Supporting Information for

Hydrogen-Bonding Induced Melamine-Core Supramolecular Discotic Liquid Crystals

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General considerations.

Cyanuric acid, 3,4-dihydroxy methyl benzoate, 3,4,5-trihydroxy-benzoic acid methyl ester, 1-bromododecane, lithium aluminum hydride, phosphorus tribromide, maleimide, azodiisobutyronitrile (AIBN), tri-n-butyltin hydride (n-Bu_3SnH), melamine, thymine, oxalyl chloride, ammonium acetate, chloroacetyl chloride, otassium o-ethyl xanthate, di-tert-butyl peroxide, dioxane, acetonitrile, o-dichlorobenzene, thymine, di-tert-butyl dicarbonate (Boc_2O), triphenylphosphine and diethylazocarboxylate (DEAD) were purchased from Aladdin Inc (Shanghai). Prior to use, dichloromethane (DCM), toluene, DMSO and DMF were distilled from CaH_2 under nitrogen. Tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl under nitrogen. Other chemical reagents were used as received without further purification. All non-aqueous reactions were conducted in oven-dried glassware, under a dry nitrogen atmosphere. All flash chromatography was performed using

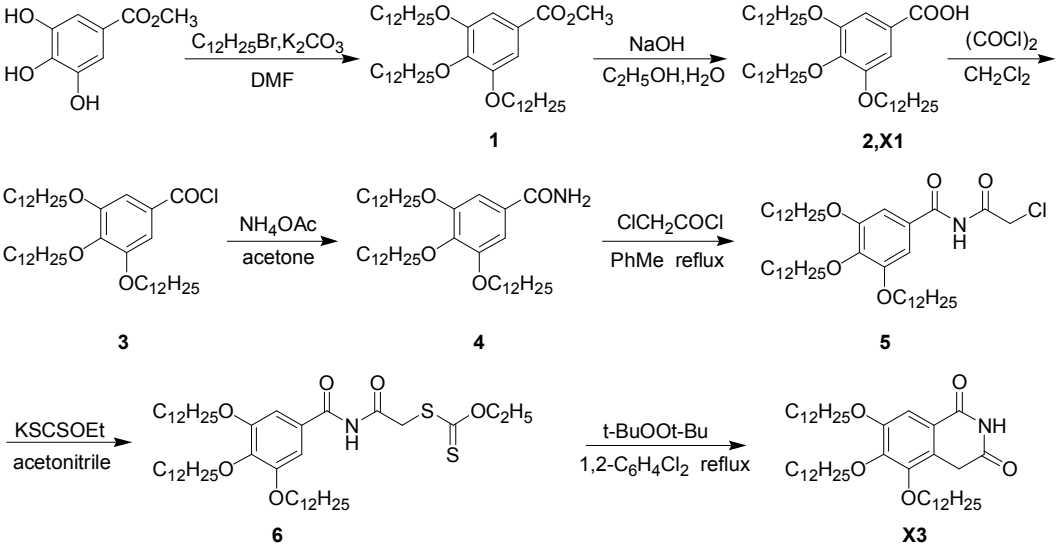
Macherey-Nagel MN Kieselgel 60 (0.063-1.2 mm). Distilled water was used in all the experiments.

In order to confirm the formation of hydrogen bonding between melamine and the synthesized compounds X, nuclear magnetic resonance (NMR) experiments of Compounds X and Mel-X complexes were performed. All ^{1}H NMR spectra were obtained using either a Bruker HW500 MHz spectrometer (AVANCE AV-500) or a Bruker HW300 MHz spectrometer (AVANCE AV-300), deuterated chloroform ($CDCl_3$, internal reference 7.26 ppm) as solvent, tetramethylsilane (TMS) as interior reference. High-resolution mass spectra were obtained with Waters Micromass Q-TOF micro system mass spectrometer in positive ion mode.

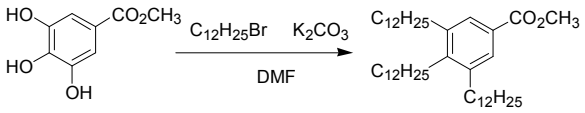
The thermotropic liquid crystalline properties of Compounds X and Mel-X complexes were investigated by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). Differential scanning calorimetry (DSC) spectra were recorded on a TA Instruments Q20 instrument (New Castle, DE) from -10 °C to 250 °C at a rate of 10 °C/min under a nitrogen atmosphere. Polarized optical microscopy (POM) observations of the liquid crystalline textures of all the compounds X and Mel-X complexes were performed on an Olympus BX53P microscope with a Mettler PF82HT hot stage. The images were captured using a Microvision MV-DC200 digital camera with Phenix Phmias2008 Cs Ver2.2 software.

X-ray scattering experiments were performed with a high-flux small angle X-ray scattering (SAXS) instrument (SAXSess, Anton Paar) equipped with Kratky block-collimation system and a temperature control unit (Anton Paar TCS300). At each single steady temperature, small angle X-ray scattering (SAXS) was simultaneously recorded on an imaging-plate (IP), which extended to high-angle range (the q range covered by the IP was from 0.06 to 29 nm^{-1}, $q= 4\pi (\sin \theta) / \lambda$, where the wavelength λ is 0.1542 nm of Cu-Kα radiation and 2θ is the scattering angle) at 40 kV and 40 mA for 30 min.

Synthesis of Compound X3



Scheme S1. The synthetic route of Compound **X3**



1

3,4,5-Tris-dodecyloxy-benzoic acid methyl ester (1). Under a nitrogen atmosphere, methyl 3,4,5-trihydroxy benzoate (3.00 g, 16.30 mmol), anhydrous potassium carbonate (8.40 g, 65.20 mmol) and dry DMF (40 mL) were added into a 150 mL three-neck flask equipped with a nitrogen inlet tube, a water-cooled condenser and a constant pressure funnel. 1-Bromododecane (14.20 g, 57.00 mmol) was then added slowly into the above flask and the mixture was stirred at 80 °C overnight. After cooling to room temperature, the reaction mixture was diluted with 40 mL diethyl ether and the resulting solids were filtered off. The filtrate was washed with 7 % HCl solution (40 mL), deionized water (40 mL) and brine (40 mL) in turn. The organic layer was dried over anhydrous magnesium sulfate, and the filtrate was then concentrated by rotary evaporation. The crude compound was recrystallized in acetone to give the desired product **1** (8.84 g, Yield: 78.8 %) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (s, 2H), 4.01 (t, J = 6.2 Hz, 6H), 3.88 (s, 3H), 1.88 – 1.67 (m, 6H), 1.46 (d, J = 7.1 Hz, 6H), 1.26 (m, 48H), 0.88 (t, J = 6.2 Hz, 9H).

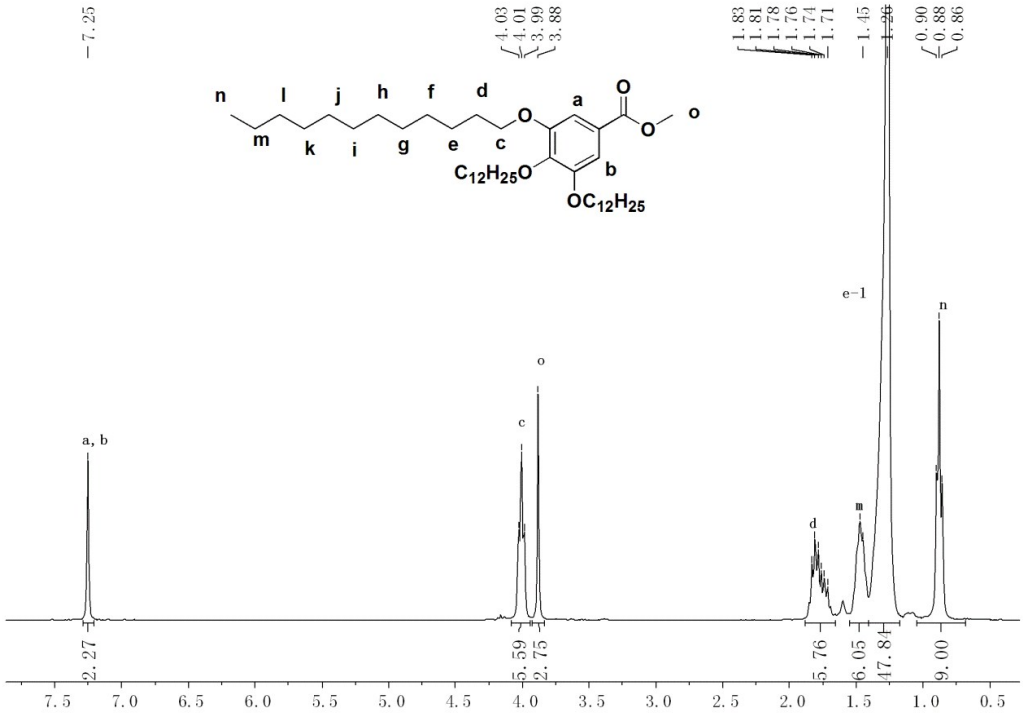
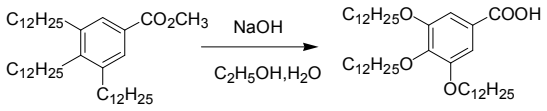


Figure S1. ^{1}H NMR spectrum of compound **1**.



1 2

3,4,5-Tris-dodecyloxy-benzoic acid (2). 3,4,5-Tris-dodecyloxy-benzoic acid methyl ester (4.00 g, 5.81 mmol), sodium hydroxide (0.47 g, 11.62 mmol), ethanol (30 mL) and water (30 mL) were added into a 150 mL round-bottom flask with a water-cooled condenser. The reaction mixture was heated to 80 °C for 10 h. After cooling to room temperature, hydrochloric acid was added into the solution to adjust the pH value to 2. The white precipitate was dissolved in CH_2Cl_2 and washed with brine. The crude mixture was purified by flash column chromatography (petroleum ether : ethyl acetate = 5 : 1) to give the desired product **2** (2.60 g, Yield: 66.4 %) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37 (s, 2H), 4.07 (s, 6H), 1.83 (m, 6H), 1.42 (m, 54H), 0.92 (d, J = 6.5 Hz, 9H).

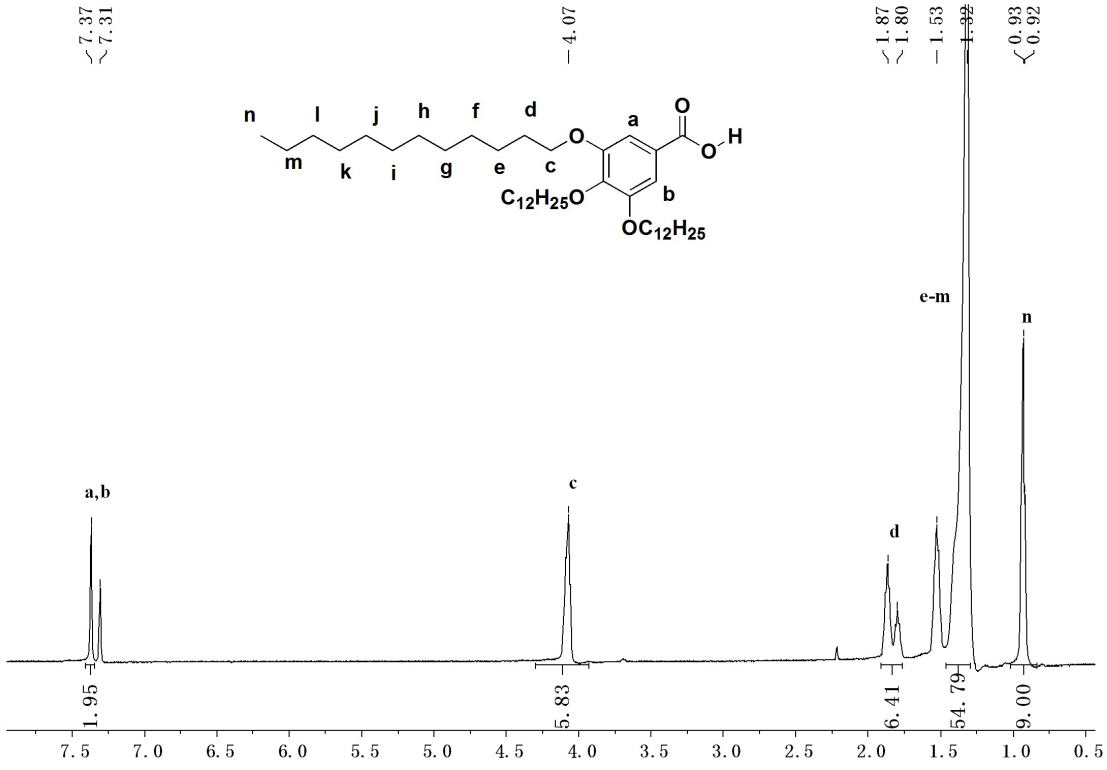
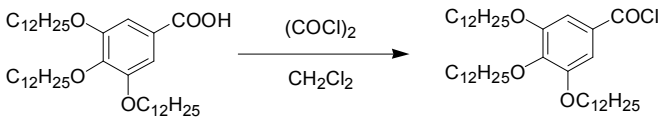
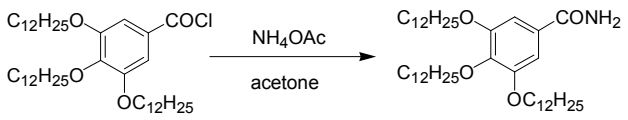


Figure S2. ^{1}H NMR spectrum of compound **2**.



