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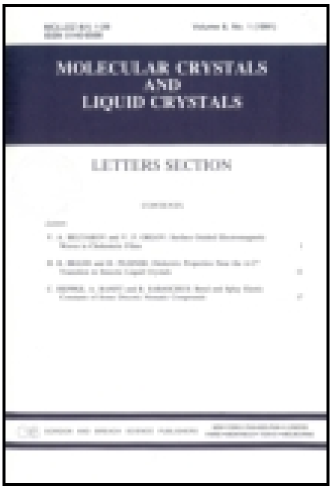

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Asymmetrical Azobenzene Liquid Crystals with High Birefringence Prepared via Click Chemistry

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Asymmetrical Azobenzene Liquid Crystals with High Birefringence Prepared via Click Chemistry

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Asymmetrical azobenzene liquid crystals with high birefringence were prepared via the click chemistry method. The chemical structures of the synthetic intermediates and compounds were confirmed by FT-IR and ^{1}H-NMR. The liquid crystal behavior, including transition temperatures and phase sequences, were investigated by DSC and POM. The effect of the alkyl substituents on liquid crystal behavior is discussed in detail. Then, the birefringence values of the liquid crystals were measured using polarizing light interferometry method. Moreover, the characteristics of selective reflection, which was associated with the value of birefringence, were studied.

Keywords Azobenzene; birefringence; click chemistry; liquid crystal; selective reflection

1. Introduction

Owing to the rich photochemistry of azobenzene chromophores, a fundamental research aspect of materials science and optical technologies [1], has received much attention because of applications in information storage [2], optical processing [3,4], holographic grating [5,6], liquid crystal alignment [7], and so on. These interesting applications cannot be separated from the photochemical trans-cis isomerization induced by UV and visible light [8], which is the most important and well-known property of azobenzene-containing species, and is usually accompanied by the structural change, as a result of the changes of dipole moment and geometry [9].

Presently, various photoresponsive systems including small-molecular azobenzene liquid crystals have been exploited [10,11]. Among them, azobenzene liquid crystals with high birefringence (Δn) were especially concerned for use as smart light-responsive materials in various potential applications [12]. Furthermore, Huisgen [3+2] cycloaddition reaction ("click chemistry" CC) plays an important role in the preparation of novel liquid crystal compounds [13]. CC, which takes place between terminal alkynes and high-energy azides under thermal condition, gives two isomer products, the 1,4- and 1,5-disubstituted

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1,2,3-triazoles [14,15]. In 2001, Kolb, Finn, and Sharpless published a landmark review describing a new strategy for CC. They used Cu(I) salt as the catalyst, and obtained the 1,5-disubstituted 1,2, 3-triazoles selectively [16]. Since then CC has been broadly used in the areas of biological, materials, and medicinal chemistry, gives high yields, tolerates many functional groups, and the reaction conditions are simple [17,18].

In the present work, our objective was to synthesize a series of azobenzene liquid crystals molecules, through CC reactions, with high Δn values. The synthesis and mesomorphic properties are presented for a variety of functional groups that were made in order to investigate the effect of these modifications.

2. Experimental

Reagents were purchased from commercial sources (Aldrich) and used without further purification. Triethylamine (TEA) and tetrahydrofuran (THF) were distilled and purged with argon before use. ^{1}H-NMR spectra of the samples were recorded with a Bruker DMS-400 spectrometer instrument. Fourier transform infrared spectroscopy (FT-IR, Perkin Elmer Spectrum One) was also measured.

