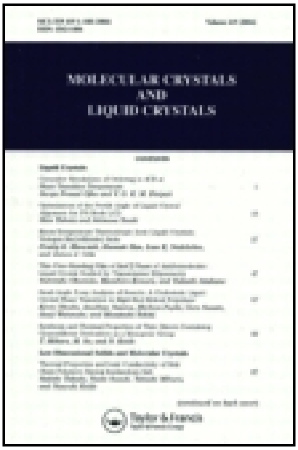

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Synthesis of Liquid-Crystalline, Highly Luminescent π-Conjugated 1,3,5-Triazine Derivatives by Palladium-Catalyzed Cross-Coupling Reaction

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Synthesis of Liquid-Crystalline, Highly Luminescent π-Conjugated 1,3,5-Triazine Derivatives by Palladium-Catalyzed Cross-Coupling Reaction

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A new class of 2,4,6-triphenyl-1,3,5-triazine derivatives having long alkoxyl side chains have been synthesized by a Pd(0)/Cu(I)-catalyzed carbon-carbon coupling reaction. These compounds behave as liquid-crystalline materials and show quantum yields higher than 70% in photoluminescence.

Keywords: 2,4,6-triphenyl-1,3,5-triazine derivatives, coupling reaction, liquid crystals, luminescent

INTRODUCTION

The preparation and characterization of compounds containing the 1,3,5-triazine unit is currently of considerable interest, and many substituted triazines have been reported [1,2]. Among these materials, disklike liquid crystals are getting much attention [3]. The liquid-crystalline materials are of great interest, especially with respect to their unique optical properties.

We herein report the synthesis of a new class of 1,3,5-triazine derivatives with terminal alkynes having long alkoxy groups.

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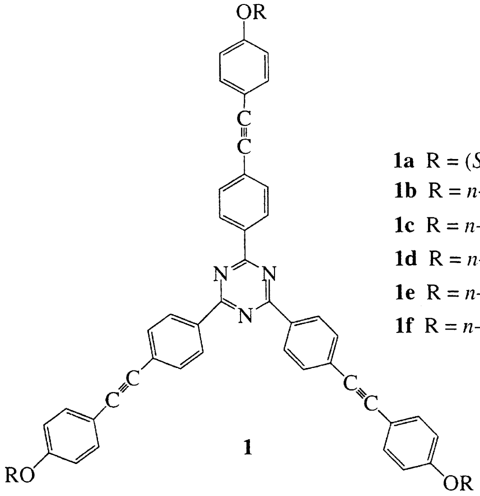


1

1a R = (S)-$C_2H_5C^*H(CH_3)CH_2$
1b R = n-C_6H_{13}
1c R = n-$C_{10}H_{21}$
1d R = n-$C_{12}H_{25}$
1e R = n-$C_{14}H_{29}$
1f R = n-$C_{16}H_{33}$

SCHEME 1 π-Conjugated 1,3,5-triazine derivatives **1** having long alkoxy groups.

The conjugated diphenylacetylene backbone [4] is a rigid rod that can act as a mesogenic unit, and the synthesized 1,3,5-triazine derivatives with the long alkoxy groups behave as liquid-crystalline materials. Long alkoxy and alkyl groups play an important role in the generation of large nonlinear optical coefficients [5] and are essential for molecular assembly [6]. It is known that various optical properties (such as electroluminescence and nonlinear optical property) associated with the delocalized π-electron system are enhanced due to the orientation of molecules induced by liquid crystal ordering [7]. Triazine is known to serve as a core of liquid crystals [3]. However, to our knowledge, no report has been published for synthesis of the π-conjugated 2,4,6-triphenyl-1,3,5-triazine derivatives that have highly photoluminescent and liquid-crystalline properties. The new 1,3,5-triazine derivatives **1** (Scheme 1) reported in this paper exhibit liquid-crystalline properties and give green-blue photoluminescence with high quantum yields (74–90%).