2 **3**

3,4,5-Tris-dodecyloxy-benzoyl chloride (3). 3,4,5-Tris-dodecyloxy-benzoic acid (2.00 g, 2.97 mmol) and dry DCM (5 mL) were added into a 50 mL three-neck flask equipped with a nitrogen inlet tuber and a constant pressure funnel. Oxalyl chloride (1.87 g, 3.70 mmol) in dry DCM (5 mL) was added slowly into the above solution (below 0 °C). The mixture was stirred at room temperature for 4 h. The reaction solution was then concentrated by rotary evaporation to give the product **3,** which was further dried under vacuum and used directly in the next step.



3 4

3,4,5-Tris-dodecyloxy-benzamide (4). 3,4,5-Tris-dodecyloxy- benzoyl chloride (2.06 g, 2.97 mmol), one portion ammonium acetate (0.69 g, 8.91 mmol) and acetone (10 mL) was added in a 50 mL round-bottom flask. After stirring for 48 h at room temperature, the mixture was filtered and the filtrate was concentrated under reduced pressure. The brown residue was recrystallized from ethanol to provide product **4** (1.16 g, Yield: 57.9 %) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33 (s, 2H), 4.05 (m, 6H), 1.95 – 1.66 (m, 6H), 1.60 – 1.13 (m, 54H), 0.90 (t, J = 6.5 Hz, 9H).

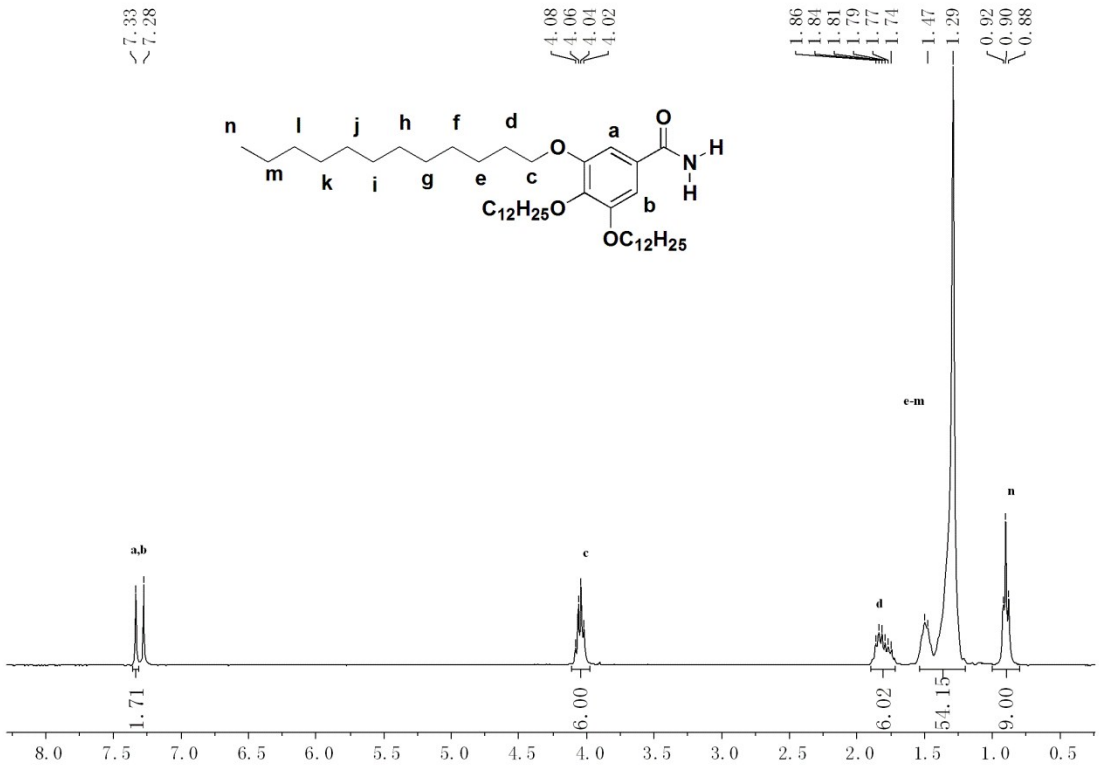
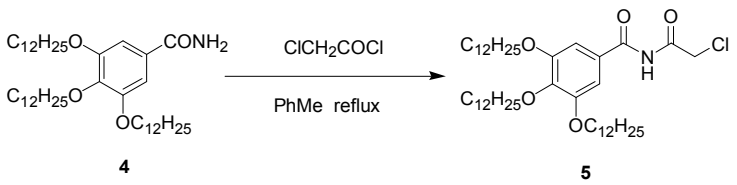


Figure S3. ^{1}H NMR spectrum of compound **4**.



N-(2-Chloroacetyl)-3,4,5-tris-dodecyloxy-benzamide (5). 3,4,5-Tris-dodecyloxy-benzamide (1.16 g, 1.72 mmol) and toluene (10 mL) were added into a 50 mL three-neck flask equipped with a nitrogen inlet tuber and a water-cooled condenser. 2-Chloroacetyl chloride (0.58 g, 5.61 mmol) was added into the above flask *via* a syringe under a nitrogen atmosphere. Then the reaction mixture was stirred at 110 °C for 4 h. The organic solution was concentrated by rotary evaporation. The crude mixture was purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1) to give the desired product **5** (0.80 g, Yield: 62.2 %) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 (s, 2H), 4.15 (s, 2H), 4.03 (m, 6H), 1.92 – 1.67 (m, 6H), 1.37 (m, 54H), 0.87 (d, J = 6.7 Hz, 9H).

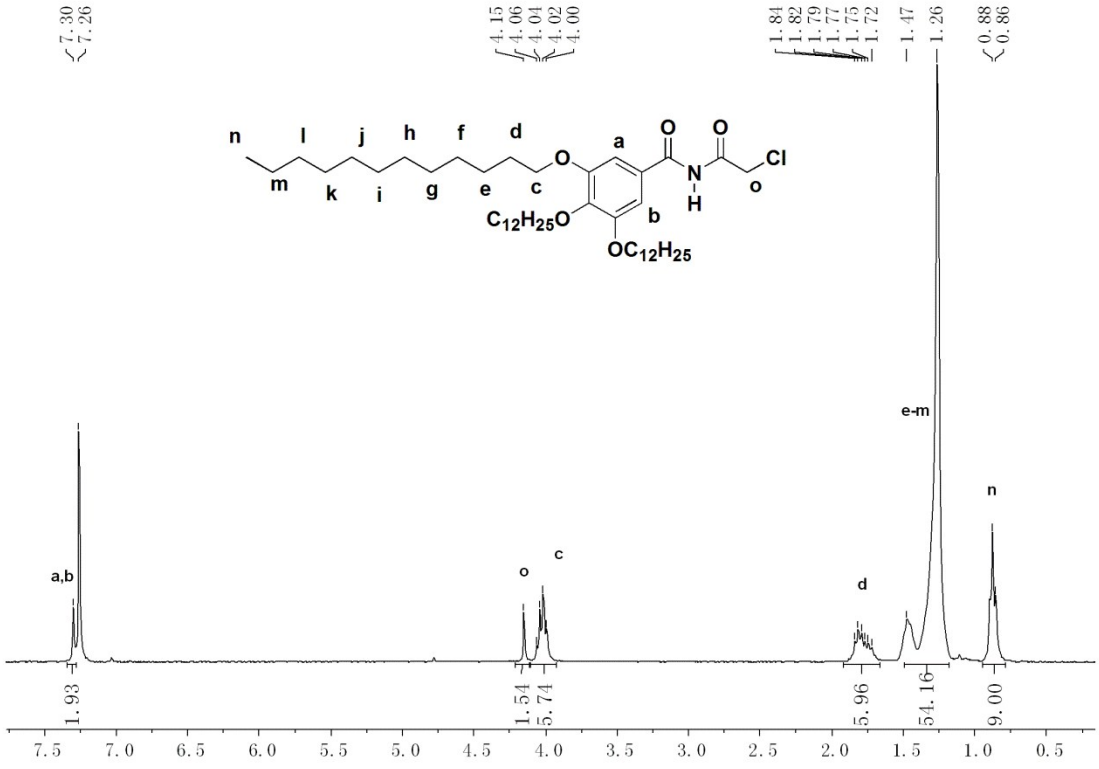
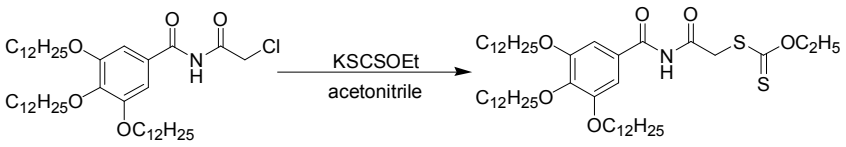


Figure S4. ^{1}H NMR spectrum of compound **5**.



5 6

Dithiocarbonic acid O-ethylester S-[2-oxo-2-(3,4,5-tris-dodecyloxy-benzoylamino) -ethyl] ester (6). Compound **5** (0.34 g, 0.45 mmol) reacted with potassium O-ethyl xanthate (0.09 g, 0.54 mmol) in acetonitrile (5 mL) under nitrogen atmosphere. After a little of water was added into the above reaction solution, precipitates appeared and were then filtered off. The final purification was carried out by column chromatography (petroleum ether : ethyl acetate = 5 : 1) to give the product **6** (0.27 g, Yield: 71.1 %) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31 (s, 2H), 4.03 (m, 8H), 3.05 (s, 2H), 1.92 – 1.65 (m, 6H), 1.37 (m, 54H), 0.88 (t, J = 6.6 Hz, 12H).

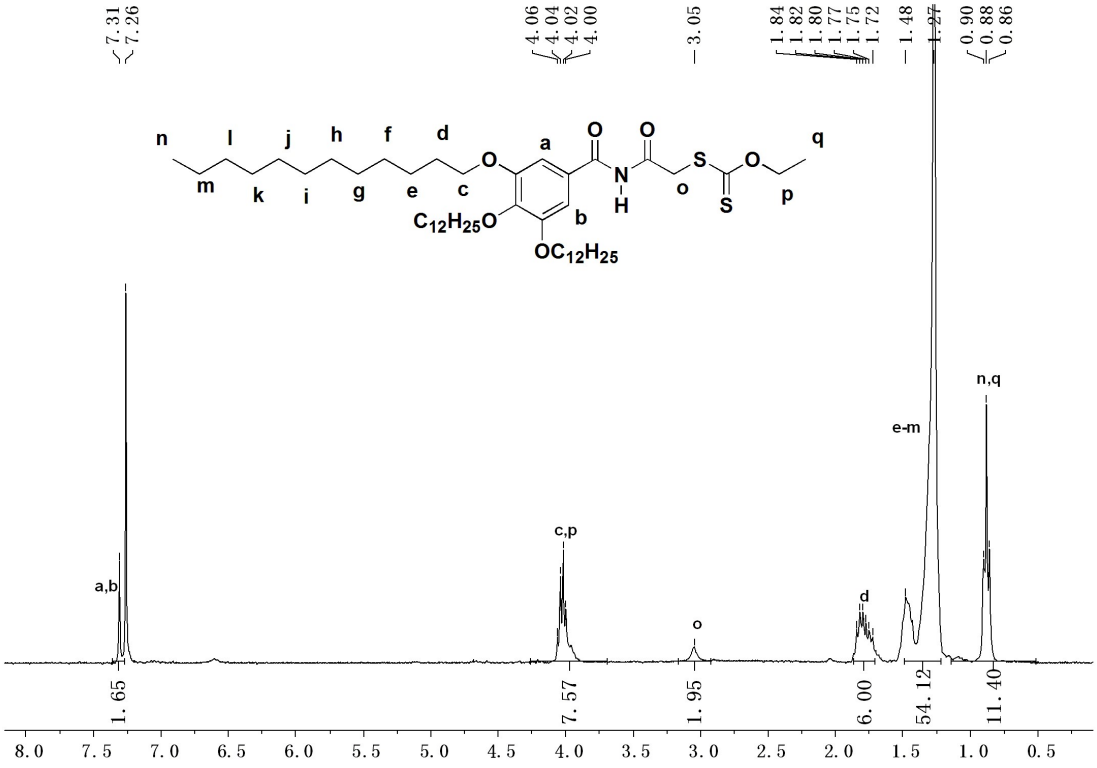
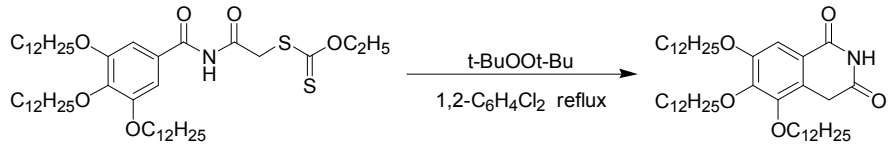


Figure S5. ^{1}H NMR spectrum of compound **6**.



