Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Synthesis and mesomorphic properties of a new series of triazole bent-core liquid crystalline molecules by "click" reaction

Yu-Zhen Zhao, Ze-Min He, Gang Chen, Zong-Cheng Miao, Dong Wang & Hai-Quan Zhang

To cite this article: Yu-Zhen Zhao, Ze-Min He, Gang Chen, Zong-Cheng Miao, Dong Wang & Hai-Quan Zhang (2016) Synthesis and mesomorphic properties of a new series of triazole bent-core liquid crystalline molecules by "click" reaction, Molecular Crystals and Liquid Crystals, 624:1, 171-179, DOI: 10.1080/15421406.2015.1044713

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1044713

Published online: 11 Feb 2016.

MOL. CRYST. LIQ. CRYST.
2016, VOL. 624, NO. 1, 171–179
http://dx.doi.org/10.1080/15421406.2015.1044713

Taylor & Francis
Taylor & Francis Group

Synthesis and mesomorphic properties of a new series of triazole bent-core liquid crystalline molecules by "click" reaction

Yu-Zhen Zhao[a], Ze-Min He[a], Gang Chen[b], Zong-Cheng Miao[c], Dong Wang[c], and Hai-Quan Zhang[a]

[a]State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao, China; [b]Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing, China; [c]Department of Materials Physics and Chemistry, University of Science and Technology Beijing, Beijing, China

ABSTRACT

The synthesis and mesomorphic properties of new triazole liquid-crystalline are presented and discussed. These triazole derivatives have been synthesized by reacting 4-hydrazoic iodobenzene with the 4-alkyl phenyl acetylene in dimethyl formamide (DMF). The molecular structure is characterized by 1H NMR, *Fourier transform infrared spectroscopy* (FTIR), *time-of-flight mass spectrometry* (TOF-MS) and the mesomorphic properties are characterized by polarizing optical microscope (POM) and (DSC). These new triazole liquid-crystallines have higher melting point and clearing point and the final compounds display both nematic and smectic liquid-crystalline phases.

KEYWORDS

Bent-core; click reaction; mesomorphic behavior; Sonogashira coupling; triazole liquid-crystalline

1. Introduction

As is known to all, chemical structure has a most significant effect on the mesophases formed by a liquid crystal material, therefore, it has become clear that what type of molecules should be able to form a mesophase. Obviously, rod-like molecules or disk-shaped can exhibit nematic phases. In addition, calamitic mesogens form lamellar phases while discotic mesogens form columnar phases. Different ways of these basic molecular structures giving rise to structural features of the mesophases can be modified. Since Niori et al. have first reported the synthesis of bent-core liquid crystals and found their special property, it seems that the bent or banana-shaped liquid crystals represent a new subfield of liquid crystals. Banana mesophases formed by bent core mesogens have become targets of great interest in academic research and their potential applications [1–7]. Due to their characteristic structure–property relationships, these have played an important role in displaying novel mesophases exhibiting polar and chiral properties.

At an early stage of the discovery of the bent-core liquid crystals, seven mesogenic phases were identified and simply designated as B1–B7, as specific phases different from conventional phases found in calamitic mesogens [8]. Sharpless and coworkers introduced "click" chemistry, a novel approach in organic synthesis that involves a handful of almost perfect chemical reactions [9].

CONTACT Hai-Quan Zhang hqzhang@ysu.edu.cn State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao, China.

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

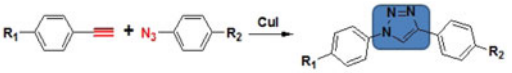


Figure 1. Schematic representation of a CuAAC reaction.

The CuI catalyzed azide–alkyne cycloaddition (CuAA C) can be considered as a typical "click" reaction [10] (Fig. 1). As part of our continuing interest in the synthesis of new liquid crystals (LCs), we explored the synthetic potential of triazole in the preparation of new LC materials.

2. Experimental

Reagents were purchased from commercial sources (Aldrich) and used without further purification, apart from triethylamine (TEA) and tetrahydrofuran (THF), which were distilled under argon before use. Reactions were carried out in an inert atmosphere (dry Ar). The structures of the various synthetic intermediates and final compounds were characterized by ^{1}H nuclear magnetic resonance (NMR) spectra of the samples with tetramethylsilane (TMS) as internal standard, which were recorded on a Bruker DMS (300 MHz) spectrometer instrument. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet-510P spectrophotometer using a powered sample on a KBr plate. MALDI-TOF mass spectra were determined on a Shimadzu AXIMA-CFR mass spectrometer.

