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Preparation and Coupling Reactions of Alkynyl(phenyl)iodonium Salts Bearing Long Alkoxy Chains. Formation of Liquid−Crystalline Diacetylenes

Tsugio Kitamura,* Chi Han Lee, Hiroshi Taniguchi, Masaru Matsumoto,† and Youich Sano†

Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University 36, Hakozaki, Fukuoka 812, Japan, and Department of Industrial Chemistry, Faculty of Engineering, Kyushu Sangyo University, Matsukadai, Fukuoka 813, Japan

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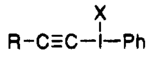
Alkynyl(phenyl)iodonium tosylates with long alkoxy chains, such as (octyloxy)-, (decyloxy)-, (dodecyloxy)-, and (tetradecyloxy)phenyl, were prepared by reaction of the corresponding alkynes with hydroxy(tosyloxy)iodobenzene. The alkynyliodonium tosylates were allowed to react with alkynylcopper reagents $(p\text{-}RC_6H_4C{\equiv}C)_2Cu(CN)Li_2$, where R = MeO, Me, H, Br, CN, and NO_2. The coupling reaction proceeded under mild conditions to provide unsymmetrical and symmetrical diacetylenes. The selectivity of the formation of these diacetylenes was dependent on the substituent on the alkynylcopper reagents. The diacetylenes prepared in this study displayed liquid−crystalline properties.

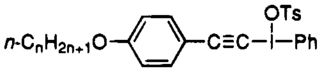
Organoiodine(III) compounds are useful in organic synthesis.[1] Alkynyl(phenyl)iodonium salts **1** especially are valuable because they contain a synthetically significant carbon−carbon triple bond.[1c,2] Previously we reported the stereoselective formation of conjugated enynes via the coupling of alkynyl(phenyl)iodonium tosylates **1** (X = OTs) with alkenylcopper reagents.[3] In addition, selective coupling reactions were conducted with alkyl- and alkynylcopper reagents.[4]

Recently, diacetylene derivatives have been found to display liquid−crystalline and nonlinear optical properties.[5−10] Long-chain alkyl groups play an important role in the formation of the molecular assembly by the intermolecular interaction, and the molecular assembly is applied to crystal engineering and molecular devices.[11] We believed that alkynyl(phenyl)iodonium salts bearing long alkyl chains were potential starting compounds for synthesizing such engineering materials. Thus, we prepared [(*p*-alkoxyphenyl)ethynyl](phenyl)iodonium tosylates **2** bearing long alkyl chains and applied the coupling reaction to synthesis of liquid−crystalline diacetylenes. Here we report the preparation of liquid−crystalline diacetylenes by means of the coupling reaction of alkynyl(phenyl)iodonium salts bearing long alkoxy chains.



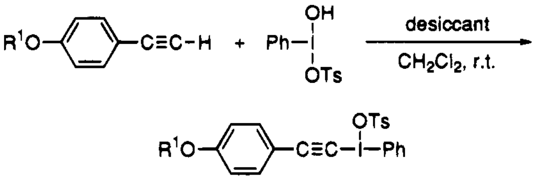
$R{-}C{\equiv}C{-}\overset{X}{I}{-}Ph$

1



2: *n* = 8, 10, 12 and 14

Preparation of Alkynyl(phenyl)iodonium Tosylates 2 with Long Alkoxy Chains. Alkynyl(phenyl)iodonium tosylates **2** bearing long alkoxy chains (R^1 = $n\text{-}C_8H_{17}$, $n\text{-}C_{10}H_{21}$, $n\text{-}C_{12}H_{25}$, and $n\text{-}C_{14}H_{29}$) were readily prepared from hydroxy(tosyloxy)iodobenzene.[12] Treatment of *p*-alkoxyphenylethynes with hydroxy(tosyloxy)iodobenzene in CH_2Cl_2 in the presence of desiccants gave crystalline alkynyl(phenyl)iodonium tosylates (**2a**, R^1 = $n\text{-}C_8H_{17}$; **2b**, R^2 = $n\text{-}C_{10}H_{21}$; **2c**, R^3 = $n\text{-}C_{12}H_{25}$; and **2a**, R^1 = $n\text{-}C_{14}H_{29}$) in 30−41% yields. Alkynyliodonium tosylates **2** were stable to air and moisture and could be used without any special precautions.



(1)

2 **a**: $R^1 = n\text{-}C_8H_{17}$
b: $R^1 = n\text{-}C_{10}H_{21}$
c: $R^1 = n\text{-}C_{12}H_{25}$
d: $R^1 = n\text{-}C_{14}H_{29}$

Coupling Reactions of Long-Chained [(*p*-Alkoxyphenyl)ethynyl]iodonium Tosylates 2 with Alkynylcopper Reagent 3. Coupling reactions were conducted under a N_2 atmosphere. A mixed alkynyl-substituted cuprate **3** was prepared from a lithium acetylide and CuCN in THF. Alkynyl(phenyl)iodonium

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† Kyushu Sangyo University.