6 X3

5,6,7-Tris-dodecyloxy-4H-isoquinoline-1, 3-dione (X3). Compound **6** (0.27 g, 0.32 mmol) and o-dichlorobenzene (5 mL) were added into a 50 mL three-neck round-bottom flask and stirred for 1 h under nitrogen atmosphere. Then the solution of di-tert-butyl peroxide (0.38 g, 2.58 mmol) in o-dichlorobenzene (2 mL) was added slowly into the above resulting mixture. After cooling the mixture to room temperature, the precipitate was collected and dried. The resulting crude solid was purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1) to give the compound **X3** (0.05 g, Yield: 21.1 %) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32 (s, 1H), 6.61(s, 1H), 4.18 – 3.86 (m, 6H), 3.05 (s, 2H), 1.95 – 1.62 (m, 6H), 1.58 – 1.09 (m, 54H), 0.88 (t, J = 6.1 Hz, 9H).

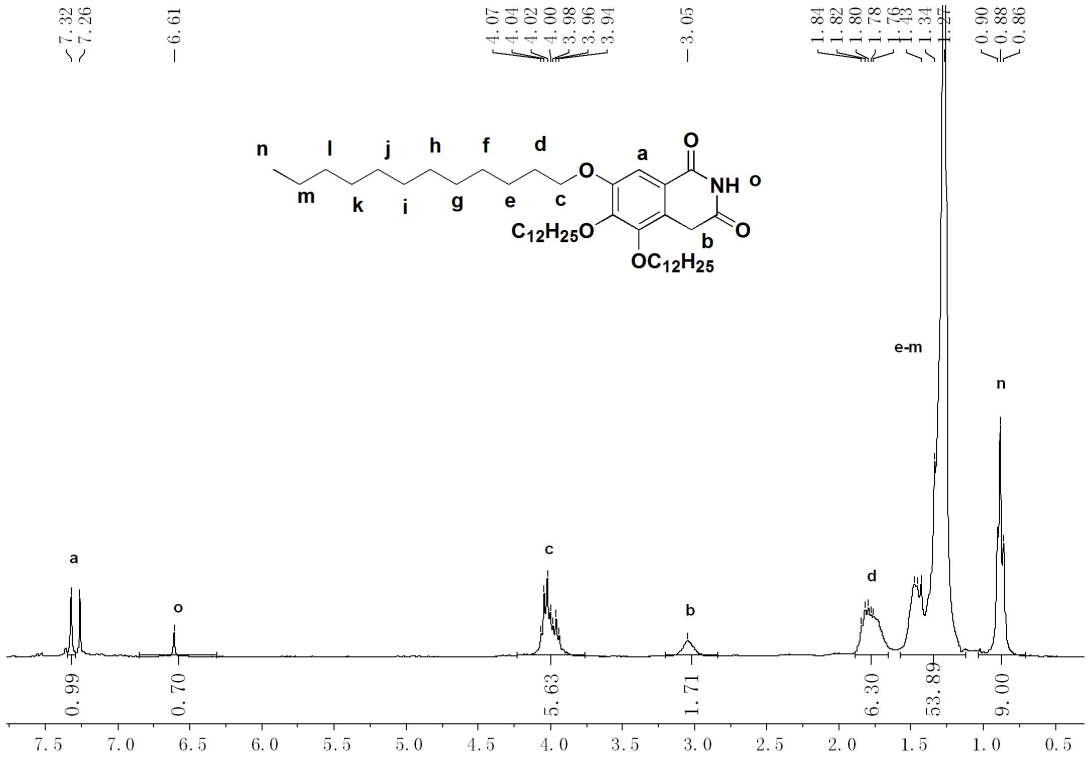
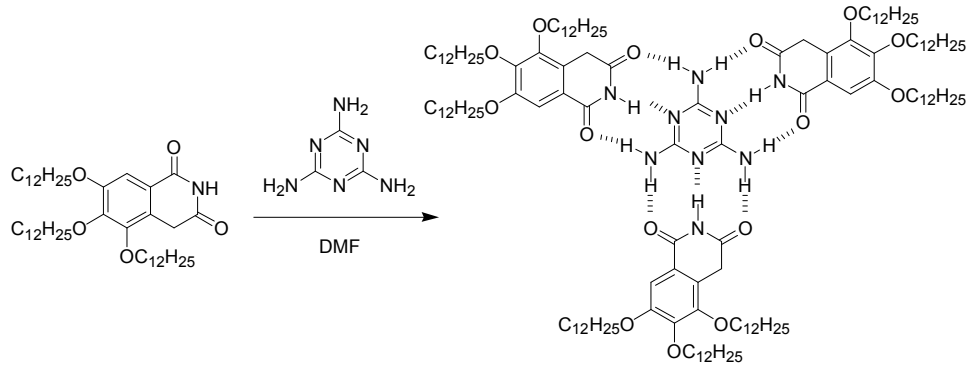


Figure S6. ^{1}H NMR spectrum of Compound **X3**.



X3 Mel-X3

Complex Mel-X3. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (s, 1H), 6.11 (s, 1H), 4.03 (m, 6H), 2.87 (d, J = 1.0 Hz, 2H), 1.95 – 1.69 (m, 6H), 1.67 – 1.05 (m, 54H), 0.88 (t, J = 8.4 Hz, 9H).

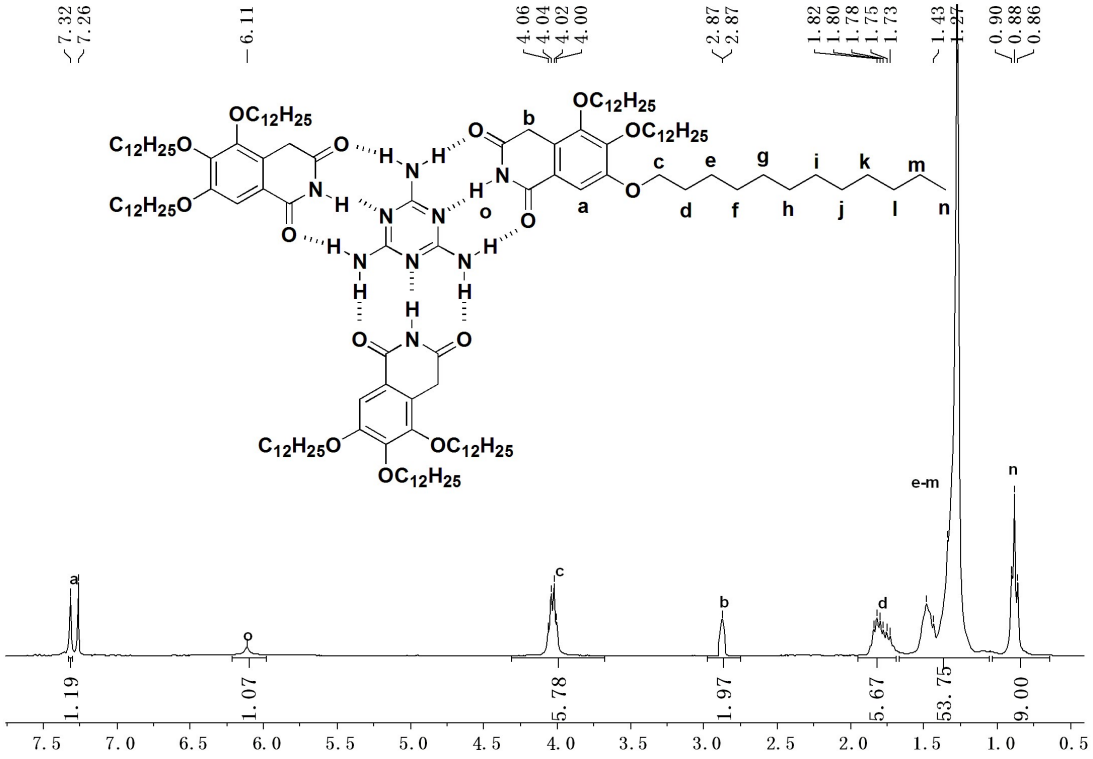
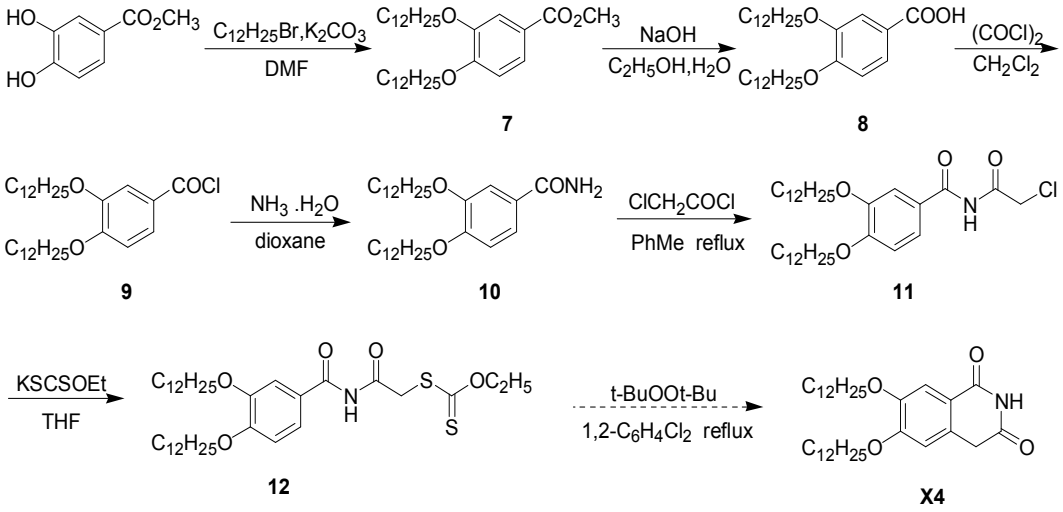
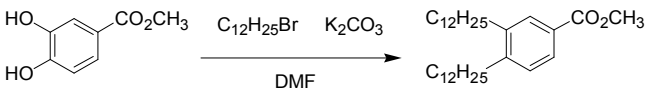


Figure S7. ^{1}H NMR spectrum of Complex **Mel-X3**.

Synthesis of Compound X4



Scheme S2. The synthetic route of Compound **X4**



7

3,4-Bis-dodecyl-benzoic acid methyl ester (7). Under a nitrogen atmosphere, methyl 3,4-dihydroxy benzoate (8.00 g , 47.61 mmol), anhydrous potassium carbonate (26.28 g, 190.44 mmol) and dry DMF (150 mL) were added into a 250 mL three-neck flask equipped with a nitrogen inlet tube, a water-cooled condenser and a constant pressure funnel. 1-Bromododecane (29.64 g, 119.02 mmol) was then added slowly into the above flask and the reaction mixture was stirred at 80 °C overnight. After cooling to room temperature, the reaction mixture was diluted with 150 mL dry ether and then the resulting solids were filtered off. The filtrate was washed with 7 % HCl solution (200 mL), deionized water (200 mL) and brine (200 mL) in turn. The organic layer was dried over anhydrous magnesium sulfate, and the filtrate was then concentrated by rotary evaporation. The crude compound was recrystallized from acetone to give the desired product **7** (18.30 g, Yield: 76.3 %) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, J = 8.3 Hz, 1H), 7.53 (s, 1H), 6.85 (d, J = 8.3 Hz, 1H), 4.03 (s, 4H), 3.87 (s, 3H), 1.82 (s, 4H), 1.46 (d, J = 6.4 Hz, 4H), 1.37 – 1.10 (m, 32H), 0.87 (t, J = 6.4 Hz, 6H).

