Electronic Supplementary Information (ESI)

Contents

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 (Φ_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$^+$/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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[1] R. Cristiano, E. Westphal, I. H. Bechtold, A. J. Bortoluzzi and H. Gallardo, *Tetrahedron*, 2007, **63**, 2851.

[2] V. N. Salimgareeva, R. M. Polevoi, V. A. Ponomareva, N. S. Sannikova, S. V. Kolesov and G. V. Leplyanin, *Russ. J. Appl. Chem.*, 2003, **76**, 1655.

[3] R.R. Gagne, C.A. Koval, G.C. Lisensky, *Inorg. Chem.*, 1980, **9**, 2854

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, 1478, 1318, 1253, 1175, 834. ^{1}H NMR (DMSO-d$_6$) 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, OCH$_3$). ^{13}C NMR (CDCl$_3$) 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 $C_{27}H_{21}N_9O_3$: 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.^{1}H NMR (CDCl$_3$) 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, -OCH$_2$-), 1,83 (m, 6H, -OCH$_2$C$\underline{H}_2$-), 1.49 – 1.37 (m, 18 H, -CH$_2$-), 0.93 (t, 9 H, -CH$_3$). ^{13}C NMR (CDCl$_3$) 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 $C_{42}H_{51}N_9O_3$: Calcd. C, 69.11; H, 7.04; N, 17.27 %, Found: C, 68.81; H, 7.63; N, 17.34.

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

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[4] H. Gallardo, R. Magnago and A. J. Bortoluzzi, *Liq. Cryst.*, 2001, **28**, 1343.

Yield: 43 %; m.p. 95.7-97.4 °C. IR (KBr pellet) ν_{max}cm^{-1}: 2923, 2852, 1592, 1480, 1255, 1175, 828. ^{1}H NMR ($CDCl_3$) δ ppm: 8.08 (d, *J* = 8.8 Hz, 6 H, Ar), 7.05 (d, *J* = 8.8 Hz, 6 H, Ar), 4.05 (t, 6H, -OCH_2-), 1.83 (m, 6H, -$OCH_2C\underline{H}_2$-), 1.48 – 1.30 (m, 30 H, -CH_2-), 0.90 (t, 9 H, -CH_3). ^{13}C NMR ($CDCl_3$) δ 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 $C_{48}H_{63}N_9O_3$: Calcd. C, 70.82; H, 7.80; N, 15.49 %; Found: C, 70.64; H, 8.51; N, 15.63.

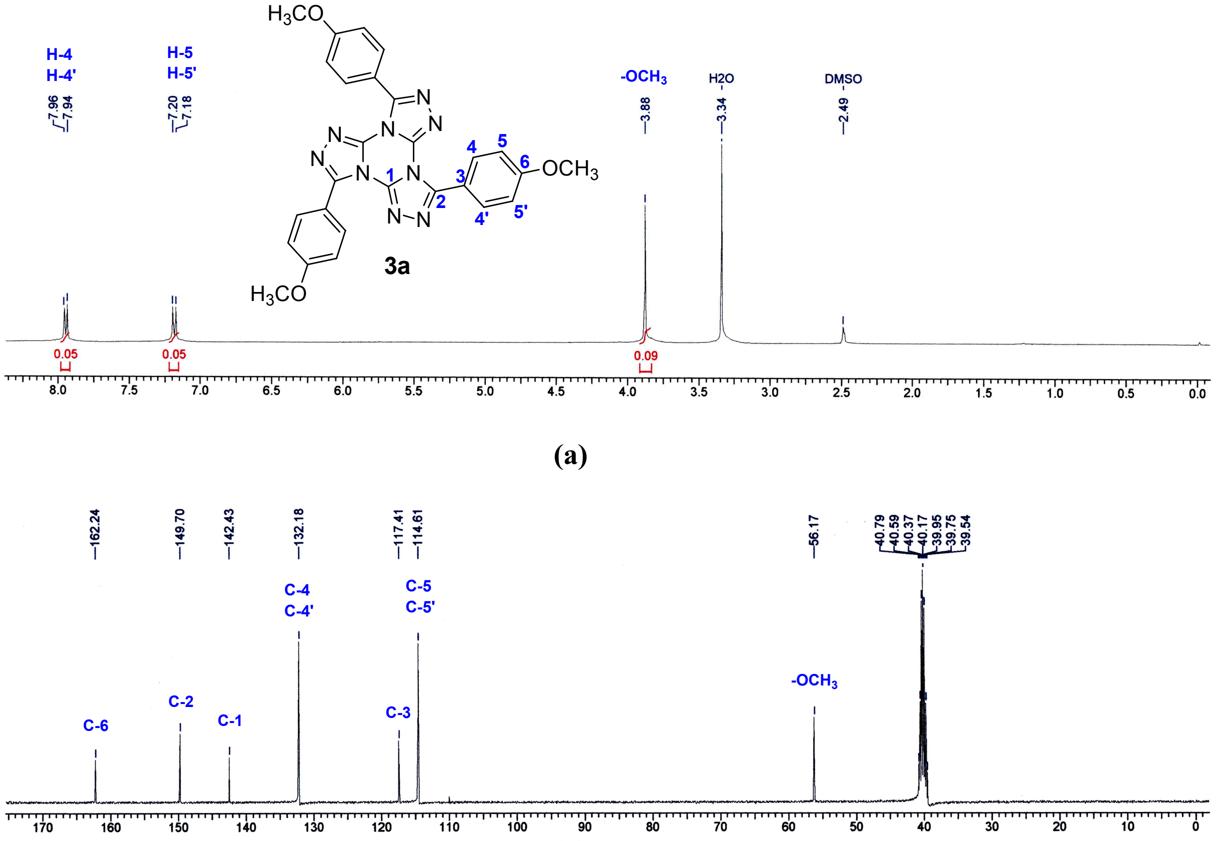
Tris-(4-dodecyloxyphen-1-yl)-[1,2,4]triazolo[1,3,5]triazine (3d)

Yield: 58 %; m.p. 85.5-87.0 °C; IR (KBr pellet) ν_{max}cm^{-1}: 3076, 2917, 2847, 1611, 1586, 1486, 1468, 1260, 1179, 828. ^{1}H NMR ($CDCl_3$) δ ppm: 8.09 (d, *J* = 8.8 Hz, 6 H, Ar), 7.06 (d, *J* = 8.8 Hz, 6 H, Ar), 4.05 (t, 6H, -OCH_2-), 1.83 (m, 6H, -$OCH_2C\underline{H}_2$-), 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 ($CDCl_3$) δ 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 $C_{60}H_{87}N_9O_3$: 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) ν_{max}cm^{-1}: 3094, 2920, 2854, 1595, 1465, 1263. ^{1}H NMR ($CDCl_3$) δ 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, -$OCH_2C\underline{H}_2$-), 1.50 (m, 12 H, -CH_2-), 1.26 (broad, 96 H, -CH_2-), 0.88 (m, 18 H, -CH_3). ^{13}C NMR ($CDCl_3$) δ 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 $C_{96}H_{159}N_9O_6$: Calcd. C, 75.10; H, 10.44; N, 8.21 %; Found: C, 74.85; H, 10.67; N, 8.26.