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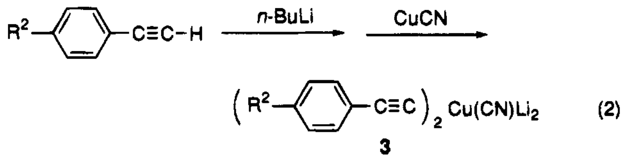
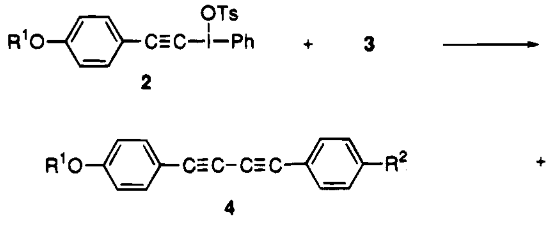
tosylate **2a** (R = n-C_8H_{17}) was added to cuprate reagent **3** in THF at −70 °C, and the reaction mixture was allowed to warm to room temperature. After workup of the reaction mixture, diacetylenes were separated either by column chromatography on silica gel with hexane−CH_2Cl_2 as the eluent or by recrystallization from ethanol. The major products were coupling products, symmetrical and unsymmetrical diacetylenes (**4** and **5**, respectively). Coupling reactions of alkynyliodonium salts **2b**, **2c**, and **2d** were conducted similarly. The results are in Table 1.





a: R^1 = n-C_8H_{17}, R^2 = Me

b: R^1 = n-C_8H_{17}, R^2 = NO_2

c: R^1 = n-C_8H_{17}, R^2 = CN

d: R^1 = n-$C_{10}H_{21}$, R^2 = Me

e: R^1 = n-$C_{10}H_{21}$, R^2 = NO_2

f: R^1 = n-$C_{10}H_{21}$, R^2 = CN

g: R^1 = n-$C_{12}H_{25}$, R^2 = MeO

h: R^1 = n-$C_{12}H_{25}$, R^2 = Me

i: R^1 = n-$C_{12}H_{25}$, R^2 = NO_2

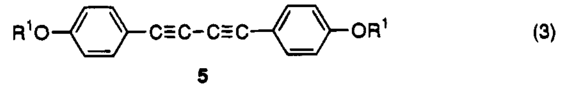
j: R^1 = n-$C_{12}H_{25}$, R^2 = CN

k: R^1 = n-$C_{14}H_{29}$, R^2 = MeO

l: R^1 = n-$C_{14}H_{29}$, R^2 = Me

m: R^1 = n-$C_{14}H_{29}$, R^2 = NO_2

n: R^1 = n-$C_{14}H_{29}$, R^2 = CN



a: R^1 = n-C_8H_{17}

b: R^1 = n-$C_{10}H_{21}$

c: R^1 = n-$C_{12}H_{25}$

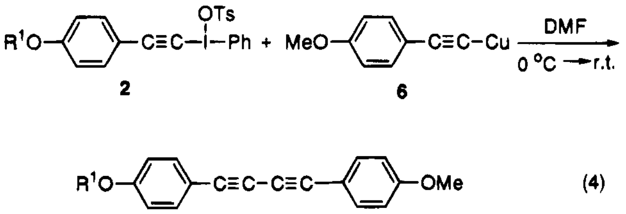
d: R^1 = n-$C_{14}H_{29}$

In the coupling reaction, the length of the alkoxy chain does not significantly affect the yield of the diacetylenes because the reaction of [(p-methoxyphenyl)ethynyl]iodonium tosylate with alkynyl cuprate **3** (R^2 = H) provides a similar yield of unsymmetrical diacetylene (75% yield).[4] However, Table 1 shows that the substituent on the aromatic ring affects the selectivity of the coupling reaction. The electron-donating groups on the aromatic ring preferentially give unsymmetrical diacetylenes **4** and increase that of symmetrical diacetylenes **5**. Although alkynyl groups are well known as popular nontransferable ligands,[13] alkynyl(phenyl)iodonium salts showed a high reactivity toward such alkynyl-substituted cuprates.

Copper(I) acetylides are also useful reagents for the synthesis of acetylenic derivatives.[14] Long-chained [(p-alkoxyphenyl)ethynyl]iodonium tosylates **2** were allowed to react with copper(I) p-methoxyphenylacetylide **6** in DMF. This reaction proceeded at room temperature to yield diacetylenes **4** in 31−43% yields. The yields of diacetylenes **4** were lower with **6** than with dialkynylcopper reagents **3**.