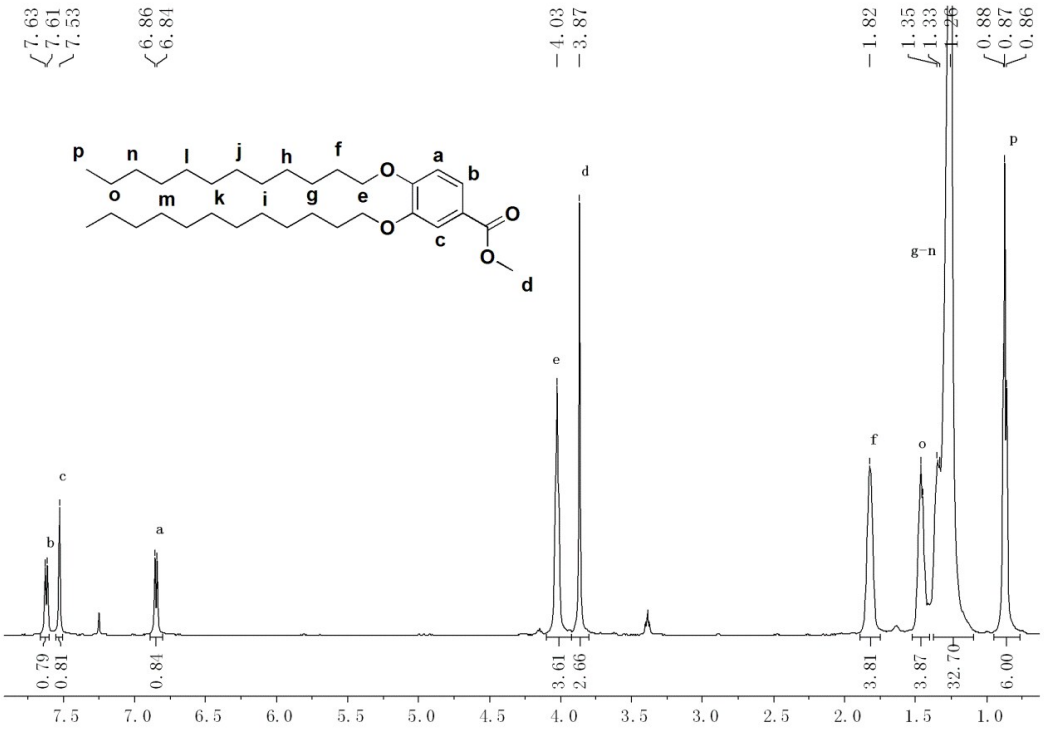
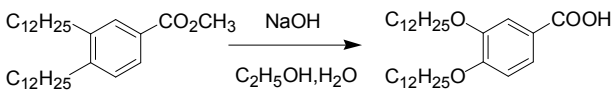


Figure S8. ^{1}H NMR spectrum of compound **7**.



7 8

3,4-Bis-dodecyloxy-benzoic acid (8). 3,4-Bis-dodecyloxy-benzoic acid methyl ester (18.00 g, 35.68 mmol), sodium hydroxide (2.85 g, 71.36 mmol) , ethanol (100 mL) and water (100 mL) were added into a 500 mL round-bottom flask with a water-cooled condenser. The reaction mixture was heated to 80 °C for 10 h. After cooling to room temperature, hydrochloric acid was added into the solution to adjust the pH value to 2. The white precipitate was dissolved in CH_2Cl_2 and washed with brine. The crude mixture was purified by flash column chromatography (petroleum ether : ethyl acetate = 5 : 1) to give the desired product **8** (13.70 g, Yield: 78.0 %) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (m, 1H), 7.58 (d, J = 1.8 Hz, 1H), 6.89 (d, J = 8.5 Hz, 1H), 4.06 (m, 4H), 1.85 (m, 4H), 1.34 (m, 36H), 0.88 (t, J = 6.6 Hz, 6H).

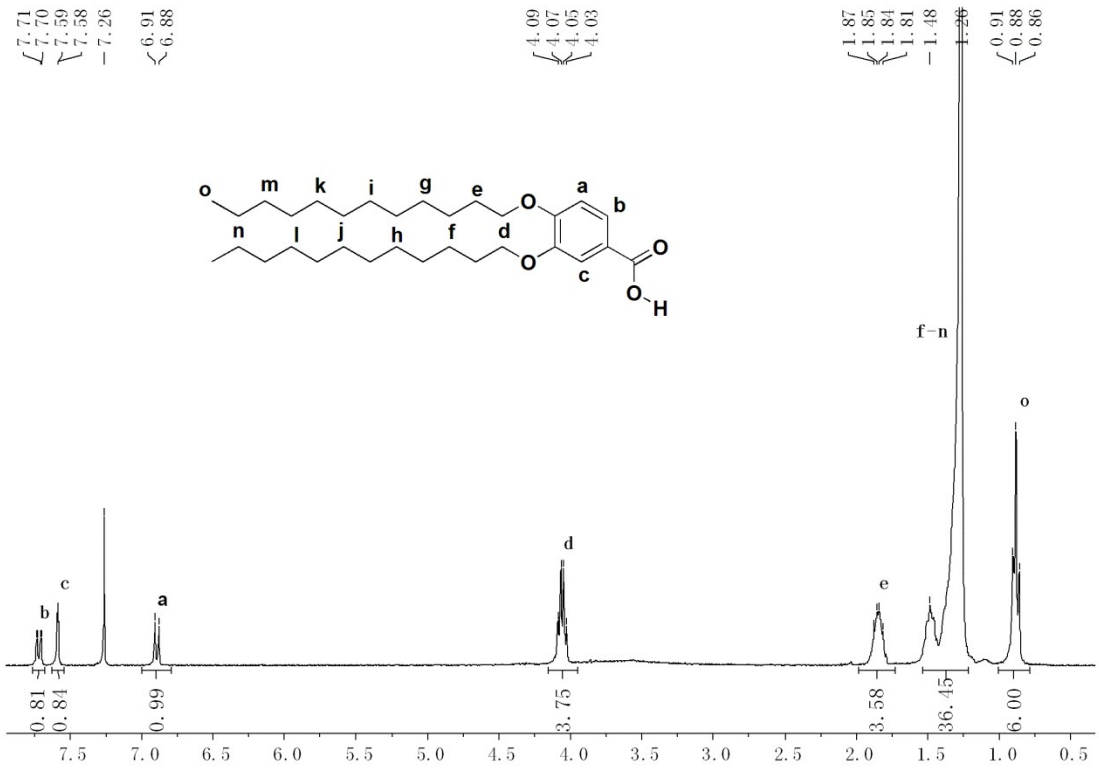
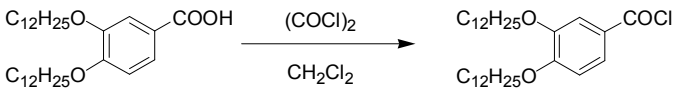
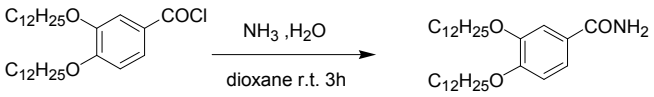


Figure S9. ^{1}H NMR spectrum of compound **8**.



8 **9**

3,4-Bis-dodecyloxy-benzoyl chloride (9). 3,4-Bis-dodecyloxy-benzoic acid (13.70 g, 27.94 mmol) and dry DCM (25 mL) were added into a 250 mL three-neck flask equipped with a nitrogen inlet tuber, a constant pressure funnel and a water-cooled condenser. Oxalyl chloride (17.73 g, 139.70 mmol) dissolved in dry DCM (100 mL) was added slowly into the above solution (below 0 °C). After adding two drops of DMF into the above reaction flask, the mixture was stirred vigorously at room temperature for 4 h. The reaction solution was then concentrated by rotary evaporation to give the desired product **9,** which was further dried under vacuum and used directly in the next step.



9 10

3,4-Bis-dodecyloxy-benzamide (10). The solution of 3,4-bis-dodecyloxy-benzoyl chloride (14.20 g, 27.90 mmol) in dry 1,4-dioxane (100 mL) was added slowly to conc. aqueous NH_3 (100 mL) (below 0 °C) in a 250 mL three-neck flask *via* a constant pressure funnel. After stirring for 4 h at room temperature, the mixture was poured into ice-cooled deionized water (100 mL). The resulting mixture was acidified by diluted HCl solution to the pH value of 3. The precipitate was then washed with deionized water until the pH value was about 7. The reaction product was recrystallized from ethyl acetate to provide the desired product **10** (9.97 g, Yield 73.0 %) as a white powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, J = 1.9 Hz, 1H), 7.34 (m, 1H), 6.91 (d, J = 8.3 Hz, 1H), 4.09 (m, 4H), 1.87 (m, 4H), 1.53 – 1.25 (m, 36H), 0.93 (t, J = 6.9 Hz, 6H).

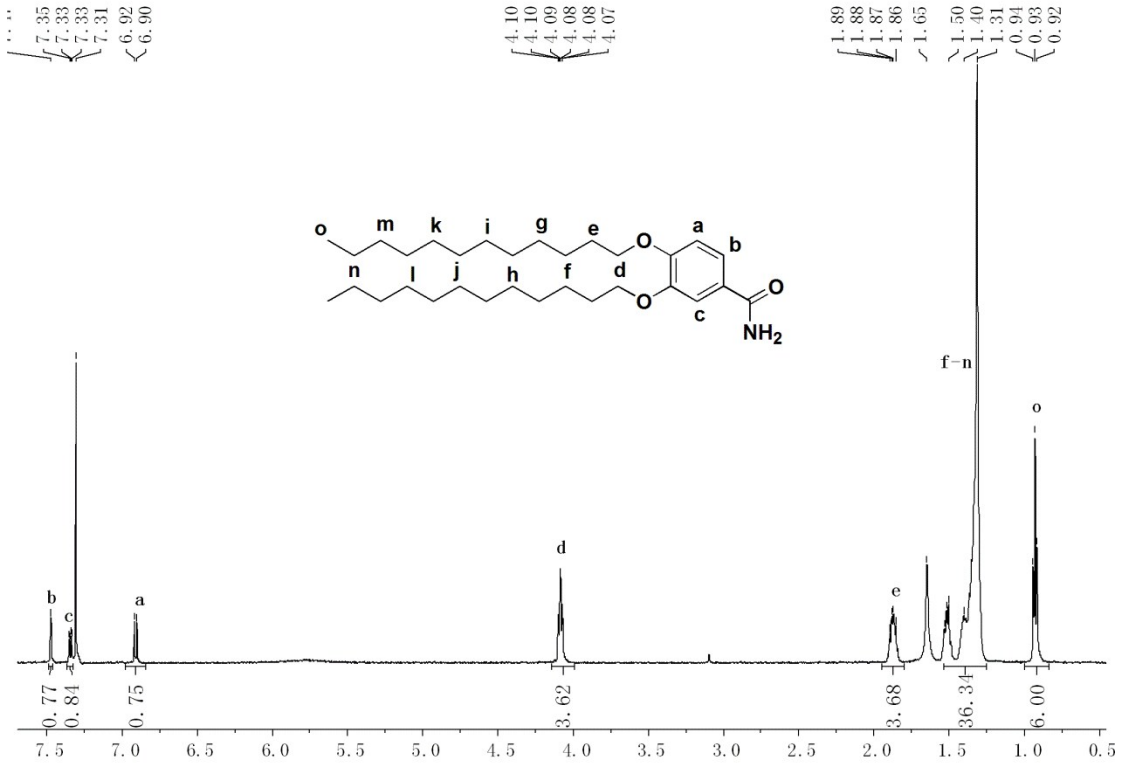
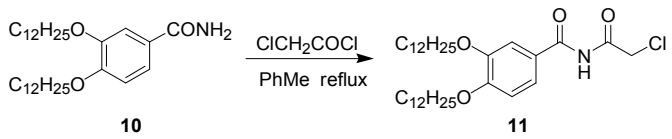


Figure S10. ^{1}H NMR spectrum of compound **10**.



10 11

N-(2-chloroacetyl)-3,4-bis-dodecyloxy-benzamide (11).

3,4-Bis-dodecyloxy-benzamide (9.97 g, 20.37 mmol) and toluene (100 mL) were added into a 250 mL three-neck flask equipped with a nitrogen inlet tuber and a water-cooled condenser. 2-Chloroacetyl chloride (6.90 g, 61.11 mmol) was added into the above flask *via* a syringe under a nitrogen atmosphere. The reaction mixture was then heated to 110 °C and stirred for 4 h. The resulting solution was concentrated by rotary evaporation. The crude mixture was purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1) to give the desired product **11** (6.50 g, Yield: 56.4 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.76 (s, 1H), 7.43 – 7.32 (m, 2H), 6.90 (d, J = 8.3 Hz, 1H), 4.77 (s, 2H), 4.05 (m, 4H), 1.84 (s, 4H), 1.63 – 1.17 (m, 36H), 0.88 (t, J = 6.4 Hz, 6H).

