Effect of regioisomerism on the mesomorphic and photophysical behavior of oxadiazole-based tris(N-salicylideneaniline): Synthesis and characterization

Suraj Kumar Pathak, a,Ψ Subrata Nath, a,Ψ Joydip De, b Santanu Kumar Pal b and Ammathnadu S. Achalkumar a*

Ψ Equal contribution

a Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati, 781039, Assam, India. b Department of Chemical Sciences, Indian Institute of Science Education and Research Mohali, Sector-81, Knowledge City, Manauli 140306, Punjab, India.

Supporting information

Table of Contents

<table>
<thead>
<tr>
<th>Serial Number</th>
<th>Contents</th>
<th>Page numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Materials and methods</td>
<td>S2</td>
</tr>
<tr>
<td>2</td>
<td>Experimental Section</td>
<td>S3-S9</td>
</tr>
<tr>
<td>3</td>
<td>NMR Spectra</td>
<td>S10-S23</td>
</tr>
<tr>
<td>4</td>
<td>Polarized Optical Microscopy</td>
<td>S24</td>
</tr>
<tr>
<td>5</td>
<td>X-ray diffraction studies</td>
<td>S25</td>
</tr>
<tr>
<td>6</td>
<td>Photophysical properties</td>
<td>S26-S27</td>
</tr>
<tr>
<td>7</td>
<td>MALDI-TOF mass spectrometry</td>
<td>S28</td>
</tr>
<tr>
<td>8</td>
<td>Thermal Gravimetric Analysis</td>
<td>S29</td>
</tr>
</tbody>
</table>
1. Materials and methods

All commercially obtained chemicals were used as received. As required the solvents were dried as per the standard protocols. Silica gel or neutral alumina used as stationery phase for column chromatography. Aluminium sheets coated with silica gel were used for thin layer chromatography (TLC) to monitor the reactions and column purifications. Infrared spectra were measured on a Perkin Elmer IR spectrometer at room temperature by preparing the KBr pellet. $^1$H and $^{13}$C NMR spectra were recorded using Varian Mercury 400 MHz (at 298K) or Bruker 600 MHz NMR spectrometer. Mass spectrometry was carried out using MALDI-TOF mass spectrometer or High Resolution Mass Spectrometer. Polarizing optical microscope (POM) (Nikon Eclipse LV100POL) in conjunction with a controllable hot stage (Mettler Toledo FP90) was used for the characterization of mesogens. The phase transitions, associated enthalpy changes were obtained by differential scanning calorimeter (DSC) (Mettler Toledo DSC1). X-ray diffraction (XRD) studies were carried out using image plate and a detector. This setup had Cu Kα ($\lambda$=0.15418 nm) radiation from a source (GeniX3D, Xenocs) operating at 50 kV and 0.6 mA in conjunction with a multilayer mirror was used to irradiate the sample. Glass capillaries containing the sample were used for the measurements. Thermogravimetric analysis (TGA) was accomplished with a thermogravimetric analyzer (Mettler Toledo, model TG/SDTA 851 e). Perkin-Elmer Lambda 750, UV/VIS/NIR spectrometer was used to obtain UV-Vis spectra, while Fluoromax-4 fluorescence spectrophotometer and Perkin Elmer LS 50B spectrometer were used to obtain emission spectra in solution state and solid thin film state respectively.
2. Experimental Section

3,4,5-trimethoxybenzonitrile (1)

3,4,5-trimethoxybenzaldehyde (10.2 mmol, 1 equiv.) was added to a solution of hydroxylamine hydrochloride (18.9 mmol, 1.85 equiv.) in DMSO (10.2 mL), and the resulting reaction solution was stirred and heated for 3 h at 100 °C. After cooling to room temperature, water was added to the reaction mixture, which was then extracted with CHCl₃ (5 × 20 mL). The combined chloroform layers were washed with water (4 × 20 mL) and dried with Na₂SO₄. Removal of chloroform by rotatory evaporation and high vacuum yielded the desired product which was then recrystallised with ethanol to get the pure product.

