Electronic Supplementary Information

Supramolecular Assembly of Fluorescent Phasmidic Diacetylene and Its Photopolymerization

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Synthesis

3,4,5-Tridodecyloxybenzoic acid ethyl ester. 51 g (0.3 mol) of gallic acid was suspended in ethanol and then, catalytic amount of H_2SO_4 was added. The mixture was refluxed for 3 h and cooled to room temperature. After pouring to cold water, white solid was collected by filtration and thoroughly dried. Obtained gallic acid ethyl ester 19.8 g (0.1 mol), 28 g (0.5mol) of KOH and catalytic amount of KI were dissolved in ethanol. The solution was heated to 60 ^{o}C with magnetic stirring and 95.8 mL (0.4 mol) of 1-bromododecane was then added dropwise. The reaction was conducted under reflux until completion in about 6 h. The reaction mixture was then poured into cold water and extracted with ethylacetate. After removal of solvent, the crude product was reprecipitated into *n*-hexane. 38.67 g of product was obtained and reaction yield was 55 %. ^{1}H-NMR ($CDCl_3$, 300MHz) δ 7.24 (s, 2H), 4.33 (q, 2H), 3.99 (m, 6H).

3,4,5-Tridodecyloxybenzoic acid hydrazide (1). 7.03 g (0.01 mol) of 3,4,5-tri-dodecyloxybenzoic acid ethyl ester was suspended in 150 mL of ethanol/H_2O (7/3 volume ratio) solution and two equivalent of KOH was added. This mixture was refluxed for 3 h and poured into excess cold water. After the solution was neutralized, precipitate was collected by filtration and dried. Obtained white solid was suspended in dichloromethane (10 mL) solution containing 7.3 mL of thionyl chloride and catalytic amount of DMF. Then, the solution was heated to 70 ^{o}C with magnetic stirring for 2 h, which was cooled to 0 ^{o}C and diluted with 15 mL of Na-dried tetrahydrofuran (THF). Reacted solution was added dropwise to a vigorously stirring mixture composed of 2.4 mL (0.05mol) of hydrazine monohydrate and 2 mL of triethylamine (TEA). After additional stirring for 20 min, it was diluted with excess THF. The yellowish salt was eliminated by filtration and solvent was removed with rotary vacuum evaporator. After impurities were eliminated through flash column of silica gel (Merck 60, 70-230 mesh) using ethyl acetate, white solid was obtained by elution with THF (Yield 79 %). ^{1}H-NMR ($CDCl_3$, 300MHz) δ 6.60 (s, 2H), 3.51 (m, 6H).

