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Synthesis and specific features of mesomorphic behavior of new polysubstituted triphenylenes

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Previously unknown 2,3,6,7,10,11-hexakis(dodecyloxy)triphenylene and -(tetradecyloxy)triphenylene were synthesized. The structures of the synthesized compounds were proved by elemental analysis and spectral methods. Polymesomorphism was found for the first time and studied for substances of the hexaalkoxytriphenylene homologic series, as well as liotropic mesomorphism in a series of organic solvents.

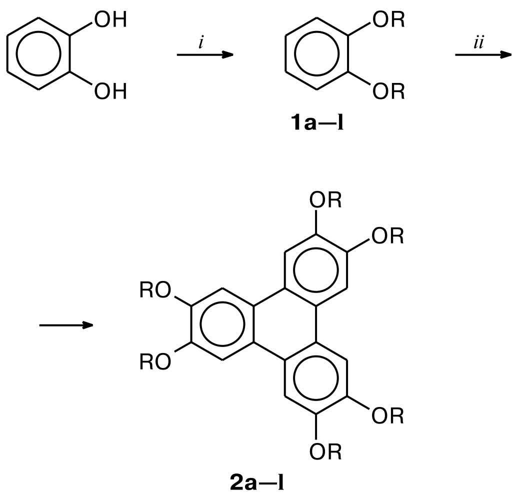
Key words: synthesis, 2,3,6,7,10,11-hexakis(dodecyloxy)triphenylene, 2,3,6,7,10,11-hexakis(tetradecyloxy)triphenylene, polymesomorphism, phase transitions, textures, liotropic mesomorphism.

Discotic compounds with columnar or nematic mesomorphism are being intensely studied recently. These compounds can be used in optoelectronics,[1—3] sensor devices,[4] and other areas.[5,6] The synthesis of the mesogenic core of discotics and purification of target products are rather labor-consuming. The main steps of the synthesis have been described previously.[7—10]

Hexaalkoxytriphenylenes can be synthesized by different methods,[11—17] including the oxidative condensation of benzene derivatives in concentrated sulfuric acid using chloranil (tetrachloro-*p*-benzoquinone)[11] or anhydrous iron chloride as oxidants.[12] However, these methods do not give triphenylene derivatives in appropriate yields.

In this work, we used a previously developed method[18] for the synthesis of hexamethoxytriphenylene (Scheme 1) to synthesize representatives of the hexaalkoxytriphenylene homologic series.

Scheme 1



Reagents and conditions: *i.* RBr, KOH, EtOH. *ii.* Chloranil, $C_{16}H_{33}NMe_3Br$, H_2SO_4, hexane.

R = *n*-C_mH_{2m+1}, *m* = 1 (**a**), 2 (**b**), 3 (**c**), 4 (**d**), 5 (**e**), 7 (**f**), 8 (**g**), 9 (**h**), 10 (**i**), 11 (**j**), 12 (**k**), 14 (**l**)

In the first step, pyrocatechol was alkylated by alkyl bromides in an alcohol-alkaline medium. Compounds **1a—l** trimerized in the second step. A phase-transfer catalyst, $C_{16}H_{33}NMe_3Br$, which can be recovered from washing waters after the separation of target products, was introduced into the reaction medium to enhance the yield of triphenylenes **2a—l**. The reaction occurred under heterogeneous conditions at room temperature in hexane as a solvent. When the alkyl substituent length increased, we had to prolong the duration of the synthesis to achieve appropriate yields of the target products, which were 20—30% in the case of compounds **2k,l** synthesized for the first time. Since it is known[11] that only triphenylene derivatives with a certain arrangement of substituents are formed under the reaction conditions, the elemental analysis data (Table 1) and coincidence of the phase transition temperatures with the published data[11] confirm unambiguously the structures of the compounds synthesized.