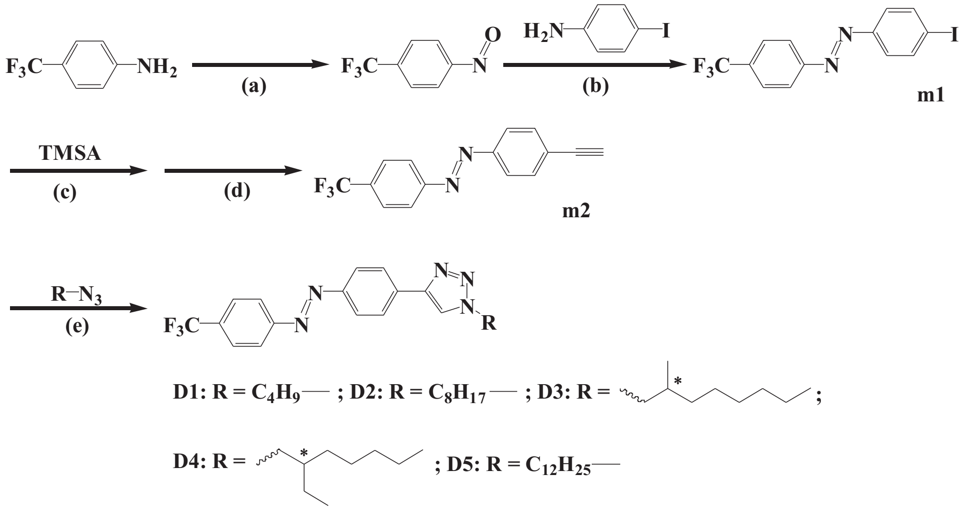
Transition temperatures and phase sequences were measured using a polarizing optical microscope (POM, Olympus BX51) equipped with a hot stage calibrated to an accuracy of ± 0.1K (Linkam LK-600PM) and then conformed using differential scanning calorimetry (DSC, Perkin Elmer Pyris 6). Δn was evaluated using the guest–host method from mixtures containing 10 wt% of each test compound in SLC 1717 (Slichem Liquid Crystal Material Co., Ltd.) and a polarized UV/VIS/NIR spectrophotometer (JASCO V-570) was used to measure the birefringence of the mixtures [19].

The reflectance characteristics were investigated by unpolarized UV/VIS/NIR spectrophotometer (JASCO V-570) in transmission mode at normal incidence. The transmittance of the blank cell was normalized as 100%. The N* LC was composed of a matrix LC, chiral dopant (specific content of 12.0 wt%), and one of the synthesized compounds (specific content of 10.0 wt%). The matrix nematic LC, SLC1717 and the chiral dopant, R811 (Merck Co., Ltd.) were used [20]. $\Delta\lambda$s were measured from the spectrum by considering respectively the peak bandwidth at half-height.

3. Results and Discussion

3.1. Synthesis

A strategy was planned for the design of azobenzene-based structures, which consist of four main units: the azobenzene group, the triazole group, the polar terminal substituent, and the alkyl terminal substituent. The polar terminal substituent could both engender the asymmetric structures and influence the intramolecular electron density [21], and the triazole could be easily obtained through Huisgen 3+2 cycloaddition reaction between phenylacetylene and RN_3 [16]. On the basis of the above methodology, a series of azobenzene derivatives with trifluoromethyl groups as terminal substituents were synthesized that connected with alkyl groups or chiral alkyl groups. The synthesis of the target compounds was accomplished mainly by three-step reactions as shown in Scheme 1: azobenzene generation procedure (a and b), phenylacetylene derivatives generation procedure (c and d) and Huisgen 3+2 cycloaddition procedures (e). All of above compounds were obtained in good yields and high purities. Their molecular structures and purities were assigned using ^{1}H-NMR and FT-IR.



Scheme 1. Reagents and conditions: (a) Oxone, CH_2Cl_2, H_2O, r. t., 15 h; (b) AcOH, r. t., 15 h; (c) TEA, THF, CuI, PPh_3, $PdCl_2(PPh_3)_2$, 30°C, 10 h; (d) MeOH, THF, K_2CO_3, r. t., 2 h; (e) CuI, DMF, 100°C, 15 h.

3.2. *FT-IR Spectra*

The FT-IR spectra of the synthesized compounds **D1**-**D5**, which were taken into KBr pellets, were shown in Fig. 1. It was indicated that the absorption peaks of **D1**-**D5** were very similar according to Fig. 1, because there were the similar molecular major structures except for the terminal alkyl substituents [22]. The position (cm^{-1}) of IR absorption peaks were in the order of 3132, 2969, 2916, 2847, 1931, 1731, 1604, 1470, 1336, 1224, 1102, 1071, 1016, 977, and 858.

3.2. *Phase Transitions*

Differential scanning calorimetry (DSC) was used to determine the phase transition temperatures during heating at a scanning rate of $10°C \cdot min^{-1}$; the phase transition temperatures

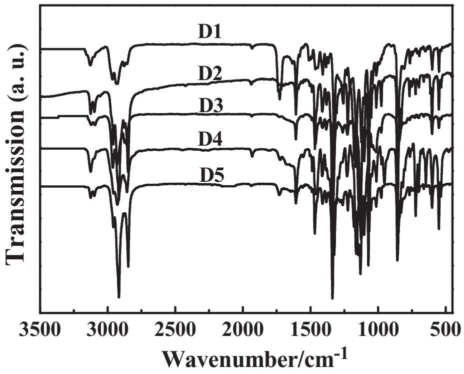


Figure 1. FT-IR spectra of **D1**-**D5**.