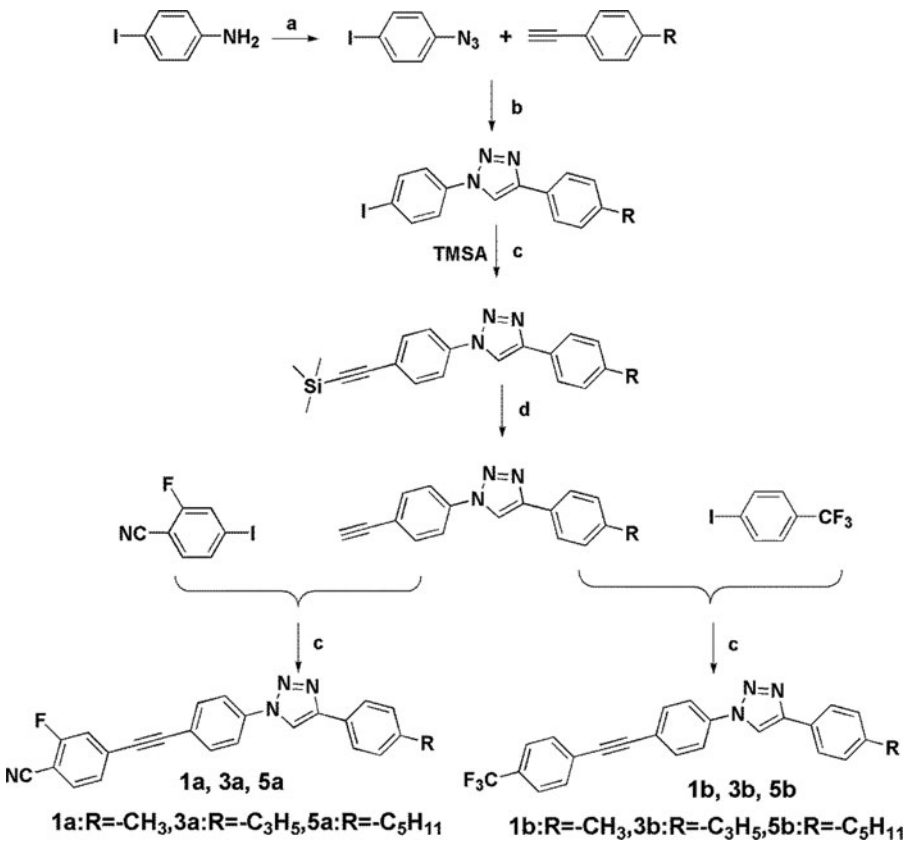
The optical textures were measured using a polarizing optical microscope (POM, Olympus BX51) equipped with a hot stage (Linkam LK-600PM) calibrated to an accuracy of ±0.1 K, and the phase transition temperatures and corresponding enthalpy changes of the target compounds were measured by differential scanning calorimetry (DSC, Perkin-Elmer Pyris 6) at a heating rate of 10.0°C min^{-1} under a dry nitrogen purge. UV-vis absorption spectra were recorded on UV-3100 spectrophotometer. Fluorescence spectra were carried out with RF-5301PC.

3. Results and discussion

The preparative routes and reagents for triazole liquid-crystalline are shown in Scheme 1, and the detailed synthetic processes are acquired elsewhere in references. In these targeted compound, the bent core of 1,2,3-triazole was synthesized through a classical reaction of CuI catalyzed azide–alkyne cycloaddition (CuAAC), which is a typical "click" reaction, and the Sonogashira coupling reaction with a palladium catalyst plays a key role in the synthesis procedure. In six compounds we synthesized, **1b** was not purified due to its low solubility.

