Support Information

Novel supramolecular liquid crystal: Cyclodextrin-triphenylene column liquid crystal based on click chemistry

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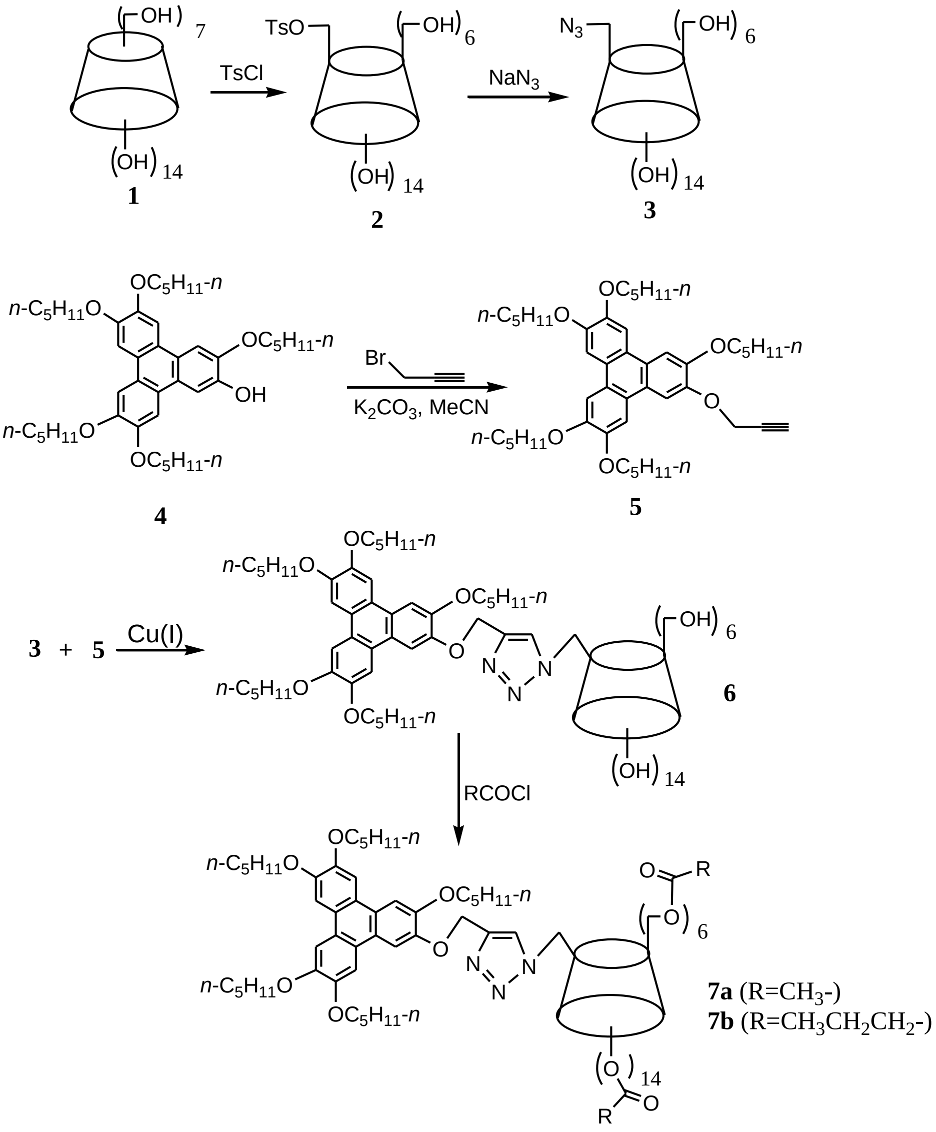
1. General

All chemical reagents were obtained from commercial suppliers and used without further purification. The other organic solvents and inorganic reagents were purified according to standard anhydrous methods before use. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed by using silica gel (200-300 mesh). NMR spectra were recorded in $CDCl_3$ on a Bruker-ARX 400 instrument at 30°C. Chemical shifts are reported in ppm, using tetramethylsilane (TMS) as internal standard. ESI-MS spectra were obtained from DECAX-30000 LCQ Deca XP mass spectrometer. Elemental analyses were performed at Vario EL III Elemental Analyzer. A polarized optical microscopy (Leica DMRX) was used along with a hot stage (Linkam THMSE 600) to examine phase transitions. Thermal analysis of the materials was carried out using a differential scanning calorimeter (DSC) (Thermal Analysis Q100) at a scanning rate of 10°C/min under N_2 atmosphere. X-ray diffraction (XRD) experiments were performed on SEIFERT-FPM (XRD7), using Cu Kα 1.5406 A ° as the radiation source with 40 kV, 30 mA power.