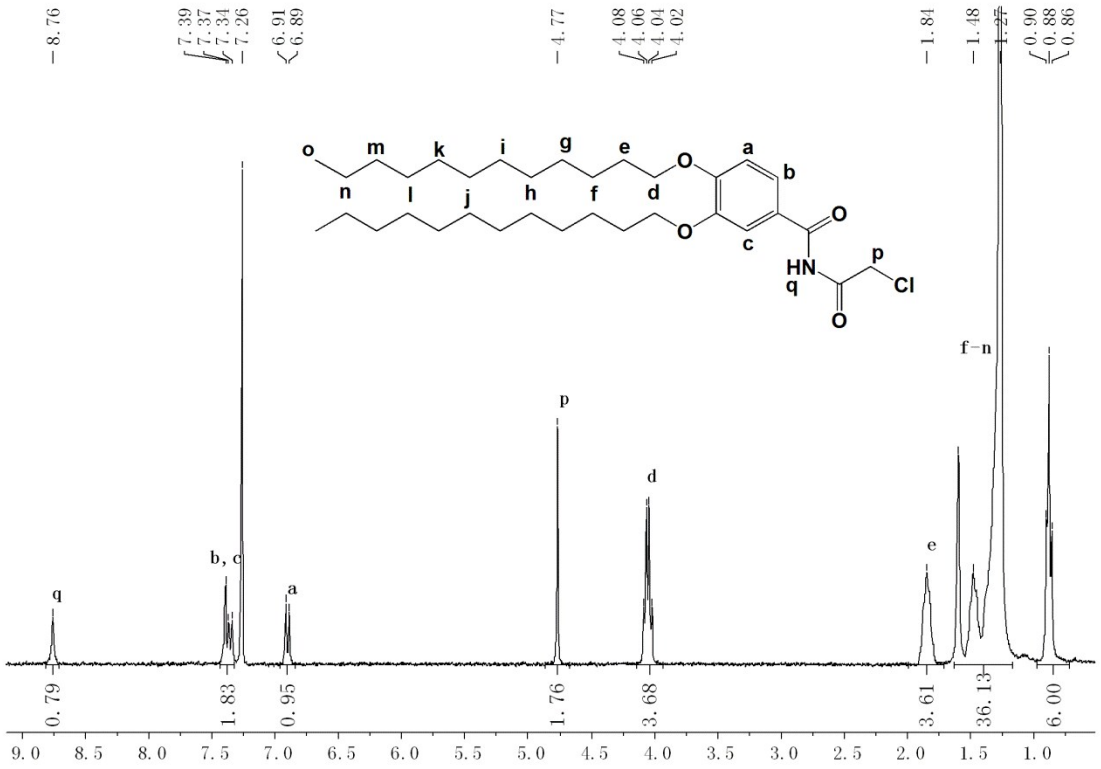
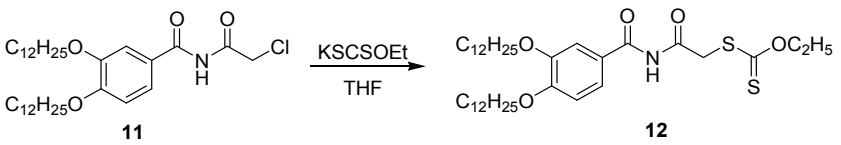


Figure S11. ^{1}H NMR spectrum of compound **11**.



Dithiocarbonic acid O-ethylester S-[2-oxo-2-(3,4 -bi-dodecyloxy-benzoylamino) -ethyl] ester (12). Compound **11** (6.50 g, 11.50 mmol) reacted with potassium O-ethyl xanthate (2.21 g, 13.80 mmol) in THF (50 mL) under a nitrogen atmosphere. The above mixture was stirred for 24 h at room temperature. The excess solvent was evaporated under reduced pressure. Then the final purification was carried out by column chromatography (petroleum ethe r: ethyl acetate = 5 : 1) to give the desired product **12** (4.20 g, Yield: 56.1 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.71 (s, 1H), 7.39 (m, 2H), 6.91 (s, 1H), 4.67 (d, J = 7.1 Hz, 2H), 4.59 (s, 2H), 4.05 (s, 4H), 1.85 (s, 4H), 1.62 – 1.17 (m, 39H), 0.87 (d, J = 6.6 Hz, 6H).

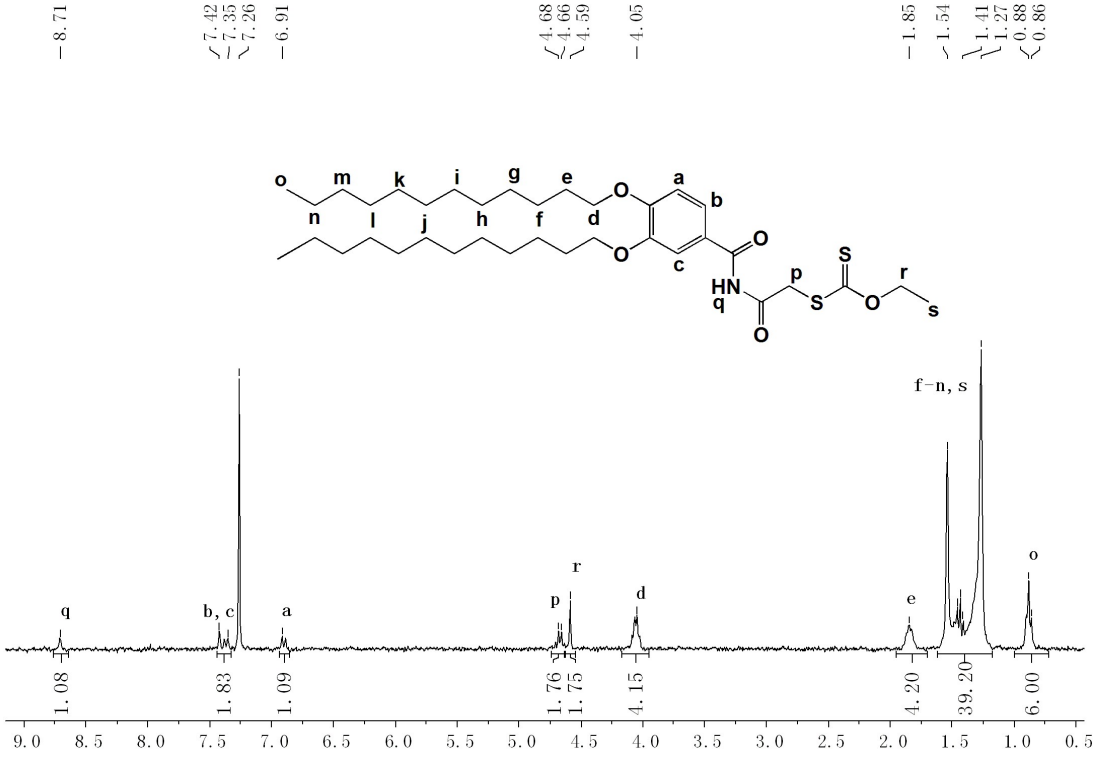
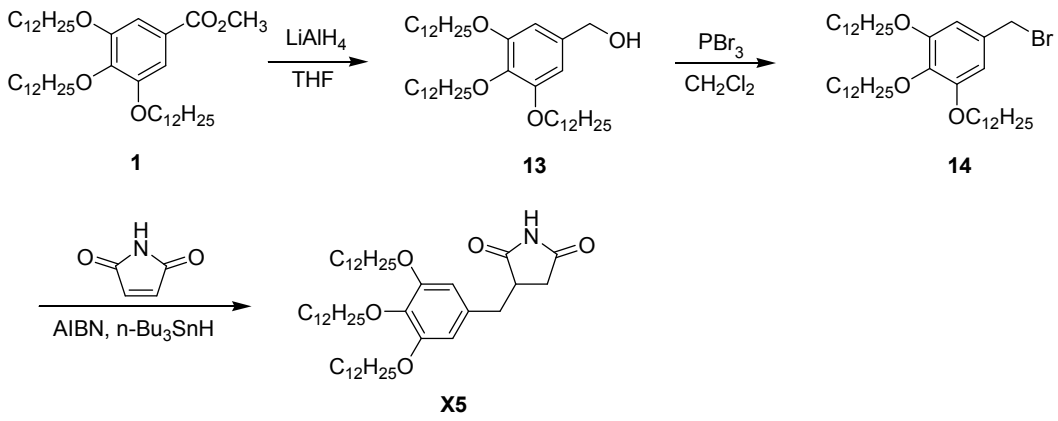
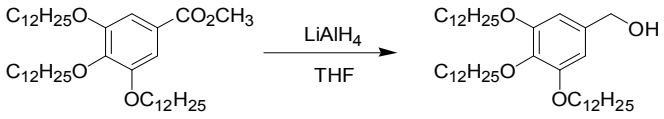


Figure S12. ^{1}H NMR spectrum of compound **12**.

Synthesis of Compound X5



Scheme S3. The synthetic route of Compound **X5**



1 **13**

3,4,5-Tris-dodecyloxy-benzyl alcohol (13). 3,4,5-tris-dodecyloxy-benzoic acid methyl ester (4.00 g, 5.81 mmol) and dry THF (20 mL) were added into a 100 mL three-neck flask equipped with a nitrogen inlet tube and a constant pressure funnel. The solution of $LiAlH_4$ (0.44 g, 11.63 mmol) in dry THF (20 mL) was added slowly into the above flask by a constant pressure funnel (below 0 °C). The resulting reaction mixture was stirred at room temperature for 12 h, which was quenched by adding a small amount of methanol and deionized water. After the residual solid was filtered off, the filtrate was concentrated by rotary evaporation. The resulting solid was dissolved in CH_2Cl_2 (60 mL) and washed with deionized water (40 mL) and brine (40 mL) in turn. The separated organic phase was dried over anhydrous magnesium sulfate and filtered, and the filtrate was concentrated under reduced pressure to give the crude product. The final purification was carried out by column chromatography (petroleum ether : ethyl acetate = 5 : 1) to give the desired product **13** (3.00 g, Yield: 78.2 %) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.56 (s, 2H), 4.59 (s, 2H), 4.14 – 3.72 (m, 6H), 1.92 – 1.62 (m, 6H), 1.46 (s, 6H), 1.26 (m, 48H), 0.88 (t, J = 6.2 Hz, 9H).

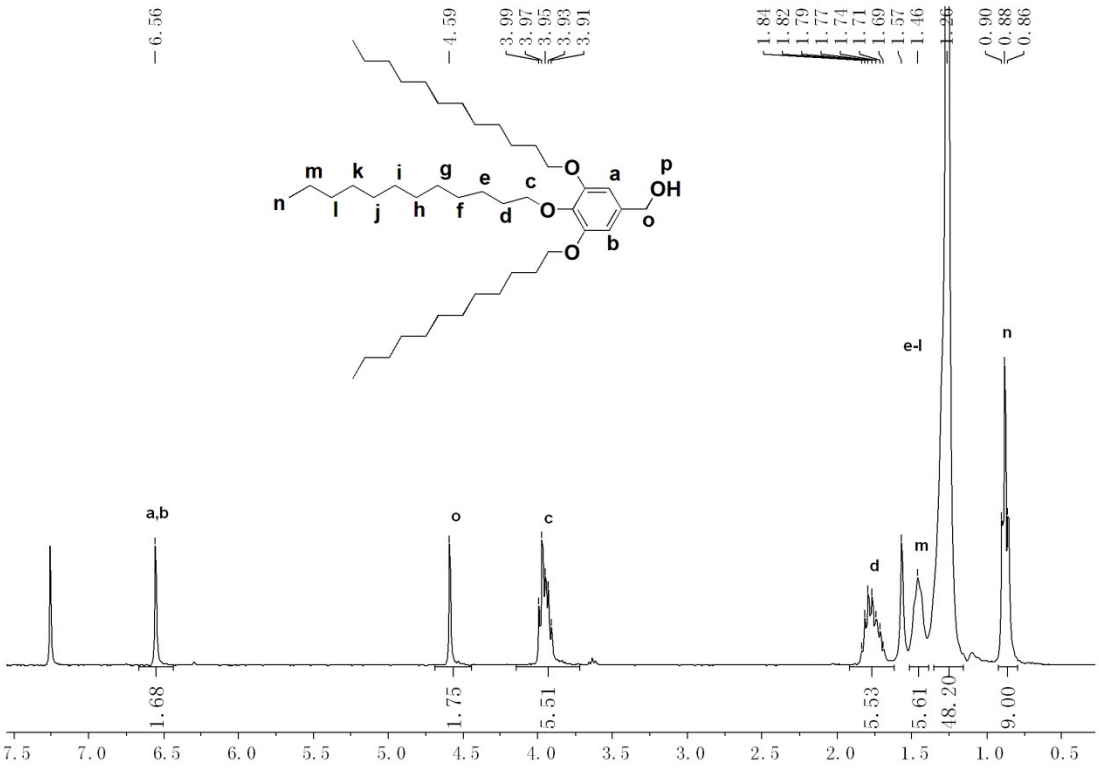
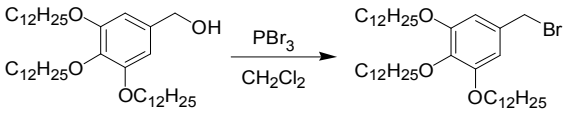


Figure S13. ^{1}H NMR spectrum of compound **13**.



13 14

5-Bromomethyl-1,2,3-tris-dodecyloxy-benzene (14). Compound **13** (2.00 g, 3.03 mmol) and dry CH_2Cl_2 (30 mL) were added into a 100 mL three-neck flask equipped with a nitrogen inlet tube and a constant pressure funnel. PBr_3 (1.64 g, 6.06 mmol) was then added slowly into the above flask by a constant pressure funnel (below 0 °C) under a nitrogen atmosphere. The reaction solution was stirred at room temperature for 5 h. The resulting mixture was then diluted with plenty of deionized water and extracted with CH_2Cl_2 for 3 times (60 mL × 3). The coalescent organic phase was washed with deionized water and saturated sodium chloride in turn, and then the organic layer was dried over anhydrous magnesium sulfate. Finally, the filtrate was concentrated under reduced pressure to give the desired product **14** (1.80 g, Yield: 82.3 %) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.57 (s, 2H), 4.43 (s, 2H), 3.95 (m, 6H), 1.79 – 1.71 (m, 6H), 1.46 (s, 6H), 1.27 (m, 48H), 0.87 (d, J = 6.5 Hz, 9H).