3.1. *Phase transitions*

DSC was used to determine the phase transition temperatures of the compounds, these are listed in Table 1. The compounds all exhibited mesophases and with high melting points. In the DSC analysis of the compounds, only the Cr–N or Cr–Sm transitions were detected while the absence of N–I or Sm–I transitions suggests a highly disordered fluid mesophase [11]. The melting point of the compounds decreased with the increase of terminal alkyl chain length. The long alkyl chain shortened the π-electron conjugation and decreased the molecule rigidity. In contrast to the previously reported [12], the compounds with terminal trifluoromethyl group have higher melting points than those with terminal cyano group, correspondingly.



Scheme 1. Reagents and conditions: (a) HCl, H_2O, $NaNO_2$, NaN_3, 0°C, 1 hr; (b) CuI, DMF, 100°C; (c) TEA, THF, CuI, PPh_3, $PdCl_2(PPh_3)_2$, 30°C, 8 hr; (d) MeOH, THF, K_2CO_3, room temperature, 2 hr.

Table 1. Phase transition temperatures (°C)/ (enthalpy/kJ mol^{-1}) of the compounds.

Compound	Phase transition temperatures (°C)/(enthalpy/kJ mol^{-1})
1a	Cr234(41.2), N, decomposition, I
3a	C 218(39.8), N, decomposition, I
5a	Cr181(44.2), N, decomposition, I
3b	Cr224(36.3), Sm, decomposition, I
5b	Cr203(40.2), Sm, decomposition, I

That is due to the fluorosubstituent decreased molecular packing density. We only report mesomorphic properties of other compounds.

3.2. *Optical textures*

The optical textures of these compounds were observed with hot-stage POM (see Fig. 2). For **3a** and **5a** with terminal cyano group, the typical schlieren texture was observed, see Fig. 2(**3a**). However, the typical fingerprint texture was found, see Fig. 2(**5a**). Possibly, this is due to that the molecules of **5a** are of asymmetric order with spontaneity [13]. The optical textures of compounds **3b** and **5b** are similar in each case, manifesting a fan-like texture together [14] with large areas of oblique arrangement texture (see Fig. 2(**3b**) and (**5b**)).

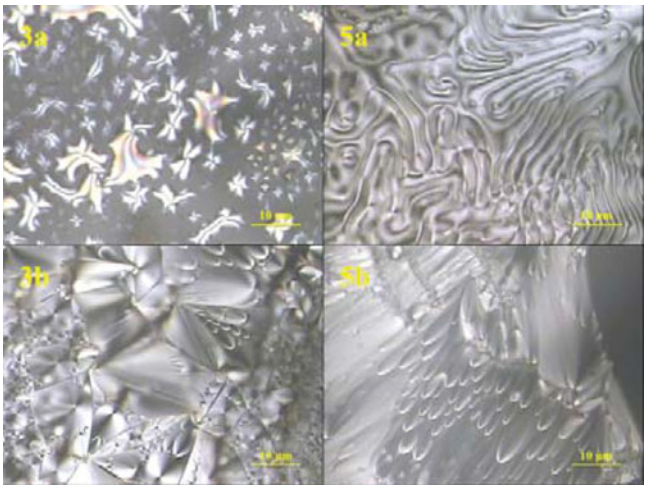


Figure 2. Microphotographs of the liquid crystalline phases of compounds **3a**, **5a**, **3b** and **5b** cooling rate: 10°C min^{-1}.

3.3. *Optical properties*

The photophysical properties of compounds **3a** and **3b** were examined by UV-vis spectroscopy and fluorescence spectroscopy in dilute CH_2Cl_2 solution at room temperature as shown in Fig. 3. All the data were summarized in Table 2 including absorption maxima (λ_{abs}), PL emission maxima (λ_{em}), and the Stokes shifts. The UV-vis absorption spectra were shown in Fig. 3(a). For **3a** and **3b**, both exhibit well-resolved absorption peaks because of π-$\pi*$ conjugation absorption [15]. The bathochromic shift from **3b** to **3a** was due to their slightly stronger polarity. For the same reason, the emission characteristics of **3a** and **3b** in Fig. 3(b) have been bathochromatically tuned obviously in the visible region. The maximum absorption edge of the compounds was 362 nm. The use of these materials would be suitable for optical display applications because such applications do not have an absorption band in the visible region.