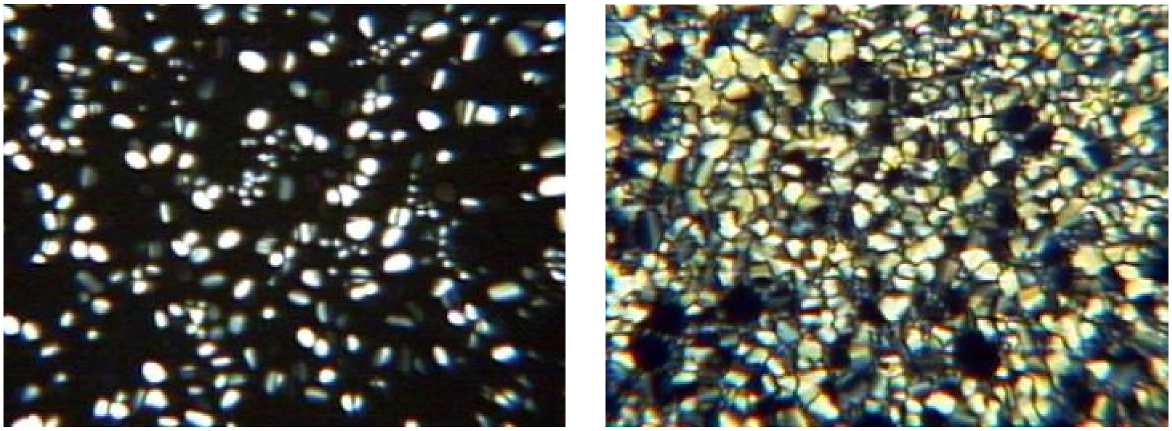
2-(4-Bromophenyl)-5-(3,4,5-tris-dodecyloxyphenyl)-[1,3,4]oxadiazole (2). 2.0 g (0.01 mol) of 4-bromobenzoic acid was suspended in dichloromethane (10 mL) solution containing 1.96 mL (0.02 mol) of thionyl chloride. After adding catalytic amounts of N,N-dimethyl formamide (DMF), the solution was heated to 70 °C with magnetic stirring for 2 h and the mixture was cooled to 0 °C with dilution of 15 mL, Na-dried tetrahydrofuran (THF). And then, this solution was added dropwise to a vigorously stirred solution containing 8.3 g (0.012 mol) of **1** and 20 mL of triethylamine (TEA). The reaction mixture was stirred for 20 min and diluted with excess THF. The yellowish salt was eliminated by filtration and solvent was removed with rotary vacuum evaporator. Yellowish solid was obtained through flash column of silica gel (Merck 60, 70-230 mesh) using ethyl acetate. Obtained yellowish solid was dissolved in 15 mL of phosphorous oxychloride, which was refluxed for 3 h for effective ring closure. Then, the solution was cooled to room temperature and poured to cold water, followed by extraction with dichloromethane. The extract was washed several times and dried with anhydrous magnesium sulfate. After removal of solvent by rotary evaporation, crude products was purified by column chromatography on silica gel using dichloromethane: ethyl acetate (3:1) as eluent. For high purity, obtained white solid was first recrystallized from acetone and second from ethyl acetate (6.65 g, Yield 78%). ^{1}H-NMR ($CDCl_3$, 300MHz) δ 8.01 (d, 2H), 7.68 (d, 2H), 7.03 (s, 2H), 4.05 (m, 6H).

2-(4-Ethynylphenyl)-5-(3,4,5-tris-dodecyloxyphenyl)-[1,3,4]oxadiazole (3). Under N_2 current, 8.54 g (0.01 mol) of **2** was dissolved in 20 mL of TEA with magnetic stirring in room temperature. 5.7 mL (0.04 mol) of trimethylsilyl acetylene and catalytic amounts of CuI and PPh_3 were added to mixture. Then, the mixture was heated to 50 °C and 0.21 g (3×10^{-4} mol) of $PdCl_2(PPh_3)_2$ was added. The reaction mixture was refluxed for 6 h and poured into cold water. After neutralization with 2N of hydrochloric acid, the precipitate was collected by filtration, and thoroughly dried. Obtained solid was dissolved in methanol solution containing 0.4 g (0.003 mol) of K_2CO_3, which was stirred for 2 h in room temperature. Then, it was poured into excess of brine and extracted with diethyl ether. The extract was dried with anhydrous magnesium sulfate and excess solvent was removed by rotary evaporation. Obtained mixture was purified by column chromatography on silica gel using ethyl acetate : *n*-hexane (1:3) as eluent and 5.12 g of white solid was obtained (Yield 64 %). ^{1}H-NMR ($CDCl_3$, 300MHz) δ 8.15 (d, 2H), 7.72 (d, 2H), 7.75 (s, 2H), 4.07 (m, 6H), 3.01 (s, 1H).

PhDO. 0.8 g (0.001mol) of **4** and catalytic amount of CuCl was added to methanol solution containing small amount of pyridine with vigorous stirring. After warming for 2 h, the mixture was cooled to room temperature and neutralized with concentrated HCl, which was poured to excess sodium chloride solution and and extracted with dichloromethane. The extract was dried with anhydrous magnesium sulfate and excess solvent was removed by rotary evaporation. Crude mixture was purified by flash column chromatography of silica gel (Merck 60, 70-230 mesh) using ethyl acetate. 0.73g of **5** was obtained and yield was 92%. ^{1}H-NMR ($CDCl_3$, 300MHz) δ 8.13 (d, 2H), 7.69 (d, 2H), 7.31 (s, 2H), 4.06 (m, 6H); MALDI-TOF (reflector, positive) m/z 1596.42 (Calcd), 1596.96 (Found); Anal. Calcd for $C_{104}H_{162}N_4O_8$: C, 78.24; H, 10.23; N, 3.51. Found: C, 78.21; H, 10.24; N, 3.53.