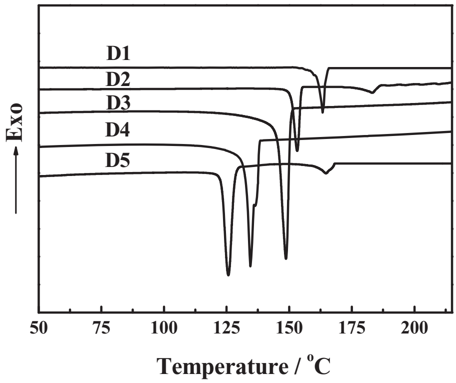


Figure 2. DSC curves of compounds **D1-D5** during heating with a scanning rate of 10°C · $\min^{-1}$, under a N_2 atmosphere.

of the compounds were shown in Fig. 2; and the associated data are listed in Table 1. It was observed that all compounds were crystals at room temperature, **D2** and **D5** formed a mesomorphic phase after melting [23]. Two endothermic peaks appeared when the compounds **D2** and **D5** were heated, which corresponded to the transformation from the crystalline (Cr) phase to an LC phase and that from the LC to the isotropic (I) liquid, respectively. However, there was only one endothermic peak during heating for the compounds **D1**, **D3**, and **D4**, which corresponded to the melting and crystallisation of the compounds. In Fig. 2, the melting points decreased with the increasing of carbon numbers of the alkyl substituents, while as to the LC monomers of **D2** and **D5**, clearing temperatures decreased and liquid crystal temperature range increased accordingly.

3.3. Mesomorphic Properties

In order to further confirm the above DSC results, the textures of the LC phase of each compound were observed using polarizing optical microscope (POM) (results shown in Fig. 3). The phases were identified through the comparison of the observed textures with reference textures [24] from POM. **D2** and **D5** developed the LC state at the first-phase transition temperature shown in the DSC curve, and a bright, colourful, and smectic phase texture could be observed. Upon further heating, the compounds entered into the I state and the field of view finally turned dark. When cooled from the I state, **D2** and **D5** developed a liquid Cr state again and then started to crystallize. The observations above indicated that **D2** and **D5** showed enantiotropic phase behavior with the existence of a smectic phase between the crystal and the I liquid, which were consistent with the DSC results.

Table 1. Phase transition temperatures and Δn of **D2** and **D5**. Cr = crystal, Sm = smectic phase, I = isotropic

Compounds	Phase transition temperature (°C)	Δn
D2	Cr 153 Sm 183 I	0.426
D5	Cr 126 Sm 165 I	0.412

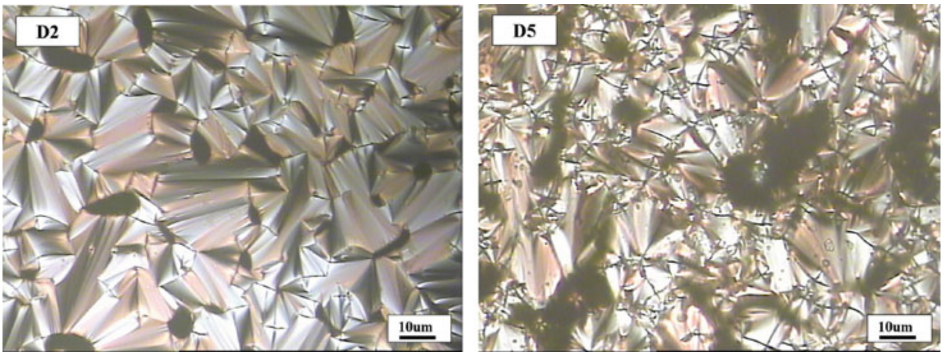


Figure 3. Polarised optical microscope images of **D2** and **D5** in mesophase. Cooling rate: 5°C · min^{-1}.

Compounds **D1**, **D3**, and **D4** could not form an LC phase during heating and cooling. This phenomenon indicated that the structure of the alkyl substituent played an important role for the azobenzene derivates to form LC phase, shorter (**D1**) and irregular (**D3**, **D4**) alkyl groups were not beneficial to the formation of LC phases.