4. Conclusions

By using the CuI catalyzed azide–alkyne cycloaddition (CuAAC) and Hagihara-Sonogashira cross-coupling reaction, a new series of 1,2,3-triazole derivatives were prepared with polar groups in excellent yield. All the compounds revealed fully characterized bent-core liquid crystalline. The compounds have relatively high melting and clearing temperatures that is due to the strong conjugate structure and the POM texture is very interesting. The results obtained by inspecting the absorption and emission spectra of these pure compounds indicated that the 1,2,3-triazole derivatives were affected by polarity of terminal group. The present study opens up a venue for click reaction in the design and synthesis of bent core liquid crystal.

Table 2. Physical properties of the materials 3a and 3b.

Compound	λ_{abs} (nm)	λ_{em} (nm)	Stokes shift (nm)
3a	323	400	77
3b	312	386	74

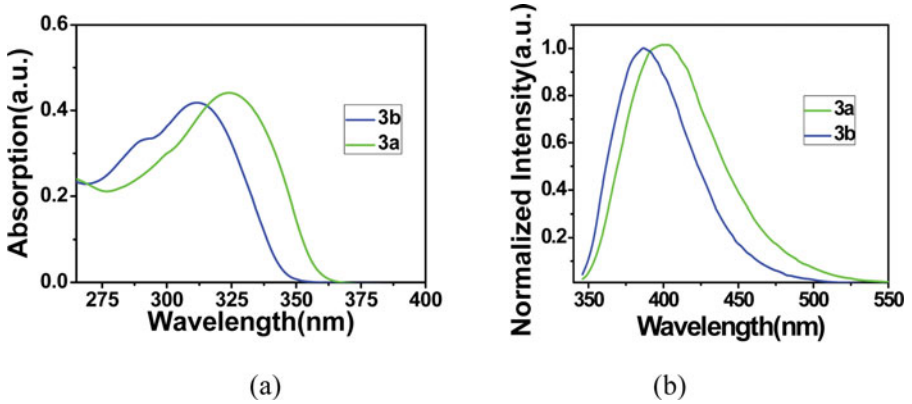


Figure 3. (a) The UV-visible spectra of synthesized compounds **3a** and **3b**. (b) The emission spectra of synthesized compound **3a** and **3b**.

5. Synthesis

1-Azido-4-iodo-benzene

A solution of 4-iodo-phenylamine (6.3 g, 28.8 mmol) in 20 ml ($HCl:H_2O$; 1:1) was cooled to 0°C in an ice-water bath. A solution of $NaNO_2$ (2.0 g, 28.8 mmol) in 100 ml water was added dropwise through a syringe to the vigorously stirred solution. After stirred at 0°C, adding a solution of NaN_3 (1.88 g, 28.8 mmol) in 20 ml water by drops into the mixed solution. After stirred at 0°C for half an hour, after the reaction was done, it was extracted with CH_2Cl_2 (3 × 50 ml) and dried over anhydrous $MgSO_4$, filtered, and concentrated. Obtain the target product as dark brownish solid (6.4 g, 91%).^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.36$ (d, J = 8.0 Hz, 2 H), 7.28 (d, J = 8.0 Hz, 2 H) ppm; FTIR (KBr): $\nu = 2109, 1692, 1604, 1568, 1522, 1483, 1462, 1415, 1402, 1368, 1293, 1207, 1183, 1145, 1060, 816, 721$ cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_6H_4IN_3$: 244.94 g mol^{-1}, found: 245.03 g mol^{-1} [MH]+.

1-(4-Iodo-phenyl)-4-(4-methyl-phenyl)-1H-[1,2,3]triazole (Procedure A)

1-Azido-4-iodo-benzene (2.44 g, 10 mmol) was reacted with 1-ethynyl-4-methylbenzene (1.16 g, 10 mmol). Then added CuI (95 mg, 0.5 mmol). The reaction mixture was then stirred at 100°C for 10 hr. After the reaction was done, remove the solvent by vacuum distillation. The crude product was purified by column chromatography (silica gel, 3:1, hexanes:CH_2Cl_2) to give target product (3.25 g, 90%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.21$ (s, 1 H), 7.96 (d, J = 8.0 Hz, 2 H), 7.87 (d, J = 8.0 Hz, 2 H), 7.64 (d, J = 8.0 Hz, 2 H), 7.35 (d, J = 8.0 Hz, 2 H) ppm; FTIR (KBr): $\nu = 3115, 2925, 2853, 1606, 1584, 1524, 1467, 1404, 1361, 1325, 1273, 1181, 1145, 1062, 956, 816, 722$ cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{15}H_{12}IN_3$: 361.01 g mol^{-1}, found: 361.18 g mol^{-1} [MH]+.