Rₛ = 0.5 (30% EtOAc-hexanes); mp: 92-93°C; yield: 85%; IR (KBr pellet): νₘₐₓ in cm⁻¹ 3098.12, 2926.86, 2845.46, 2224.93, 1585.18, 1505.73, 1337.93, 998.37, 853.94, 777.52; ¹H NMR (CDCl₃, 600 MHz): δ 6.85 (s, 2H, Ar), 3.89 (s, 3H, 1× OCH₃), 3.87 (s, 6H, 2× OCH₃); ¹³C NMR (CDCl₃, 150 MHz): 153.74, 142.50, 119.16, 109.61, 106.89, 61.24, 56.57; HRMS (ESI+) exact mass calculated for C₁₀H₁₁NO₃ (M+1): 194.0812, Found: 194.0826.

(Z)-N'-hydroxy-3,4,5-trimethoxybenzimidamide (2)

To a stirred solution of 3,4,5-trimethoxybenzonitrile (5.5 mmol, 1 equiv.) in ethanol (6 mL) was added hydroxylamine hydrochloride (12.1 mmol, 2.2 equiv.) and then Et₃N (12.7 mmol, 2.3 equiv.). The solution was stirred under reflux for 18 h. Ethanol was removed under reduced pressure and then diluted with water and the aqueous layer extracted 4 times with DCM. The combined organic phases were dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by recrystallization with ethanol to get the pure product as white solid.

Rₛ = 0.5 (pure EtOAc); mp: 155-157°C; yield: 90%; IR (KBr pellet): νₘₐₓ in cm⁻¹ 3463.70, 3333.55, 3004.33, 2936.41, 2834.30, 1660.83, 1585.58, 1304.12, 854.03; ¹H NMR (CDCl₃, 600 MHz): δ 6.85 (s, 2H, Ar), 4.87 (s, 2H, NH₂), 3.88 (s, 6H, 2× OCH₃); ¹³C NMR (CDCl₃, 150 MHz): 153.74, 153.13, 139.73, 128.23, 103.48, 61.11, 56.43; HRMS (ESI+) exact mass calculated for C₁₀H₁₄N₂O₄ (M+1): 227.1026, Found: 227.1033.

5-(4-nitrophenyl)-3-(3,4,5-trimethoxyphenyl)-1,2,4-oxadiazole (3)

A mixture of Compound 2 (4.9 mmol, 1 equiv.) and dry pyridine (5 mL) was stirred under Ar-atmosphere at 0 °C. To this, solution of 4-nitrobenzoyl chloride (5.3 mmol, 1.1 equiv.) in dry THF was added dropwise. The reaction mixture was refluxed for 12 h and then poured into cold water. The whole mass (a mixture of solid and water) was extracted with CHCl₃ (4 × 30
mL). The combined extract was washed with water, brine and dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on neutral alumina. Elution with 50% DCM-Hexane system to DCM yielded the desired product. Recrystallisation with ethylacetate give the pure product.

\[ R_f = 0.32 \text{ (80\% EtOAc-hexane); mp: 208-209°C; yield: 80\%; IR (KBr pellet): } v_{\text{max}} \text{ in cm}^{-1} 3120.56, 2924.21, 2852.29, 1596.21, 1569.35, 1360.65, 851.48, 770.49, 704.94, 672.20; \]
\[ ^1H \text{ NMR (CDCl}_3, 600 MHz): \delta 8.42 (s, 4H, Ar), 7.41(s, 2H, Ar), 3.98(s, 6H, 2× OCH}_3, 3.93(s, 2H, 1×OCH}_3); ^13C \text{ NMR (CDCl}_3, 150 MHz): 173.80, 169.44, 153.86, 150.42, 141.13, 129.69, 129.45, 124.55, 121.64, 104.93, 61.20, 56.55; \]
\[ \text{HRMS (ESI+) exact mass calculated for } C_{17}H_{15}N_{3}O_{6}(M+1): 358.1034, \text{ Found: 358.1047.} \]

5-(5-(4-nitrophenyl)-1,2,4-oxadiazol-3-yl)benzene-1,2,3-triol (4)

A solution of Compound 3 (3.6 mmol, 1 equiv) in dry DCM (20 mL) was cooled to -80 °C. Then BBr₃ (13.03 mmol, 3.6 equiv.) was added slowly to the cooled solution. The reaction mixture was then allowed to warm to room temperature and stirred for additional 12h. Subsequently, the mixture was poured into the ice-water dropwise and precipitate was formed. The precipitate was filtered and washed with water. The crude product was recrystallized from ethanol to get the pure product.