1.3. NMR spectra



(a)

(b)

Figure 1. (a) ^{1}H NMR and **(b)** ^{13}C NMR spectra of compound **3a** (DMSO-d6).

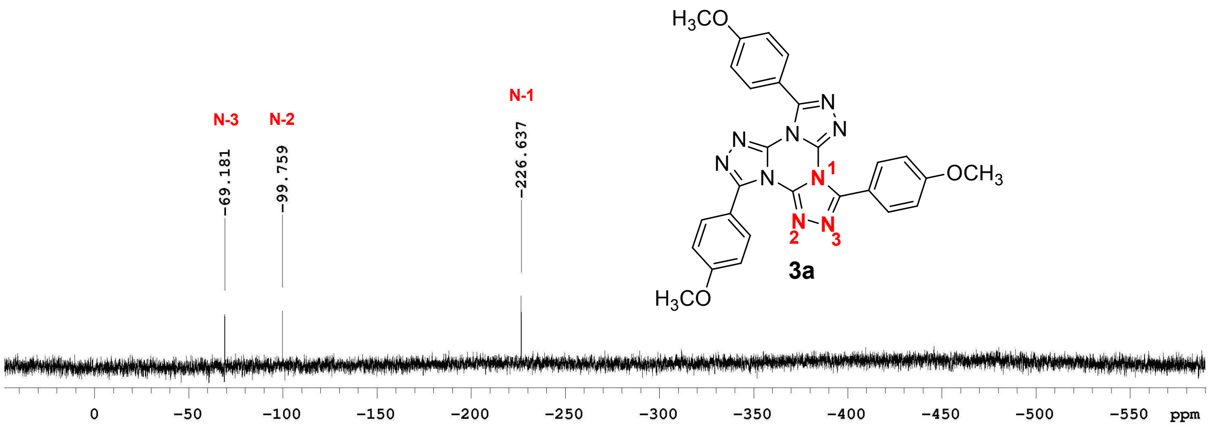


Figure 2. ^{15}N NMR spectrum of **3a** (DMSO-d6, external standard nitromethane).

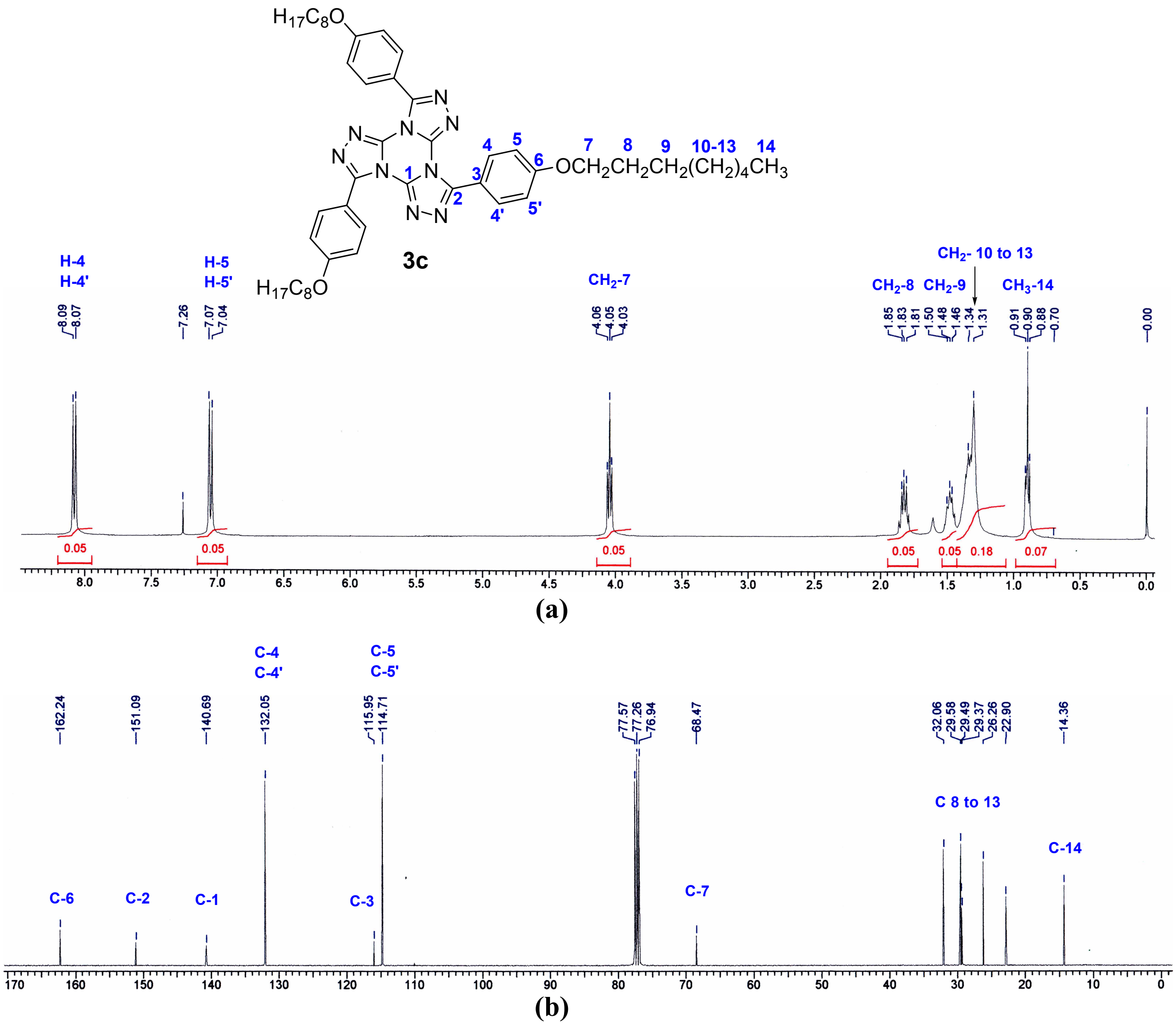


Figure 3. (a) ^{1}H NMR and **(b)** ^{13}C NMR spectra of compound **3c** ($CDCl_3$).

