%; IR (KBr pellet): v_{max} in cm⁻¹ 2922, 2851, 1587, 1507, 1121; ¹H NMR (CDCl₃, 400 MHz): δ 8.13 (s, 4H, Ar), 7.23 (s, 4H, Ar), 4.02 - 4.09 (m, 12H, 6 × OCH₂), 1.26 – 1.87 (m, 168H, 84 × CH₂), 0.86 – 0.89 (m, 18H, 6 × CH₃). ¹³C NMR (CDCl₃, 100 MHz): 169.09, 166.73, 153.83, 141.40, 132.64, 128.69, 124.93, 106.81, 73.88, 69.65, 32.15, 30.57, 29.95, 29.88, 29.81, 29.63, 29.60, 26.32, 22.92, 14.33. HRMS (ESI+) exact mass calculated for C₁₁₈H₂₀₇N₄O₆S₂ (M+1): 1840.5452, Found: 1840.5267.

(ii) NMR spectra



Figure S1. ¹H NMR (400 MHz) spectra of 1a in CDCl₃



Figure S2. ¹³C NMR (100 MHz) spectra of 1a in CDCl₃



Figure S3. ¹H NMR (400 MHz) spectra of **1b** in CDCl₃



Figure S4. ¹³C NMR (100 MHz) spectra of 1b in CDCl₃



Figure S5. ¹H NMR (400 MHz) spectra of 1c in CDCl₃



Figure S6. ¹³C NMR (100 MHz) spectra of 1c in CDCl₃



Figure S7. ¹H NMR (600 MHz) spectra of 2a in CDCl₃



Figure S8. ¹³C NMR (100 MHz) spectra of 2a in CDCl₃



Figure S9. ¹H NMR (400 MHz) spectra of 2b in CDCl₃



Figure S10. ¹³C NMR (100 MHz) spectra of **2b** in CDCl₃



Figure S11. 1 H NMR (400 MHz) spectra of 2c in CDCl₃



Figure S12. ¹³C NMR (100 MHz) spectra of 2c in CDCl₃



Figure S13. ¹H NMR (400 MHz) spectra of 6a in CDCl₃



Figure S14. ¹³C NMR (100 MHz) spectra of 6a in CDCl₃



Figure S16. ¹³C NMR (150 MHz) spectra of 6b in CDCl₃



Figure S17. ¹H NMR (400 MHz) spectra of 6c in CDCl₃



Figure S18. ¹³C NMR (100 MHz) spectra of 6c in CDCl₃



Figure S19. $\,^1\text{H}$ NMR (400 MHz) spectra of 5a in CDCl_3



Figure S20. ¹³C NMR (100 MHz) spectra of 5a in CDCl₃



Figure S21. ¹H NMR (400 MHz) spectra of 5b in CDCl₃



Figure S22. ¹³C NMR (100 MHz) spectra of 5b in CDCl₃



Figure S23. ¹H NMR (600 MHz) spectra of 5c in CDCl₃



Figure S24. $\rm ^{13}C$ NMR (150 MHz) spectra of Sc in CDCl3

iii) Polarized Optical Microscopy



Figure S25. POM images of polycatenars **1a-c** and **2a-c** on a cooling process from isotropic melt. (a) **1a** at 82.7 °C, Col_h phase; (b) **1b** at 85 °C, Col_{ob} phase; (c) **1c** at 46 °C, Cr phase; (d) **2a** at 96.3 °C, Col_{ob} phase; (e) **2a** at 50 °C, Cr phase; (f) **2b** at 93 °C, Col_{ob} phase; (g) **2b** at 60 °C, Col_{ob} phase; (h) **2c** at 87 °C, Col_{ob} phase; (i) **2c** at 82 °C, Col_{ob} phase.



Figure S26. DSC thermograms of polycatenars **1a-c** (a-c) and **2a-c** (d-f) showing the second heating (bottom) and the first cooling (top) cycle at a scanning rate of 5.0 $^{\circ}$ C min⁻¹.