The electronic absorption spectra of compounds **1k** and **2k** contain two absorption bands corresponding to the π—π*-transitions of the aromatic moieties (Fig. 1). In the spectrum of compound **2k**, a shorter-wave band has λ_{max} = 279 nm (ε = 33100) and is characterized by a

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Table 1. Elemental analysis data for compounds **2a—l**

Compound	Found / Calculated (%) C	Found / Calculated (%) H	Molecular formula
2a	70.58	5.92	$C_{24}H_{24}O_6$
	69.73	5.95	
2b	73.15	7.37	$C_{30}H_{36}O_6$
	74.25	7.48	
2c	74.97	8.39	$C_{36}H_{48}O_6$
	76.09	8.51	
2d	76.33	9.15	$C_{42}H_{60}O_6$
	77.37	9.28	
2e	77.38	9.74	$C_{48}H_{72}O_6$
	79.47	8.79	
2f	78.95	10.61	$C_{60}H_{96}O_6$
	80.52	9.72	
2g	79.46	10.91	$C_{66}H_{108}O_6$
	80.01	11.04	
2h	79.94	11.18	$C_{72}H_{120}O_6$
	80.24	11.35	
2i	80.35	11.41	$C_{78}H_{132}O_6$
	81.52	10.69	
2j	80.71	11.61	$C_{84}H_{144}O_6$
	80.71	11.75	
2k	81.02	11.78	$C_{90}H_{156}O_6$
	81.02	11.96	
2l	81.54	12.07	$C_{102}H_{180}O_6$
	82.76	12.24	

Table 2. Electronic absorption spectra of compounds **2a,e—l**

Compound	λ_1/nm (shoulder) [logε_1]	λ_2/nm (max) [logε_2]	λ_3/nm (max) [logε_3]	λ_4/nm (max) [logε_4]	λ_5/nm (shoulder) [logε_5]
2a	303	279	270	260	—
	[5.51]	[5.71]	[5.60]	[5.43]	
2e	290	282	275	265	—
	[4.46]	[4.27]	[4.10]	[4.10]	
2f	307	278	270	260	250
	[4.09]	[4.74]	[4.56]	[4.36]	[3.79]
2g	308	280	271	262	252
	[4.35]	[4.90]	[4.82]	[4.60]	[4.30]
2h	307	277	273	265	257
	[4.20]	[4.88]	[4.75]	[4.58]	[4.30]
2i	290	280	272	263	—
	[4.45]	[4.92]	[4.76]	[4.58]	
2j	307	278	270	260	250
	[4.38]	[5.05]	[4.85]	[4.68]	[4.38]
2k	308	279	271	263	253
	[3.37]	[4.52]	[4.34]	[4.15]	[3.78]
2l	306	278	272	262	252
	[3.48]	[4.54]	[4.32]	[4.20]	[3.81]

Note. For known compounds (**2a—j**), the constants are presented in Refs 11 and 12.

vibrational structure. In the spectrum of compound **1k**, a longer-wave band lies at λ_{max} = 278 nm (ε = 34700). The increase in the intensity of the absorption bands and their bathochromic shift indicate the appearance of a new chromophore with a higher degree of conjugation, namely, a triphenylene moiety, because the electronic absorption spectra of earlier described[11] compound **2f** and compound **2k** are similar (see Fig. 1, curves *2* and *3*).