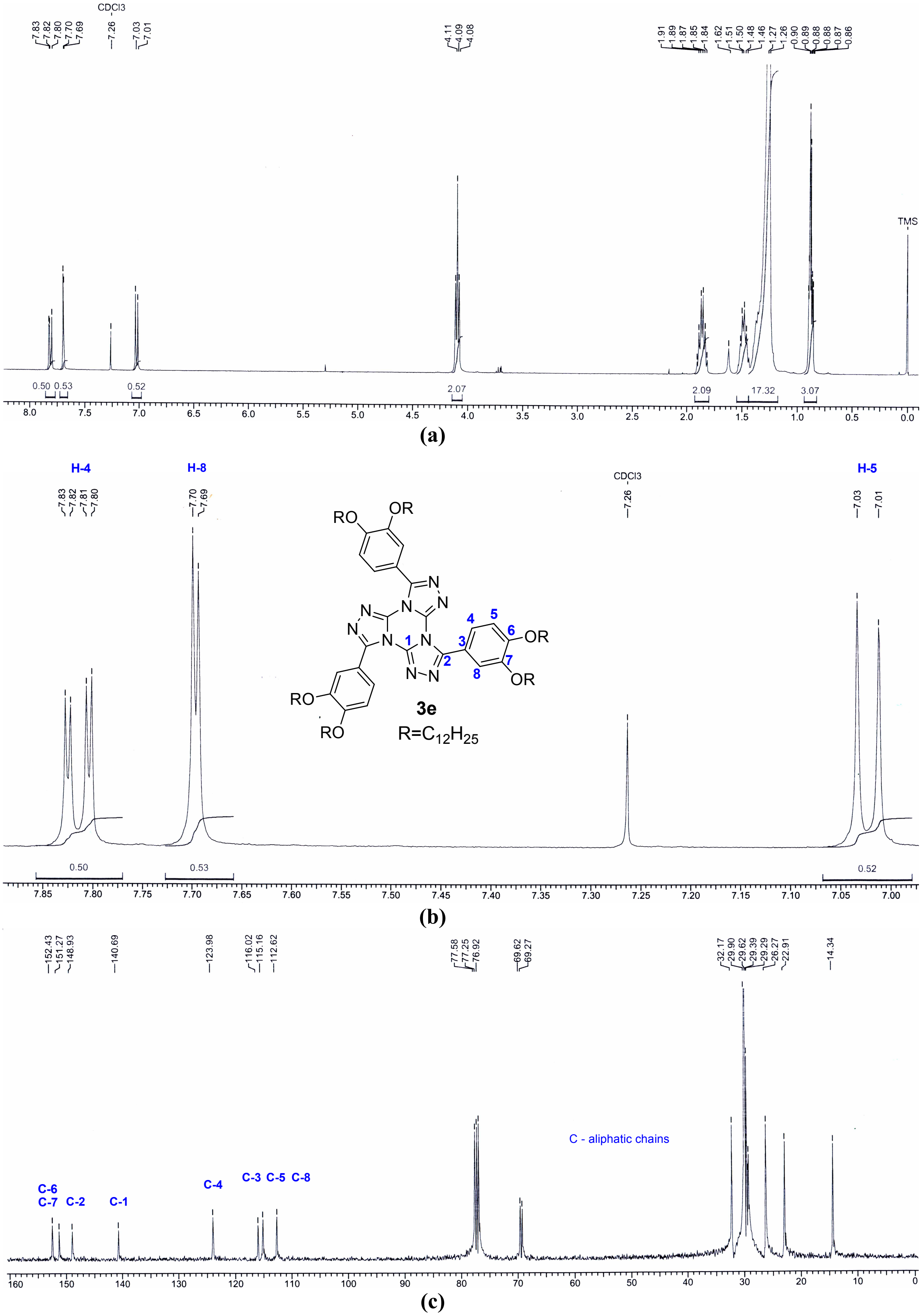
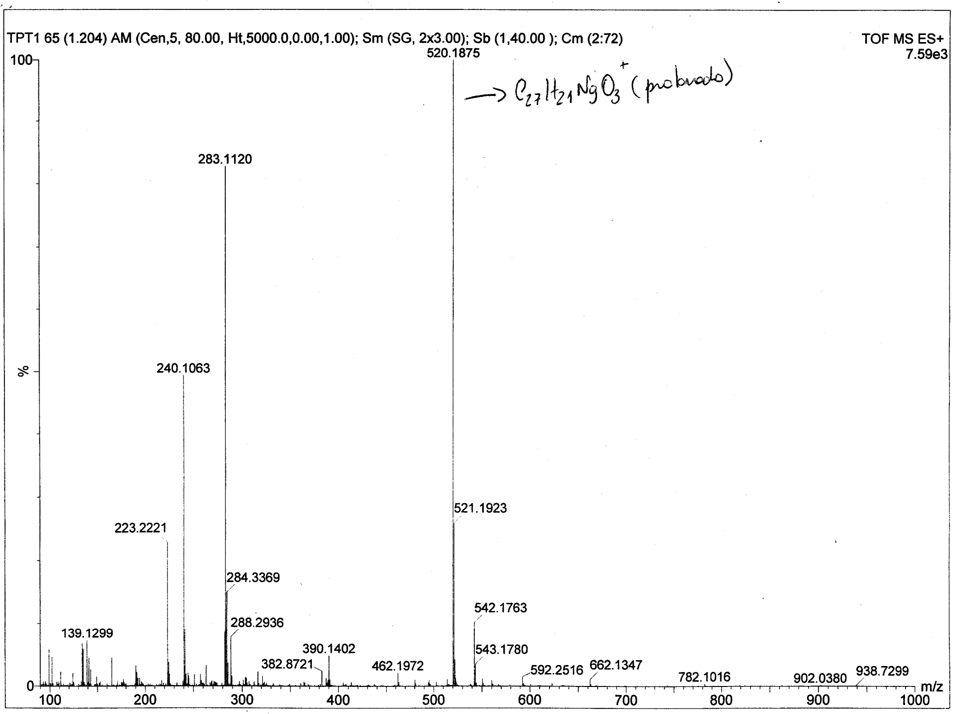


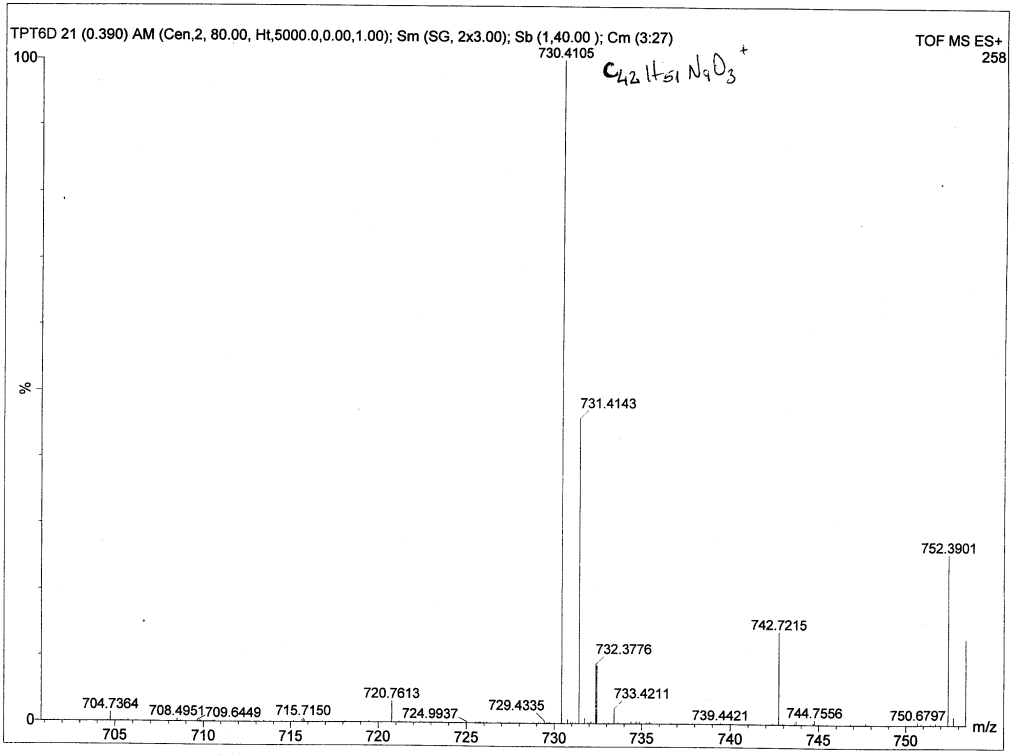
Figure 4. **(a)** ^{1}H NMR spectrum, **(b)** expanded aromatic region in the ^{1}H NMR spectrum and **(c)** ^{13}C NMR spectrum of compound **3e** ($CDCl_3$).