3.4. Optical Anisotropy

After confirming the LC phase of **D2** and **D5**, we turned our attention to their birefringent (Δn) properties, because there was a certain number of π-electron conjugation in **D2** and **D5**. Δn was evaluated as extrapolated values from mixtures containing 10 wt% of each test compound in SLC 1717. Δn data of the compounds were collected in Table 1. Among compound **D2** and **D5**, the length of alkyl chain was important evaluation factor for Δn. Longer carbon chain decreased electron cloud density slightly, the Δn value decreased correspondingly [24].

3.5. Photophysical Properties

D2 and **D5** showed the similar absorption spectra for the same rigid segment structure. The photochemical responses to UV or visible light exposure were monitored by the unpolarized

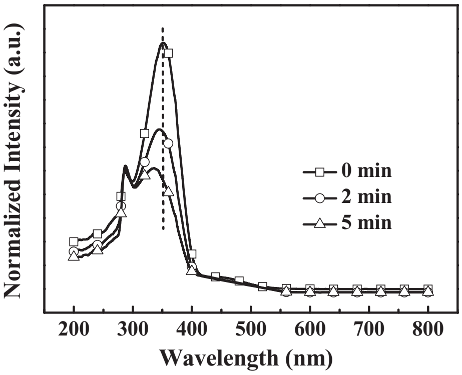


Figure 4. UV-Vis absorption spectra of **D2** in CH_2Cl_2 exposed to UV (8.5 mW·cm^{-2}) for 0 min, 2 min, and 5 min at room temperature.

Table 2. The composition and content of the N*-LC

Compound	Weight ratio[a]
Black sample	0.0/78.0/12.0
D2	10.0/68.0/12.0
D5	10.0/68.0/12.0

[a]Weight ratio of Compound/SLC1717/S811.

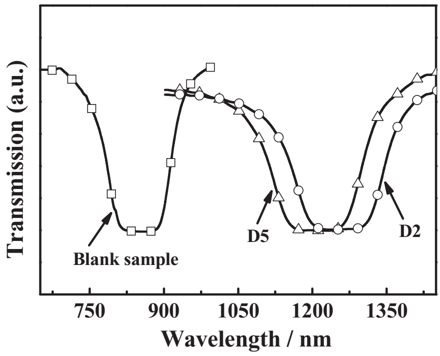


Figure 5. Dependence of the reflection band on **D2** and **D5**.

UV/VIS/NIR spectrophotometer (JASCO V-570) in absorption mode at normal incidence. In this paper, **D2** was used to study the photophysical properties of the azobenzene derivates in dilute CH_2Cl_2 solution at room temperature, the results were depicted in Fig. 4. All displayed a characteristic pattern of two absorption bands between 280 and 350 nm before UV lighting. When UV light ($\lambda = 365$ nm, 8.5 mW·cm^{-2}) was applied to the sample for 2 min and 5 min at room temperature, the absorption at 350 nm dropped as a result the trans-cis isomerization, and revealed significant blue shifts, that was about 6 nm for lighting 2 min and 15 nm for 5 min. However, when visible light ($\lambda = 440$ nm, 4.5 mW·cm^{-2}) was turned on (UV turned off) to induce the reverse cis-trans isomerization, the absorption returned to the initial state again.

3.6. Selective Reflection

In order to investigate the effect of **D2** and **D5** on the reflection behaviors of the N*-LC, the spectra of N*-LC samples with **D2** or **D5** were shown in Fig. 5. The composition and content of the N*-LC were shown in Table 2. In Fig. 5, $\Delta\lambda$ was about 140 nm for **Blank sample**, whereas it was 196, 210 nm for **D2** and **D5**, respectively. It was clearly seen that the reflection band remarkably become more broad with the increasing in Δn of the synthetic compound.

4. Conclusions

The compounds of asymmetrical azobenzene liquid crystals with high birefringence were designed and synthesized as potential new mesogens via click chemistry. The effect of these replaced modifications had been presented, that shorter and irregular alkyl groups weren't benefit to the formation of LC phases. From the Δn values of the series, it was shown that the length of alkyl chain was important evaluation factor for Δn, longer side chain decreased electron cloud density conjugation slightly, the Δn value decreased correspondingly. The compound with higher Δn was usually benefit to increase the broad reflection band of the N*-LC.