Polarized Optical Micrographic (POM) Textures

Taken at the indicated temperature on cooling from the isotropic melt.



85 °C (mesophase)

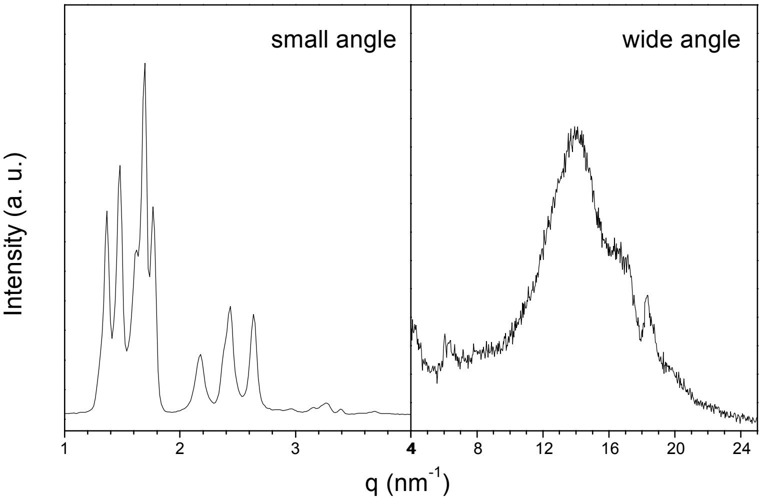
40 °C (crystalline phase)

Characterization on X-ray Diffraction (XRD) of PhDO Mesophase

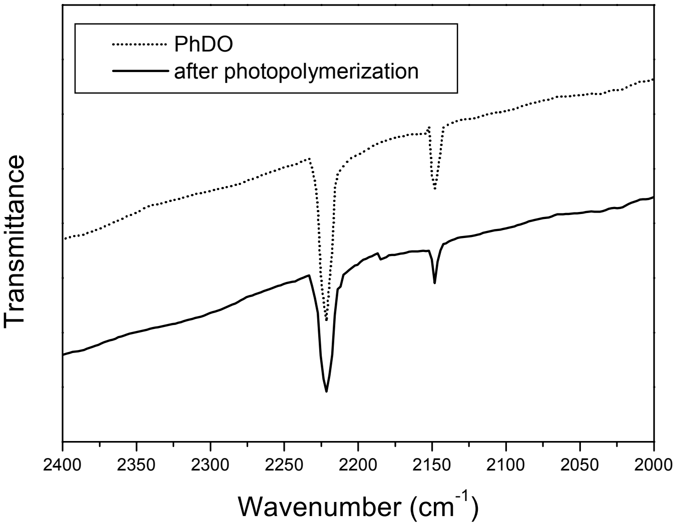
h	*k*	*l*	q_{calc} (nm^{-1})	q_{obsd} (nm^{-1})
1	0	0	1.367	1.367
0	1	0	1.481	1.481
0	0	1	1.623	1.623
1	0	-1	1.666	1.666
1	-1	0	1.766	1.766
1	-1	-1	1.972	
0	1	1	2.165	2.165
1	1	0	2.221	2.378
1	0	1	2.449	2.435
2	-1	-1	2.613	2.62
1	0	-2	2.99	2.976
1	-1	-2	3.154	3.118
0	0	2	3.246	3.261
0	2	1	3.325	3.346
2	0	1	3.673	3.673

Triclinic structure (P1)
a: 51.8 Å b: 44.1 Å c: 42.44 Å
α=83.45° β=114.1° γ=105.21°

XRD Pattern of PhDO after Photopolymerization



IR spectra before and after photopolymerization



Absorption Change of PhDO Film Depending on Exposure Time