\[ R_f = 0.2 \text{ (20\% CH}_3OH-CHCl}_3); \text{ mp: 256-258°C; yield: 87%; IR (KBr pellet): } v_{\text{max}} \text{ in cm}^{-1} 3633.33, 3379.18, 3108.52, 2924.07, 2853.26, 1619.94, 1506.07, 1340.70, 1216.63, 1108.73, 857.55, 768.57; \]
\[ ^1H \text{ NMR (DMSO-d}_6, 600 MHz): \delta 9.38 (brs, 2H, 2×OH), 8.85(brs, 1H, 1×OH), 8.46(d, 2H, J = 6Hz, Ar), 8.39(d, 2H, J = 12Hz, Ar), 7.08(s, 2H, Ar); ^13C \text{ NMR (DMSO-d}_6, 150 MHz): 173.16, 168.74, 149.85, 146.41, 136.88, 129.32, 128.91, 124.60, 115.47, 106.29; \]
\[ \text{HRMS (ESI+) exact mass calculated for } C_{14}H_{9}N_{3}O_{6} \text{ (M+1): 315.0491, Found: 315.0137.} \]

5-(4-nitrophenyl)-3-(3,4,5-tris(hexadecyloxy)phenyl)-1,2,4-oxadiazole (5)

A mixture of compound 4 (1.6mmol, 1equiv.), n-bromohexadecane (5.23 mmol, 3.3equiv.), anhyd. K₂CO₃ (10.47 mmol, 6.6 equiv.) and DMF (10mL) was heated at 80 °C for 17h under N₂ atmosphere. Then the reaction mixture poured into ice-water and extracted with EtOAc (3 × 50 mL). The combined organic layer was washed with water, brine and dried over anhyd. Na₂SO₄. Evaporation of the solvent and the purification of crude product over neutral alumina using hexanes followed by 50% CH₂Cl₂-hexanes to CH₂Cl₂ as eluents furnished the desired product, which was further purified by recrystallisation with ethylacetate.
\[ R_f = 0.7 \ (80\% \text{ CH}_2\text{Cl}_2-\text{hexane}) \; \text{mp: } 86-88^\circ \text{C} \; \text{yield: } 64\%; \text{ IR (KBr pellet): } \nu_{\text{max}} \text{ in cm}^{-1} \ 2919.31, 2850.08, 1588.82, 1565.43, 1467.89, 1356.29, 1231.14, 1111.03, 743.03; \text{ }^1\text{H NMR (CDCl}_3, 600 \text{ MHz): } \delta \ 8.42 \ (s, 4\text{H, Ar}), 7.37 \ (s, 2\text{H, Ar}), 4.08 \ (t, 4\text{H, } J = 6\text{Hz, } 2\times \text{OCH}_2), 4.04 \ (t, 2\text{H, } J = 6\text{Hz, } 1\times \text{OCH}_2), \ 1.25-1.85 \ (m, 84\text{H, } 42\times \text{CH}_2), 0.86-0.89 \ (m, 9\text{H, } 3\times \text{CH}_3); \text{ }^{13}\text{C NMR (CDCl}_3, 150 \text{ MHz): } 173.66, 169.65, 160.55, 153.78, 150.40, 141.30, 129.46, 124.55, 121.11, 106.12, 73.80, 69.50, 32.16, 30.58, 29.98, 29.95, 29.89, 29.83, 29.65, 29.59, 26.34, 22.92, 14.34; \text{ HRMS (ESI+) exact mass calculated for } \text{C}_{62}\text{H}_{105}\text{N}_3\text{O}_6 (\text{M}^+) : 987.8003, \text{ Found: } 987.7330. \]

4-(3-(3,4,5-tris(hexadecyloxy)phenyl)-1,2,4-oxadiazol-5-yl)aniline (6)

To a solution of nitro compound 5 (0.47mmol, 1equiv.) in dry THF was added 10\% Pd-C (0.046g) (10\% wt. of compound 5) and stirred under hydrogen atmosphere (balloon) for 12h (monitored by TLC). The reaction mixture was then filtered through a celite bed. Evaporation of the solvent under reduced pressure to get the crude product. The crude product was further purified by neutral alumina using hexanes followed by 10\% ethylacetate-hexanes as eluents furnished the desired pure amine.