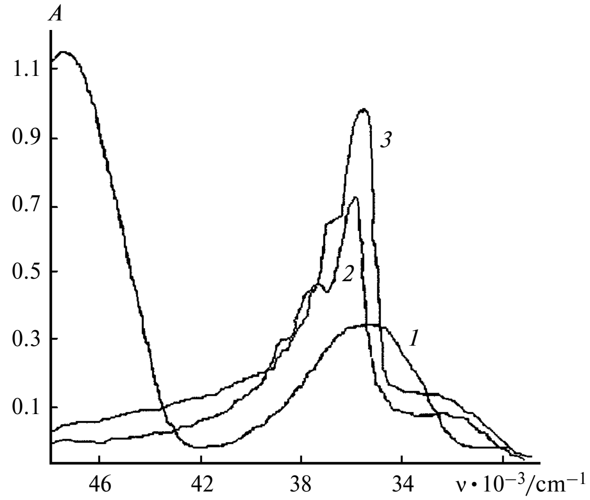

Fig. 1. Electronic absorption spectra of compounds **1k** (*1*), **2k** (*2*), and **2f** (*3*). $C = 3.10 \cdot 10^{-4}$ (*1*), $2.99 \cdot 10^{-5}$ (*2*), and $1.30 \cdot 10^{-5}$ mol L^{-1} (*3*).

The spectral parameters of triphenylene derivatives **2a,e—l** are presented in Table 2. The IR spectra of compounds **2c—j** synthesized in this work agree well with the published data.[19]

A comparison of the IR spectra of compounds **1k** and **2k** confirmed additionally the structure of triphenyl-

Table 3. Comparative characterization of the main absorption bands in the IR spectra of compounds **1k** and **2k**

Type of vibrations	ν/cm^{-1} **1k**	ν/cm^{-1} **2k**
ν(CH arom.)	3005 sh (v.w)	3080 (w)
$\nu^{as}(CH_3)$	2980	2956
$\nu^{as}(CH_2)$	2966	2920
$\nu^{s}(CH_3)$	2880	2880
$\nu^{s}(CH_2)$	2856	2852
ν(C—C arom.)	1590, 1516	1592, 1518, 1476
$\delta^{as}(CH_2)$, $\delta^{as}(CH_3)$	1464, 1450 sh	1465, 1452
$\delta^{s}(CH_2)$, $\delta^{s}(CH_3)$	1392, 1380 sh	1392, 1384
ν(C—O—C)	1260	1258
δ(C—H arom.)*	1220	1225
ν^{s}(Ar—O)	1124	1122
ν(C—O—C)	1050	1064
δ(C—H arom.)**	812	856
$\delta((CH_2)_n)$	736	740

* Plane vibrations.

** Out-of-plane vibrations.

ene **2k** (Table 3). The absorption bands in the regions of stretching (2960—2850 cm^{-1}) and bending (1465—1392 cm^{-1}) vibrations of the Me and CH$_2$ groups confirm that compound **2k** contains hydrocarbon substituents. A slight difference in positions of the absorption bands is observed only in the region of asymmetric stretching vibrations of the Me and CH$_2$ groups, which occurs due to a high shift of the electron density to the triphenylene ring in compound **2k**, compared to the benzene moiety of compound **1k**, and thus decreases the force constant of the C—H bond. The presence of a C—O—C group is confirmed by absorption bands at 1260—1050 cm^{-1} in the spectra of both compounds, indicating that ether bonds are retained in compound **2k**. Rocking vibrations of CH$_2$ groups in hydrocarbon substituents are observed in the IR spectra of both compounds at 736—740 cm^{-1}.

Substantial spectral distinctions are observed in an absorption region of stretching and bending out-of-plane vibrations of the C—H groups of the aromatic ring. Very weak absorption bands of stretching vibrations of the C—H groups are observed at 3005 cm^{-1} in the case of the benzene derivative (**1k**), while, after the benzene rings trimerized to the triphenylene cycle (compound **2k**), the band intensity increased and the bands shifted toward a high-frequency spectral region (see Table 3). The absorption band of bending vibrations of the C—H groups shifts in the same direction, which indicates a stronger conjugated system of the triphenylene ring compared to the benzene ring.

The mesomorphic behavior of the synthesized compounds was studied by thermal polarization microscopy. It was found that only compounds **2a—c** do not form a thermotropic liquid-crystalline phase (Table 4).

