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 aluminium 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 \(^1\)H 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 \(\alpha\)-cyano-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 CuK\(\alpha\) 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)

A mixture of ethyl gallate (15.1 mmol, 1equiv.), anhyd K₂CO₃ (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): ν_max in cm⁻¹ 2920, 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)

A mixture of ethyl gallate (10.1 mmol, 1equiv.), anhyd K₂CO₃ (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% EtOAc-hexanes); Low melting colorless solid; yield: 90%; IR (KBr pellet): ν_max in cm⁻¹ 2924, 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 × OCH₂), 1.23-1.83 (m, 60H, 30 × CH₂), 0.87-0.89 (m, 12H, 4 × CH₃); 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)

A mixture of ethyl gallate (10.1 mmol, 1equiv.), anhyd K₂CO₃ (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 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 2 - 5% ethylacetate-hexanes yielded the desired product. Rf = 0.81(10% EtOAc-hexanes); colorless solid, m.p.: 54-56 °C; yield: 85%; IR (KBr pellet): νmax 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 × OCH₂), 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)

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. Rf = 0.45 (20% EtOAc-hexanes); colorless solid, m.p.: 113-115 °C; yield: 80%; IR (KBr pellet): νmax 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_{2}O_{4} (M+1): 605.5257, Found: 605.5171.

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

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): $\nu_{\text{max}}$ in cm$^{-1}$ 3449, 3248, 2922, 2851, 1635, 1580, 1466, 1428, 1239, 1122; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.32 (br s, 1H, CONH), 6.92 (s, 2H, Ar), 3.99 (m, 8H, 1× NH$_2$, 3× OCH$_2$), 1.26 – 1.83 (m, 60H, 30× CH$_2$), 0.86-0.89 (m, 9H, 3× CH$_3$); $^{13}$C NMR (CDCl$_3$, 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 C$_{43}$H$_{81}$N$_2$O$_4$ (M+1): 689.6191, Found: 689.6189.

**Procedure for the synthesis of 3,4,5-tri-n-hexadecyloxy benzohydrazide (5c)**

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): $\nu_{\text{max}}$ in cm$^{-1}$ 3449, 3248, 2922, 2851, 1635, 1580, 1466, 1428, 1239, 1122; $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 7.22 (br s, 1H, CONH), 6.92 (s, 2H, Ar), 4.07 (s, 2H, NH$_2$), 3.99 (m, 6H, 3× OCH$_2$), 1.26 – 1.80 (m, 84H, 42× CH$_2$), 0.88 (m, 9H, 3× CH$_3$); $^{13}$C NMR (CDCl$_3$, 150 MHz): HRMS (ESI+) exact mass calculated for C$_{55}$H$_{105}$N$_2$O$_4$ (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)\textsuperscript{4,5,6}

Isophthalic acid (1 mmol) 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 \textit{in vacuo} and used for the next reaction without further purification and characterization. The solution of Isophthaloyl dichloride (0.9 mmol, 1 equiv.) in THF was added dropwise to a solution of 3,4,5-tri-\textit{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 Na\textsubscript{2}SO\textsubscript{4} and concentrated. The resulting crude product (3a) was directly used for next reaction. The solution of crude product 3a (0.4 mmol, 1 equiv.) 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 \textit{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): \(\nu_{\text{max}}\) in cm\textsuperscript{-1} 2924, 2853, 1589, 1512, 1187; \(^1\)H NMR (CDCl\textsubscript{3}, 600 MHz): \(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta\) 8.59 (s, 1H, Ar), 8.15 (d, 2H, \(J = 6\) Hz, Ar), 7.64 (t, 1H, Ar), 7.23 (s, 4H, Ar), 4.08 (t, 8H, 4 \times OCH\textsubscript{2}), 4.04 (t, 4H, 2 \times OCH\textsubscript{2}), 1.24 – 1.88 (m, 96H, 48 \times CH\textsubscript{2}), 0.87 – 0.89 (m, 18H, 6 \times CH\textsubscript{3}); \(^{13}\)C NMR (CDCl\textsubscript{3}, 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 C\textsubscript{82}H\textsubscript{135}N\textsubscript{4}O\textsubscript{6}S\textsubscript{2}(M+1): 1335.9818, Found: 1335.9711.

Procedure for the synthesis of 1,3-bis(5-(3,4,5-tris(dodecyloxy)phenyl)-1,3,4-thiadiazol-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, 1 equiv.) 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): \( \nu_{\text{max}} \) in cm\(^{-1}\) 2923, 2852, 1589, 1512, 1124; \(^1\)H NMR (CDCl₃, 400 MHz): \(^1\)H NMR (CDCl₃, 400 MHz): \( \delta \) 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, \( 6 \times \text{OCH}_2 \)), 1.27 – 1.89 (m, 120H, \( 60 \times \text{CH}_2 \)), 0.86 – 0.89 (m, 18H, \( 6 \times \text{CH}_3 \)). \(^{13}\)C 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)-1,3,4-thiadiazol-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 Na₂SO₄ and concentrated. The resulting crude product (4c) was directly used for next reaction. The solution of crude product 3c (0.5mmol, 1equiv.) 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.