\[ R_f = 0.3 \ (20\% \text{ EtOAc-hexanes}) \; \text{mp: } 85-87^\circ \text{C} \; \text{yield: } 70\%; \text{ IR (KBr pellet): } \nu_{\text{max}} \text{ in cm}^{-1} \ 3327.26, 2918.85, 2849.80, 1620.08, 1501.42, 1466.38, 1362.53, 1236.53, 1127.24, 866.02, 720.82; \text{ }^1\text{H NMR (CDCl}_3, 600 \text{ MHz): } \delta \ 8.01 \ (d, 2\text{H, } J = 6\text{Hz, Ar}), 7.35 \ (s, 2\text{H, Ar}), 6.75 \ (d, 2\text{H, } J = 12\text{Hz, Ar}), 4.15 \ (brs, 2\text{H, NH}_2), 4.07 \ (t, 4\text{H, } J = 6\text{Hz, } 2\times \text{OCH}_2), 4.02 \ (t, 2\text{H, } J = 6\text{Hz, } 1\times \text{OCH}_2), 1.14-1.86 \ (m, 84\text{H, } 42\times \text{CH}_2), 0.86-0.89 \ (m, 9\text{H, } 3\times \text{CH}_3); \text{ }^{13}\text{C NMR (CDCl}_3, 150 \text{ MHz): } 176.03, 168.86, 153.60, 150.79, 140.67, 130.28, 122.23, 114.69, 106.01, 100.20, 73.73, 69.40, 32.16, 30.57, 29.98, 29.94, 29.89, 29.84, 29.65, 29.60, 26.33, 22.92, 14.34; \text{ HRMS (ESI+) exact mass calculated for } \text{C}_{62}\text{H}_{107}\text{N}_3\text{O}_4 (\text{M}^+) : 958.8334, \text{ Found: } 958.9782. \]

TSAN (1b)

A mixture of triformylphloroglucinol (0.09 mmol, 1equiv.) and aniline 6 (0.31mmol, 3.3 equiv.) in absolute ethanol (20 mL) was heated for reflux under inert atmosphere for 6h with vigorous stirring. The dull yellow solid separated upon cooling the reaction mixture was collected by filtration, repeatedly washed with ethanol and air-dried. The crude product was purified by repeated recrystallizations with ethylacetate.

\[ R_f = 0.6 \ (80\% \text{ CH}_3\text{OH-CHCl}_3) \; \text{yield: } 67\%; \text{ IR (KBr pellet): } \nu_{\text{max}} \text{ in cm}^{-1} \ 2950.81, 2919.85, 2850.52, 1631.21, 1602.79, 1509.14, 1467.61, 1434.10, 1289.74, 1179.34, 1120.16, 1016.19, 845.97, 760.76; \text{ }^1\text{H NMR (CDCl}_3, 600 \text{ MHz): } \delta \ 13.39-13.43 \ (m, =\text{CNH}), 13.27 \ (s, =\text{CNH}), \text{ Found: } 958.7330. \]
12.95 (s, –CNH), 8.62-8.75 (m, 3H, –CHN), 8.14-8.18 (m, 6H, Ar), 7.21-7.38 (m, 12H, Ar),
4.01 (broad s, 18H, 9 × OCH$_2$), 1.26-1.83 (m, 252H, 126 × CH$_2$), 0.87-0.89 (m, 27H, 9 ×
CH$_3$). MALDI-TOF exact mass calculated for C$_{195}$H$_{323}$N$_9$O$_{15}$ (M+2): 3031.4789, Found:
3031.4320.

4-nitrobenzonitrile (9)

4-nitrobenzaldehyde (13.23 mmol, 1 equiv.) was added to a solution of hydroxylamine
hydrochloride (24.48 mmol, 1.85 equiv.) in DMSO (13 mL), and the resulting reaction
solution was stirred and heated for 3h in an oil bath maintained at 100 °C. After cooling to
room temperature, water (20 mL) was added to the reaction mixture, which was then
extracted with CHCl$_3$ (5 × 20 mL). The combined organic layers were washed with water and
dried over sodium sulphate. The organic layer was concentrated to get the crude product
which was recrystallized with ethanol to get the pure product.