1.4. MS spectra



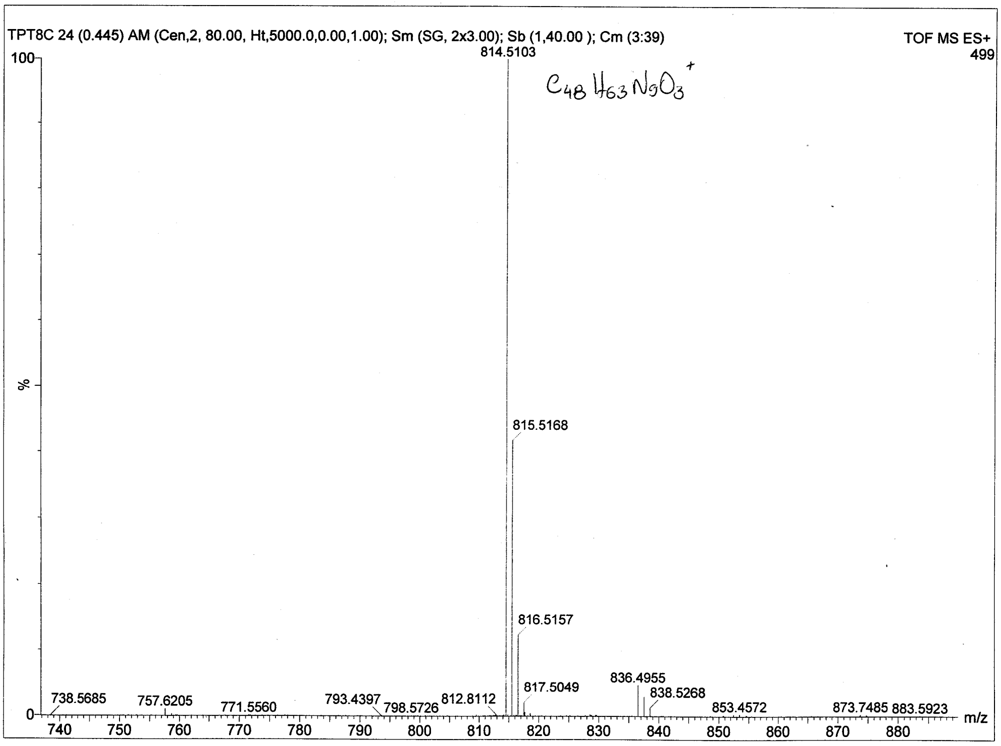
$\rightarrow C_{27}H_{21}N_9O_3^+$ (protonado)

(a)

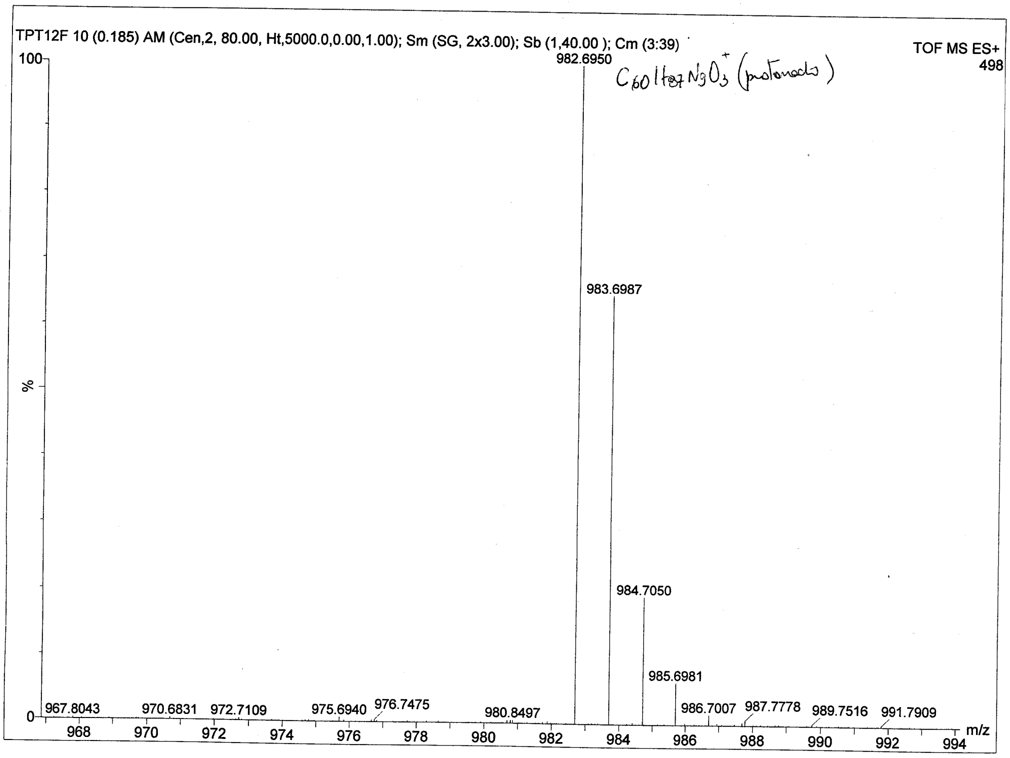


$C_{42}H_{51}N_9O_3^+$

(b)



(c)



(d)

