Electronic Supplementary Information (ESI)

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1. Experimental Details

1.1. General

Infrared spectra were recorded on a Perkin-Elmer model 283 spectrometer in KBr discs or films. $^1$H NMR spectra were obtained with a Varian Mercury Plus 400-MHz instrument using tetramethylsilane (TMS) as the internal standard. $^{13}$C NMR spectra were recorded on a Varian Mercury Plus 100-MHz spectrometer. Elemental analyses were carried out using a Carlo Erba model E-1110 instrument. Mesomorphic textures were determined using an Olympus BX50 microscope equipped with a Mettler Toledo FP-82 hot stage and a PM-30 exposure control unit. Thermal transitions and enthalpies were determined by DSC measurements carried out using Shimadzu equipment with a DSC-50 module. TGA measurements were carried out using Shimadzu equipment with a TGA-50 module. ESI/MS spectra were obtained on a Micromass Q-TOFmicro and APPI/MS/MS Acquity TQD Waters. An HP UV-Vis model 8453 spectrophotometer was used to record absorption spectra. Fluorescence spectra were recorded on a Hitachi-F-4500 and relative quantum yields were obtained according to published method$^1$ using PBD as standard ($\Phi_F = 0.83$)$^2$. The electrochemical measurements were carried out with an EPSILON potentiostat (BAS). Cyclic voltammograms were recorded at scan rates of 50, 100, 200 and 500 mV s$^{-1}$ from a solution of 3a ($10^{-3}$ mol.dm$^{-3}$) in acetonitrile containing 0.1 mol.dm$^{-3}$ TBAPF$_6$, using a gastight single-compartment three-electrode cell equipped with carbon working, platinum wire auxiliary, and Ag/AgCl pseudo-reference electrodes. The potentials are reported against the saturated calomel electrode using the redox pair (Fc$^{+/0}$/Fc) as an internal standard, (0.400 V vs. NHE) and the relation SCE=NHE - 0.241V.$^3$

All the reagents were obtained from commercial sources and used without further purification. The organic solvents were of commercial grade quality and all were dried by traditional methods. In general, all the intermediates and final compounds were purified by column chromatography on silica gel (60–120 mesh), and crystallization

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from analytical grade solvents. The purity of the sample was checked by thin-layer chromatography (Merck Kieselgel 60F254).

1.2. Synthesis

The 5-(4-alkoxyphenyl)tetrazoles 1a-e have been prepared according to published procedures.4

Synthesis of tris[1,2,4]triazolo[1,3,5]triazines (3a-e).

A mixture of corresponding tetrazole (9 mmol), cyanuric chloride (3 mmol), and anhydrous potassium carbonate (36 mmol) in butanone (80 mL) was heated at temperature of reflux under argon atmosphere and vigorous stirring for 20 h. The still hot reaction mixture was filtered off washing with dichloromethane. The solvents were evaporated furnishing the crude product which was purified by column chromatography on silica-gel (eluant dichloromethane).

Tris-(4-methoxyphen-1-yl)-[1,2,4]triazolo[1,3,5]triazine (3a)

Yield: 46 %; m.p. 278 °C. IR (KBr pellet) ν_max cm⁻¹: 2934, 1601, 1318, 1253, 1175, 834. 1H NMR (DMSO-d₆) δ ppm: 7.96 (d, J = 8.6 Hz, 6 H, Ar), 7.20 (d, J = 8.6 Hz, 6 H, Ar), 3.89 (s, 9H, OCH₃). 13C NMR (CDCl₃) δ ppm: 162.2, 149.7, 142.4, 132.2, 117.4, 114.6, 56.2. ESI/MS: m/z 520.18 [(M + H), 100%]. Elemental analysis for C₂₇H₂₁N₉O₃: Calcd. C, 62.42; H, 4.07; N, 24.27 %; Found: C, 62.06; H, 4.36; 23.95.

Tris-(4-hexyloxyphen-1-yl)-[1,2,4]triazolo[1,3,5]triazine (3b)

Yield: 55 %; m.p. 127.4-127.8 °C. IR (KBr pellet) ν_max cm⁻¹: 2928, 2860, 1599, 1476, 1313, 1257, 1175, 828. 1H NMR (CDCl₃) δ ppm: 8.08 (d, J = 8.8 Hz, 6 H, Ar), 7.06 (d, J = 8.8 Hz, 6 H, Ar), 4.05 (t, 6H, -OCH₂-), 1.83 (m, 6H, -OCH₂CH₂-), 1.49 – 1.37 (m, 18 H, -CH₂-), 0.93 (t, 9 H, -CH₃). 13C NMR (CDCl₃) δ ppm: 162.2, 151.1, 140.7, 132.1, 116.0, 114.7, 68.5, 31.8, 29.3, 25.9, 22.8, 14.3. ESI/MS: m/z 730.41 [(M + H)+, 100%]. Elemental analysis for C₄₂H₅₁N₉O₃: Calcd. C, 69.11; H, 7.04; N, 17.27 %, Found: C, 68.81; H, 7.63; N, 17.34.