Table 1. Yields of Diacetylenes 4 and 5 by Coupling Reaction of Iodonium Tosylates 2 with Alkynylcopper Reagents 3

iodonium tosylate 2 R^1	copper reagent 3 R^2	diacetylenes (isolated yield, %) 4	5
n-C_8H_{17}	Me	66 (**4a**)	20 (**5a**)
	NO_2	36 (**4b**)	40 (**5a**)
	CN	26 (**4c**)	35 (**5a**)
n-$C_{10}H_{21}$	Me	54 (**4d**)	13 (**5b**)
	NO_2	20 (**4e**)	46 (**5b**)
	CN	37 (**4f**)	33 (**5b**)
n-$C_{12}H_{25}$	MeO	90 (**4g**)	7 (**5c**)
	Me	63 (**4h**)	32 (**5c**)
	NO_2	38 (**4i**)	52 (**5c**)
	CN	29 (**4j**)	36 (**5c**)
n-$C_{14}H_{29}$	MeO	67 (**4k**)	12 (**5d**)
	Me	59 (**4l**)	12 (**5d**)
	NO_2	26 (**4m**)	60 (**5d**)
	CN	10 (**4n**)	54 (**5d**)



4o: R^1 = n-C_8H_{17}, 31%

4p: R^1 = n-$C_{10}H_{21}$, 43%

4g: R^1 = n-$C_{12}H_{25}$, 40%

Diacetylenes **4** and **5** are mesogenic. The liquid phase transition temperature and the phase types of the diacetylenes were examined by optical microscopy and were confirmed by differential scanning calorimetry (DSC). The results are given in Table 2. Only cyano-substituted diacetylenes **4c**, **4f**, **4j**, and **4n** were monotropic liquid crystals and showed smectic phases on cooling. Other diacetylenes were enantiotropic liquid crystals. Methyl- and methoxy-substituted diacetylenes **4d**, **4g**, **4f**, **4k**, and **4l** exhibited smectic and nematic phases. Only smectic phases were observed in the cases of nitro-substituted diacetylenes **4b**, **4e**, **4i**, and **4m** and short alkoxy-chained diacetylenes **4a**, **4o**, and **4p**.

Symmetrical diacetylenes with long alkyl chains, which can be easily prepared by the Glaser coupling reactions,[10] have been shown to be mesogenic. Preparations of unsymmetrical diacetylenes present some difficulties with selectivity and purification. The formation of the donor−acceptor type of coupling product proceeds in particularly low yields (4−10%).[15] The present procedure using alkynyliodonium salts in the coupling reaction to give diacetylene derivatives has advantageous selectivity and reactivity, although it can be only applied to diacetylenes with electron-donating groups.

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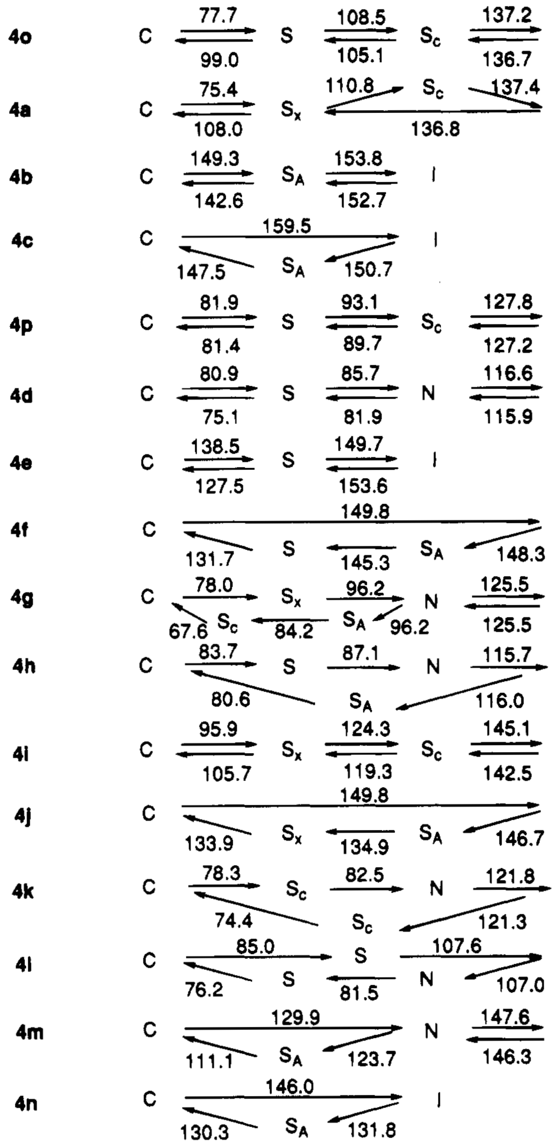
Table 2. Liquid Crystal Phases and Transition Temperature of Unsymmetrical Diacetylenes 4[a]



[a] Key: C, crystal; S, smectic; S$_A$, smectic A; S$_C$, smectic C; S$_X$, higher order smectic; N, nematic, and I, isotropic.