R$_f$ = 0.7 (50% EtOAc-hexanes); mp:147-149 °C; yield: 95%; IR (KBr pellet): $\nu_{\text{max}}$ in cm$^{-1}$
2231.80, 1645.66, 859.74, 747.49; $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 8.36 (d, 2H, $J$ = 12Hz, Ar),
7.89(d, 2H, $J$ = 12Hz, Ar); $^{13}$C NMR (CDCl$_3$, 150 MHz): 150.18, 133.67, 124.47, 118.48,
116.99; HRMS (ESI+) exact mass calculated for C$_{10}$H$_{11}$NO$_3$ (M+1): 194.0812, Found:
194.0826.

(Z)-N’-hydroxy-4-nitrobenzimidamide (10)

To a stirred solution of 4-nitrobenzonitrile (6.75 mmol, 1equiv.) in ethanol (10 mL) was
added hydroxylamine hydrochloride (14.85 mmol, 2.2 equiv.) and then Et$_3$N (15.53 mmol,
2.3 equiv.). The solution was stirred under reflux for 18h. Ethanol was removed under
reduced pressure and then diluted with water and the aqueous layer extracted 4 times with
DCM. The combined organic phases were dried over Na$_2$SO$_4$ and concentrated under reduced
pressure. The crude product was further purified by recrystallization with ethanol to get the
pure product as yellow solid.

R$_f$ = 0.5 (50% EtOAc); mp: 155-157°C; yield: 90%; IR (KBr pellet): $\nu_{\text{max}}$ in cm$^{-1}$ 3463.01,
3359.87, 2923.99, 2852.99, 2596.37, 2508.31, 2459.38, 1659.83, 1600.43, 1340.46, 862.17;
$^1$H NMR (CD$_3$OD, 400 MHz): $\delta$ 8.25 (d, 2H, $J$ = 12Hz, Ar), 7.88 (d, 2H, $J$ = 12Hz, Ar);$^{13}$C
NMR (CDCl$_3$, 150 MHz): 153.98, 150.59, 141.30, 128.98, 125.33; HRMS (ESI+) exact mass
calculated for C$_{10}$H$_{14}$N$_2$O$_4$ (M+1): 227.1026, Found: 227.1033.

3-(4-nitrophenyl)-5-(3,4,5-trimethoxyphenyl)-1,2,4-oxadiazole (11)
A mixture of Compound 10 (5.5mmol, 1equiv.) and dry pyridine (5mL) was stirred under Ar-atmosphere at 0 °C. To this, solution of 3,4,5-trimethoxy benzoxyld chloride (6.07 mmol, 1.1 equiv.) in dry THF was added dropwise. The reaction mixture was refluxed for 12h and then poured into cold water. The whole mass (a mixture of solid and water) was extracted with CHCl₃ (4 × 40 mL). The combined extract was washed with water, brine and dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on neutral alumina. Elution with 50% DCM-Hexane system to DCM yielded the desired product. Recrystallisation with ethylacetate gives the pure product.

\[ R_f = 0.34 \text{(80\% EtOAc-hexane);} \text{ mp: 205-207°C; yield: 61%; IR (KBr pellet): } \nu_{\text{max}} \text{ in cm}^{-1} 2924.02, 2852.00, 1569.38, 1360.69, 851.36, 770.39, 704.68, 672.16; \text{ } ^1\text{H NMR (CDCl}_3, 600 MHz): \delta 8.37 \text{ (s, 4H, Ar), 7.45(s, 2H, Ar), 3.99(s, 6H, 2× OCH}_3, 3.96(s, 2H, 1×OCH}_3); \text{ } ^13C NMR (CDCl}_3, 150 MHz): 176.52, 167.64, 153.92, 149.68, 142.60, 133.07, 128.73, 124.30, 118.88, 105.66, 61.31, 56.65; \text{ HRMS (ESI+)} \text{ exact mass calculated for C}_{17}H_{15}N_3O_6 (M+1): 358.1034, Found: 358.1047.\]

5-(3-(4-nitrophenyl)-1,2,4-oxadiazol-5-yl)benzene-1,2,3-triol (12)

A solution of Compound 11 (2.8 mmol, 1equiv) in dry DCM (40 mL) was cooled to -80 °C. Then, BBr₃ (10.08 mmol, 3.6 equiv.) was added slowly to the cooled solution. The reaction mixture was then allowed to warm to room temperature and stirred for additional 12 h. Subsequently, the mixture was poured into the ice cold water dropwise and precipitate was formed. The precipitate was filtered and washed with water. The crude product was recrystallized from ethanol to get the pure product.