Tris-(4-octyloxyphen-1-yl)-[1,2,4]triazolo[1,3,5]triazine (3c)

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Yield: 43%; m.p. 95.7-97.4 °C. IR (KBr pellet) \( \nu_{\text{max}} \text{cm}^{-1} \): 2923, 2852, 1592, 1480, 1255, 1175, 828. \(^1\)H NMR (CDCl\(_3\)) \( \delta \text{ ppm} \): 8.08 (d, \( J = 8.8 \) Hz, 6 H, Ar), 7.05 (d, \( J = 8.8 \) Hz, 6 H, Ar), 4.05 (t, 6 H, -OCH\(_2\)-), 1.83 (m, 6 H, -OCH\(_2\)CH\(_2\)-), 1.48 – 1.30 (m, 30 H, -CH\(_2\)-), 0.90 (t, 9 H, -CH\(_3\)). \(^{13}\)C NMR (CDCl\(_3\)) \( \delta \text{ ppm} \): 162.2, 151.1, 140.7, 132.1, 116.0, 114.7, 68.5, 32.1, 29.6, 29.5, 29.4, 26.3, 22.9, 14.3. ESI/MS: m/z 814.51 [(M + H\(^+\)), 100%]. Elemental analysis for C\(_{48}\)H\(_{63}\)N\(_9\)O\(_3\): Calcd. C, 70.82; H, 7.80; N, 15.49 %; Found: C, 70.64; H, 8.51; N, 15.63.

Tris-(4-dodecyloxyphen-1-yl)-[1,2,4]triazolo[1,3,5]triazine (3d)

Yield: 58%; m.p. 85.5-87.0 °C; IR (KBr pellet) \( \nu_{\text{max}} \text{cm}^{-1} \): 3076, 2917, 2847, 1611, 1586, 1486, 1468, 1260, 1179, 828. \(^1\)H NMR (CDCl\(_3\)) \( \delta \text{ ppm} \): 8.09 (d, \( J = 8.8 \) Hz, 6 H, Ar), 7.06 (d, \( J = 8.8 \) Hz, 6 H, Ar), 4.05 (t, 6 H, -OCH\(_2\)-), 1.83 (m, 6 H, -OCH\(_2\)CH\(_2\)-), 1.49 (m, 6 H, -CH\(_2\)-), 1.28 (s broad, 48 H, -CH\(_2\)-), 0.89 (t, 9 H, -CH\(_3\)). \(^{13}\)C NMR (CDCl\(_3\)) \( \delta \text{ ppm} \): 162.3, 151.1, 140.7, 132.1, 116.0, 114.7, 68.49, 32.16, 29.92, 29.88, 29.85, 29.83, 29.63, 29.60, 29.38, 26.27, 22.93, 14.37. ESI/MS: m/z 982.69 [(M + H\(^+\)), 100%]. Elemental analysis for C\(_{60}\)H\(_{87}\)N\(_9\)O\(_3\): Calcd. C, 73.36; H, 8.93; N, 12.83 %; Found: C, 73.13; H, 9.19; N, 12.99.

Tris-(3,4-didodecyloxyphen-1-yl)-[1,2,4]triazolo[1,3,5]triazine (3e)

Yield: 57%; IR (KBr pellet) \( \nu_{\text{max}} \text{cm}^{-1} \): 3094, 2920, 2854, 1595, 1465, 1263. \(^1\)H NMR (CDCl\(_3\)) \( \delta \text{ ppm} \): 7.81 (dd, \( J = 8.4 \) and 2.1 Hz, 3 H, Ar), 7.70 (d, \( J = 2.1 \) Hz, 3 H, Ar), 7.03 (d, \( J = 8.6 \) Hz, 3 H, Ar), 4.09 (t, 12 H, -OCH\(_2\)-), 1.86 (m, 12 H, -OCH\(_2\)CH\(_2\)-), 1.50 (m, 12 H, -CH\(_2\)-), 1.26 (broad, 96 H, -CH\(_2\)-), 0.88 (m, 18 H, -CH\(_3\)). \(^{13}\)C NMR (CDCl\(_3\)) \( \delta \text{ ppm} \): 152.4, 151.3, 148.9, 140.7, 124.0, 116.0, 115.2, 112.6, 69.62, 69.27, 32.17, 29.20, 29.62, 29.39, 29.29, 26.27, 22.91, 14.34. APPI/MS/MS: m/z 1536.2 [(M + H\(^+\)), 100%]. Elemental analysis for C\(_{96}\)H\(_{159}\)N\(_9\)O\(_6\): Calcd. C, 75.10; H, 10.44; N, 8.21 %; Found: C, 74.85; H, 10.67; N, 8.26.
1.3. NMR spectra

Figure 1. (a) $^1$H NMR and (b) $^{13}$C NMR spectra of compound 3a (DMSO-d$_6$).