The unsymmetrical diacetylenes have received much attention because of their important application for liquid crystals, electronic, and nonlinear optical materials. The most mesogenic diacetylenes prepared in the present study display smectic and nematic phases suitable for use in liquid−crystal display devices. Diacetylenes **4** have mesogenic properties, and the unsymmetrical diacetylenes have potent, interesting optical properties. The coupling reaction using alkynyliodonium salts exhibits a large substituent effect on the selectivity for the formation of diacetylenes **4** and **5**.

Experimental Section

General. Melting points were measured with a Yanaco micro melting apparatus and are uncorrected. ^{1}H NMR spectra were obtained with HITACHI R-600 (60 MHz) and BRUKER AC-250P (250 MHz) spectrometers and ^{13}C NMR spectra with a BRUKER AC-250P (62.9 MHz) spectrometer. Chemical shifts are given in ppm. IR spectra were recorded with a HITACHI 270-30 spectrometer. Microanalyses were performed by the Service Center of the Elementary Analysis of Organic Compounds, Faculty of Science, Kyushu University. Some terminal acetylenes were prepared according to the reported procedures. *p*-Methoxyphenylacetylene:[16] IR (neat) 2108 (C≡C), 3319 cm^{-1} (C≡CH); ^{1}H NMR (60 MHz, CDCl$_3$) δ 2.98 (s, 1 H, C≡CH), 3.86 (s, 3 H, OMe), 6.81−7.42 (m, 4 H, ArH). *p*-Bromophenylacetylene:[17] IR (Nujol) 2106 cm^{-1}; ^{1}H NMR (60 MHz, CDCl$_3$) δ 3.10 (s, 1 H, C≡CH), 7.37−7.40 (m, 4 H, ArH). *p*-Nitrophenylacetylene:[18] IR (Nujol) 1512, 1593, 2106 (C≡C), 3251 cm^{-1} (C≡CH); ^{1}H NMR (60 MHz, CDCl$_3$) δ 3.34 (s, 1 H, C≡CH), 7.55−8.28 (m, 4 H, ArH). *p*-Cyanophenylacetylene:[18] IR (Nujol) 2102 (C≡C), 2222 (C≡N), 3251 cm^{-1} (C≡CH); ^{1}H NMR (60 MHz, CDCl$_3$) δ 3.29 (s, 1 H, C≡CH), 7.60 (s, 4 H, ArH).

Preparation of Long-Chained Alkoxyphenylacetylenes. General Procedure. After NaH (60% in oil, 12 g, 0.3 mol) was washed with hexane, 120 mL of DMF was added to it. A solution of *p*-hydroxyacetophenone (40.85 g, 0.3 mol) in DMF (100 mL) was added dropwise with stirring at 0 °C, and the mixture was stirred with cooling for an additional 1 h. 1-Bromoalkane (0.3 mol) was added, and the reaction mixture was then stirred for 22 h. The reaction mixture was poured into water, and the product was extracted with ether. The ether extract was washed with water and saturated brine, dried over Na$_2$SO$_4$, and concentrated. The product was separated by column chromatography on alumina with ether−hexane eluent.

POCl$_3$ (25 mL) was added dropwise to a solution of dichloromethane (80 mL) and DMF (25 mL) at 0 °C, and the mixture was stirred until the solution turned red. *p*-Alkoxyacetophenone (0.1 mol) prepared above was dropwise to the POCl$_3$ solution. The mixture was refluxed for 5 h with stirring and poured onto a mixture of ice and water. The mixture was hydrolyzed with CH$_3$COONa·H$_2$O until the solution became neutral and then extracted with ether. The ether extract was washed with water and saturated brine, dried over Na$_2$SO$_4$, and concentrated. The residue was dissolved in dioxane (30 mL), and the solution was added dropwise to a refluxing solution of 0.2 M NaOH (100 mL) in dioxane (60 mL). The mixture was refluxed for an additional 24 h and then poured into water and extracted with ether. The ether extract was washed with water and saturated brine, dried over Na$_2$SO$_4$, and concentrated. The colorless liquid was purified by column chromatography on alumina with ether−benzene (2:1) as an eluent.

***p*-(Octyloxy)phenylacetylene:**[10,19] yield, 76%; IR (neat) 2108 (C≡C), 3292 cm^{-1} (C≡CH); ^{1}H NMR (60 MHz, CDCl$_3$) δ 0.89 (br s, 3 H, Me), 1.29 (br s, 12 H, CH$_2$), 2.95 (s, 1 H, CH), 3.91 (t, J = 7.0 Hz, 2 H, OCH$_2$), 6.86−7.33 (m, 4 H, ArH).