2. The synthetic procedure of β-Cyclodextrin-triphenylene 6, 7a and 7b



2.1 Synthesis of compound 2

According to the published method [*Journal of Chromatography A*, **2009**, 1216(2),257-63], to a NaOH solution (3.6 g, 0.09mol of NaOH in water120mL)was added β-CD (6.0 g, 5.3mmol) at

0-5℃. p-Tolylsulfonyl chloride (TsCl,1.2 g, 6.3mmol) was added into the solution with vigorous stirring at 0-5℃. After 5h at 0-5℃, the precipitate was removed by filtration. 10% HCl was added into the filtrate, and the pH was adjusted to pH=7. The mixture was kept in the refrigerator overnight to afford a white solid product. The white solid was recrystallized in hot water to afford 2.3 g of product (yield 38.3%). The characteristic data were in accordance with literature[*Journal of Chromatography A*, **2009**, 1216(2),257-63].

2.2 Synthesis of compound 3

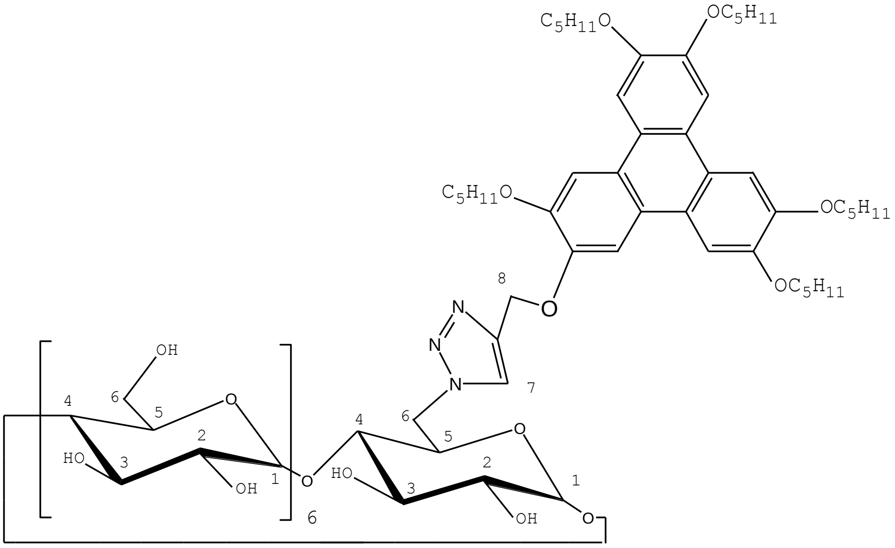
According to the published method [*Journal of Controlled Release*, **2007**, 122(1): 54–62], the compound **2** (3g, 2.2mmol) and sodium azide (0.94g, 14.5mmol) dissolves into the DMF(20mL) and H_2O(3mL). The mixture was stirred at 80℃for 5h and then cooled to room temperature. The resulting solution was precipitated into acetone (80mL) to produce the raw azide product as a white powder. The crude product was recrystallized with little hot water and acetone to give white compound **3** in yield of 65%. The characteristic data were in accordance with literature[*Journal of Controlled Release*, **2007**, 122(1): 54–62].

2.3 Synthesis of compound 5

Monohydroxytriphenylene **4** (0.674g, 1mmol), propargyl bromide (0.2g, 1mmol) and K_2CO_3 (0.5g, 3.6mmol) were refluxed in 30 mL anhydrous acetonitrile for overnight purged with N_2. TLC detection indicated the disappearance of materials. Then the solvent was evaporated under reduced pressure. The residue was treated with 30 mL HCl (10%) and extracted with 40 mL $CHCl_3$. The organic layer was separated, dried over anhydrous $MgSO_4$, and then filtered, concentrated. The residue was recrystallized by MeOH/$CHCl_3$. The compound **5** was obtained as beige solid in yield of 90%. The characteristic data were in accordance with literature [K. Q. Zhao, H. Zhou, W. H. Yu, P. Hu, B. Q. Wang, H. Monobe, Y. Shimizu, *Sci. Sinica. Chimica*., **2011**, *41*, 1565-1574].