Figure 2. $^{15}$N NMR spectrum of 3a (DMSO-d$_6$, external standard nitromethane).
Figure 3. (a) $^1$H NMR and (b) $^{13}$C NMR spectra of compound 3c (CDCl$_3$).
Figure 4. (a) $^1$H NMR spectrum, (b) expanded aromatic region in the $^1$H NMR spectrum and (c) $^{13}$C NMR spectrum of compound 3e (CDCl$_3$).
1.4. MS spectra

(a)

(b)
Figure 5. ESI-MS spectra of (a) 3a, (b) 3b, (c) 3c, (d) 3e.
Figure 6. APPI/MS/MS spectra of 3e.

1.5. DSC thermograms

Figure 7. DSC curves of 3b, 10 °C/min., first (a) and second (b) scans.
Figure 8. DSC curves of 3c, 10 °C/min., first (a) and second (b) scans.

Figure 9. DSC curves of 3d, 10 °C/min., first (a) and second (b) scans.

Figure 10. DSC curves of 3e, 10 °C/min., first and second scans.
1.6. TGA curves

**Figure 11.** TGA curves of final compounds 3a-e.
1.7. Cyclic Voltammetry

![Cyclic Voltammetry Graph](image)

**Figure 12.** Representative cyclic voltammogram of 3a measured in acetonitrile solution, containing 0.1 M TBAPF₆ at 25 °C. Scan rate 200 mV/s. $HOMO = E_{\text{onset}}^{\text{ox}} \text{(SCE)} + 4.4$

$HOMO = 1.36 + 4.4 = 5.8 \text{ eV}$

1.8. X-ray crystallography – Compound 3a

A prismatic colorless crystal of 3a, with dimensions of 0.50 x 0.30 x 0.13 mm, was selected and mounted at goniometer head for X-ray measurements. The crystallographic analysis was carried out on a CAD4 diffractometer using graphite-monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073 \text{ Å}$), at room temperature. Unit cell parameters were determined on the setting angles of 25 centered reflections in the range $5.77^\circ \leq \theta \leq 17.48^\circ$. The intensities of 4194 reflections were collected from $\omega/2\theta$ scans in the range $1.43^\circ \leq \theta \leq 25.07^\circ$.

**Solution and Refinement of the structure:**

The collected reflections were corrected for Lorentz and polarization effects. No absorption correction was applied to the intensities. The structure was solved by direct methods with SIR-97 and refined by full-matrix least-squares procedure based on

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A drawing of molecular structure presented in the article was carried out with PLATON program. All non-hydrogen atoms were refined anisotropically. H atoms were placed at idealized positions, with C-H distances and Ueq values taken from the default settings of the refinement program. Full table of crystallographic data is presented below.

Table 1. Crystal data and structure refinement for 3a.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{27}$H$</em>{21}$N$_9$O$_3$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>519.53</td>
</tr>
<tr>
<td>Temperature</td>
<td>293(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71069 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P$\bar{i}$</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>6.418(3) Å</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>80.73(2)$^\circ$.</td>
</tr>
<tr>
<td>b</td>
<td>12.867(2) Å</td>
</tr>
<tr>
<td>$\beta$</td>
<td>86.34(5)$^\circ$.</td>
</tr>
<tr>
<td>c</td>
<td>14.500(9) Å</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>89.67(3)$^\circ$.</td>
</tr>
<tr>
<td>Volume</td>
<td>1179.4(9) Å</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.463 Mg/m$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.101 mm$^{-1}$</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>540</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.50 x 0.30 x 0.13 mm$^3$</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.43 to 25.07$^\circ$.</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-7 $\leq$ h $\leq$ 7, -15 $\leq$ k $\leq$ 15, -17 $\leq$ l $\leq$ 0</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>4375</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>4194 [R(int) = 0.0462]</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>None</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on $F^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>4194 / 0 / 353</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.026</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0642, wR2 = 0.1577</td>
</tr>
</tbody>
</table>

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R indices (all data) \( R_1 = 0.1102, \) wR2 = 0.1834

Extinction coefficient 0.022(5)

Largest diff. peak and hole 0.395 and -0.355 e Å\(^{-3}\)

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**Figure 13.** Molecular structure of compound 3a with hydrogen atoms.