\[ R_f = 0.68 \text{ (20% EtOAc-hexanes); colorless solid, yield: 44%}; \]

IR (KBr pellet): \( \nu_{\text{max}} \) in cm⁻¹ 2921, 2852, 1586, 1510, 1122; \(^1\)H NMR (CDCl₃, 400 MHz): \(^1\)H NMR (CDCl₃, 400 MHz): \( \delta \) 8.60 (s, 1H, Ar), 8.15(d, 2H, \( J =8\)Hz, Ar), 7.64 (t, 1H, Ar), 7.23(s, 4H, Ar), 4.02 – 4.09 (m, 12H, 6 \( \times \)OCH₂), 1.25 – 1.85 (m, 168H, 84 \( \times \)CH₂), 0.86 – 0.89 (m, 18H, 6 \( \times \)CH₃). \(^13\)C 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 terephthaloyldichloride (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 the next reaction. The solution of crude product 4a (0.6mmol, 1equiv.) in dry toluene (12 mL) was added dropwise to a solution of Lawesson’s reagent (1.4 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 5-10% ethylacetate-hexanes yielded the desired product.

\[ R_f = 0.38 \text{ (20\% EtOAc-hexanes)} \]; yellowish green solid, yield: 50\%; IR (KBr pellet): 

\[ \nu_{\text{max}} \text{ in cm}^{-1} 2922, 2851, 1583, 1510, 1127; \quad ^1\text{H NMR (CDCl}_3, 400 \text{ MHz)}: \delta \ 8.13 \text{ (s, 4H, Ar), 7.23 (s, 4H, Ar), 4.02 - 4.09 (m, 12H, 6 × OCH}_2\text{), 1.28 – 1.87 (m, 96H, 48 × CH}_2\text{), 0.88 (m, 18H, 6 × CH}_3\text{).} \]

\[ ^{13}\text{C NMR (CDCl}_3, 100 \text{ MHz)}: 168.91, 166.55, 153.70, 141.28, 132.44, 128.49, 124.79, 106.61, 73.75, 69.51, 32.08, 30.53, 29.91, 29.85, 29.82, 29.77, 29.60, 29.57, 29.53, 26.26, 22.84, 14.24. \]

HRMS (ESI+) exact mass calculated for \( \text{C}_{82}\text{H}_{135}\text{N}_4\text{O}_6\text{S}_2\text{(M+1): 1335.9818, Found: 1335.9850.} \]

Procedure for the synthesis of 1,4-bis(5-(3,4,5-tris(dodecyloxy)phenyl)-1,3,4-thiadiazol-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 (terephthaloyldichloride) was dried \textit{in vacuo} and used for the next reaction without further purification and characterization. The terephthaloyldichloride (0.8 mmol, 1equiv.) was added dropwise to a solution of 3,4,5-tri-\(n\)-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 Na\(_2\)SO\(_4\) 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 \textit{in vacuo}, the crude product was further purified through column chromatography on neutral alumina. Elution with 5-10% ethylacetate-hexanes yielded the desired product.

\[ R_f = 0.62 \text{ (20\% EtOAc-hexanes)} \]; yellowish green solid, yield: 55\%; IR (KBr pellet): 

\[ \nu_{\text{max}} \text{ in cm}^{-1} 2923, 2851, 1585, 1511, 1121; \quad ^1\text{H NMR (CDCl}_3, 400 \text{ MHz)}: \delta \ 8.11 \text{ (s, 4H, Ar), 7.21 (s, 4H, Ar), 4.02 - 4.08 (m, 12H, 6 × OCH}_2\text{), 1.27 – 1.88 (m, 120H, 60 × CH}_2\text{), 0.88 (m, 18H, 6 × CH}_3\text{).} \]

\[ ^{13}\text{C NMR (CDCl}_3, 100 \text{ MHz)}: 168.84, 166.49, 153.59, 141.15, 132.38, 128.43, 124.68, 106.54, 73.65, 69.41, 31.92, 30.34, 29.74, 29.70, 29.66, \]

135.9818, Found: 1335.9850.
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\textsubscript{94}H\textsubscript{159}N\textsubscript{4}O\textsubscript{6}S\textsubscript{2}(M+1):1504.1696, Found: 1504.1868.

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

Terephthalic 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 (terephthaloyl dichloride) was dried \textit{in vacuo} and used for the next reaction without further purification and characterization. The terephthaloyldichloride (0.7 mmol, 1 equiv.) was added dropwise to a solution of 3,4,5-tri-n-hexadecyloxy benzhydrazide (1.4 mmol, 2.05 equiv.), triethylamine (1.4 mmol, 2 equiv.) 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 Na\textsubscript{2}SO\textsubscript{4} and concentrated. The resulting crude product (4c) was directly used for next reaction.