1-(4-Iodo-phenyl)-4-(4-propyl-phenyl)-1H-[1,2,3]triazole

The synthesized process of product as described in procedure A in a yield of (92%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.17$ (s, 1 H), 7.88 (d, J = 8.0 Hz, 2 H), 7.81 (d, J = 8.0 Hz, 2 H), 7.57 (d, J = 8.0 Hz, 2 H), 7.28 (d, J = 8.0 Hz, 2 H) ppm; FTIR (KBr): $\nu = 3113, 2925, 2851, 1606, 1584, 1524, 1467, 1404, 1362, 1325, 1273, 1182, 1145, 1062, 956, 812,$

720 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{17}H_{16}IN_3$: 389.04 g mol^{-1}, found: 389.23 g mol^{-1} [MH]+.

1-(4-Iodo-phenyl)-4-(4-pentyl-phenyl)-1H-[1,2,3]triazole

The synthesized product as described in procedure A in a yield of (93%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.11$ (s, 1 H), 7.85 (d, J = 8.0 Hz, 2 H), 7.78 (d, J = 8.0 Hz, 2 H), 7.54 (d, J = 8.0 Hz, 2 H), 7.25 (d, J = 8.0 Hz, 2 H), 2.62 (t, 2 H), 1.27 (m, 2 H), 1.53 (m, 2 H), 1.62 (m, 2 H), 0.87 (t, 3 H) ppm; FTIR (KBr): $\nu = 3116$, 2923, 2852, 1644, 1605, 1568, 1522, 1483, 1466, 1415, 1402, 1368, 1293, 1203, 1183, 1144, 1060, 816, 721 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{19}H_{20}IN_3$: 417.07 g mol^{-1}, found: 417.26 g mol^{-1} [MH]+.

1-(4-Trimethylsilanylethynyl-phenyl)-4-(4-methyl-phenyl)-1H-[1,2,3]triazole (Procedure B)

1-(4-Iodo-phenyl)-4-(4-methyl-phenyl)-1H-[1,2,3]triazole (2.89 g, 8 mmol) and Trimethylsilylacetylene (TMSA) (0.87 g, 8.8 mmol) dissolved in 120 ml dry Et3N:THF (1:1) in a 250 ml round-bottom flask. Add $PdCl_2(PPh_3)_2$ (0.12 g, 0.16 mmol) and CuI (0.06 g, 0.32 mmol). The reaction mixture was then stirred at room temperature for 8 hr under an Ar atmosphere. Upon completion, the solvent was removed in vacuo and the crude material was purified by chromatography on silica gel (2:1, hexanes:CH_2Cl_2) to give target compound (2.1 g, 81%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.14$ (s, 1 H), 7.77 (d, J = 8.0 Hz, 2 H), 7.73 (d, J = 8.0 Hz 2 H), 7.61 (d, J = 8.0 Hz, 2 H), 7.25 (d, J = 8.0 Hz, 2 H), 2.38 (s, 3 H), 0.26 (s, 9 H) ppm; FTIR (KBr): $\nu = 3108$, 2924, 2852, 2205, 1581, 1522, 1466, 1399, 1349, 1181, 961, 862, 720 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{20}H_{21}N_3Si$: 331.15 g mol^{-1}, found: 331.4 g mol^{-1} [MH]+.

1-(4-Trimethylsilanylethynyl-phenyl)-4-(4-propyl-phenyl)-1H-[1,2,3]triazole

The synthesized product as described in procedure B in a yield of (82%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.17$ (s, 1 H), 7.81 (d, J = 8.0 Hz, 2 H), 7.76 (d, J = 8.0 Hz, 2 H), 7.65 (d, J = 8.0 Hz, 2 H), 7.28 (d, J = 8.0 Hz, 2 H), 2.65 (t, 2 H), 1.70 (m, 2 H), 0.98 (t, 3 H) ppm; FTIR (KBr): $\nu = 3109$, 2923, 2852, 2199, 1606, 1584, 1523, 1467, 1404, 1363, 1325, 1273, 1183, 1145, 1062, 957, 814, 720 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{22}H_{25}N_3Si$: 359.18 g mol^{-1}, found: 359.54 g mol^{-1} [MH]+.