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

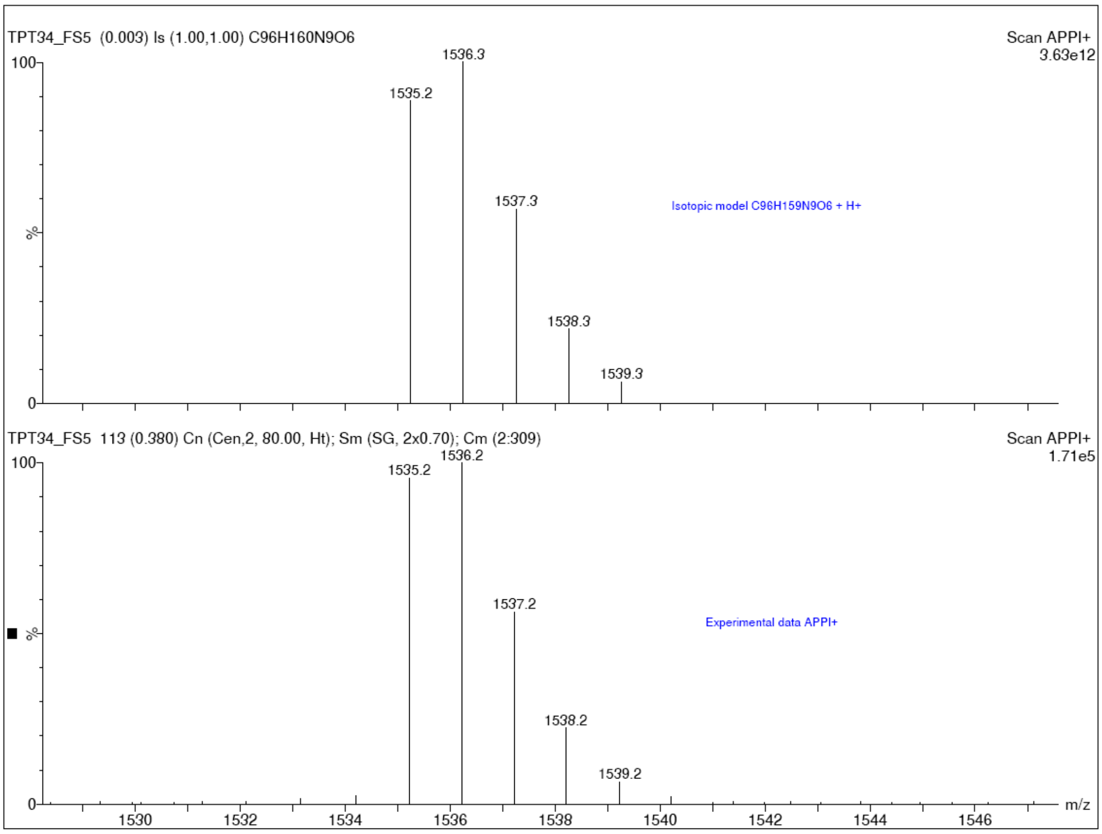


Figure 6. APPI/MS/MS spectra of **3e**.

1.5. DSC thermograms

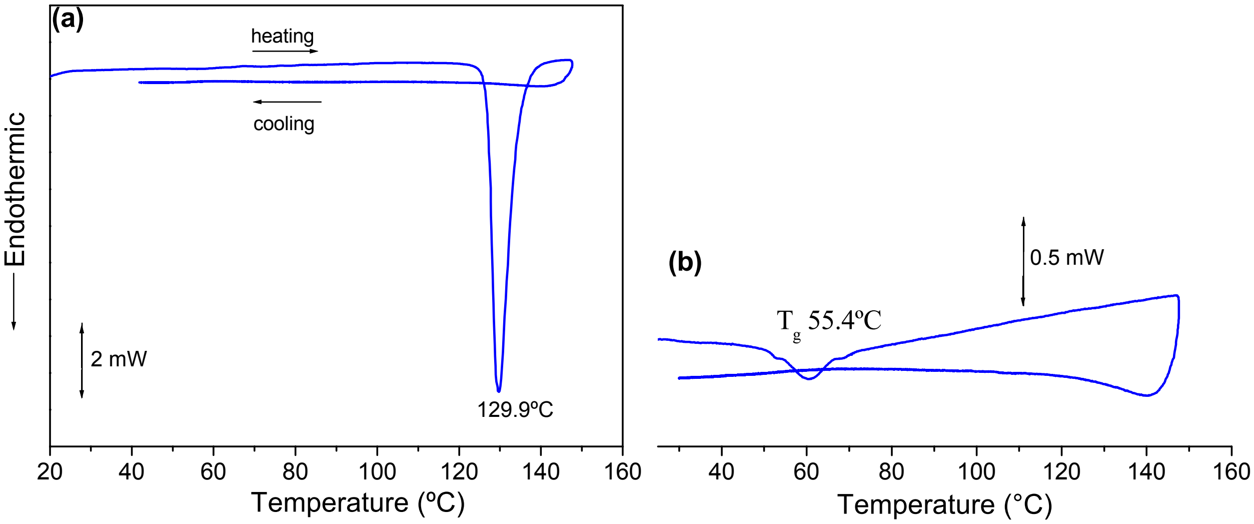


Figure 7. DSC curves of **3b**, 10 °C/min., first **(a)** and second **(b)** scans.

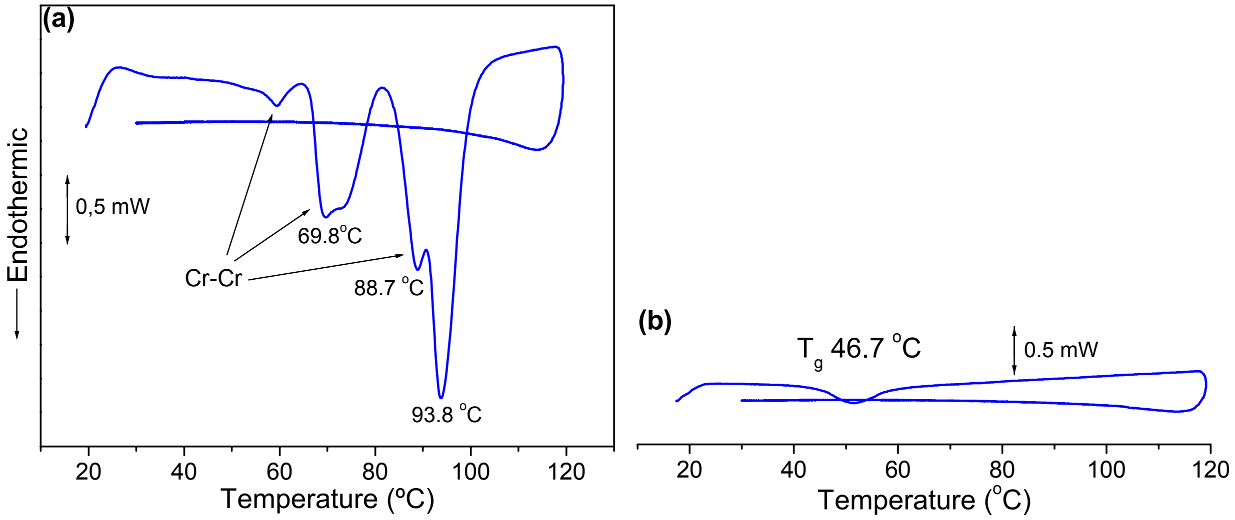


Figure 8. DSC curves of **3c**, 10 °C/min., first **(a)** and second **(b)** scans.