***p*-(Decyloxy)phenylacetylene:**[10,19] yield, 36%; IR (neat) 2108 (C≡C), 3292 cm^{-1} (C≡CH); ^{1}H NMR (60 MHz, CDCl$_3$) δ 0.88 (br s, 3 H, Me), 1.27 (br s, 16 H, CH$_2$), 2.96 (s, 1 H, CH), 3.94 (t, J = 7.0 Hz, 2 H, OCH$_2$), 6.73−7.48 (m, 4 H, ArH).

***p*-(Dodecyloxy)phenylacetylene:**[19] yield, 55%; mp 25−26 °C; IR (CDCl$_3$) 2108 (C≡C), 3319 cm^{-1} (C≡CH); ^{1}H NMR (60 MHz, CDCl$_3$) δ 0.87 (br s, 3 H, Me), 1.27 (br s, 20 H, CH$_2$), 2.96 (s, 1 H, CH), 3.93 (t, J = 7.0 Hz, 2 H, OCH$_2$), 6.73−7.48 (m, 4 H, ArH).

***p*-(Tetradecyloxy)phenylacetylene:**[10] yield, 36%; mp 32−34 °C; IR (CDCl$_3$) 2108 (C≡C), 3319 cm^{-1} (C≡CH); ^{1}H NMR (60 MHz, CDCl$_3$) δ 0.87 (br s, 3 H, Me), 1.27 (br s, 24 H, CH$_2$), 2.96 (s, 1 H, CH), 3.95 (t, J = 7.0 Hz, 2 H, OCH$_2$), 6.73−7.48 (m, 4 H, ArH).

Long-Chained (*p*-Alkoxyphenyl)ethynyliodonium Tosylates 2. General Procedure. A solution of hydroxy(tosyloxy)iodobenzene (7.84 g, 20 mmol), *p*-alkoxyphenylacetylene (21 mmol), and desiccant (silica gel, granular, 12 g) in CH$_2$Cl$_2$ (120 mL) was stirred at rt for 1 h. After removal of the silica gel and the solvent, dry ether was added to the

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residue to crystallize it. The crystals were filtered, washed with ether and hexane, and dried in vacuo. Crystalline long-chained (*p*-alkoxyphenyl)ethynyliodonium tosylates **2** were obtained in 30–41% yields.

[[*p*-(Octyloxy)phenyl]ethynyl]iodonium tosylate 2a: yield, 30%; mp 136–139 °C; IR (Nujol) 2158 cm^{-1} ($C\equiv C$); ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.88 (br s, 3 H, Me), 1.32 (br s, 12 H, CH_2), 2.30 (s, 3 H, Me), 3.96 (t, J = 7.0 Hz, 2 H, OCH_2), 6.77–8.05 (m, 13 H, ArH). Anal. Calcd for $C_{29}H_{33}IO_4S$: C, 57.64; H, 5.46. Found: C, 57.67; H, 5.44.

[[*p*-(Decyloxy)phenyl]ethynyl]iodonium tosylate 2b: yield, 30%; mp 103–106 °C; IR (Nujol) 2158 cm^{-1} ($C\equiv C$); ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.87 (br s, 3 H, Me), 1.30 (br s, 16 H, CH_2), 2.31 (s, 3 H, Me), 3.96 (t, J = 7.0 Hz, 2 H, OCH_2), 6.97–8.19 (m, 13 H, ArH). Anal. Calcd for $C_{31}H_{37}IO_4S$: C, 58.86; H, 5.90. Found: C, 58.59; H, 5.71.

[[*p*-(Dodecyloxy)phenyl]ethynyl]iodonium tosylate 2c: yield, 37%; mp 93–95 °C; IR (Nujol) 2158 cm^{-1} ($C\equiv C$); ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.87 (br s, 3 H, Me), 1.26 (br s, 20 H, CH_2), 2.32 (s, 3 H, Me), 4.02 (t, J = 7.0 Hz, 2 H, OCH_2), 7.07–8.26 (m, 13 H, ArH). Anal. Calcd for $C_{33}H_{41}IO_4S$: C, 60.02; H, 6.21. Found: C, 59.72; H, 6.18.

[[*p*-(Tetradecyloxy)phenyl]ethynyl]iodonium tosylate 2d: yield, 41%; mp 87–92 °C; IR (Nujol) 2156 cm^{-1} ($C\equiv C$); ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.87 (br s, 3 H, Me), 1.26 (br s, 24 H, CH_2), 2.33 (s, 3 H, Me), 3.96 (t, J = 7.0 Hz, 2 H, OCH_2), 6.91–8.20 (m, 13 H, ArH). Anal. Calcd for $C_{35}H_{45}IO_4S$: C, 61.07; H, 6.54. Found: C, 60.86; H, 6.56.