5. Synthesis

5.1. General Procedure for the Synthesis of Intermediate m1

4-Trifluoromethyl-aniline (16.1 g, 0.100 mol) dissolved in 200 mL of CH_2Cl_2 and oxone (123.0 g, 0.200 mol) dissolved in 200 mL of water were added in a round-bottom flask, the reaction mixture then stirred at room temperature for 15 h under an N_2 atmosphere. After separation of the layers, the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with 1 N HCl, saturated sodium bicarbonate solution, water, brine, and dried with $MgSO_4$. After filtration, removal of the solvent from the filtrate in vacuo yielded the corresponding labile nitrosoarene, which was submitted to the next condensation step without further purification. To the nitrosoarene dissolved in 200 mL of acetic acid was added 4-Iodo-aniline (21.9 g 0.100 mol). The resulting mixture was stirred at room temperature for 15 h. The precipitate was separated by filtration and the collected solid was washed with acetic acid and water and dried in a desiccator over P_2O_5 under reduced pressure for 24 h [25,26].

(4-Iodo-phenyl)-(4-trifluoromethyl-phenyl)-diazene (**m1**). Yellow solid, yield: 72.3%, 27.2 g. ^{1}H-NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.66 (d, 2H, $J = 8.8$ Hz), 7.76 (d, 2H, $J = 8.4$ Hz), 7.88 (d, 2H, $J = 8.8$ Hz), 7.98 (d, 2H, $J = 8.4$ Hz). IR (cm^{-1}): 2109, 1932, 1600, 1492, 1409, 1326, 1174, 1139, 1066, 856.

5.2. General Procedure for the Synthesis of Intermediate m2

m1 (3.76 g, 10 mmol) was dissolved in the mixed solvent of 100 mL TEA and 100 mL THF in a round-bottom flask. The solution was purged for 30 min with bubbling Ar followed by addition of $Pd(PPh_3)_3Cl_2$ (0.211 g, 0.300 mmol) and CuI (0.033 g, 0.300 mmol). The addition of TMSA (1.96 g, 20 mol) occurred via injection after Ar purge. The reaction mixture was then stirred at 30°C for 10 h under an Ar atmosphere. Upon completion, the mixture was concentrated, rediluted with CH_2Cl_2, and filtered through a plug of silica gel. The solvent was removed in vacuo and then dissolved in THF: MeOH (7: 3, 100 mL), added K_2CO_3 (3 equiv per silyl group). The reaction mixture was stirred at 20°C for 3 h. Upon completion, the mixture was diluted with Et_2O, washed with aq. NH_4Cl and H_2O, dried ($MgSO_4$) [27,28]. The solvent was removed in vacuo and the crude product was purified by chromatography of silica gel (3:1, hexanes: CH_2Cl_2).

(4-Ethynyl-phenyl)-(4-trifluoromethyl-phenyl)-diazene (**m2**). Yellow solid, yield: 91.4%, 2.51 g. ^{1}H-NMR (400 MHz, $CDCl_3$) (δ, ppm): $\delta = 3.12$ (s, 1H), 7.66 (d, 2H, $J = 8.8$ Hz), 7.76 (d, 2H, $J = 8.8$ Hz), 7.88 (d, 2H, $J = 8.8$ Hz), 7.98 (d, 2H, $J = 8.4$ Hz). IR (cm^{-1}): 3307, 2142, 2906, 1594, 1415, 1333, 1174, 1136, 1059, and 856 [27].

5.3. General Procedure for the Synthesis of R-N$_3$

R-Br (10 mmol) and NaN3 (3.25 g, 50 mmol) were dissolved in dry DMF) (50 mL). The mixture was stirred at 80°C for 20 h. After cooling, the solution was poured into H_2O (150 mL).

The resulting mixture was extracted with Et_2O (3 × 20 mL) and the combined organic phases were washed three times with saturated aqueous NaCl solution (3 × 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo [28,29]. The obtained oil was diluted with CH_2Cl_2, and the solution was filtered with a short silica gel column. Concentration of the filtered solution gave the corresponding azides in 85%–92% yield.

5.4. General Procedure for the Synthesis of the Azobenzene Liquid Crystals via Click Chemistry

To a 100 mL round-bottomed flask were charged **m2** (1.37 g, 5 mmol), R-N_3 (10 mmol), CuI (57.0 mg, 0.3 mmol), and DMF (50 mL). The mixture was heated to 100°C for 24 h, and then cooled to room temperature. The solution was poured into H_2O (150 mL) and then extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Upon completion, the mixture was rediluted with CH_2Cl_2, and filtered with a short silica gel column [30,31]. The solvent was removed in vacuo and the crude material was purified by chromatography of silica gel (1:1, hexanes: CH_2Cl_2).