2.4 Synthesis of compound 6

Compound **3** (0.31 g, 0.43mmol) with compound **5** (0.5 g, 0.43mmol) was carried out in DMF(20mL) in the presence of Cu(I) generated by the reduction of copper sulfate (0.011g, 0.043mmol) with sodium ascorbate (0.043g, 0.22mmol). The mixture was stirred at 60°C for 8h then cooled to room temperature. TLC detection indicated the disappearance of materials. Then 20 mL distilled water and 30mL of $CHCl_3$ were added into the solution with vigorous stirring at room temperature. Then the solution were formed with three layers: upper layer(DMF and water), middle layer (solid), and lower layer($CHCl_3$).The middle layer was separated out and was further purified by flash column chromatography on silica gel using a mixture of n-butanol: ethanol: water=5:4:3 as eluant. Compound **6** was obtained as green solid in yield of 80%. Compound **6**: ^{1}HNMR(400MHz, DMSO) δppm: 0.93(t, 15H, *J*=6.6Hz, CH_3), 1.41~1.85(m, 30H, CH_2), 3.44~3.65(m, 40H, H2~H6), 4.24(bs, 12H, TpOCH_2 and NCH_2), 4.50~5.88(m, 29H, CH_2, CH and OH), 7.90-8.29(m, 7H, TpH and CH); IR/cm^{-1}: 3395, 2930, 2869, 1690, 1616, 1508, 1432, 1366, 1261, 1156, 1035, 583; MS *m*/*z* (%): 1896.0(MNa$^+$, 100). Anal. calcd. for $C_{88}H_{133}N_3O_{40}$: C 56.43, H 7.16, N 2.24; found C 56.39, H 7.21, N 2.22%.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C5H11O
OC5H11
OC5H11
8
O
N
N
N
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OH
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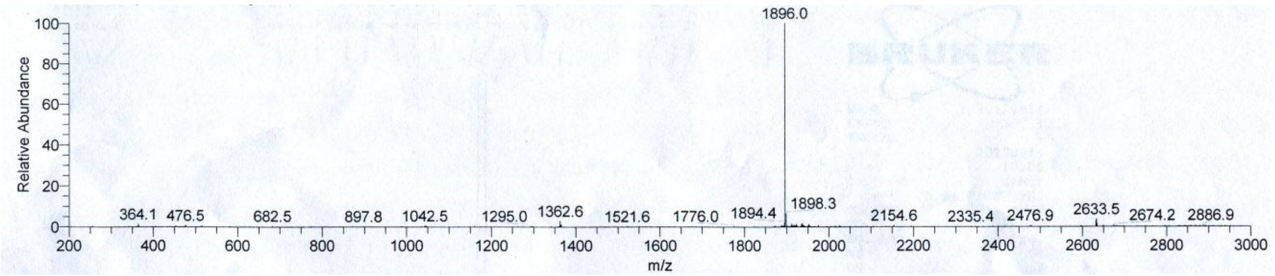
HO
3
2
1
OH
O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1521.6
1776.0
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1898.3
2154.6
2335.4
2476.9
2633.5
2674.2
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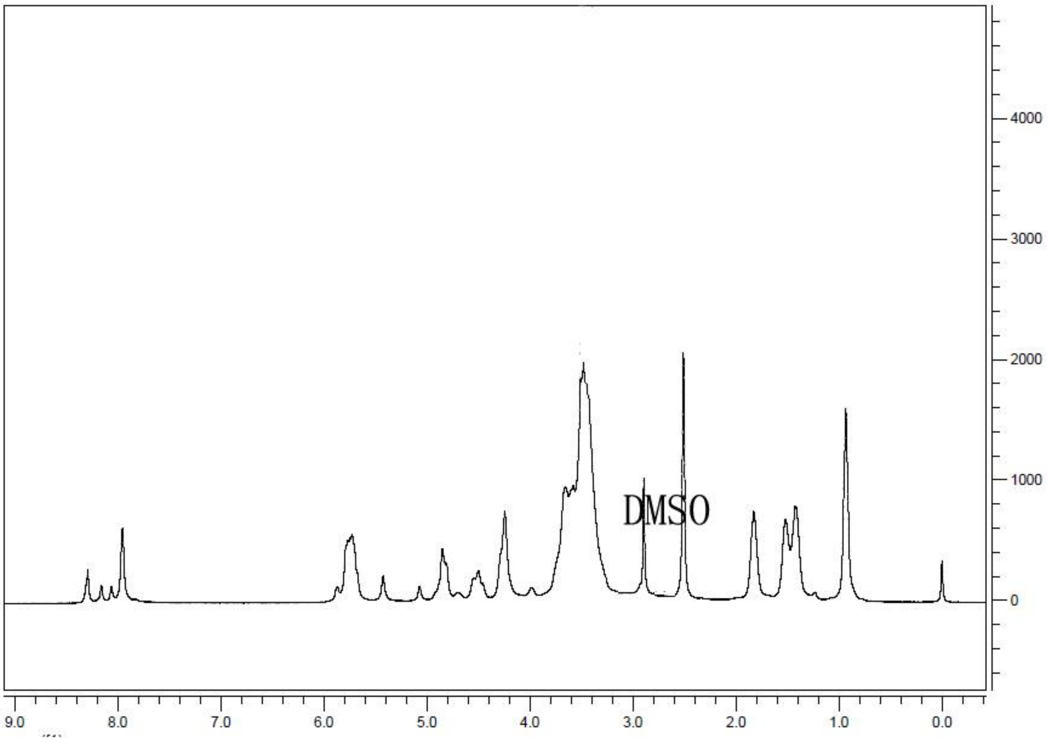
2600
2800
3000
m/z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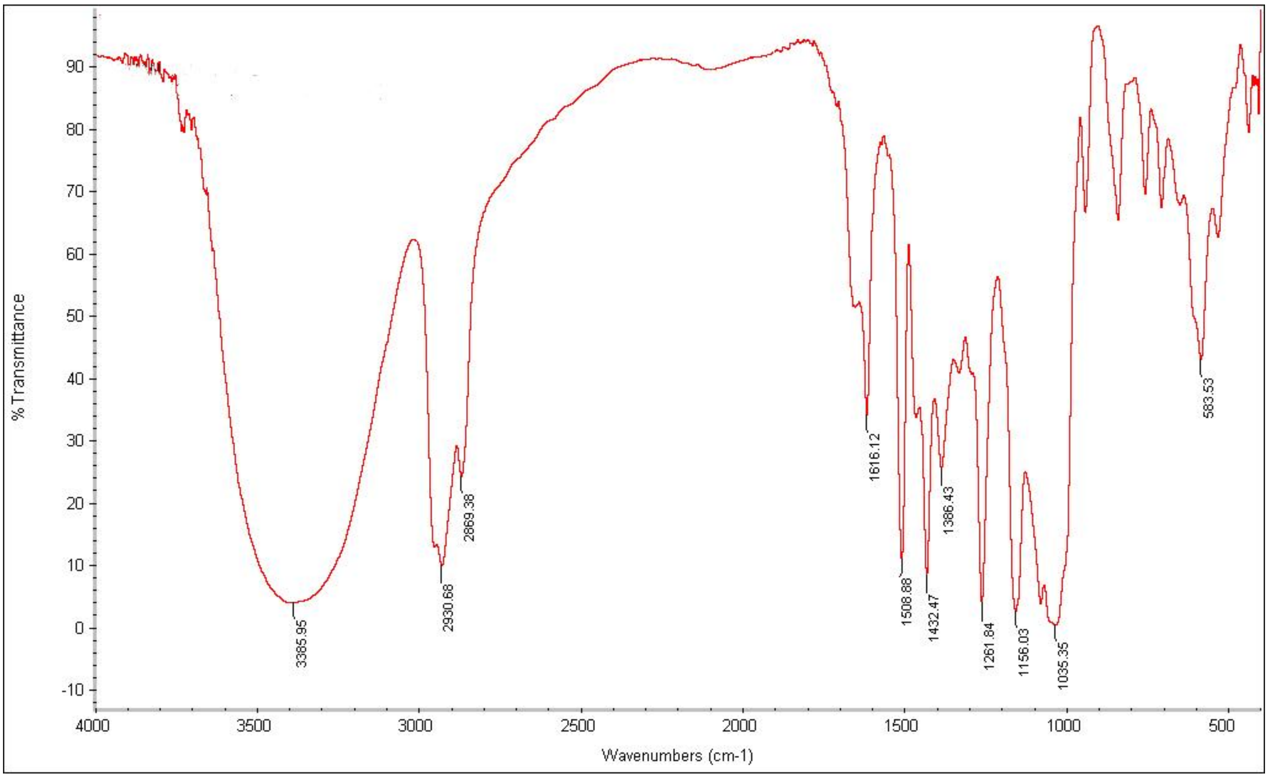
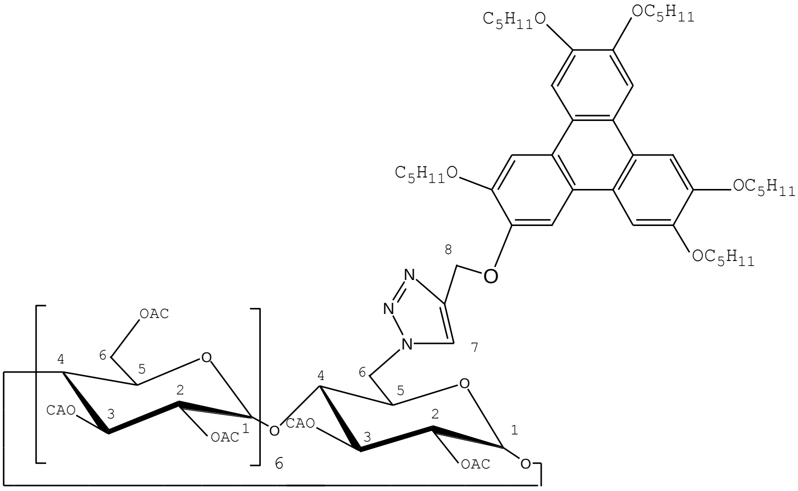
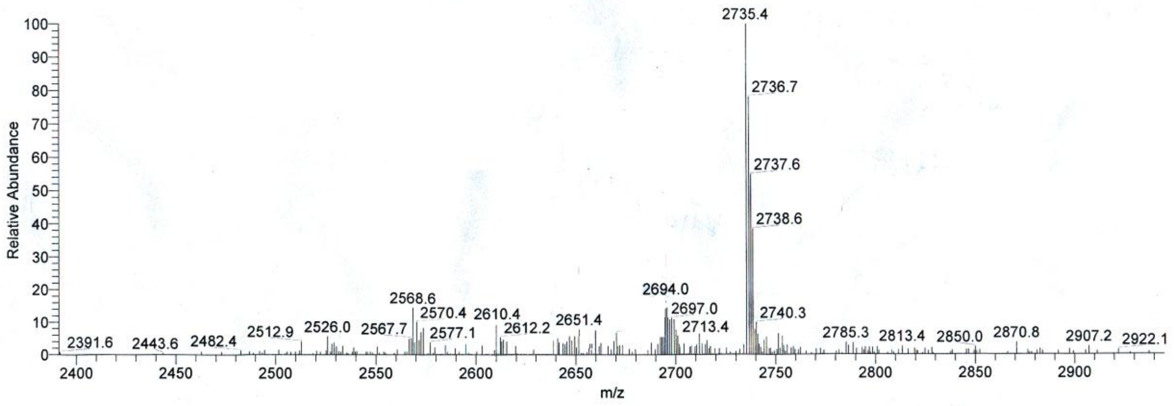
0.0