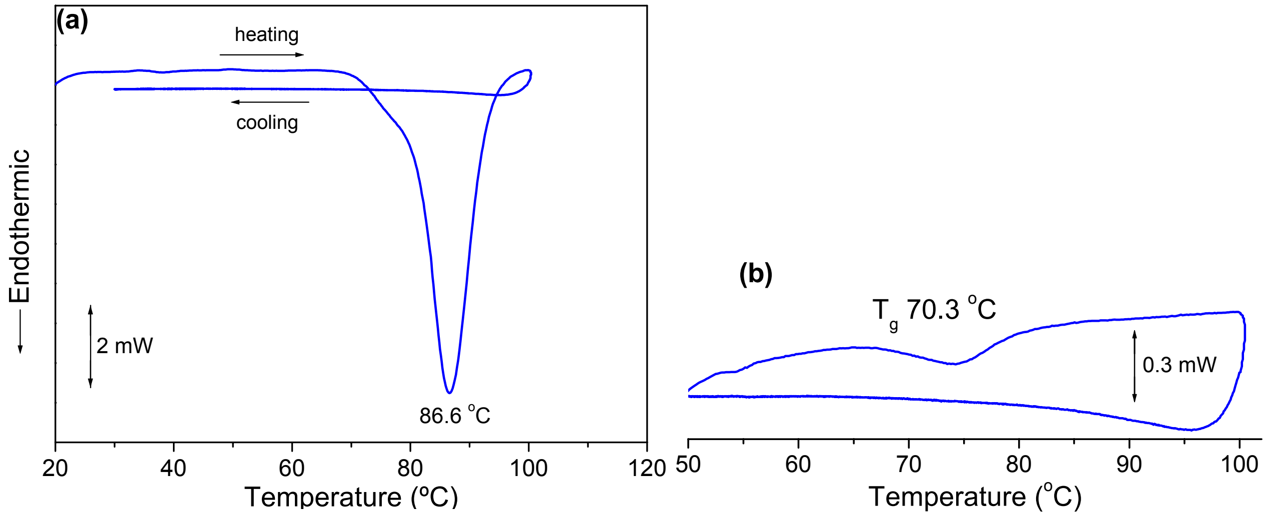


Figure 9. DSC curves of **3d**, 10 °C/min., first **(a)** and second **(b)** scans.

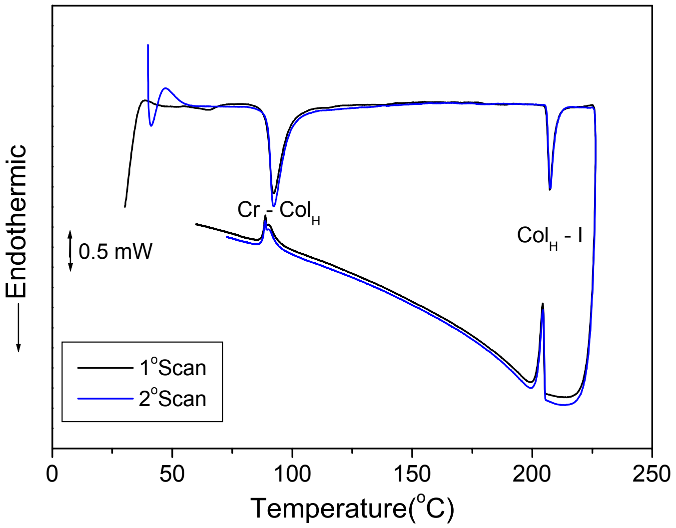
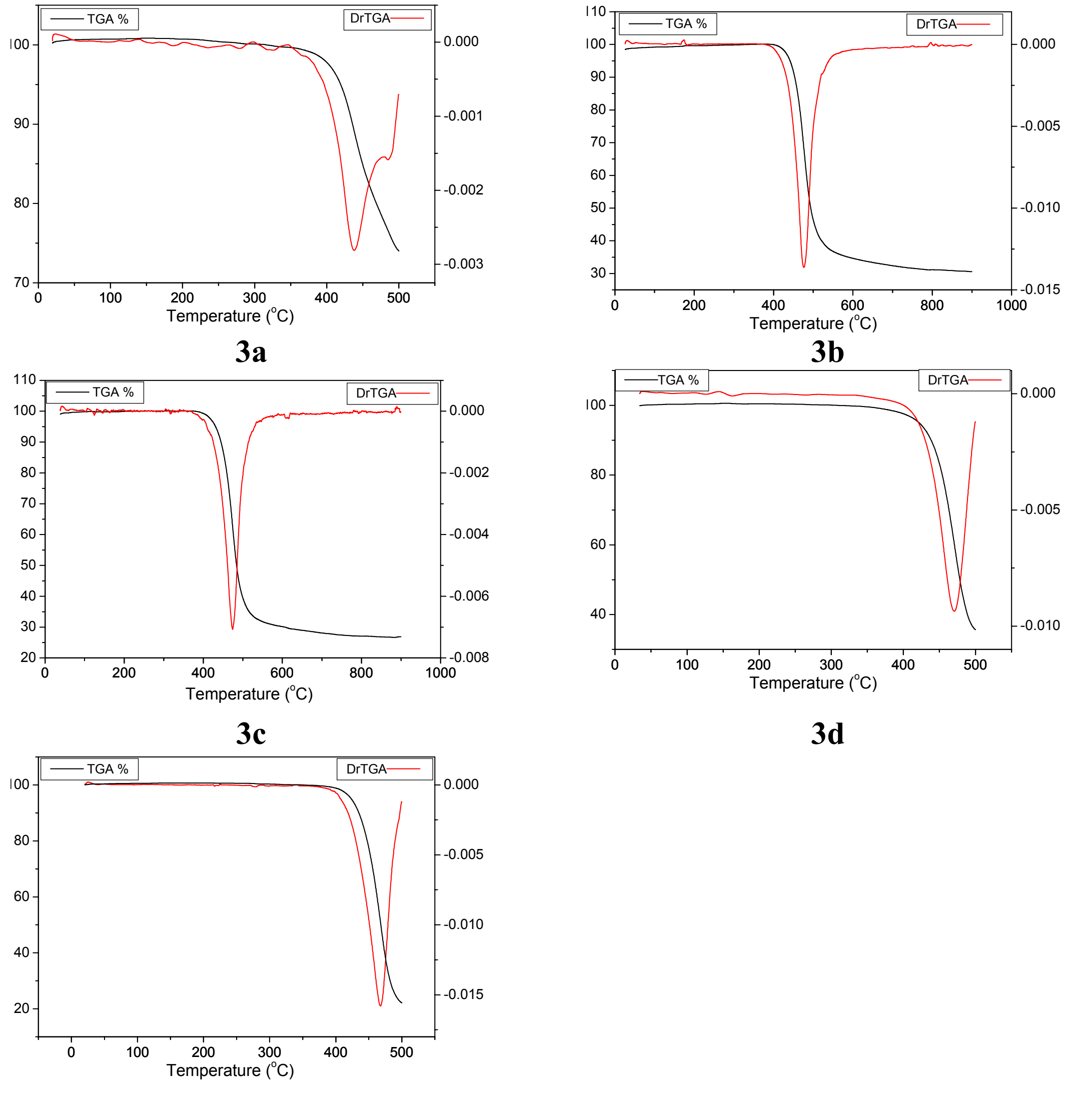


Figure 10. DSC curves of **3e**, 10 °C/min., first and second scans.