\[ R_f = 0.21 \text{(20\% CH}_3OH-CHCl}_3); \text{ mp: } >300°C; \text{ yield: 57%; IR (KBr pellet): } \nu_{\text{max}} \text{ in cm}^{-1} 3637.16, 3379.32, 2952.39, 2924.13, 2853.19, 1619.88, 1506.00, 1340.63, 1216.51, 1108.65, 1032.40 857.57, 768.55; \text{ } ^1\text{H NMR (CD}_3OD, 600 MHz): 8.34(d, 2H, J = 12Hz, Ar), 8.26(d, 2H, J = 12Hz, Ar), 7.15(s, 2H, Ar); \text{ } ^13C NMR (CD}_3OD, 150 MHz): 179.12, 169.23, 151.61, 148.22, 140.88, 135.05, 130.20, 125.89, 115.91, 109.39; \text{ HRMS (ESI+)} \text{ exact mass calculated for C}_{14}H_{9}N_3O_6 (M+1): 315.0491, Found: 315.0137.\]

3-(4-nitrophenyl)-5-(3,4,5-tris(hexadecyloxy)phenyl)-1,2,4-oxadiazole (13)

A mixture of compound 12 (1.22 mmol, 1 equiv.), n-bromohexadecane (4.01 mmol, 3.3 equiv.), anhyd. K₂CO₃ (8.02mmol, 6.6equiv.) and DMF (5mL) was heated at 80°C for 17h under N₂ atmosphere. Then the reaction moisture poured on to ice-water and extracted with
EtOAc (4 × 50 mL). The combined organic layer was washed with water, brine and dried over anhyd. Na₂SO₄. Evaporation of the solvent and the purification of residue over neutral alumina using hexanes followed by 50% CH₂Cl₂-hexanes to CH₂Cl₂ as eluents furnished the desired product, which was further purified by recrystallization with ethylacetate.

\[ R_f = 0.69 \] (80% CH₂Cl₂-hexane); mp: 83-85°C; yield: 42%; IR (KBr pellet): \( \nu_{\text{max}} \text{ in cm}^{-1} \) 2920.08, 2851.17, 1640.29, 1560.09, 1526.22, 1466.88, 1357.53, 1243.16, 1121.72, 746.09; ¹H NMR (CDCl₃, 600 MHz): \( \delta \) 8.37 (s, 4H, Ar), 7.40 (s, 2H, Ar), 4.06-4.08 (m, 6H, 3×OCH₂), 1.21-1.88 (m, 84H, 42×CH₂), 0.86-0.89 (m, 9H, 3×CH₃); ¹³C NMR (CDCl₃, 150 MHz): 176.80, 167.59, 153.84, 149.67, 142.84, 133.23, 128.73, 124.28, 118.43, 106.81, 73.92, 69.62, 32.16, 30.58, 29.94, 29.90, 29.80, 29.63, 29.60, 29.52, 26.32, 22.29, 22.92, 14.34; HRMS (ESI+) exact mass calculated for C₆₂H₁₀₅N₃O₆ (M+1): 988.8076, Found: 988.8176.

**4-(5-(3,4,5-tris(hexadecyloxy)phenyl)-1,2,4-oxadiazol-3-yl)aniline (14)**

To a solution of nitro compound 13 (0.3 mmol, 1 equiv.) in dry THF was added 10% Pd-C (0.030g) (10% wt. of compound 13) and stirred under hydrogen atmosphere (balloon) for 12h (monitored by TLC). The reaction mixture was then filtered through a celite bed. Evaporation of the solvent under reduced pressure to get the crude product. The crude product was further purified by neutral alumina using hexanes followed by ethylacetate-hexanes (10%) as eluents furnished the desired pure amine.