Samples of compounds **2d—l** were shown to transit on melting to a very viscous birefringent phase, and the sample viscosity decreases to form a mesophase with the typical finely domain texture with the further temperature increase. Such a texture is characteristic of columnar (Col) two-dimensionally ordered phases. The phase transition temperatures of compounds **2a—j** (see Table 4) agree satisfactorily with the published data.[11]

Based on both textural and X-ray diffraction studies,[20] the authors found that compounds **2d—j** form only one hexagonal columnar mesophase with an ordered arrangement of molecules in columns. We have shown (see Table 4) that the further elongation of the hydrocarbon substituent results in the appearance of two mesomorphic transitions of compounds **2k,l**, *i.e.*, polymesomorphism appears.

All types of textures characteristic of compounds **2d—l** are indicated in Table 4. Finger-shaped domains appeared upon very slow cooling near the phase transition from the isotropic liquid (I) to the mesophase. Nuclei had a pronounced shape of a regular hexagon, and upon further cooling each element of the flower texture formed lateral branches, and the nuclei resembled snowflakes with rounded ends.

Table 4. Temperatures of phase transitions (PT) and textures of mesophases for compounds **2a—l**, determined by polarization microscopy

Compound	PT	T*/°C	Texture
2a	Cr → I	310	—
2b	Cr → I	247	—
2c	Cr → I	176	—
2d	Cr → Col	86	Mosaic
	Col → I	145	
2e	Cr → Col	68	Mosaic
	Col → I	123	
2f	Cr → Col	67	Banded-mosaic
	Col → I	92	(finger-shaped**)
2g	Cr → Col	64	Flower
	Col → I	85	
2h	Cr → Col	56	Banded-mosaic
	Col → I	75	
2i	Cr → Col	57	Flower
	Col → I	67	
2j	Cr → Col	54	Flower
	Col → I	65	(finger-shaped**)
2k	Cr → Col$_{X_1}$	55	Broken-fan (55 °C),
	Col$_{X_1}$ → Col$_{X_2}$	58	basket (58 °C)
	Col$_{X_2}$ → I	63	
2l	Cr → Col$_{X_1}$	55	Filiform-cellular (55 °C),
	Col$_{X_1}$ → Col$_{X_2}$	58	filiform-
	Col$_{X_2}$ → I	64	reticulate (58 °C)

Note. Cr is crystal, Col is the columnar phase, and I is the isotropic liquid. The textures were identified in the cooling regime. For compounds **2a—j**, textural studies are presented in Ref. 11.

* The PT temperatures were determined in the heating regime.

** The texture is formed near the PT and characteristic of mesophases with columnar hexagonal supramolecular structures.

It has previously been shown[21—24] that the appearance of finger-shaped nuclei of regular shape near the phase transition from the isotropic liquid to the mesophase (the study was carried out in the nonpolarized light) allows one to assign the mesophase to the columnar type with hexagonal packing of columns.

In this work, we showed that samples of compounds **2k,l**, except for textures characteristic of columnar hexagonal mesophases, form textures, whose analogs are unknown. These textures obtained in the cooling regime are presented in Figs 2 and 3. In the case of compound **2k**, a basket texture is formed (see Fig. 2, *a*), whereas compound **2l** is characterized by a filiform-reticulate texture (see Fig. 3, *a*). On further cooling of the sample, the first texture is transformed into a broken-fan texture (see Fig. 2, *b*), while the second texture forms a filiform-cellular one (see Fig. 3, *b*). Under a shear deformation of a