2.5 Synthesis of compound 7a

Compound **6** (0.3 g, 0.16mmol) and I_2 (0.05g, 0.2mmol) was stirred in acetic anhydride(6mL) for overnight under N_2 atmosphere. Then the mixture was stirred at 40℃ and cooled to room temperature. TLC detection indicated the disappearance of materials. Then 20mL distilled water and sodium thiosulphate(0.05g, 0.2mmol）were added into the solution with vigorous stirring, and the pH was adjusted to pH=7 with $NaHCO_3$. The organic layer was separated with 30mL CH_2Cl_2, dried over anhydrous $MgSO_4$, and then filtered, concentrated and recrystallized in MeOH/CH_2Cl_2. Compound **7a** was obtained as beige solid in yield of 72%. Compound **7a**: ^{1}HNMR (400MHz, $CDCl_3$)δppm: 0.97 (bs, 15H, CH_3), 1.47~1.96(m, 30H, CH_2), 2.10(s, 60H, $COCH_3$), 3.53~5.52 (m, 61H, CH1-5, NCH_2 and OCH_2), 7.84(s, 6H, TpH), 8.11(s, 1H, H7); IR/cm^{-1}: 2929, 2867, 1747, 1616, 1509, 1433, 1372, 1238, 1166, 1042, 699, 603; MS *m/z* (%): 2735.4 (MNa$^+$, 100). Anal. calcd. for $C_{128}H_{173}N_3O_{60}$: C 56.65, H 6.43, N 1.55; found C 56.61, H 6.491, N 1.49%.