**Figure 14.** Molecular packing of compound 3a.
1.9. X-Ray diffraction (XRD) of the mesophase

**Sample preparation:** The XRD measurements were performed on samples produced with the 3e powder compound. The samples were prepared by heating 3e on a glass plate (using a directional heater) to an isotropic liquid (208 °C), followed by an air-cooling process until the solidification occurred. As a result ~1 mm thick film was obtained.

**Powder X-ray diffraction (XRD):** X-Ray diffraction experiments were carried out with the XPERT-PRO diffractometer, X'Celerator detector and Cu Kα radiation (λ = 1.5418 Å). The scan was performed in continuous mode from 2° to 30° with scan step size of 0.0167° and scan step time of 5 seconds. The samples were heated to an isotropic liquid, and then inserted immediately in the diffractometer. The temperature of the plate was monitored with a thermometer to assure the sample in the mesophase during the short total scan time (78 seconds).

![Figure 15](image)

**Figure 15.** X-ray diffraction patterns of tristriazolotriazine 3e. Col₈ mesophase: the reflections (100), (110), and (200) are due to the long-range intercolumnar ordering. B-I, a broad halo at 4.5 Å indicating the mean distance between the molten alkyl chains within one column. Another broad diffuse band, B-II, at 3.5 Å, which is a characteristic distance usually found between flat aromatic cores.
Figure 15 shows the powder X-ray diffractogram of compound 3e in the temperature range identified to be liquid crystalline. It showed typical diffraction patterns that can be attributed to a columnar phase of a discotic compound, the diffractogram showed a strong fundamental reflection at spacing $d_{100} = 26.0 \text{ Å}$. Other discernible features of the diffractogram are two very weak, higher-order reflections in the approximate spacing ratio of $d_{100}/\sqrt{3}$ and $d_{100}/\sqrt{4}$, that allow the lattice to be indexed to 110 and 200 reflections of two-dimensional hexagonal lattice, ($d_{110} = 15.3$ and $d_{200} = 13.3 \text{ Å}$). In the wide-angle data is shown a halo diffuse peak B-I at 4.5 Å which arises from correlations between molten alkyl chains. Another broad diffuse band, B-II, at 3.5 Å, which is a characteristic distance usually found between cores. All the reflections observed support the phase assignment as hexagonal columnar (Colh).9,10,11,12

Table 2. Powder X-Ray diffraction data of tristriazolotriazine 3e.

<table>
<thead>
<tr>
<th>$d_{obs}$ (Å)</th>
<th>Hkl</th>
<th>$d_{calc}$ (Å)</th>
<th>Cell const. (Å)</th>
<th>$S$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.0</td>
<td>100</td>
<td>26.3</td>
<td>$a = 30.4^a$</td>
<td>800</td>
</tr>
<tr>
<td>15.3</td>
<td>110</td>
<td>15.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.3</td>
<td>200</td>
<td>13.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>Halo</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.4</td>
<td>001</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The $p6mm$ Col$_h$ cell parameter, $a$, as well as the columnar surface, $S$, were calculated from the position of the most intense reflections at the smallest Bragg angle according to the equations $a = (2/[3\sqrt{3}]) (d_{100} + \sqrt{3}d_{110} + 2d_{200})$ and $S = (\sqrt{3}/2)a^2$, respectively. $d_{obs}$ and $d_{calc}$ are the observed and calculated $d$-spacings, respectively.

The cell parameter $a$ is smaller than the van der Waals diameter of the molecule (43 Å) in the most extended conformation. This indicates either interdigitation or partial folding of the chains.

1.10. Fluorescence measurement in the Col\textsubscript{h} phase of 3e

The spin coated film of compound 3e was heated to an isotropic liquid (208 °C) and then cooled into its mesophase. The fluorescence spectra were collected upon cooling using a Varian Cary Eclipse equipment (conditions: 600 V, slit width 2.5). The temperatures of the glass slide upon cooling were estimated by its time of cooling (plot of temperature versus seconds), previously obtained by using a thermopar in the same conditions.

![Fluorescence spectra of mesogen 3e in its columnar and crystal phases. I and II are different samples. Exc. wavelengths were at 316 nm.](image)

**Figure 15.** Fluorescence spectra of mesogen 3e in its columnar and crystal phases. I and II are different samples. Exc. wavelengths were at 316 nm.