Coupling Reaction of Alkynyl(phenyl)iodonium Tosylates 2 with Alkynylcopper Reagents 3. General Procedure. To a solution of arylacetylene (1.5 mmol) in THF (30 mL) at −70 °C was added dropwise n-BuLi in hexane solution (0.65 mL, 1.5 mmol) under a nitrogen atmosphere. CuCN (0.067 g, 0.75 mmol) was then added at −70 °C, and the mixture was stirred at −40 °C for 2 h. The mixture was cooled to −70 °C, and a solution of [(*p*-alkoxyphenyl)ethynyl]iodonium tosylate **2** (0.75 mmol) in THF (10 mL) was added dropwise to the cooled mixture, which was then allowed to warm to rt. The whole was poured into saturated aqueous ammonium chloride, and the resulting precipitate was filtered off. The filtrate was extracted with ether, and the extract was washed with saturated brine, dried over Na_2SO_4, and concentrated. The products were separated by column chromatography on silica gel with hexane–dichloromethane as an eluent.

1-[4-(Octyloxy)phenyl]-3-(4-methylphenyl)-1,3-butadiyne (4a): IR (Nujol) 2135 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.87 (t, J = 6.8 Hz, 3 H, Me), 1.29–1.45 (m, 10 H, CH_2), 1.76 (quint, J = 6.8 Hz, 2 H, CH_2), 3.96(t, J = 6.5Hz, 2 H, OCH_2), 6.83 (d, J = 8.5 Hz, 2 H, ArH), 7.13 (d, J = 8.0 Hz, 2 H, ArH), 7.40–7.46 (m, 4 H, ArH). Anal. Calcd for $C_{25}H_{28}O$: C, 87.16; H, 8.19. Found: C, 86.72; H, 8.53.

1-[4-(Octyloxy)phenyl]-3-(4-nitrophenyl)-1,3-butadiyne (4b): IR (Nujol) 2138 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.87 (t, J = 6.8 Hz, 3 H, Me), 1.29–1.44 (m, 10 H, CH_2), 1.79 (quint, J = 6.5 Hz, 2 H, CH_2), 3.97(t, J = 6.5Hz, 2 H, OCH_2), 6.86 (d, J = 8.8 Hz, 2 H, ArH), 7.47 (d, J = 8.8 Hz, 2 H, ArH), 7.64 (d, J = 8.8 Hz, 2 H, ArH), 8.20 (d, J = 8.8 Hz, 2 H, ArH). Anal. Calcd for $C_{24}H_{25}NO_3$: C, 76.77; H, 6.71; N, 3.73. Found: C, 76.76; H, 6.72; N, 3.69.

1-[4-(Octyloxy)phenyl]-3-(4-cyanophenyl)-1,3-butadiyne (4c): IR (Nujol) 2139, 2222 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3 H, Me), 1.28–1.45 (m, 10 H, CH_2), 1.79 (quint, J = 6.7 Hz, 2 H, CH_2), 3.97 (t, J = 6.5Hz, 2 H, OCH_2), 6.85 (d, J = 8.8 Hz, 2 H, ArH), 7.64 (d, J = 8.8 Hz, 2 H, ArH), 7.56–7.64 (m, J = 8.8 Hz, 4 H, ArH). Anal. Calcd for $C_{25}H_{25}NO$: C, 84.47; H, 7.09; N, 3.94. Found: C, 84.23; H, 7.10; N, 3.88.

1-[4-(Decyloxy)phenyl]-3-(4-methylphenyl)-1,3-butadiyne (4d): IR (Nujol) 2137 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.88 (t, J = 6.5 Hz, 3 H, Me), 1.27–1.43 (m, 14 H, CH_2), 1.77 (quint, J = 6.8 Hz, 2 H, CH_2), 2.36 (s, 3 H, Me), 3.95 (t, J = 6.5Hz, 2 H, OCH_2), 6.83 (d, J = 8.5 Hz, 2 H, ArH), 7.13 (d, J = 8.0 Hz, 2 H, ArH), 7.39–7.46 (m, 4 H, ArH). Anal. Calcd for $C_{27}H_{32}O$: C, 87.05; H, 8.66. Found: C, 87.19; H, 8.92.

1-[4-(Decyloxy)phenyl]-3-(4-nitrophenyl)-1,3-butadiyne (4e): IR (Nujol) 2210 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.86 (t, J = 6.8 Hz, 3 H, Me), 1.27–1.46 (m, 14 H, CH_2), 1.77 (quint, J = 7.5 Hz, 2 H, CH_2), 3.97 (t, J = 6.5Hz, 2 H, OCH_2), 6.86 (d, J = 8.8 Hz, 2 H, ArH), 7.47 (d, J = 8.8 Hz, 2 H, ArH), 7.64 (d, J = 8.8 Hz, 2 H, ArH), 8.20 (d, J = 8.8 Hz, 2 H, ArH). Anal. Calcd for $C_{26}H_{29}NO_3$: C, 77.39; H, 7.24; N, 3.47. Found: C, 77.02; H, 7.19; N, 3.19.