The solution of crude product 4c (0.2 mmol, 1 equiv.) 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 24 h. After the reaction, toluene was evaporated under reduced pressure. After removal of solvent \textit{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): \(\nu_{\text{max}}\) in cm\(^{-1}\) 2922, 2851, 1587, 1507, 1121; \(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta\) 8.13 (s, 4H, Ar), 7.23 (s, 4H, Ar), 4.02 - 4.09 (m, 12H, 6 \times OCH\textsubscript{2}), 1.26 – 1.87 (m, 168H, 84 \times CH\textsubscript{2}), 0.86 – 0.89 (m, 18H, 6 \times CH\textsubscript{3}). \(^{13}\)C NMR (CDCl\textsubscript{3}, 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 C\textsubscript{118}H\textsubscript{207}N\textsubscript{4}O\textsubscript{6}S\textsubscript{2}(M+1): 1840.5452, Found: 1840.5267.
(ii) NMR spectra

Figure S1. $^1$H NMR (400 MHz) spectra of 1a in CDCl$_3$

Figure S2. $^{13}$C NMR (100 MHz) spectra of 1a in CDCl$_3$
Figure S3. $^1$H NMR (400 MHz) spectra of 1b in CDCl$_3$

Figure S4. $^{13}$C NMR (100 MHz) spectra of 1b in CDCl$_3$
Figure S5. $^1$H NMR (400 MHz) spectra of 1c in CDCl$_3$

Figure S6. $^{13}$C NMR (100 MHz) spectra of 1c in CDCl$_3$
**Figure S7.** $^1$H NMR (600 MHz) spectra of 2a in CDCl$_3$

**Figure S8.** $^{13}$C NMR (100 MHz) spectra of 2a in CDCl$_3$
Figure S9. $^1$H NMR (400 MHz) spectra of 2b in CDCl$_3$

Figure S10. $^{13}$C NMR (100 MHz) spectra of 2b in CDCl$_3$
Figure S11. $^1$H NMR (400 MHz) spectra of 2c in CDCl$_3$

Figure S12. $^{13}$C NMR (100 MHz) spectra of 2c in CDCl$_3$
Figure S13. $^1$H NMR (400 MHz) spectra of 6a in CDCl$_3$

Figure S14. $^{13}$C NMR (100 MHz) spectra of 6a in CDCl$_3$
**Figure S15.** $^1$H NMR (600 MHz) spectra of 6b in CDCl$_3$

**Figure S16.** $^{13}$C NMR (150 MHz) spectra of 6b in CDCl$_3$
Figure S17. $^1$H NMR (400 MHz) spectra of 6c in CDCl$_3$

Figure S18. $^{13}$C NMR (100 MHz) spectra of 6c in CDCl$_3$
Figure S19. $^1$H NMR (400 MHz) spectra of 5a in CDCl$_3$

Figure S20. $^{13}$C NMR (100 MHz) spectra of 5a in CDCl$_3$
**Figure S21.** $^1$H NMR (400 MHz) spectra of 5b in CDCl$_3$

**Figure S22.** $^{13}$C NMR (100 MHz) spectra of 5b in CDCl$_3$
Figure S23. $^1$H NMR (600 MHz) spectra of 5c in CDCl$_3$

Figure S24. $^{13}$C NMR (150 MHz) spectra of 5c in CDCl$_3$
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, Colh phase; (b) 1b at 85 °C, Colob phase; (c) 1c at 46 °C, Cr phase; (d) 2a at 96.3 °C, Colob phase; (e) 2a at 50 °C, Cr phase; (f) 2b at 93 °C, Colob phase; (g) 2b at 60 °C, Colob phase; (h) 2c at 87 °C, Colob phase; (i) 2c at 82 °C, Colob phase.
(iv) Differential Scanning Calorimetry

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 °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_{ab} 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 properties

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

**Relative Quantum Yield Calculation**

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:

\[ Q_S = Q_R \times \left( \frac{m_S}{m_R} \right) \times \left( \frac{n_S}{n_R} \right)^2 \]

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 H₂SO₄ and subscript S refers to the sample under investigation. In order to minimize re-absorption 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.

\[ Q_S = 0.54 \times \left( \frac{m_S}{2.71} \right) \times (1.407/1.33)^2 \]

\[ = 0.223 \times m_S \]

<table>
<thead>
<tr>
<th>Entry</th>
<th>( m_S )</th>
<th>( m_R )</th>
<th>( Q_S^{a,b,c} )</th>
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<tr>
<td>1a</td>
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</tr>
<tr>
<td>2a</td>
<td>( 1.58 \times 10^9 )</td>
<td>( 2.71 \times 10^9 )</td>
<td>0.35</td>
</tr>
</tbody>
</table>

\(^a\) Measured in THF.
\(^b\) Excited at absorption maxima.
\(^c\) Standard 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$_2$SO$_4$ 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
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 ($\text{Fc/Fc}^+$) redox couple ($E_{1/2, \text{Fc/Fc}^+}$) was found to be 0.57 V relative to the Ag/Ag$^+$ reference electrode.

References