\[ R_f = 0.25 \] (20% EtOAc-hexanes); mp: 78-79°C; yield: 41%; IR (KBr pellet): \( \nu_{\text{max}} \text{ in cm}^{-1} \) 3327.11, 2918.86, 2849.80, 1620.14, 1501.38, 1466.36, 1362.50, 1236.47, 1188.64, 1013.51, 866.43, 762.27, 720.86; ¹H NMR (CDCl₃, 400 MHz): \( \delta \) 7.87 (d, 2H, \( J = 6 \)Hz, Ar), 7.62 (s, 2H, Ar), 6.72 (d, 2H, \( J = 12 \)Hz, Ar), 4.10 (brs, 2H, NH₂), 4.01-4.09 ( m, 6H, 3×OCH₂), 1.19-1.84 (m, 84H, 42×CH₂), 0.86-0.89 (m, 9H, 3×CH₃); ¹³C NMR (CDCl₃, 100 MHz): 179.83, 166.30, 152.73, 150.79, 141.77, 133.30, 129.45, 124.25, 114.52, 108.30, 73.64, 69.28, 32.15, 30.55, 29.98, 29.95, 29.90, 29.84, 29.62, 29.60, 26.37, 26.31, 22.92, 14.35; HRMS (ESI+) exact mass calculated for C₆₂H₁₀₇N₃O₄ (M+3): 960.8485, Found: 960.8528.

**TSAN (1c)**

A mixture of triformylphloroglucinol (0.03mmol, 1 equiv.) and aniline 14 (0.11mmol, 3.3 equiv.) in absolute ethanol (20mL) was heated for reflux under inert atmosphere for 6h with vigorous stirring. The dull yellow solid separated upon cooling the reaction mixture was collected by filtration, repeatedly washed with ethanol and air dried. The crude product was purified by repeated recrystallizations with ethylacetate.
\[ R_f = 0.61 \text{ (80\% CH}_3\text{OH-CHCl}_3); \text{ yield: 67\%; IR (KBr pellet): } \nu_{\text{max}} \text{ in cm}^{-1}; \] 
\[ ^1\text{H NMR (CDCl}_3, \text{ 600 MHz): } \delta 13.40 \text{ (bs, =CNH), 13.32 (bs, =CNH), 12.98(bs, =CNH), 8.70 (m, 3H, =CHN), 8.04 (bs, 6H, Ar), 7.60 (s, 6H, Ar), 7.26-7.34 (m, 6H, Ar), 3.99-4.08 (m, 18H, 9 } \times \text{ OCH}_2\text{), 1.24-1.85(m, 352H, 126 } \times \text{ CH}_2\text{), 0.85 – 0.89 (m, 27H, 9 } \times \text{ CH}_3\text{); MALDI-TOF exact mass calculated for C}_{195}\text{H}_{322}\text{N}_9\text{O}_{15}(\text{M+1): 3030.4705, Found: 3030.4780.} \]
3. NMR spectra

Figure S1. $^1$H NMR (600 MHz) spectra of 1 in CDCl$_3$

Figure S2. $^{13}$C NMR (150 MHz) spectra of 1 in CDCl$_3$
Figure S3. $^1$H NMR (600 MHz) spectra of 2 in CDCl$_3$

Figure S4. $^{13}$C NMR (150 MHz) spectra of 2 in CDCl$_3$
Figure S5. $^1$H NMR (600 MHz) spectra of 3 in CDCl$_3$

Figure S6. $^{13}$C NMR (150 MHz) spectra of 3 in CDCl$_3$
Figure S7. $^1$H NMR (600 MHz) spectra of 4 in DMSO-D$_6$.

Figure S8. $^{13}$C NMR (150 MHz) spectra of 4 in DMSO-D$_6$.
Figure S9. $^1$H NMR (600 MHz) spectra of 5 in CDCl$_3$

Figure S10. $^{13}$C NMR (150 MHz) spectra of 5 in CDCl$_3$
Figure S11. $^1$H NMR (600 MHz) spectra of 6 in CDCl$_3$.

Figure S12. $^{13}$C NMR (150 MHz) spectra of 6 in CDCl$_3$. 

S15
Figure S13. $^1$H NMR (600 MHz) spectra of 1b in CDCl$_3$ (Ratio of the integrated area under the signals corresponding to $H_a$ (from $C_{3h}$ isomer) and $H_c$ (from $C_i$ isomer) are in the ratio of 2:1)
Figure S14. $^1$H NMR (600 MHz) spectra of 9 in CDCl$_3$

Figure S15. $^{13}$C NMR (150 MHz) spectra of 9 in CDCl$_3$

Figure S16. $^1$H NMR (400 MHz) spectra of 10 in CD$_3$OD
**Figure S17.** $^{13}$C NMR (100 MHz) spectra of 10 in CD$_3$OD

**Figure S18.** $^1$H NMR (600 MHz) spectra of 11 in CDCl$_3$
**Figure S19.** $^{13}$C NMR (150 MHz) spectra of 11 in CDCl$_3$