1-[4-(Decyloxy)phenyl]-3-(4-cyanophenyl)-1,3-butadiyne (4f): IR (Nujol) 2214, 2229 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.87 (t, J = 6.5 Hz, 3 H, Me), 1.27–1.46 (m, 14 H, CH_2), 1.77 (quint, J = 7.5 Hz, 2 H, CH_2), 3.97(t, J = 6.5Hz, 2 H, OCH_2), 6.86 (d, J = 8.8 Hz, 2 H, ArH), 7.47 (d, J = 8.8 Hz, 2 H, ArH), 7.56–7.65 (m, J = 8.8 Hz, 4 H, ArH). Anal. Calcd for $C_{27}H_{29}NO$: C, 84.11; H, 7.81; N, 3.77. Found: C, 83.95; H, 7.75; N, 3.43.

1-[4-(Dodecyloxy)phenyl]-3-(4-methoxyphenyl)-1,3-butadiyne (4g): IR (Nujol) 2137 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.88 (t, J = 6.6 Hz, 3 H, Me), 1.26–1.43 (m, 18 H, CH_2), 1.77 (quint, J = 6.5 Hz, 2 H, CH_2), 3.81 (s, 3 H, OMe), 3.96 (t, J = 6.5Hz, 2 H, OCH_2), 6.81–6.87 (m, 4 H, ArH), 7.42–7.47(m, 4 H, ArH). Anal. Calcd for $C_{29}H_{36}O_2$: C, 83.61; H, 8.71. Found: C, 83.45; H, 8.40.

1-[4-(Dodecyloxy)phenyl]-3-(4-methylphenyl)-1,3-butadiyne (4h): IR (Nujol) 2139 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.89 (t, J = 6.2 Hz, 3 H, Me), 1.28–1.46 (m, 18 H, CH_2), 1.78 (quint, J = 6.4 Hz, 2 H, CH_2), 2.37 (s, 3 H, Me), 3.96 (t, J = 6.4Hz, 2 H, OCH_2), 6.84 (d, J = 8.5 Hz, 2 H, ArH), 7.14 (d, J = 7.8 Hz, 2 H, ArH), 7.40–7.47(m, 4 H, ArH). Anal. Calcd for $C_{29}H_{36}O$: C, 86.95; H, 9.06. Found: C, 86.68; H, 9.39.

1-[4-(Dodecyloxy)phenyl]-3-(4-nitrophenyl)-1,3-butadiyne (4i): IR (Nujol) 2139 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.88 (t, J = 6.3 Hz, 3 H, Me), 1.26–1.45 (m, 18 H, CH_2), 1.79 (quint, J = 6.4 Hz, 2 H, CH_2), 3.99 (t, J = 6.4Hz, 2 H, OCH_2), 6.86 (d, J = 8.5 Hz, 2 H, ArH), 7.47 (d, J = 8.5 Hz, 2 H, ArH), 7.64 (d, J = 8.4 Hz, 2 H, ArH), 8.20 (d, J = 8.4 Hz, 2 H, ArH). Anal. Calcd for $C_{28}H_{33}NO_3$: C, 77.93; H, 7.71. Found: C, 77.60; H, 7.65.

1-[4-(Dodecyloxy)phenyl]-3-(4-cyanophenyl)-1,3-butadiyne (4j): IR (Nujol) 2139, 2229 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.88 (t, J = 6.5 Hz, 3 H, Me), 1.26–1.45 (m, 18 H, CH_2), 1.79 (quint, J = 6.5 Hz, 2 H, CH_2), 3.97(t, J = 6.5Hz, 2 H, OCH_2), 6.86 (d, J = 8.8 Hz, 2 H, ArH), 7.47 (d, J = 8.8 Hz, 2 H, ArH), 7.56–7.64 (m, 4 H, ArH). Anal. Calcd for $C_{29}H_{33}NO$: C, 84.63; H, 8.08; N, 3.40. Found: C, 84.62; H, 8.12; N, 3.36.

1-[4-(Tetradecyloxy)phenyl]-3-(4-methoxyphenyl)-1,3-butadiyne (4k): IR (Nujol) 2162 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.88 (t, J = 6.4 Hz, 3 H, Me), 1.26–1.45 (m, 22 H, CH_2), 1.78 (quint, J = 6.5 Hz, 2 H, CH_2), 3.82 (s, 3 H, OMe), 3.95 (t, J = 6.5Hz, 2 H, OCH_2), 6.81–6.86 (m, 4 H, ArH), 7.42–7.48(m, 4 H, ArH). Anal. Calcd for $C_{31}H_{40}O_2$: C, 83.74; H, 9.07. Found: C, 83.72; H, 9.11.