[4-(1-Butyl-1H-[1,2,3]triazol-4-yl)-phenyl]-(4-trifluoromethyl-phenyl)-diazene (**D1**). Yellow solid, yield: 68.2%, 1.27 g. ^{1}H-NMR (400 MHz, $CDCl_3$) (δ, ppm): $\delta = 0.98$ (t, 3H), 1.46 (m, 2H), 1.75 (m, 2H), 4.43 (t, 2H), 7.77 (d, 2H, $J = 8.4$ Hz), 7.85 (s, 1H), 7.99 (d, 2H, $J = 8.0$ Hz), 8.01 (s, 4H). IR (cm^{-1}): 3132, 2969, 2916, 2847, 1931, 1731, 1604, 1470, 1336, 1224, 1102, 1071, 1016, 977, and 858.

[4-(1-Octyl-1*H*-[1,2,3]triazol-4-yl)-phenyl]-(4-trifluoromethyl-phenyl)-diazene (**D2**). Yellow solid, yield: 74.9%, 1.61 g. ^{1}H-NMR (400 MHz, $CDCl_3$) (δ, ppm): $\delta = 0.88$ (t, 3H), 1.26 (m, 2H), 1.33 (m, 8H), 1.94 (m, 2H), 4.34 (t, 2H), 7.77 (d, 2H, $J = 8.4$ Hz), 7.84 (s, 1H), 7.99 (d, 2H, $J = 8.0$ Hz), 8.01 (s, 4H). IR (cm^{-1}): 3132, 2969, 2916, 2847, 1931, 1731, 1604, 1470, 1336, 1224, 1102, 1071, 1016, 977, and 858.

{4-[1-(1-Methyl-heptyl)-1*H*-[1,2,3]triazol-4-yl]-phenyl}-(4-trifluoromethyl-phenyl)-diazene (**D3**). Yellow solid, yield: 42.3%, 0.908 g. ^{1}H-NMR (400 MHz, $CDCl_3$) (δ, ppm): $\delta = 0.84$ (t, 3H), 1.23 (m, 6H), 1.28 (m, 2H), 1.60 (d, 3H), 1.90 (m, 2H), 4.72 (m, 1H), 7.77 (d, 2H, $J = 8.4$ Hz), 7.84 (s, 1H), 7.99 (d, 2H, $J = 8.0$ Hz), 8.02 (s, 4H). IR (cm^{-1}): 3132, 2969, 2916, 2847, 1931, 1731, 1604, 1470, 1336, 1224, 1102, 1071, 1016, 977, and 858.

{4-[1-(1-Ethyl-hexyl)-1*H*-[1,2,3]triazol-4-yl]-phenyl}-(4-trifluoromethyl-phenyl)-dia zene (**D4**). Yellow solid, yield: 56.2%, 1.21 g. ^{1}H-NMR (400 MHz, $CDCl_3$) (δ, ppm): $\delta =$ 0.87 (t, 3H), 0.94 (t, 3H), 1.27 (m, 4H), 1.30 (m, 2H), 1.60 (d, 3H), 1.94 (m, 2H), 4.33 (m, 1H), 7.77 (d, 2H, $J = 8.4$ Hz), 7.82 (s, 1H), 7.99 (d, 2H, $J = 8.0$ Hz), 8.01 (s, 4H). IR (cm^{-1}): 3132, 2969, 2916, 2847, 1931, 1731, 1604, 1470, 1336, 1224, 1102, 1071, 1016, 977, and 858.

[4-(1-Dodecyl-1*H*-[1,2,3]triazol-4-yl)-phenyl]-(4-trifluoromethyl-phenyl)-diazene (**D5**). Yellow solid, yield: 76.5%, 1.86 g ^{1}H-NMR (400 MHz, $CDCl_3$) (δ, ppm): $\delta = 0.85$ (t, 3H), 1.23 (m, 16H), 1.33 (m, 2H), 1.95 (m, 2H), 4.41 (t, 2H), 7.77 (d, 2H, $J = 8.4$ Hz), 7.84 (s, 1H), 7.99 (d, 2H, $J = 8.0$ Hz), 8.01 (s, 4H). IR (cm^{-1}): 3132, 2969, 2916, 2847, 1931, 1731, 1604, 1470, 1336, 1224, 1102, 1071, 1016, 977, and 858.

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