EXPERIMENTAL

General

^{1}H NMR spectra were obtained with a JEOL JNM-LA 300 (300 MHz) spectrometer. Chemical shifts are given in ppm. Elemental analyses were carried out with a Yanagimoto CHN Autocoder, Type MT-2. IR spectra were recorded on a JASCO IR-810 spectrometer with KBr pellets. The transition temperatures were determined by a polarizing microscope (OLYMPUS, BHSP) equipped with a hot stage and a controller (JAPAN HYTECH, TH-600RH) and also on the basis of the thermograms recorded on a differential scanning calorimeter (RIGAKU, THERMOFLEX, DSC 8230).

General Procedure for Synthesis of the π-Conjugated 1,3,5-Triazine Derivatives 1

All new compounds showed satisfactory spectroscopic and analytical data. Typical procedure for product **1d**: A mixture of 2,4,6-tris(*p*-bromophenyl)triazine **3** (55 mg, 0.1 mmol), $Pd(PPh_3)_4$ (12 mg, 0.01 mmol), CuI (2 mg, 0.01 mmol), (4-dodecyloxy)phenyl-acetylene (**2d**) (95 mg, 0.33 mmol), freshly distilled triethylamine (1 mL), and anhydrous THF (10 mL) was degassed and stirred at 50°C for 15 h under argon. After cooling to room temperature, the mixture was evaporated, washed with saturated aqueous NH_4Cl, and extracted with chloroform. The combined extracts were washed with water and brine, and then dried over anhydrous Na_2SO_4 and evaporated. The product was purified by silica gel column chromatography, using chloroform as the eluent, and recrystallization (MeOH/ethyl acetate = 1/1) to afford a pale yellow powder of pure **1d** in 86% yield.

2,4,6-Tris[[((S)-4-(3-methyl)butyloxyphenyl)ethynyl]]benzene-1,3,5-triazine (1a)

^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 0.94 - 1.05$ (m, 18 H), 1.21–1.66 (m, 6 H), 1.83–1.94 (m, 3 H), 3.74–3.88 (m, 6 H), 6.88 (d, 6 H, *J* 8.8 Hz), 7.52 (d, 6 H, *J* 8.8 Hz), 7.69 (d, 6 H, *J* 8.6 Hz), 8.73 (d, 6 H, *J* 8.6 Hz). IR (KBr) 2210 cm^{-1}. Anal. Calcd for $C_{60}H_{57}N_3O_3$: C, 83.06; H, 6.57; N, 4.84. Found: C, 82.81; H, 6.62; N, 4.82.

2,4,6-Tris[(4-hexyloxyphenyl)ethynyl]benzene-1,3,5-triazine (1b)

^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 0.92$ (t, 9 H, *J* 6.4 Hz), 1.26 (br s, 18 H), 1.80 (quint, 6 H, *J* 6.4 Hz), 3.99 (t, 6 H, *J* 6.6 Hz), 6.89 (d, 6 H, *J* 8.8 Hz), 7.51 (d, 6 H, *J* 8.8 Hz), 7.69 (d, 6 H, *J* 8.6 Hz), 8.73 (d, 6 H *J* 8.6 Hz). IR (KBr) 2210 cm^{-1}. Anal. Calcd for $C_{63}H_{63}N_3O_3$: C, 83.18; H, 6.93; N, 4.62. Found: C, 82.96; H, 6.78; N, 4.44.

2,4,6-Tris[(4-decyloxyphenyl)ethynyl]benzene-1,3,5-triazine (1c)

^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 0.89$ (t, 9 H, *J* 6.4 Hz), 1.29 (br s, 42 H), 1.80 (quint, 6 H, *J* 6.4 Hz), 3.99 (t, 6 H, *J* 6.6 Hz), 6.89 (d, 6 H, *J* 8.8 Hz), 7.52 (d, 6 H, *J* 8.8 Hz), 7.70 (d, 6 H, *J* 8.6 Hz), 8.74 (d, 6 H *J* 8.6 Hz). IR (KBr) 2210 cm^{-1}. Anal. Calcd for $C_{75}H_{87}N_3O_3$: C, 83.58; H, 8.07; N, 3.90. Found: C, 83.39; H, 7.97; N, 3.79.