1-[4-(Tetradecyloxy)phenyl]-3-(4-methylphenyl)-1,3-butadiyne (4l): IR (Nujol) 2135 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.89 (t, J = 6.2 Hz, 3 H, Me), 1.28–1.46 (m, 22 H, CH_2), 1.78 (quint, J = 6.5 Hz, 2 H, CH_2), 2.36 (s, 3 H, Me), 3.95 (t, J = 6.5Hz, 2 H, OCH_2), 6.84 (d, J = 8.7 Hz, 2 H, ArH), 7.14 (d, J = 8.0 Hz, 2 H, ArH), 7.40–7.46 (m, 4 H, ArH). Anal. Calcd for $C_{31}H_{40}O$: C, 86.86; H, 9.41. Found: C, 86.93; H, 9.78.

1-[4-(Tetradecyloxy)phenyl]-3-(4-nitrophenyl)-1,3-butadiyne (4m): IR (Nujol) 2139 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.88 (t, J = 6.6 Hz, 3 H, Me), 1.26–1.45 (m, 22 H, CH_2), 1.79 (quint, J = 6.5 Hz, 2 H, CH_2), 3.97 (t, J = 6.5Hz, 2 H, OCH_2), 6.86 (d, J = 8.8 Hz, 2 H, ArH), 7.48 (d, J = 8.8 Hz, 2 H, ArH), 7.65 (d, J = 8.9 Hz, 2 H, ArH), 8.21 (d, J = 8.9 Hz, 2 H, ArH). Anal. Calcd for $C_{30}H_{37}NO_3$: C, 78.40; H, 8.11; N, 3.05. Found: C, 78.45; H, 8.07; N, 2.88.

1-[4-(Tetradecyloxy)phenyl]-3-(4-cyanophenyl)-1,3-butadiyne (4n): IR (Nujol) 2139, 2214 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.86 (t, J = 6.8 Hz, 3 H, Me), 1.26–1.45 (m, 22 H, CH_2), 1.79 (quint, J = 6.5 Hz, 2 H, CH_2), 3.97(t, J = 6.5Hz, 2 H, OCH_2), 6.86 (d, J = 8.7 Hz, 2 H, ArH), 7.47 (d, J = 8.7 Hz, 2 H, ArH), 7.56–7.64 (m, 4 H, ArH). Anal. Calcd for $C_{31}H_{37}NO$: C, 84.69; H, 8.48; N, 3.19. Found: C, 84.65; H, 8.37; N, 2.93.

1,4-Bis[4-(octyloxy)phenyl]-1,3-butadiyne (5a):[10] IR (Nujol) 2135 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.89 (br, s, 6 H, Me), 1.31–1.54 (m, 24 H, CH_2), 3.99 (t, J = 7 Hz, 4 H, OCH_2), 6.79–7.61 (m, 8 H, ArH).

1,4-Bis[4-(decyloxy)phenyl]-1,3-butadiyne (5b):[10] ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.88 (t, J = 6.5 Hz, 6 H, Me), 1.22–1.41 (m, 28 H, CH_2), 1.78 (quint, J = 6.8 Hz, 4 H, CH_2), 3.96 (t, J = 6.5Hz, 4 H, OCH_2), 6.83 (d, J = 8.8 Hz, 4 H, ArH), 7.44 (d, J = 8.8 Hz, 4 H, ArH).

1,4-Bis[4-(dodecyloxy)phenyl]-1,3-butadiyne (5c): ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.88 (t, J = 6.6 Hz, 6 H, Me), 1.26–1.41 (m, 36 H, CH_2), 1.75 (quint, J = 6.8 Hz, 4 H, CH_2), 3.95 (t, J = 6.5Hz, 4 H, OCH_2), 6.83 (d, J = 8.6 Hz, 4 H, ArH), 7.43 (d, J = 8.6 Hz, 4 H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 14.13, 22.69, 25.98, 29.12, 29.36 (×2), 29.58 (×2), 29.64 (×2), 31.92, 68.08, 72.84, 81.29, 113.60, 114.58, 133.99, 159.80. Anal. Calcd for $C_{40}H_{58}O_2$: C, 84.15; H, 10.24. Found: C, 84.07; H, 10.23.

1,4-Bis[4-(tetradecyloxy)phenyl]-1,3-butadiyne (5d):[10] $_1$H NMR (250 MHz, $CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 6 H, Me), 1.26–1.45 (m, 44 H, CH_2), 1.78 (quint, J = 6.8 Hz, 4 H, CH_2), 3.95 (t, J = 6.5Hz, 4 H, OCH_2), 6.83 (d, J = 8.7 Hz, 4 H, ArH), 7.44 (d, J = 8.7 Hz, 4 H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 14.15, 22.71, 25.99, 29.13, 29.37 (×2), 29.60 (×2), 29.60 (×2), 29.68 (×4), 31.93, 68.10, 72.86, 81.30, 113.62, 114.60, 134.00, 159.82.

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