1-(4-Trimethylsilanylethynyl-phenyl)-4-(4-pentyl-phenyl)-1H-[1,2,3]triazole

The synthesized product as described in procedure B in a yield of (82%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.14$ (s, 1 H), 7.79 (d, J = 8.0 Hz, 2 H), 7.74 (d, J = 8.0 Hz, 2 H), 7.61 (d, J = 8.0 Hz, 2 H), 7.25 (d, J = 8.0 Hz, 2 H), 2.63 (t, 2 H), 1.63 (m, 2 H), 1.60 (m, 2 H), 1.32 (m, 2 H), 0.87 (t, 3 H), 0.25 (s, 9 H) ppm ; FTIR (KBr): $\nu = 3109$, 2924, 2853, 2213, 1604, 1483, 1466, 1345, 1212, 1184, 995, 882, 800, 724 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{24}H_{29}N_3Si$: 387.21 g mol^{-1}, found: 387.4 g mol^{-1} [MH]+.

1-(4-Ethynyl-phenyl)-4-(4-methyl-phenyl)-1H-[1,2,3]triazole (Procedure C)

1-(4-Trimethylsilanylethynyl-phenyl)-4-(4-methyl-phenyl)-1H-[1,2,3]triazole (1.6 g, 5 mmol) was dissolved in 100 ml of THF: MeOH (7:3) and K_2CO_3 (1.38 g, 10 mmol) was added. The reaction mixture was stirred at room temperature for 3 hr. On completion the mixture was suction filtered. The solvent was removed in vacuo and the crude product was purified by chromatography on silica gel (CH_2Cl_2) to give target compound (1.1 g, 90%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (s, 1 H), 7.78 (d, J = 8.0 Hz, 2 H), 7.76 (d, J = 8.0 Hz, 2 H), 7.64 (d, J = 8.0 Hz, 2 H), 7.26 (d, J = 8.0 Hz, 2 H), 3.17 (s, 1 H), 2.35 (s, 3 H) ppm; FTIR (KBr): ν = 3295, 3110, 2918, 2861, 2198, 2192, 1601, 1568, 1522, 1484, 1466, 1415, 1402, 1365, 1294, 1217, 1184, 1144, 1060, 817, 725 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{17}H_{13}N_3$: 259.17 g mol^{-1}, found: 259.31 g mol^{-1} [MH]+.

1-(4-Ethynyl-phenyl)-4-(4-propylphenyl)-1H-[1,2,3]triazole

The synthesized product as described in procedure C in a yield of (91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (s, 1 H), 7.79 (d, J = 6.0 Hz, 2 H), 7.76 (d, J = 6.0 Hz, 2 H), 7.64 (d, J = 6.0 Hz, 2 H), 7.27 (d, J = 6.0 Hz, 2 H), 3.15 (s, 1 H), 2.61 (t, 2 H), 1.62 (m, 2 H), 0.89(t, 3 H) ppm; FTIR (KBr): ν = 3293, 3111, 2913, 2860, 2198, 2190, 1611, 1568, 1522, 1484, 1466, 1415, 1402, 1365, 1293, 1217, 1184, 1144, 1060, 817, 726 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{19}H_{17}N_3$: 287.14 g mol^{-1}, found: 287.26 g mol^{-1} [MH]+.

1-(4-Ethynyl-phenyl)-4-(4-pentylphenyl)-1 H-[1,2,3]triazole

The synthesized product as described in procedure C in a yield of (93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (s, 1 H), 7.79 (d, J = 6.0 Hz, 2 H), 7.76 (d, J = 6.0 Hz, 2 H), 7.64 (d, J = 6.0 Hz, 2 H), 7.27 (d, J = 6.0 Hz, 2 H), 3.17 (s, 1 H), 2.62 (t, 2 H), 1.63 (m, 2 H), 1.33 (m, 2 H), 1.31 (m, 2 H), 0.88 (t, 3 H) ppm; FTIR (KBr): ν = 3294, 3111, 2913, 2861, 2198, 2190, 1601, 1568, 1522, 1484, 1466, 1415, 1402, 1365, 1293, 1217, 1184, 1144, 1060, 817, 724 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{21}H_{21}N_3$: 315.17 g mol^{-1}, found: 315.4 g mol^{-1} [MH]+.