2,4,6-Tris[(4-dodecyloxyphenyl)ethynyl]benzene-1,3,5-triazine (1d)

^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 0.89$ (t, 9 H, *J* 6.4 Hz), 1.27 (br s, 54 H), 1.80 (quint, 6 H, *J* 6.4 Hz), 3.99 (t, 6 H, *J* 6.6 Hz), 6.89 (d, 6 H, *J* 8.8 Hz), 7.52 (d, 6 H, *J* 8.8 Hz), 7.70 (d, 6 H, *J* 8.6 Hz), 8.74 (d, 6 H *J* 8.6 Hz). IR (KBr) 2210 cm^{-1}. Anal. Calcd for $C_{81}H_{99}N_3O_3$: C, 83.73; H, 8.52; N, 3.61. Found: C, 83.73; H, 8.63; N, 3.34.

2,4,6-Tris[(4-tetradecyloxyphenyl)ethynyl]benzene-1,3,5-triazine (1e)

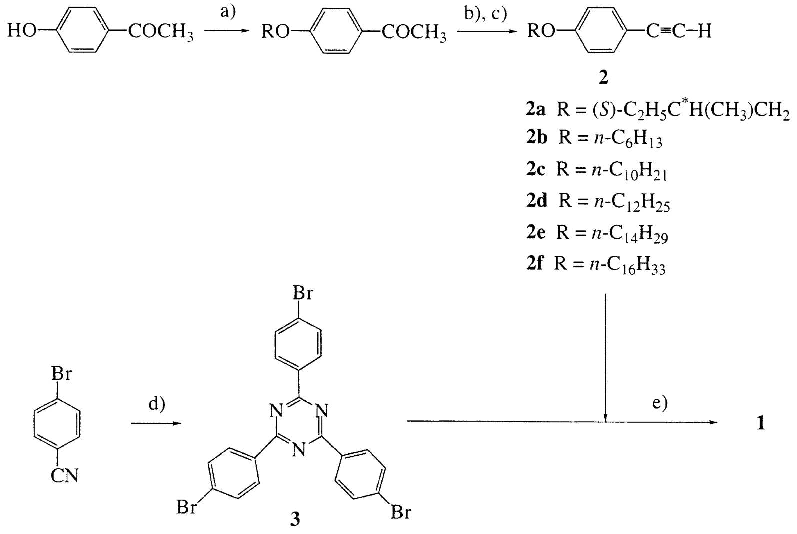
^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 0.89$ (t, 9 H, *J* 6.4 Hz), 1.27 (br s, 66 H), 1.80 (quint, 6 H, *J* 6.4 Hz), 3.99 (t, 6 H, *J* 6.6 Hz), 6.89 (d, 6 H, *J* 8.8 Hz), 7.52 (d, 6 H, *J* 8.8 Hz), 7.70 (d, 6 H, *J* 8.6 Hz), 8.74 (d, 6 H *J* 8.6 Hz). IR (KBr) 2210 cm^{-1}. Anal. Calcd for $C_{87}H_{111}N_3O_3$: C, 83.87; H, 8.91; N, 3.37. Found: C, 83.68; H, 8.77; N, 3.44.

2,4,6-Tris[(4-hexadecyloxyphenyl)ethynyl]benzene-1,3,5-triazine (1f)

^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 0.88$ (t, 9 H, *J* 6.4 Hz), 1.26 (br s, 78 H), 1.80 (quint, 6 H, *J* 6.4 Hz), 3.99 (t, 6 H, *J* 6.6 Hz), 6.88 (d, 6 H, *J* 8.8 Hz), 7.52 (d, 6 H, *J* 8.8 Hz), 7.69 (d, 6 H, *J* 8.6 Hz), 8.73 (d, 6 H, *J* 8.6 Hz). IR (KBr) 2210 cm^{-1}. Anal. Calcd for $C_{93}H_{123}N_3O_3$: C, 83.99; H, 9.25; N, 3.16. Found: C, 83.75; H, 9.00; N, 3.10.