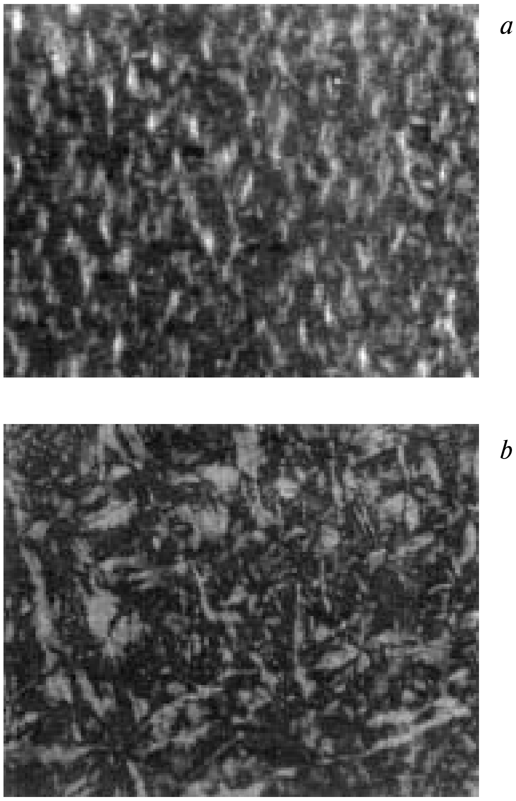

Fig. 2. Textures of a sample of compound **2k** obtained in the cooling regime (crossed polarizers, magnification ×160): basket of the columnar phase (Col_{X_2}) (*a*) and broken-fan of the columnar phase (Col_{X_1}) (*b*) at 58 and 55 °C, respectively.

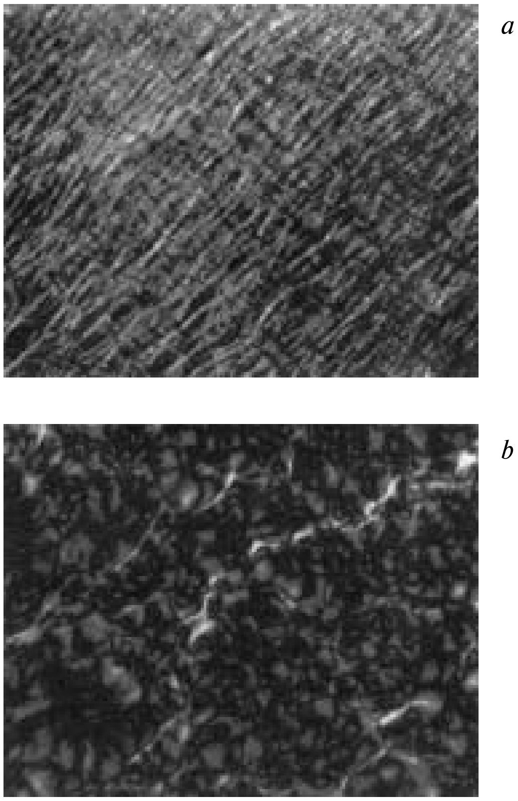

Fig. 3. Textures of a sample of compound **2l** obtained in the cooling regime (crossed polarizers, magnification ×200): filiform-reticulate of the columnar phase (Col_{X_2}) (*a*) and filiform-cellular of the columnar phase (Col_{X_1}) (*b*) at 58 and 55 °C, respectively.

sample of compound **2k**, the basket texture is modified to a texture of the parquet type.

At this stage of studies, the mesophases mentioned above can be identified as columnar with an unknown packing type of both columns themselves (Col_X) and molecules in the columns (Col_{X_y}, $y = 1, 2$). It should be emphasized that the results of preliminary prediction of columnar mesomorphism initiated our intention to synthesize compounds **2k,l** with the number of C atoms in the alkyl substituent >11.

An X-ray diffraction study of the oriented samples is needed to establish more exactly the structural organization of these mesophases. At this stage, we studied a miscibility of triphenylene **2l** with compounds that possess columnar mesomorphism according to published data. In addition, lamination was found on mixing compounds **2k** and **2l**.