2-Fluoro-4-[4-(4-p-tolyl-[1,2,3]triazol-1-yl)-phenylethynyl]-benzonitrile (Procedure D)

1-(4-Ethynyl-phenyl)-4-(4-methyl-phenyl)-1H-[1,2,3]triazole (0.9 g, 3.5 mmol) and 2-fluoro-4-iodo-benzonitrile (0.86 g, 3.5 mmol) were dissolved in 120 ml dry Et3N:THF (1:1) in a 250 ml round-bottom flask. Add $PdCl_2(PPh_3)_2$ (0.12 g, 0.16 mmol) and CuI (0.06 g, 0.32 mmol). The reaction mixture was then stirred at room temperature for 8 hr under an Ar atmosphere. Upon completion, the solvent was removed in vacuo and the crude material was purified by chromatography on silica gel (CH_2Cl_2) to give target compound (1.0 g, 79%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (s, 1 H), 7.84 (d, J = 8.0 Hz, 2 H), 7.80 (d, J = 8.0 Hz, 2 H), 7.70 (d, J = 8.0 Hz, 2 H), 7.61 (t, 1 H), 7.38 (m, 2 H), 7.27 (d, J = 6.0 Hz, 2 H), 2.39 (s, 3 H) ppm; FTIR (KBr): ν = 3112, 2923, 2852, 2235, 2207, 2190, 1604, 1568, 1522, 1484, 1466, 1415, 1402, 1368, 1293, 1207, 1183, 1144, 1060, 816, 721 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{24}H_{15}FN_4$: 378.19 g mol^{-1}, found: 378.34 g mol^{-1} [MH]+.

2-Fluoro-4-(4-[4-(4-propyl-phenyl)-[1,2,3]triazol-1-yl]-phenylethynyl)-benzonitrile

The synthesized product as described in procedure D in a yield of (75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.17 (s, 1 H), 7.84 (d, J = 6.0 Hz, 2 H), 7.80 (d, J = 6.0 Hz, 2 H), 7.70 (d, J = 6.0 Hz, 2 H), 7.61 (t, 1 H), 7.38 (m, 2 H), 7.27 (d, J = 6.0 Hz, 2 H), 2.62 (t, 2 H), 1.65 (m, 2 H), 0.93 (t, 3 H) ppm; FTIR (KBr): ν = 3112, 2924, 2853, 2241, 2213, 1604, 1483, 1466, 1345, 1212, 1184, 995, 882, 800, 724 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{26}H_{19}FN_4$: 406.16 g mol^{-1}, found: 406.30 g mol^{-1} [MH]+.

4-(4-Propyl-phenyl)-1-[4-(4-trifluoromethyl-phenylethynyl)-phenyl]-1H-[1,2,3]triazole

The synthesized product as described in procedure D in a yield of (75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.17 (s, 1 H), 7.82 (d, J = 6.0 Hz, 2 H), 7.80 (d, J = 6.0 Hz, 2 H), 7.70 (d, J = 6.0 Hz, 2 H), 7.64 (d, J = 6.0 Hz, 2 H), 7.61 (d, J = 6.0 Hz, 2 H), 7.26 (d, J = 6.0 Hz, 2 H), 2.62 (t, 2 H), 1.65 (m, 2 H), 0.95 (t, 3 H) ppm; FTIR (KBr): ν = 3101, 2921, 2853, 2209, 1606, 1584, 1523, 1466, 1404, 1363, 1325, 1273, 1183, 1144, 1062, 959, 814, 722 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{26}H_{20}F_3N_3$: 431.16 g mol^{-1}, found: 431.3 g mol^{-1} [MH]+.