RESULTS AND DISCUSSION

Synthesis of the π-conjugated 1,3,5-triazine derivatives **1** (Scheme 1) is possible due to the development of the palladium-catalyzed carbon-carbon cross-coupling reaction [8–10]; in the present case, the cross-coupling reaction of terminal alkynes having long alkoxy groups with 2,4,6-tris(*p*-bromophenyl)triazine **3** (Scheme 2). Terminal phenylalkynes **2** that have



SCHEME 2 Preparation of 1,3,5-triazine derivatives **1**: a) NaH, 1-bromoalkane, DMF, reflux; b) $POCl_3$, DMF, CH_2Cl_2, reflux; c) NaOH, H_2O, 1,4-dioxane, reflux; d) CF_3SO_3H, $CHCl_3$, room temperature; e) Terminal phenylalkynes, $Pd(PPh_3)_4$, CuI, NEt_3, THF, 50°C, 15 h.

long alkoxy groups were prepared in three steps from 4-hydroxyacetophenone, as previously reported [11].

The compounds **1a–f** were synthesized by a Pd (0)/Cu (I)-catalyzed coupling reaction of the corresponding terminal alkynes **2a–f** which have the long alkoxyl groups with 2,4,6-tris(*p*-bromophenyl)triazine **3**, prepared from *p*-bromobenzonitrile according to the reported method [2c] at 50°C in THF/NEt_3 (Scheme 2). All compounds **1** are readily soluble in organic solvents such as tetrahydrofuran, chloroform, and dichloromethane, and can be characterized by NMR spectroscopy. All results of the spectroscopic studies and elemental analysis were consistent with the proposed molecular structures. Compounds **1a–f** are air-stable solids that can be stored at ambient temperature for prolonged periods of time of more than 3 months. Simple MM2 molecular modeling indicates that the three-side diphenylacetylene groups and the 1,3,5-triazine core form a flat disklike structure.

Mesogenic Properties of the π-Conjugated 1,3,5-Triazine Derivatives

The phase assignments [12] and transition temperatures of compounds **1a–f** were studied by differential scanning calorimetry (DSC) and polarized optical microscopy (POM) measurements. The heating and cooling rates were 5°C/min. The DSC thermograms of compounds **1a–f** were measured by heating and subsequent cooling. Results of the DSC and POM experiments are summarized in Table 1.

The POM observations revealed that **1a** was not a liquid-crystalline material. The DSC peak at the higher temperature side is responsible for the melting and crystallization transitions, while that at the lower temperature is associated with crystal-crystal (k-k) transitions in the solid state. When **1a** was cooled from its isotropic state, it solidified and its crystalline phase displayed mosaic textures. However, no liquid birefringent phases were observed upon heating or cooling, indicating that **1a** was not a liquid-crystalline material.

Compound **1b** also did not show liquid-crystalline behavior. This is attributable to weak intermolecular interaction caused by relatively short hexyloxy groups.

In contrast to the cases of compounds **1a** and **1b**, **1c–f** exhibited a columnar hexagonal disordered (D_{hd}) mesophase [3a,c]. When the crystalline sample of **1c** was heated, it showed three endothermic peaks at 57.2°C, 66.9°C, and 141.1°C before melting into the isotropic state. The transitions are enantiotropic, and two exothermic peaks are observed at 67.4°C and 111.2°C in the DSC thermogram when the sample is cooled. Compound **1d** has mesogenic properties similar to those of compound **1c**. The POM examinations of **1c** and **1d** clearly revealed the formation of two liquid-crystalline phases, S_X and D_{hd}, between the crystalline and the isotropic

TABLE 1 Phase transition temperatures and corresponding enthalpies (kJ mol^{-1}) of π-conjugated 1,3,5-triazine derivatives **1**