**Figure S20.** $^1$H NMR (600 MHz) spectra of 12 in CD$_3$OD
Figure S21. $^{13}$C NMR (150 MHz) spectra of 12 in CD$_3$OD

Figure S22. $^1$H NMR (600 MHz) spectra of 13 in CDCl$_3$
**Figure S23.** $^{13}$C NMR (150 MHz) spectra of 13 in CDCl$_3$

**Figure S24.** $^1$H NMR (400 MHz) spectra of 14 in CDCl$_3$
Figure S25. $^{13}$C NMR (100 MHz) spectra of 14 in CDCl$_3$.

Figure S26. $^1$H NMR (600 MHz) spectra of 1c in CDCl$_3$ (Ratio of the integrated area under the signals corresponding to $\text{H}_a$ (from $C_{3h}$ isomer) and $\text{H}_c$ (from $C_i$ isomer) are in the ratio of 1.8:1.)
4. Polarized Optical Microscopy

Figure S27. POM images of discotics 1b on a cooling process from isotropic melt.  
- 1b at 218°C
- 1b at 180°C
- 1b at 98.2°C
- 1b at 30°C

1c at 175.1°C
1c at 143.6°C
1c at 60.5°C
1c at 30°C

Figure
POM images of discotics 1b on a cooling process from isotropic melt.
**Figure S28.** POM images of discotics 1c on a cooling process from isotropic melt

**5. X-ray diffraction studies**

![Graph showing XRD profiles with 2θ values for 180°C, 100°C, and 28°C](image)

**Figure S29.** XRD profiles depicting the intensity against the 2θ obtained for the Col$_h$ phase of compound 1b at 180°C, 100°C and at 28°C (b); (inset shows the XRD image pattern obtained).
Figure S30. XRD profiles depicting the intensity against the $2\theta$ obtained for the Col$_1$ phase of compound 1c at 140°C (inset shows the XRD image pattern obtained).

6. Photophysical properties
Relative Quantum Yield Calculation

Relative quantum yield of compound was measured with respect to tetrakis(octyl)-1H-phenanthro[1,10,9,8]carbazole-3,4,9,10-tetracarboxylate in THF solution as the standard, which is having the relative quantum yield of 1 with respect to fluorescein ($Q_f = 0.79$) in 0.1M NaOH). 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).

The subscript R refers to the reference fluorophore i.e. compound carbazole solution in THF 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 442 nm.

Quantum Yield of compound carbazole is 1.01. Simplified equation for the calculation after substituting the appropriate values is given below and values obtained are given in table below.

$$Q_S = 1.01 \times \left(\frac{m_S}{m_R}\right) \times (1.407/1.407)^2$$

$$= 1.01 \times \left(\frac{m_S}{m_R}\right)$$

<table>
<thead>
<tr>
<th>Entry</th>
<th>$m_S$</th>
<th>$m_R$</th>
<th>$Q_S^{a,b,c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1a</td>
<td>2.63082 x 10^8</td>
<td>7.2271 x 10^8</td>
<td>0.37</td>
</tr>
<tr>
<td>-----</td>
<td>----------------</td>
<td>----------------</td>
<td>------</td>
</tr>
<tr>
<td>1b</td>
<td>2.18814 x 10^8</td>
<td>7.2271 x 10^8</td>
<td>0.31</td>
</tr>
<tr>
<td>1c</td>
<td>1.90912 x 10^8</td>
<td>7.2271 x 10^8</td>
<td>0.27</td>
</tr>
</tbody>
</table>

\(^a\) Measured in THF.
\(^b\) Excited at absorption maxima.
\(^c\) Standard carbazole \((Q_f = 1.01)\) in THF solution.

**Figure S32.** Plots of integrated photoluminescence intensity vs absorbance of tetrakis(octyl)-1H-phenanthro[1,10,9,8]carbazole-3,4,9,10-tetracarboxylate (micromolar THF solution) and compounds 1a-c (micromolar THF solution).

7. MALDI-TOF mass spectrometry
Figure S33. MALDI-TOF mass spectrum of TSAN 1b

Figure S34. MALDI-TOF mass spectrum of TSAN 1c

8. Thermal Gravimetric Analysis (TGA)
Figure S35. TGA curves of TSAN 1b and 1c