Relative Abundance
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2650
2700
2750
2800
2850
2900
2735.4
2736.7
2737.6
2738.6
2740.3
2694.0
2697.0
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2610.4
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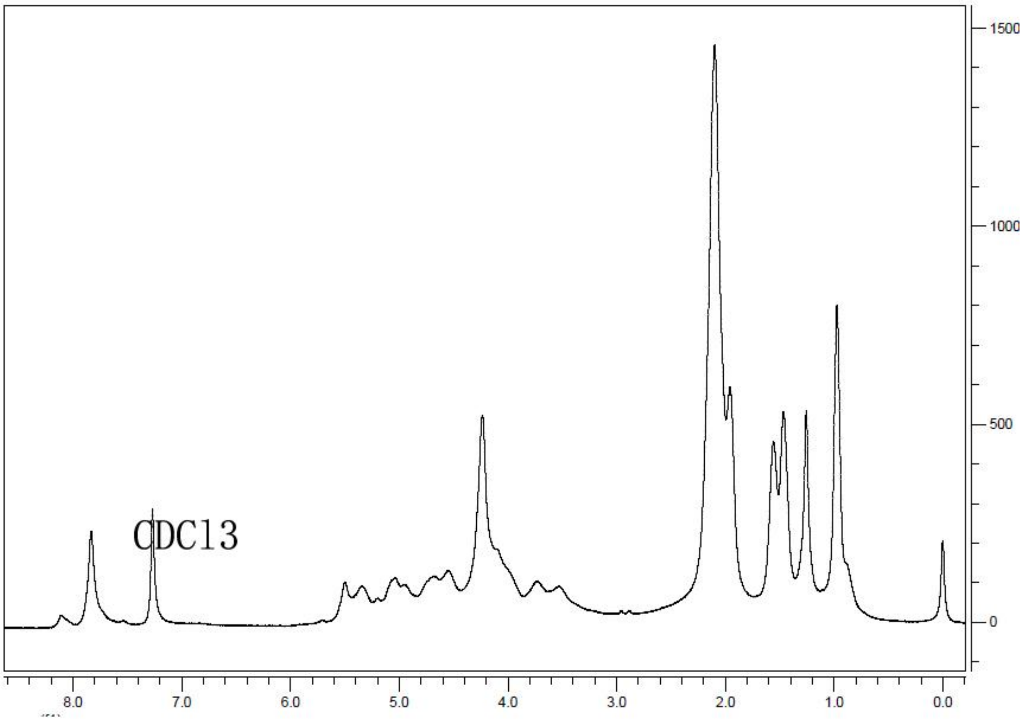
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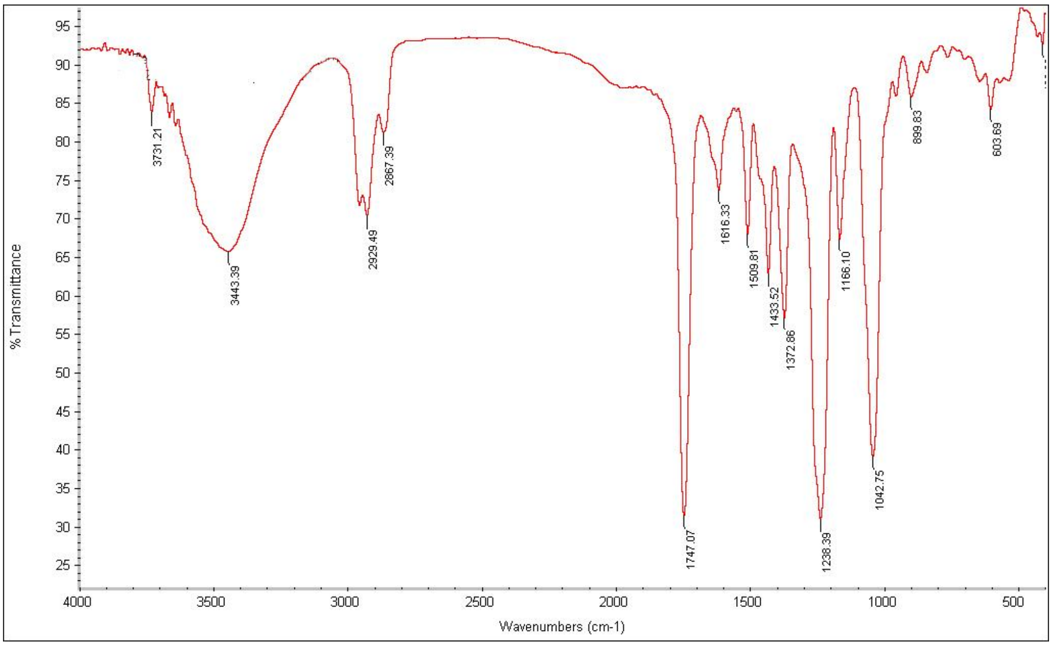