Compound	*T/°C (ΔH/ kJ mol^{-1})*[a]
1a	$K_1 \xrightarrow{246.9(0.2)} K_2 \ {}^{254.2(0.4)}\ I$
1b	$K \xrightarrow{156.1(0.5)} I$
1c	$K \xrightleftharpoons[48.5(0.1)]{57.2(0.1)} S_X \xrightleftharpoons[67.4(0.3)]{66.9(0.2)} D_{hd} \xrightleftharpoons[111.2(1.0)]{141.1(0.9)} I$
1d	$K \xrightleftharpoons[111.5(0.9)]{116.3(0.5)} S_X \xrightleftharpoons[120.1(1.3)]{124.7(1.3)} D_{hd} \xrightleftharpoons[121.9(1.3)]{129.3(0.5)} I$
1e	$K \xrightleftharpoons[69.5(0.6)]{66.4(0.3)} D_{hd} \xrightleftharpoons[106.3(0.7)]{104.8(0.5)} I$
1f	$K \xrightleftharpoons[85.8(0.8)]{105.1(0.3)} D_{hd} \xrightleftharpoons[116.7(0.6)]{116.2(0.9)} I$

[a] K, K_1, K_2, crystal; S_X, higher order smectic; D_{hd}, columnar hexagonal disordered; I, isotropic.

phases. Slow cooling of the sample from the isotropic liquid to the mesophase gave rise to a mosaic texture [14] and homeotropic areas. Based on these observations, the two mesophases are identified as enantiotropic smectic S_X and discotic D_{hd} phases, respectively. When compound **1e** is heated, it shows two endothermic peaks at 66.4°C and 104.8°C before melting into the isotropic state. The transition is enantiotropic, and a single exothermic peak is observed at 106.3°C in the DSC thermogram when the sample is cooled. Compound **1f** has mesogenic properties similar to those of compound **1e**, as shown in Table 1.

Photoluminescent Properties

The UV-vis absorption peak of compound **1d** is shifted to a longer wavelength ($\lambda_{\max} = 359$ nm) from that of 1,3,5-triazine ($\lambda_{\max} = 272$ nm) due to the expansion of the π-conjugation system. Other compounds show UV-vis absorption peaks at essentially the same places (Table 2). The UV-vis absorption peaks of **1a–d** are shifted by 22–45 nm to longer wavelengths in the solid film, presumably due to intermolecular π-π interaction between the planar core π-systems assisted by the side-chain crystallization effect of the long alkoxyl group. Similar bathochromic shifts in the solid have been reported for transition metal complexes with organic ligands having long alkoxyl side chains [13].

The emission spectroscopic data of compounds **1a–f** are also listed in Table 2. Compounds **1a–f** exhibit a sharp emission around 432 nm; the peak position essentially agrees with the onset position of the UV-vis absorption band usually observed for π-conjugated molecules and polymers [15]. Similar results were observed with compounds **1a, 1b, 1c, 1e**, and **1f**. As shown in Table 2, compounds **1a–f** give large photoluminescence quantum yields of 74–90%. Such high quantum yield and chemical stability of **1a–f**

TABLE 2 UV-vis and photoluminescence data of **1a–f**

	$CHCl_3$ solution		*Cast film*		
Compound	λ_{max} *(nm)*	λ_{em} *(nm)*	λ_{max} *(nm)*	λ_{em} *(nm)*	Φ_f(%)[a]
1a	359	432	382	500	80
1b	361	432	406	491	74
1c	360	432	384	491	86
1d	359	432	385	491	90
1e	361	432	383	490	85
1f	359	432	391	490	84

[a] Quantum yield in chloroform.

indicate the potential applicability of the compounds in optical devices such as a dye laser.

The photoluminescence peak is shifted to a longer wavelength in the solid cast film. Such a redshift in the solid phase has been observed with various π-conjugated compounds and polymers [15] and is associated with the formation of an excimer-like adduct. For the present compounds, the molecular assembly assisted by the side-chain crystallization will assist the formation of the excimer-like adduct. The intensity of the photoluminescence is weakened in the solid phase, as is usually observed with aromatic compounds forming the excimer or excimer-like adduct.

CONCLUSION

A new class of 1,3,5-triazine derivatives, **1a–f**, having long alkoxy side chains can be easily synthesized. These compounds behave as liquid-crystalline materials and are highly luminescent. The present findings that the 1,3,5-triazine-based core can serve as the new mesogenic unit and that the compounds obtained have highly luminescent properties are expected to pave the way for the development of new optical devices using the luminescent and liquid-crystalline materials.

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