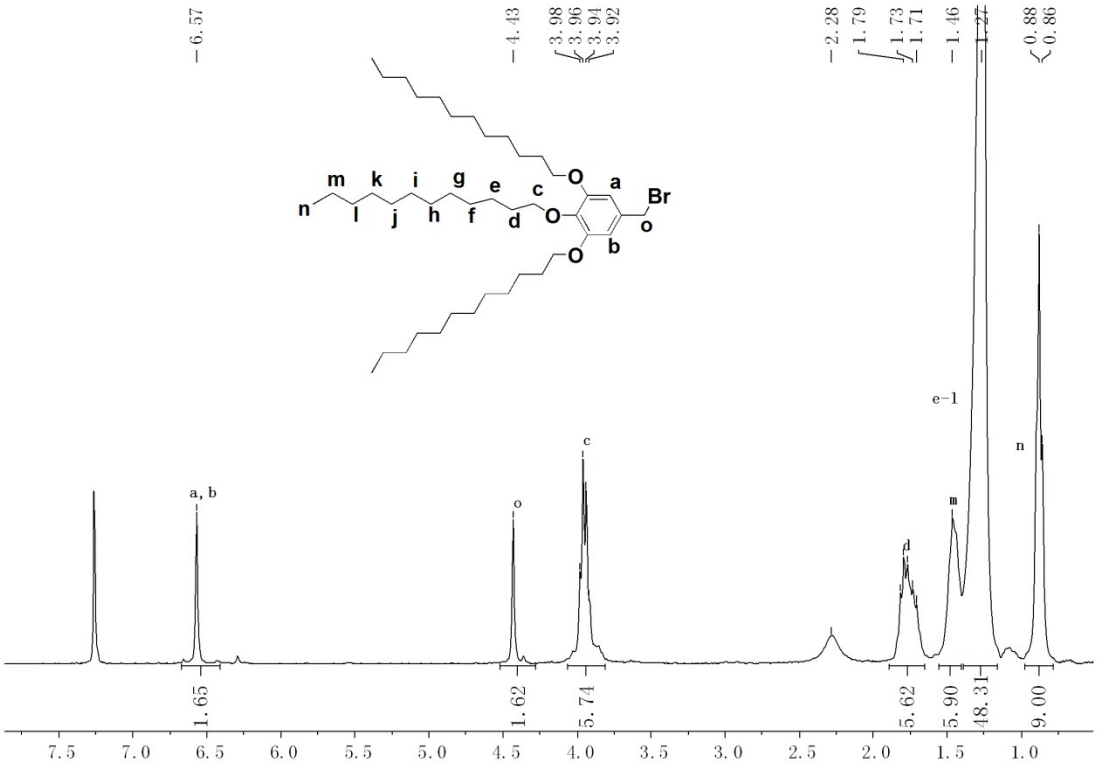
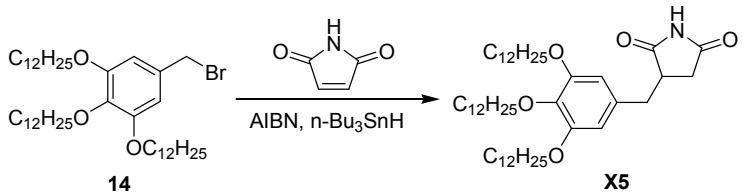


Figure S14. ^{1}H NMR spectrum of compound **14**.



14 X5

3-(3,4,5-Tris-dodecyloxy-benzyl)-pyrrolidine-2,5-dione (X5). Under a nitrogen atmosphere, compound **14** (1.20 g, 1.66 mmol), maleimide (0.16 g, 1.66 mmol), AIBN (0.03 g, 0.17 mmol) and anhydrous toluene (10 mL) were added into a 50 mL three-neck flask. n-Bu_3SnH (0.58 g, 1.99 mmol) was then added slowly into the above flask *via* a syringe under a nitrogen atmosphere. The reaction mixture was heated to 65 °C and stirred at 65 °C for 20 h. After cooling to room temperature, the resulting solution was concentrated by rotary evaporation, and then the precipitate was dissolved into diethyl ether (20 mL) and washed twice with deionized water (20mL × 2). Then the resulting organic layer was dried over anhydrous magnesium sulfate. After filtering off the precipitate, the reaction mixture was stirred at room temperature for another 30 min. The excess solvent was then removed by rotary evaporation and the resulting crude solid was purified by column chromatography (petroleum ether : ethyel acetate=5 : 1) to give the desired product **X5** (0.10 g, Yield: 8.1 %) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (s, 1H), 6.34 (s, 2H), 3.93 (t, J = 6.2 Hz, 6H), 3.13 (s, 2H), 2.90 – 2.68 (m, 2H), 2.53 (m, 1H), 1.86 – 1.64 (m, 6H), 1.36 (m, 54H), 0.88 (t, J = 6.3 Hz, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.25, 176.17, 153.36, 137.46, 132.02, 107.61, 73.39, 69.28, 42.92, 31.88, 29.49, 26.07 , 22.63, 14.03. ESI-MS m/z: 740.5 $[m + H]^+$, calculated for X5: 741.6.

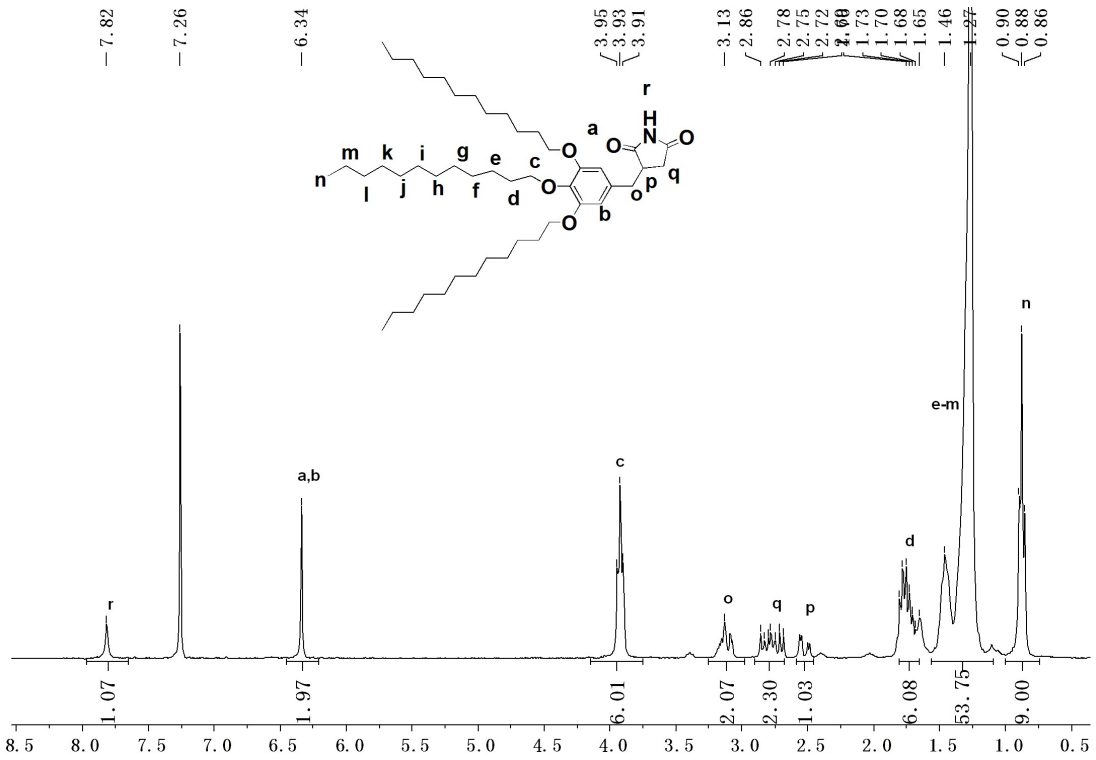


Figure S15. ^{1}H NMR spectrum of Compound **X5**.

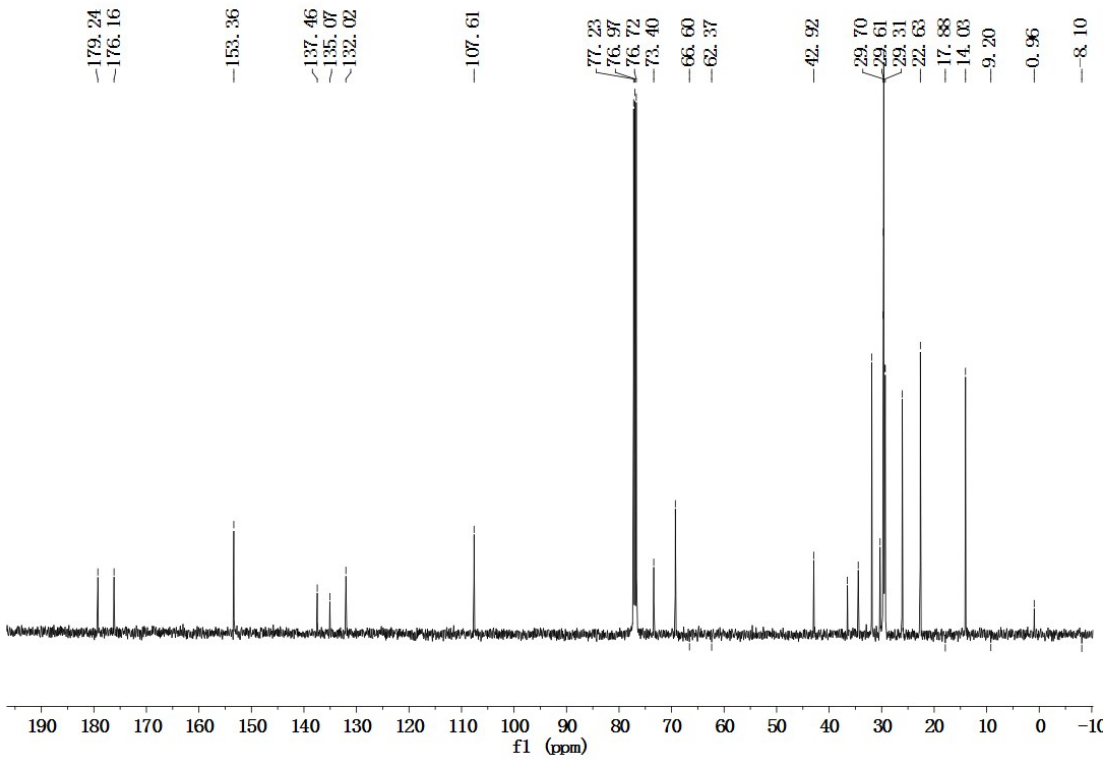


Figure S16. ^{13}C NMR spectrum of Compound **X5**.

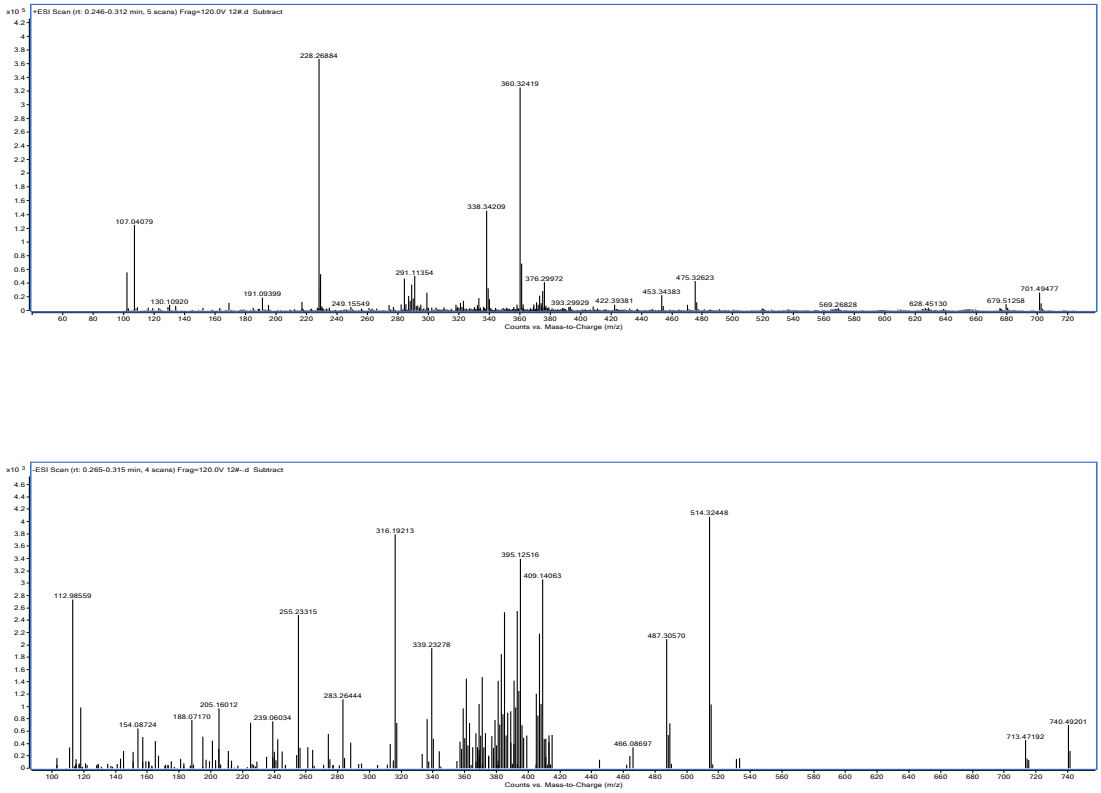
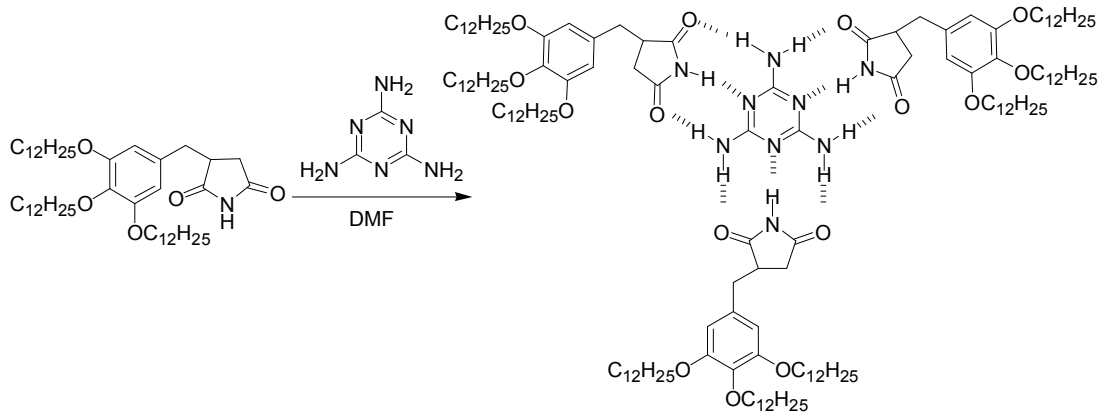