Thus, the thermal microscopic observations performed in the framework of this study made it possible to establish the phase transition temperatures for compounds **2k,l** in both the heating (see Table 4) and cooling regimes: $\mathrm{I}\rightarrow\mathrm{Col}_{X_2}$ (58 °C), $\mathrm{Col}_{X_2}\rightarrow\mathrm{Col}_{X_1}$ (56 °C), $\mathrm{Col}_{X_1}\rightarrow\mathrm{Cr}$ (50 °C) for compound **2k** and $\mathrm{I}\rightarrow\mathrm{Col}_{X_2}$ (59 °C), $\mathrm{Col}_{X_2}\rightarrow\mathrm{Col}_{X_1}$ (55 °C), $\mathrm{Col}_{X_1}\rightarrow\mathrm{Cr}$ (49 °C) for compound **2l** (Cr is the crystalline phase).

It should be mentioned that the type of supramolecular packings of thermotropic mesogens can be concluded from the ability to form liotropic mesophases.[20,25] In this work, liotropic mesomorphism of compounds **2a—c,f,h—j,l** has been studied for the first time in systems with normal and cyclic alkanes, cyclohexene, benzene, and chloroform. For this purpose, we used the method of contact preparations. Liotropic mesomorphism was found only for compounds **2f,h—j,l** (thermotropic mesomorphism). It was found that the liotropic systems are characterized by the appearance of a broken-fan texture and confocal domains in addition to textures characteristic of the thermotropic liquid-crystalline state.

All samples demonstrate the formation of the same type of a liomesophase with different variants of the texture characteristic of hexagonal columnar phases, depending on the concentration gradient. Compounds **2f,h—j,l** possess a liomesophase, as a rule, with a nongeometric texture already at room temperature. At a high solvent concentration, *i.e.*, nearer to the zone of isotropic liquid,

Table 5. Clarification temperatures (T_c) of compounds **2f,h—j,l** in contact preparations with different solvents

Solvent	T_c/°C				
	2f	**2h**	**2i**	**2j**	**2l**
Hexane	50	49	55	46	58
Decane	50	40	54	45	59
Cyclohexane	72	49	52	51	45
Cyclohexene	70	46	40	40	57
Benzene	50	49	49	55	48
Chloroform	50	48	58	20	46

Note. For all samples, only T_c are presented, because crystallization temperatures lie in a low-temperature region.

the textures look like enlarged broken fans. In addition, the experimental data indicate that the solvent nature exerts no substantial effect on the texture type. A thermotropic polymorphic samples of compound **2l** do not change the number of phases when a solvent is added, and only the clarification temperature decreases considerably and the interval of mesophase existence extends (Table 5).

The data presented in Tables 4 and 5 indicate that the solvent nature has an aligning effect on the clarification temperatures, which range, as a rule, from 40 to 59 °C. Only when cyclohexane or cyclohexene is added to compound **2f**, the clarification temperature decreases insignificantly compared to that of the thermotropic samples.

It should be noted that the addition of solvents to samples of compounds **2f,h—j,l** extends substantially the intervals of existence of columnar mesophases without significant rearrangements of their supramolecular structures.

Thus, new triphenylene derivatives, *viz.*, compounds **2k,l**, were synthesized in this work, and their polymesomorphism was shown. It was found that, for binary systems of organic solvents with samples of compounds **2f,h—j,l**, the temperatures of liomesophase formation shift considerably to the low-temperature region, and the destruction of the supramolecular structure of the initial columnar thermotropic mesophase is observed in some cases.

Experimental

Electronic absorption spectra were recorded on a Specord UV—VIS spectrophotometer (200—750 nm) in petroleum ether (fraction with b.p. ~58 °C). IR spectra were recorded on a Specord M-80 spectrometer at 400—4000 cm^{-1} in a thin film or in KBr pellets. ^1H NMR spectra were obtained in $CDCl_3$ on a Bruker AC-200 spectrometer (200.13 MHz) using Me_4Si as an internal standard.

Thermal polarization microscopy studies were carried out on a BIOLAR polarization interference microscope with a heating stage of original design and a Zorkii photoattachment and on a Leitz Laborlux 12 Pol microscope with a Mettler FP 82 heating stage. The heating rate was 2 °C min^{-1}. Photographs of textures were obtained by a microphotoattachment (24×36 mm^2) of a Wild MPS 51 camera.