1500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50
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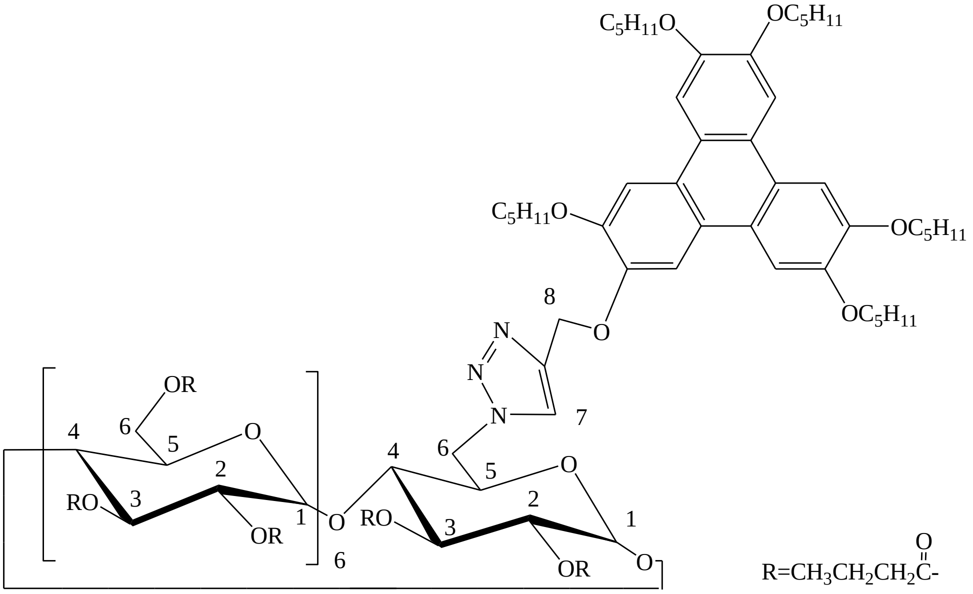
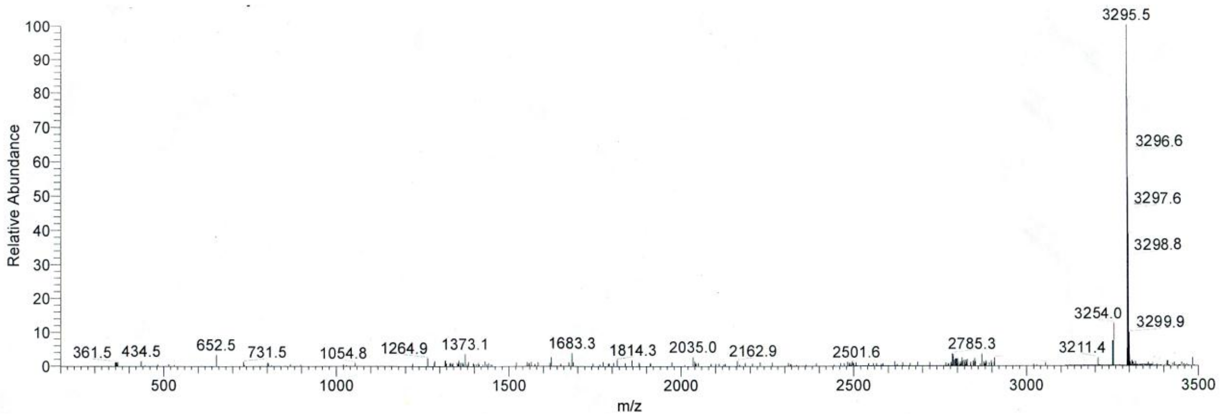
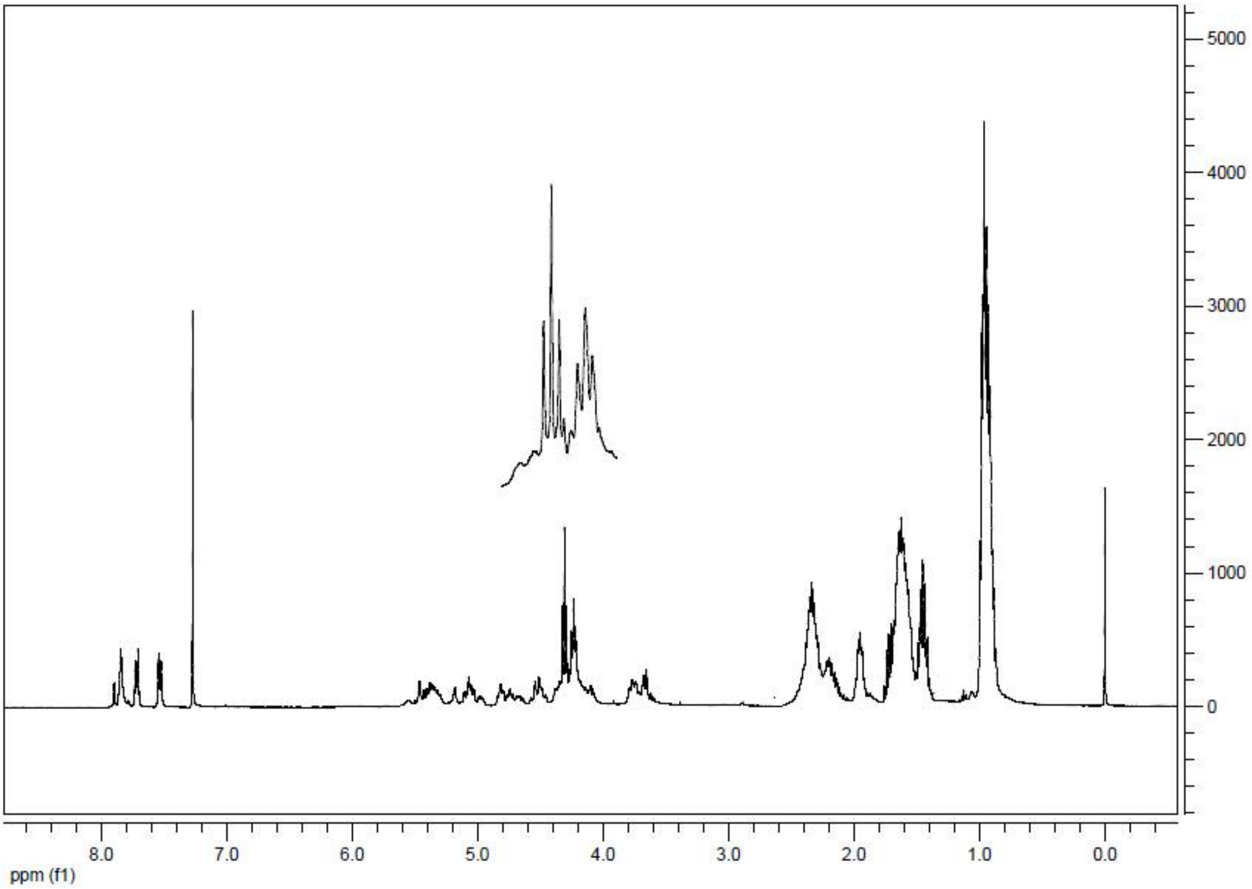
25
4000
3500
3000
2500
2000
1500
1000
500
3731.21
3443.39
2929.49
2867.39
1747.07
1616.33
1509.81
1433.52
1372.86
1238.39
1166.10
1042.75
899.83
603.69