(v) X-ray diffraction studies



Figure S27. XRD profiles depicting the intensity against the 2θ obtained for the Col phases of compounds **1a**, **1b** and **1c**. The insets show the diffuse profile in the wide-angle region.



Figure S28. XRD profiles depicting the intensity against the 2θ obtained for the Col_{ob} phases of compounds **2a**, **2b** and **2c**. The insets show the diffuse profile in the wide-angle region.

(vi) Thermogravimetric Analysis



Figure S29. TGA curves of the compounds **1a-c (a)** and **2a-c (b)** carried out at a rate of 10 °C/min.

(vii) Photophysical proerties



Figure S30. Pictures of micromolar solutions of compounds **1a-c** and **2a-c** in THF as seen with the illumination of 365 nm UV light.



Figure S31. Absorption (black trace) and emission (red trace) spectra of compounds **1a**-**c**(a-c) and **2a-c** (d-f) in micromolar THF solution



Figure S32. Normalized absorption (solid line) and emission spectra (dotted line) in THF solution obtained for **1a-c** (a) and **2a-c** (b)



Figure S33. Absorption spectra of compounds **1a** (a) and **2a** (c) as a function of concentration in THF solution. Emission spectra of compounds **1a** (b) and **2a** (d) as a function of concentration in THF solution.



Figure S34. Normalized emission spectra of compounds **1a** and **2a** as a function of concentration in THF solution.

Relative Quantum Yield Calculation⁶

Quantum yield was measured according to established procedure by using quinine sulfate in 0.1 M H₂SO₄ solution as the standard. Absolute values were calculated according to the following equation: $Q_s = Q_R x (m_s / m_R) x (n_s / n_R)^2$

Where, Q: Quantum yield, m: Slope of the plot of integrated fluorescence intensity vs absorbance

n: refractive index (1.407 for THF and 1.33 for distilled water).

The subscript R refers to the reference fluorophore *i.e.* quinine sulphate solution in 0.1 M H_2SO_4 and subscript S refers to the sample under investigation. In order to minimize reabsorption effects, absorbance was kept below 0.15 at the excitation wavelength of 347 nm. Quantum Yield of quinine sulphate is 0.54. Simplified equation for the calculation after substituting the appropriate values is given below and values obtained are given in table 1. $Q_{S=}0.54 \times (m_S / 2.71) \times (1.407/1.33)^2$

$$= 0.223 \text{ x m}_{\text{s}}$$

Entry	ms	m _R	Q s ^{a,b,c}
1a	1.78×10 ⁹	2.71×10 ⁹	0.40
2a	1.58×10 ⁹	2.71×10 ⁹	0.35

^a Measured in THF.

^bExcited at absorption maxima .

^cStandard quinine sulphate ($Q_f = 0.54$) in 0.1M H₂SO₄.



Figure S35. Plots of integrated photoluminescence intensity vs absorbance of Quinine sulphate (0.1M H_2SO_4 solution), compounds **1a** and **2a** (micromolar THF solution)

(viii) Cyclic Voltammetry



Figure S36. Cyclic voltammograms of the compounds **1a** (a) and **2a** (b) in anhydrous THF solution of tetra-*n*-butylammonium perchlorate (0.1 M) at a scanning rate 0.5mV/s



 $(E_{1/2, FC/Fc}^{+}) = (E_{anodic peak potential} + E_{cathodic peak potential})/2$ = (0.609 + 0.521)/2= 0.565 V

Figure S37. Cyclic voltammograms of ferrocene in anhydrous THF solution of tetra-*n*-butylammonium perchlorate (0.1 M). The half-wave potential of the ferrocene/ ferrocenium (Fc/Fc⁺) redox couple ($E_{1/2}$, $_{Fc,Fc}^+$) was found to be 0.57 V relative to the Ag/Ag⁺ reference electrode.

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