Phase transition temperatures were determined in heating and cooling regimes, using different rates of temperature change in both regimes. Samples were prepared as a thin film between the object-plate and cover glass.

For the structural identification of mesophases of some compounds, we additionally used the shear deformation method,[26] which makes it possible to reveal specific features of textures of mesogenic samples by miscibility.[11] Liotropic mesomorphism was studied using contact preparations.[27] Solvents used for studies of liotropic mesomorphism and chromatography were additionally dried and distilled. Alkyl bromides were purified chromatographically on Al_2O_3 (hexane or benzene as eluants). 1,2-Bis(dodecyloxy)benzene (**1k**) is commercially available. Pyrocatechol (reagent grade) was recrystallized from an EtOH—H_2O mixture. Synthesized compounds were purified by column chromatography on silica gel L (100—250 or 40—100 μm) or Al_2O_3 (activity grade II according to Brockmann) using gradient elution with mixtures of organic solvents ($CHCl_3$, hexane, benzene, CCl_4); for more detail, see purification of compound **2k**. Ethers **2a—k** were additionally recrystallized (EtOH—benzene) to constant temperatures of phase transitions.

2,3,6,7,10,11-Hexakis(dodecyloxy)triphenylene (2k). Freshly distilled hexane (215.0 mL) and 1,2-bis(dedecyloxy)benzene (**1k**) (8.0 g, 0.1 mol) were mixed in a conic 500-cm^3 flask with a magnetic stirrer and a reflux condenser. Sulfuric acid (44.6 mL, 81%, d = 1.83 g cm^{-3}) and then $C_{16}H_{33}NMe_3Br$ (0.61 g, 0.69 mol) were added. Chloranil (44.6 g, 50.2 mol) was added to the mixture with stirring. After gaseous HBr stopped evolving (in ~1 h), the flask was equipped with a reflux condenser, and the reaction mixture was magnetically stirred at ~20 °C. The color of the reaction mixture changed from yellow-pink to green and then to dark blue. After 10—12 days, the reaction mixture was neutralized on cooling with an aqueous solution of NH_4OH, and the organic layer was separated, washed with water to the neutral reaction, and dried with calcined Na_2SO_4. After excess solvent was distilled off, the product was isolated by column chromatography on silica gel (using hexane and then hexane—benzene—CCl_4 (1 : 1 : 1) and hexane—benzene (1 : 1) mixtures are eluents). The first hexane fraction containing compound **1k** was rejected. Other fractions were combined, and the solvent was distilled off almost to dryness. An air-dry residue was dissolved in benzene with weak heating, and 95% EtOH was added until a white flaky precipitate began to form. After some time (~5 min), the precipitate that formed was filtered off and washed with a small amount of a 95% EtOH—benzene (1 : 1) mixture and then with EtOH. After drying *in vacuo*, compound **2k** was obtained in 25—30% yield (3.5—4.2 g). Recrystallization was repeated until constant phase transition temperatures were achieved. ^1H NMR, δ: 0.86 (t, 18 H, Me, J = 6.1 Hz); 1.25—1.93 (m, 120 H, CH_2); 4.21 (t, 12 H, CH_2O, J = 6.1 Hz); 7.82 (s, 6 H, Ar).

Compounds **2a—j,l** were synthesized using a similar procedure.

2,3,6,7,10,11-Hexakis(tetradecyloxy)triphenylene (2l). ^1H NMR, δ: 0.87 (t, 18 H, Me, J = 6.1 Hz); 1.25—1.56 (m, 144 H, CH_2); 4.21 (t, 12 H, CH_2O, J = 6.1 Hz); 7.82 (s, 6 H, Ar).

The elemental analysis data and physicochemical characteristics of the compounds synthesized are presented in Tables 1—4.

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