2-Fluoro-4-(4-[4-(4-pentyl-phenyl)-[1,2,3]triazol-1-yl]-phenylethynyl)-benzonitrile

The synthesized product as described in procedure D in a yield of (80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18 (s, 1 H), 7.84 (d, J = 6.0 Hz, 2 H), 7.80 (d, J = 6.0 Hz, 2 H), 7.70 (d, J = 6.0 Hz, 2 H), 7.61 (t, 1 H), 7.38 (m, 2 H), 7.27 (d, J = 6.0 Hz, 2 H), 2.63 (t, 2 H), 1.63 (m, 2 H), 1.61 (m, 2 H), 1.32 (m, 2 H), 0.88 (t, 3 H) ppm; FTIR (KBr): ν = 3116, 2923, 2852, 2239, 2211, 2190, 1604, 1568, 1522, 1484, 1466, 1415, 1402, 1368, 1293, 1207, 1183, 1144, 1060, 816, 720 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{28}H_{23}FN_4$: 434.19 g mol^{-1}, found: 435.2 g mol^{-1} [MH]+.

4-(4-Pentyl-phenyl)-1-[4-(4-trifluoromethyl-phenylethynyl)-phenyl]-1H-[1,2,3]triazole

The synthesized product as described in procedure D in a yield of (76%). ^{1}H NMR (300 MHz, CDCl3): δ = 8.17 (s, 1 H), 7.82 (d, J = 6.0 Hz, 2 H), 7.80 (d, J = 6.0 Hz, 2 H), 7.70 (d, J = 6.0 Hz, 2 H), 7.64 (d, J = 6.0 Hz, 2 H), 7.61 (d, J = 6.0 Hz, 2 H), 7.27 (d, J = 6.0 Hz, 2 H), 2.63 (t, 2 H), 1.63 (m, 2 H), 1.33 (m, 2 H), 1.22 (m, 2 H), 0.88 (t, 3 H) ppm ; FTIR (KBr): ν = 3113, 2924, 2851, 2213, 2191, 1603, 1568, 1522, 1484, 1466, 1412, 1402, 1368, 12935, 1207, 1183, 1144, 1063, 816, 723 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{28}H_{24}F_3N_3$: 459.19 g mol^{-1}, found: 459.4 g mol^{-1} [MH]+.

Funding

This work was supported by the National Science Foundation of China (Grant 51173155) and the Major Project of Beijing Science & Technology Program (Grant Z121100006512002).

References

[1] Matsuda, T., & Matsunaga, Y. (1991). *Bull. Chem. Soc. Jpn.*, *64*, 2192.
[2] Akutagawa, T., Matsunaga, Y., & Yasuhara, K. (1994). *Liq. Cryst.*, *17*, 659.
[3] Yu, F. C., & Yu, L. (2006). *J. Chem. Mater.*, *18*, 5410.
[4] Hideo, T., & Yoichi, T. (2006). *Jpn. J. Appl. Phys.*, *45*, 597.

[5] Matsuzaki, H., & Matsunaga, Y. (1993). *Liq. Cryst*., *14*, 105.
[6] Niori, T., Sekine, T., Watanabe, J., Furukawa, T., & Takezoe, H. (1996). *J. Mater. Chem*., *6*, 1231.
[7] Sekine, T., Takanishi, Y., Niori, T., Watanabe, J., & Takezoe, H. (1997). *Jpn. J. Appl. Phys*., *36*, 1201.
[8] Hideo, T., & Yoichi, T. (2006). *Jpn. J. Appl. Phys*., *45*, 597.
[9] Kolb, H. C., Finn, M. G., & Sharpless, K. B. (2001). *Angew. Chem*., *113*, 2056.
[10] Lutz, J. F., & Zarafshani, Z. (2008). *Adv. Drug. Delivery. Rev*., *60*, 958.
[11] Hsu, H. F., Lai, Y. H., Lin, S. Y., Lin, W. C., & Chen, J. F. (2003). *Liq. Cryst*., *3*, 325.
[12] Zhang, Y. M., Wang, D., Miao, Z. C., Jin, S. K., & Yang, H. (2012). *Liq. Cryst*., *39*, 1330.
[13] Kentischer, F., Macdonald, R., & Warnick, P. (1998). *Liq. Cryst*., *25*, 341.
[14] Pelzl, G., Diele, S., & Weissflog, W. (1999). *Adv. Mater*., *11*, 707.
[15] Li, Y., *et al.* (2012). *J. Lumin*., *132*, 1010.