Figure S17. MS diagrams of Compound **X5**.



Complex Mel-X5. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (s, 1H), 6.34 (s, 2H), 3.93 (t, J = 6.3 Hz, 6H), 3.13 (s, 2H), 2.86 – 2.68 (m, 2H), 2.53 (m, 1H), 1.84 – 1.68 (m, 6H), 1.50 – 1.21 (m, 54H), 0.88 (t, J = 6.4 Hz, 9H).

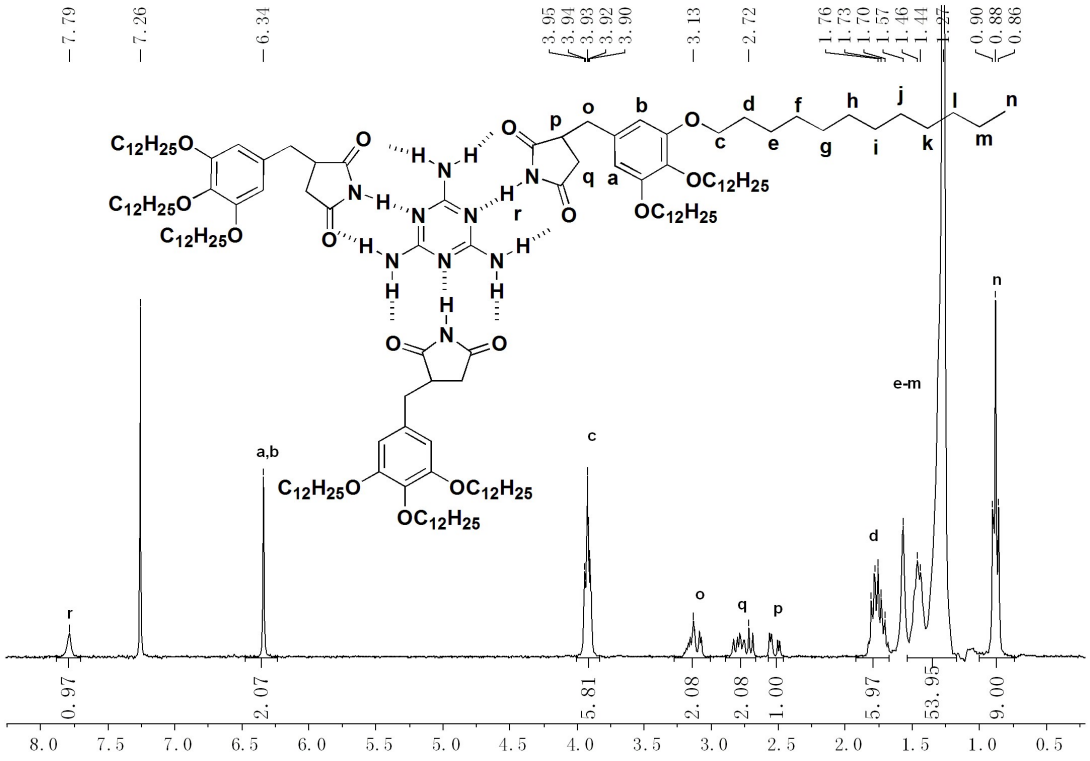
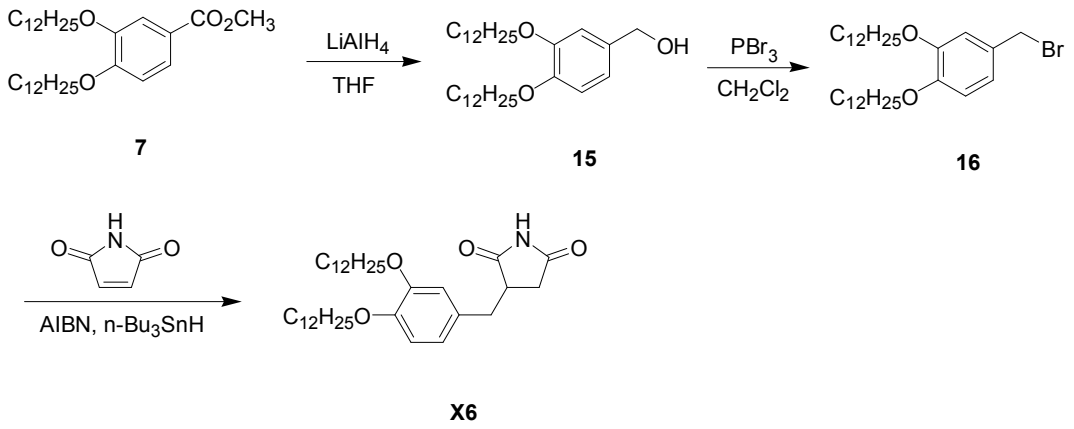
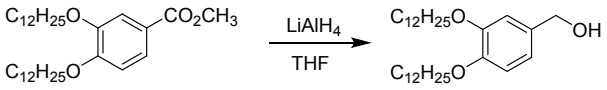


Figure S18. ^{1}H NMR spectrum of Complex **Mel-X5**.

Synthesis of Compound X6



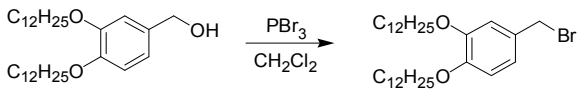
Scheme S4. The synthetic route of Compound **X6**.



7 15

(3,4-Bis-dodecyloxy-benzyl alcohol (15). Under a nitrogen atmosphere, compound **7** (5.20 g, 10.31 mmol) and dry THF (25 mL) were added into a 100 mL three-neck flask equipped with a nitrogen inlet tube and a constant pressure funnel. The solution of $LiAlH_4$ (0.78 g, 20.62 mmol) in dry THF (25 mL) was added slowly into the above flask by a constant pressure funnel (below 0 °C). The resulting reaction mixture was stirred at room temperature for 12 h, which was quenched by adding a small amount of methanol and deionized water. After the residual solid was filtered off, the filtrate was concentrated by rotary evaporation. The resulting solid was dissolved in CH_2Cl_2 (60 mL) and washed with deionized water (60 mL) and brine (60 mL), respectively. The separated organic phase was dried over anhydrous magnesium sulfate and filtered, and the filtrate was concentrated under reduced pressure to give the crude product. The final purification was carried out by column chromatography (petroleum ether : ethyl acetate = 5 : 1) to provide the desired product **15** (2.10 g, Yield: 42.8 %) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.91 (s, 1H), 6.84 (s, 2H), 4.58 (s, 2H), 3.98 (m, 4H), 1.80 (m, 4H), 1.68 (s, 1H), 1.45 (d, J = 6.5 Hz, 4H), 1.30 (m, 32H), 0.88 (t, J = 6.7 Hz, 6H).

Figure S19. ^{1}H NMR spectrum of compound **15**.



15 16

4-Bromomethyl-1,2-bis-dodecyloxy-benzene (16). Compound **15** (1.00 g, 2.52 mmol) and dry CH_2Cl_2 (30 mL) were added into a 100mL three-neck flask equipped with a nitrogen inlet tube and a constant pressure funnel. Then PBr_3 (1.13 g, 5.03mmol) was added slowly into the above flask by a constant pressure funnel (below 0 °C) under a nitrogen atmosphere. The reaction solution was stirred at room temperature for 5 h. Then the resulting mixture was then diluted with plenty of deionized water and extracted with CH_2Cl_2 for 3 times (60 mL × 3). The coalescent organic phase was washed with deionized water and saturated sodium chloride in turn, and then the organic layer was dried over anhydrous magnesium sulfate. Finally, the filtrate was concentrated under reduced pressure to give the desired product **16** (0.92 g, Yield: 81.4 %) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (d, J = 6.8 Hz, 2H), 6.82 (d, J = 8.4 Hz, 1H), 4.49 (s, 2H), 4.01 (m, 4H), 1.83 (m, 4H), 1.48 (d, J = 6.5 Hz, 4H), 1.29 (m, 32H), 0.91 (t, J = 6.3 Hz, 6H).

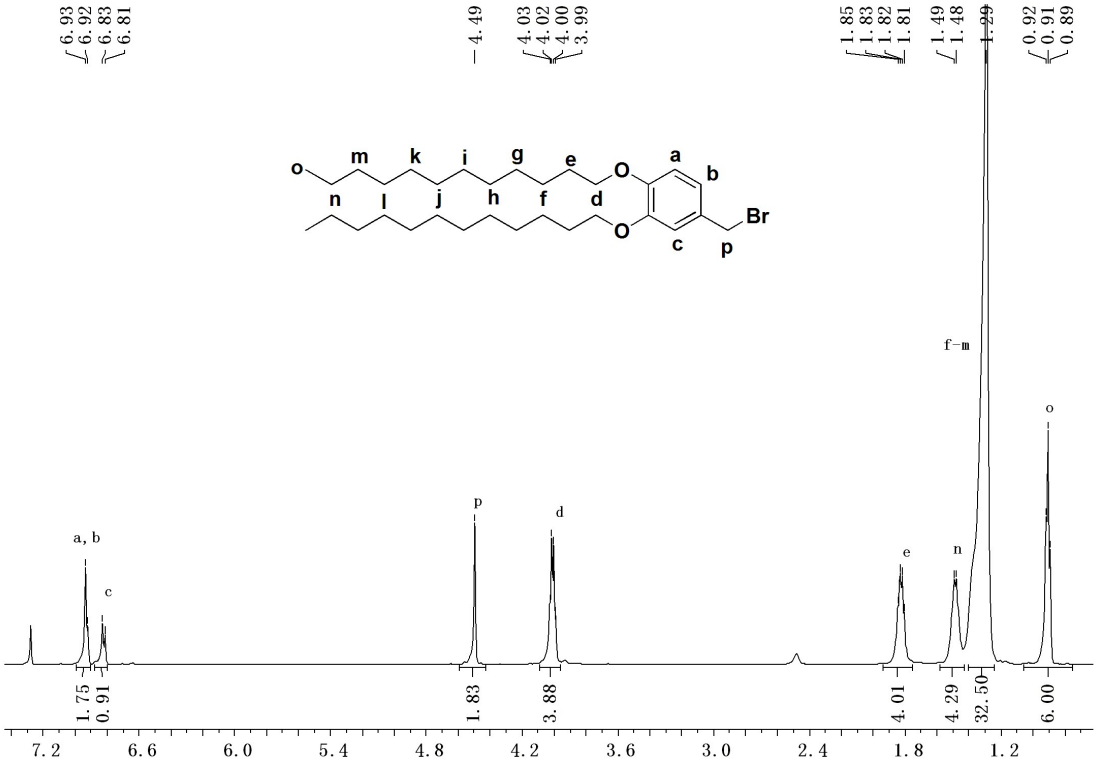
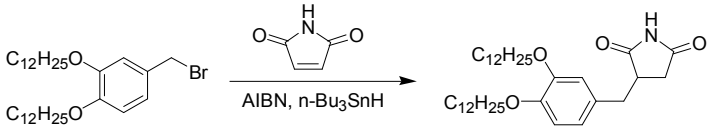


Figure S20. ^{1}H NMR spectrum of compound **16**.