2.6 Synthesis of compound7b

Compound **6**(0.3 g, 0.16mmol) and I_2(0.05g, 0.2mmol) was stirred in n-butyric anhydride (6mL) for overnight under N_2 atmosphere. Then the mixture was stirred at 40℃ and cooled to room temperature. TLC detection indicated the disappearance of materials. Then 20mL distilled water and sodium thiosulphate(0.05g,0.2mmol）were added into the solution with vigorous stirring, and the pH was adjusted to pH=7 with $NaHCO_3$. The organic layer was separated with 30mL CH_2Cl_2, dried over anhydrous $MgSO_4$, and then filtered, concentrated. By the purification of column chromatography on silica gel (100-200 mesh), the column was eluted initially with petroleum ether and then with methyl alcohol as an eluent. Compound **7b** was obtained in the yield of 65%. Compound **7b**: ^{1}HNMR (400MHz,$CDCl_3$) δppm: 0.89~0.99 (t, 75H, CH_3), 1.43~2.27 (m, 110H, CH_2 and CH_2CO), 3.62~5.47 (m, 61H, CH2-5, NCH_2 and $TpOCH_2$), 7.52-7.84(m, 6H, TpH), 7.89(s, 1H, H7); IR/cm^{-1}: 2962, 2874, 1744, 1614, 1510, 1433, 1262, 1170, 1043, 959, 749; MS *m/z* (%): 3295.5 (MNa$^+$, 100). Anal. calcd. for $C_{168}H_{253}N_3O_{60}$: C 61.61, H 7.79, N 1.28; found C 61.66, H 7.89, N 1.26%.



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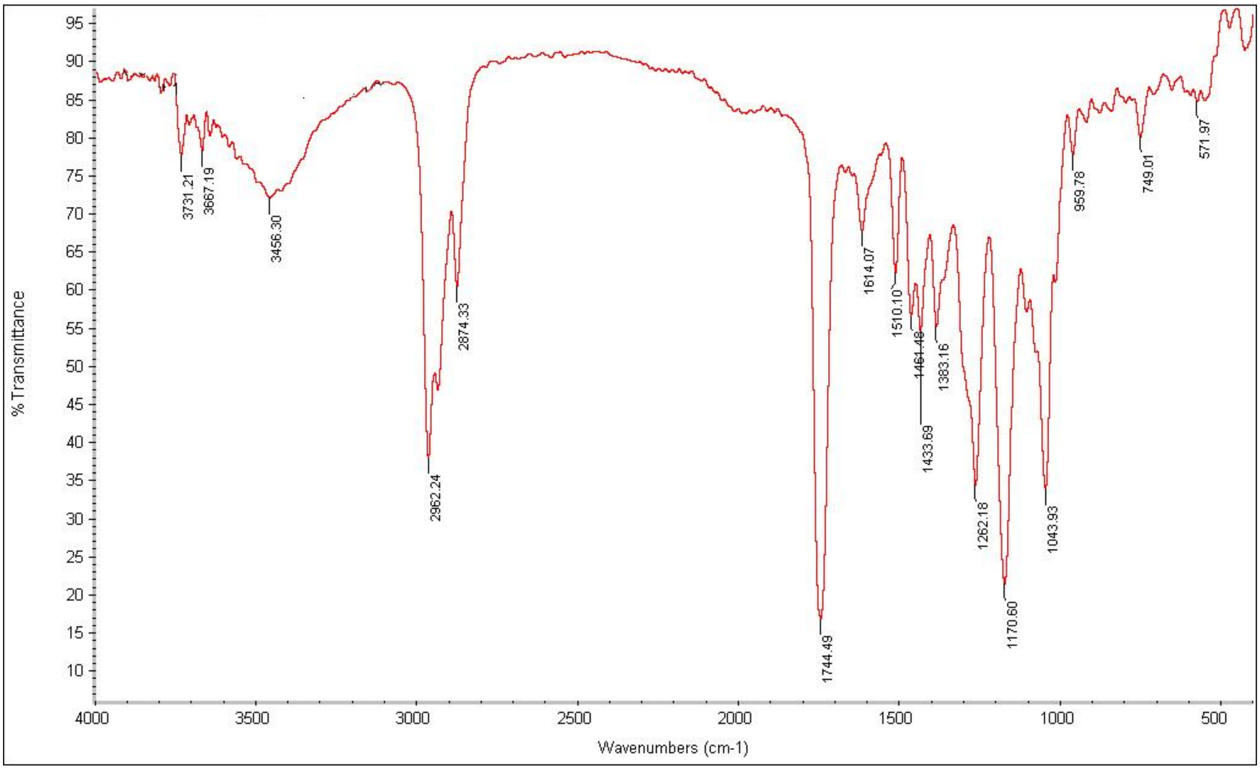
% Transmittance
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