1.6. TGA curves



3a

3b

3c

3d

3e

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

1.7. Cyclic Voltammetry

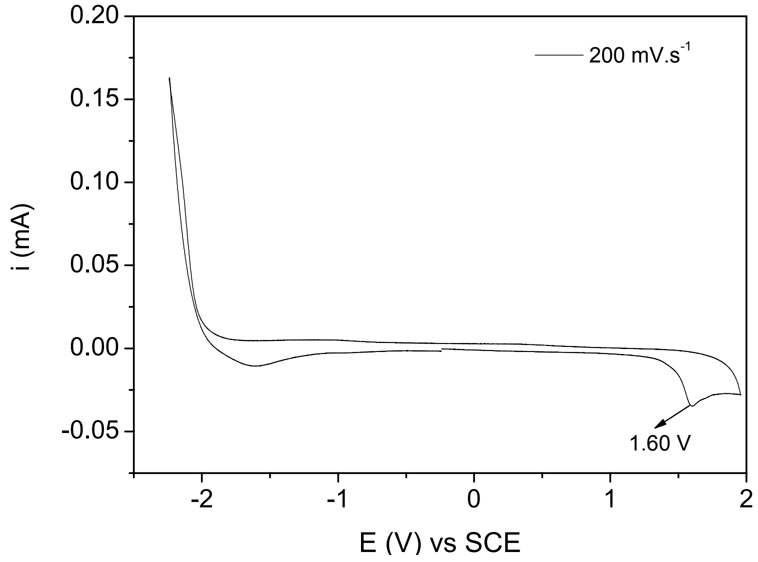


Figure 12. Representative cyclic voltammogram of **3a** measured in acetonitrile solution, containing 0.1 M TBAPF$_6$ at 25 ºC. Scan rate 200 mV/s. *HOMO =* E^{ox}_{onset} *(SCE) + 4.4*
HOMO = 1.36 + 4,4 = 5,8 eV

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 (λ = 0.71073 Å), at room temperature. Unit cell parameters were determined on the setting angles of 25 centered reflections in the range $5.77^o \leq \theta \leq 17.48^o$. The intensities of 4194 reflections were collected from $\omega/2\theta$ scans in the range $1.43^o \leq \theta \leq 25.07^o$.

Solution and Refinement of the structure:

The collected reflections were corrected for Lorentz and polarization effects.[5] No absorption correction was applied to the intensities. The structure was solved by direct methods with SIR-97[6] and refined by full-matrix least-squares procedure based on

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[5] A. L. Spek, HELENA; CAD-4 Data Reduction Program, 1996. Univ. of Utrecht, The Netherlands.

[6] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.* 1999, **32**, 115-119.

F^2 with SHELXL-97.[7] A drawing of molecular structure presented in the article was carried out with PLATON program.[8] 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**.

Empirical formula	$C_{27}H_{21}N_9O_3$	
Formula weight	519.53	
Temperature	293(2) K	
Wavelength	0.71069 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 6.418(3) Å	α = 80.73(2)°.
	b = 12.867(2) Å	β = 86.34(5)°.
	c = 14.500(9) Å	γ = 89.67(3)°.
Volume	1179.4(9) $Å^3$	
Z	2	
Density (calculated)	1.463 Mg/m^3	
Absorption coefficient	0.101 mm^{-1}	
F(000)	540	
Crystal size	0.50 x 0.30 x 0.13 mm^3	
Theta range for data collection	1.43 to 25.07°.	
Index ranges	$-7 \le h \le 7$, $-15 \le k \le 15$, $-17 \le l \le 0$	
Reflections collected	4375	
Independent reflections	4194 [R(int) = 0.0462]	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4194 / 0 / 353	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.0642, wR2 = 0.1577	

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[7] G. M. Sheldrick, SHELXL97; Program for the Refinement of Crystal Structures, 1997. Univ. of Göttingen, Germany.

[8] A. L. Spek, Acta Crystallogr., Sect A 1990, 46, C34.

R indices (all data)	R1 = 0.1102, wR2 = 0.1834
Extinction coefficient	0.022(5)
Largest diff. peak and hole	0.395 and -0.355 e.Å^{-3}

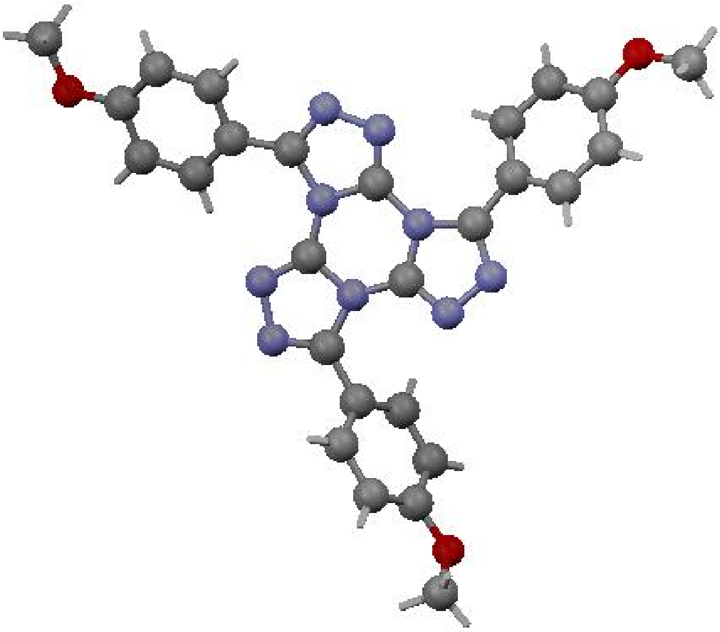

Figure 13. Molecular structure of compound 3a with hydrogen atoms.

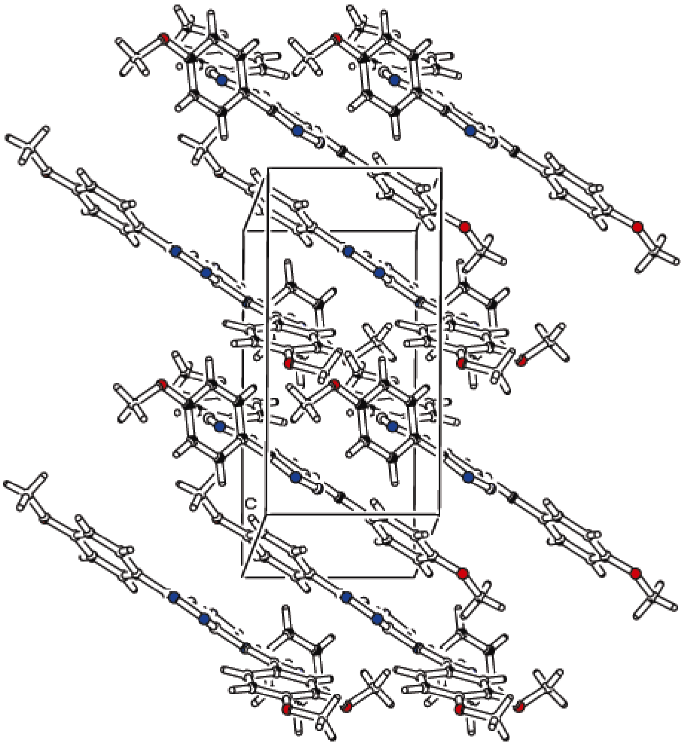

Figure 14. Molecular packing of compound **3a**.

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 ºC), 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^{o} to 30^{o} 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).

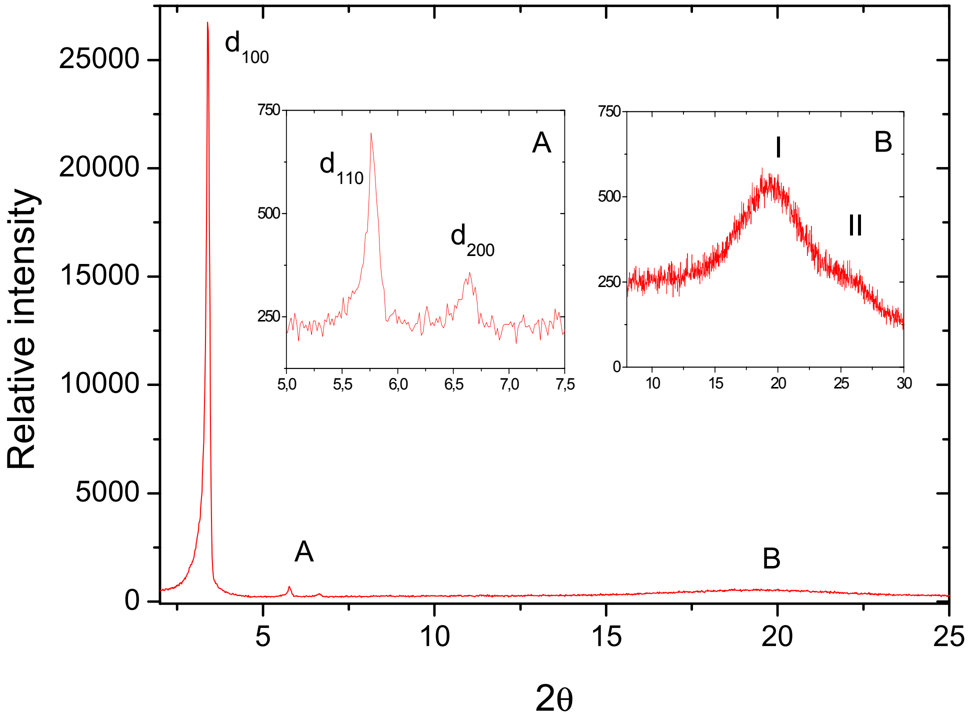

Figure 15. X-ray diffraction patterns of tristriazolotriazine **3e**. Col$_h$ mesophase: the reflections (100), (110), and (200) are due to the long-range intercolumnar ordering. B-I, a broad halo at 4,5 Å indicating the mean distance between the molten alkyl chains within one column. Another broad diffuse 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 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 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 (Col_h).[9,10,11,12]

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

d_{obs} (Å)	Hkl	d_{cal} (Å)	Cell const. (Å)	S (Å^2)
26.0	100	26.3	$a = 30.4^a$	800
15.3	110	15.2		
13.3	200	13.2		
4.5	Halo			
3.4	001			

^{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.

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[9] K. Binnemans, J. Sleven, S. De Feyter, F. C. De Schryver, B. Donnio, and D. Guillon. *Chem. Mater.* 2003**, 15***,* 3930.

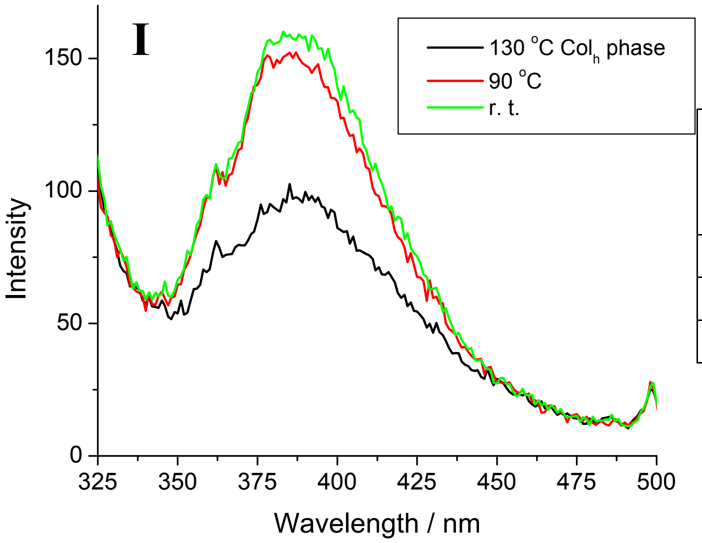
[10] M. J. Sienkowska, H. Monobe, P. Kaszynski and Y. Shimizu. *J. Mater. Chem*., 2007, **17**, 1392.

[11] K. Venkatesan, P. H. J. Kouwer, S. Yagi, P. Mu¨ller and T. M. Swager. *J. Mater. Chem.,* 2008, **18**, 400.

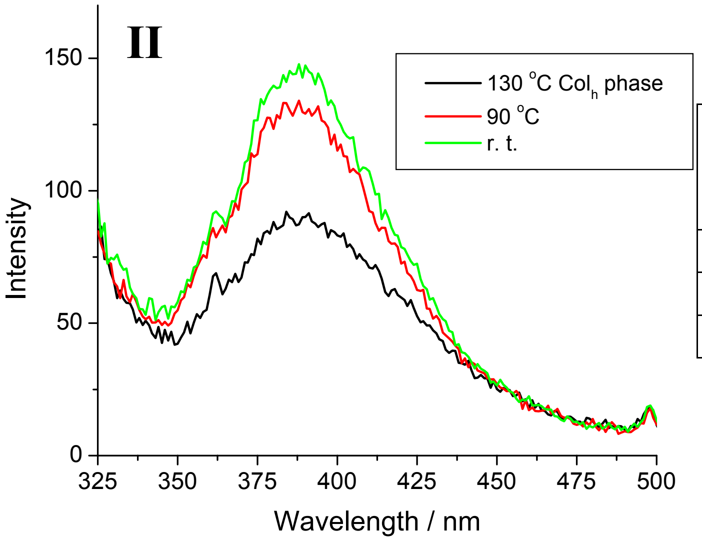
[12] S. K. Prasad, D. S. Shankar Rao, S. Chandrasekhar, S. Kumar, *Mol. Cryst. Liq. Cryst.*, 2003**, 396**, 121.

1.10. Fluorescence measurement in the Col$_h$ phase of 3e

The spin coated film of compound **3e** was heated to an isotropic liquid (208 ºC) 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.



Temperature / ºC	Intensity (at 388 nm)	Area	% Area
130	97.1	12321	77
90	150.1	15306	95
25	159.1	15971	100



Temperature / ºC	Intensity (at 388 nm)	Area	% Area
130	87.3	10486	76
90	134.0	12724	93
25	147.8	13729	100

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.