16 X6

3-(3,4-Bis-dodecyloxy-benzyl)-pyrrolidine-2,5-dione (X6). Compound **16** (0.33 g, 0.61 mmol), maleimide (0.06 g, 0.61 mmol), AIBN (0.01 g, 0.06 mmol) and anhydrous toluene (5 mL) were added into a 50 mL three-neck flask. n-Bu_3SnH (0.20 g, 0.07 mmol) was then added slowly into the above flask *via* a syringe under a nitrogen atmosphere. The reaction mixture was heated to reflux for 20 h. After cooling to room temperature, the resulting solution was concentrated by rotary evaporation, and then the precipitate was dissolved into diethyl ether (20 mL) and washed twice with deionized water (20 mL × 2). Then the resulting organic layer was dried over anhydrous magnesium sulfate. After filtering off the precipitate, the mixture was stirred at room temperature for additional 30 min. The excess solvent was then removed by rotary evaporation and the resulting crude solid was purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1) to give the desired product **X6** (0.07 g, Yield: 20.6 %) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (s, 1H), 6.80 (d, J = 7.9 Hz, 1H), 6.67 (d, J = 10.8 Hz, 2H), 3.95 (t, J = 6.3 Hz, 4H), 3.11 (m, 2H), 2.89 – 2.63 (m, 2H), 2.54 (d, J = 4.6 Hz, 1H), 1.78 (m, 4H), 1.36 (m, 36H), 0.88 (t, J = 6.2 Hz, 6H). ^{13}C NMR (75 MHz, DMSO) δ 180.04, 176.98, 149.79, 148.77, 129.92, 121.76, 115.26, 114.57, 77.84, 77.42, 76.99, 69.80, 43.34, 36.23, 34.79, 32.31, 29.93, 26.45, 23.07, 14.48. ESI-MS m/z: 556.4 $[m + Na]^+$, calculated for X6, 557.4.

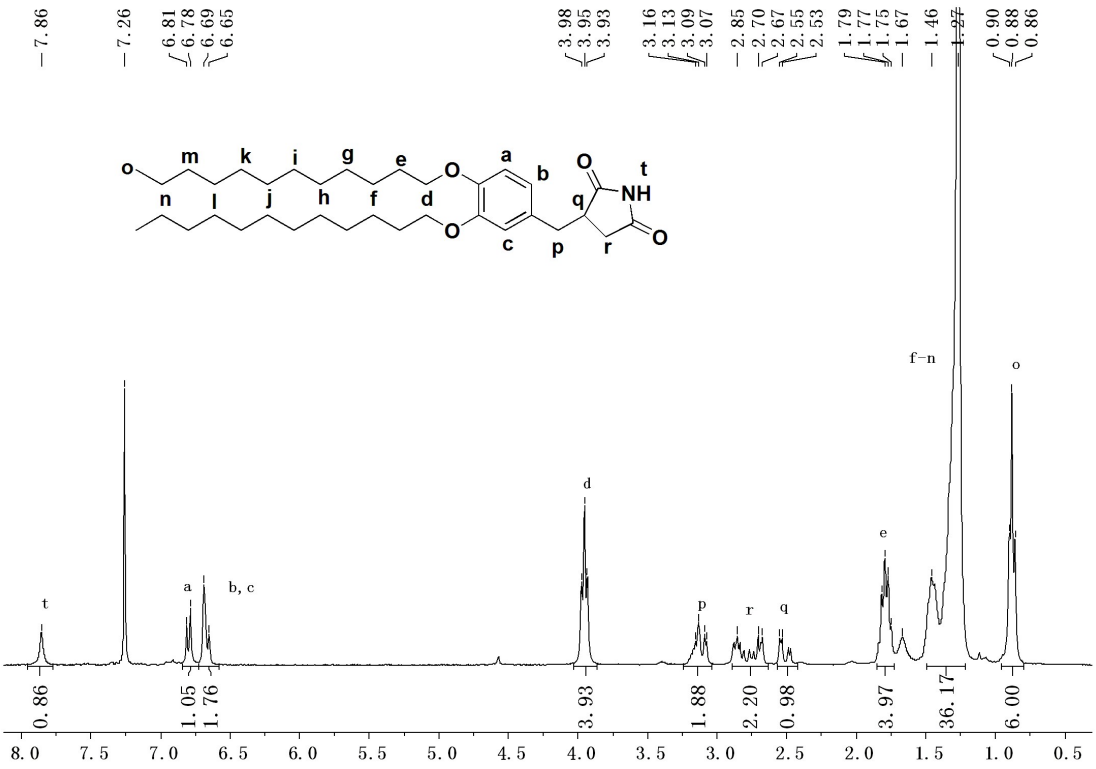


Figure S21. ^{1}H NMR spectrum of Compound **X6**.

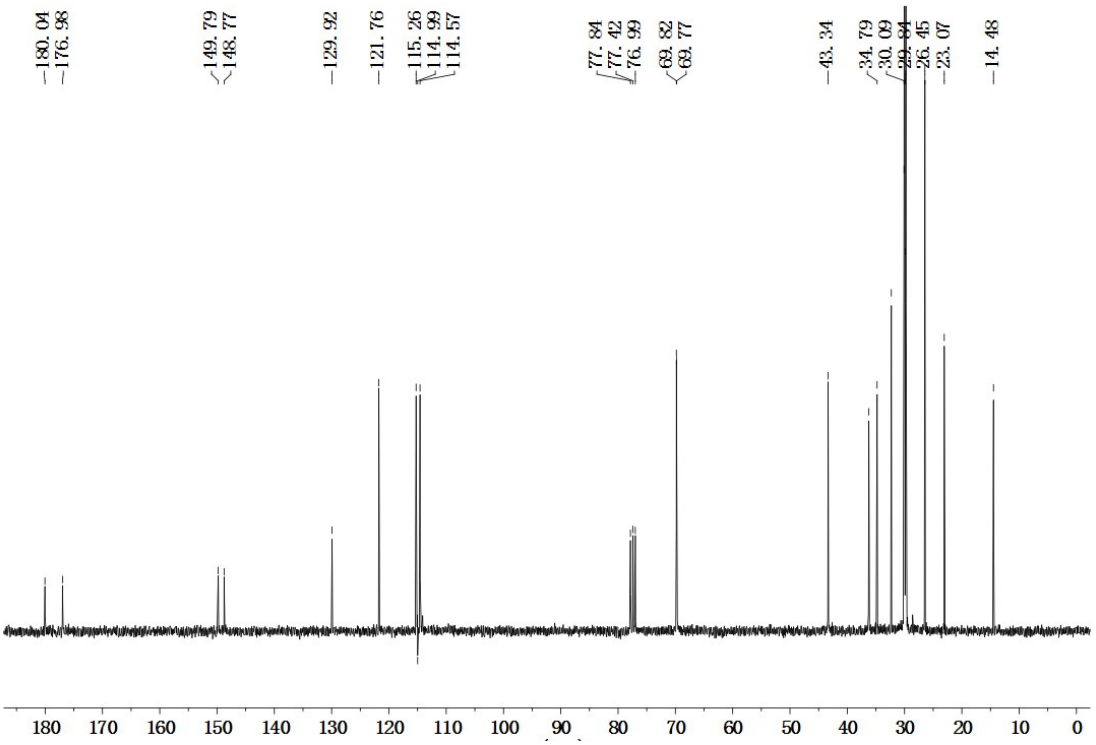


Figure S22. ^{13}C NMR spectrum of Compound **X6**.

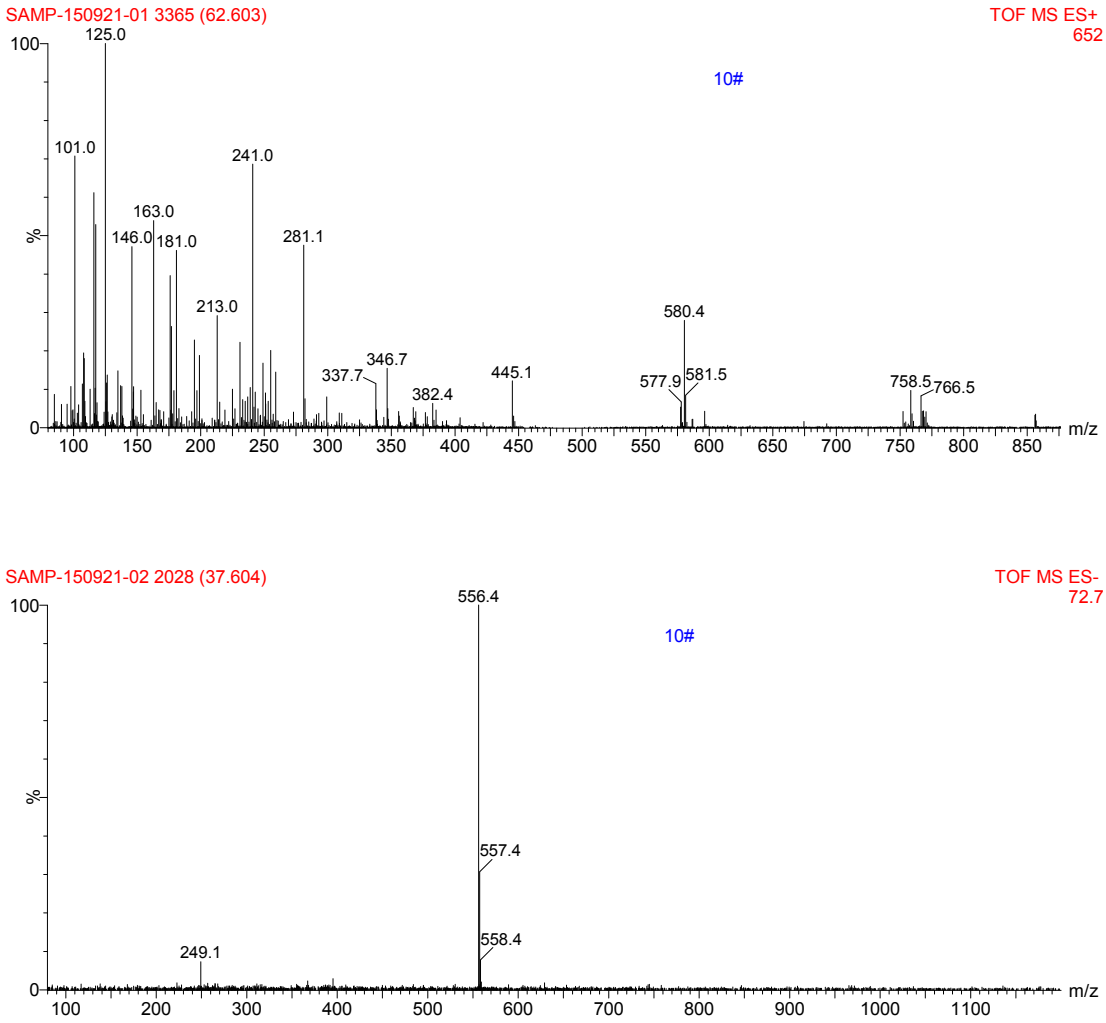
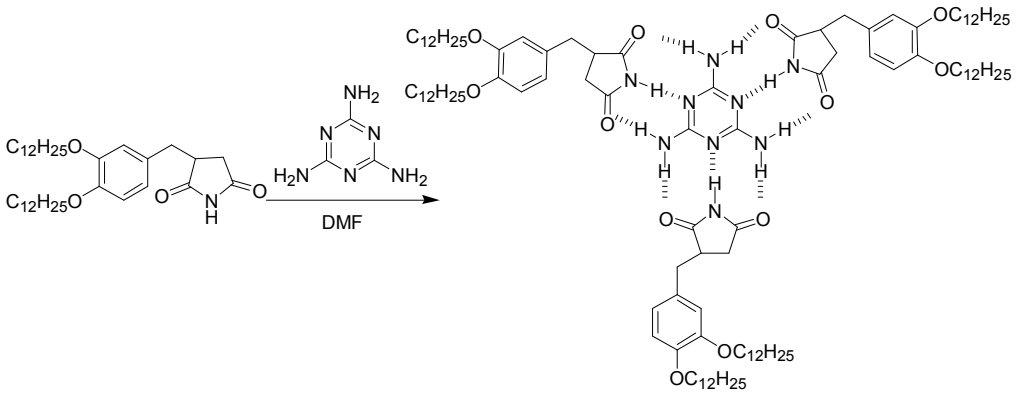


Figure S23. MS diagrams of Compound X6.



X6 Mel-X6-3

Complex Mel-X6-3. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (s, 1H), 6.80 (d, J = 7.9 Hz, 1H), 6.67 (d, J = 10.4 Hz, 2H), 3.96 (t, J = 6.1 Hz, 4H), 3.11 (d, J = 13.5 Hz, 2H), 2.71 (s, 2H), 2.59 – 2.41 (m, 1H), 1.82 – 1.66 (m, 4H), 1.28 (m, 32 H), 0.88 (t, J = 6.3 Hz, 6H).

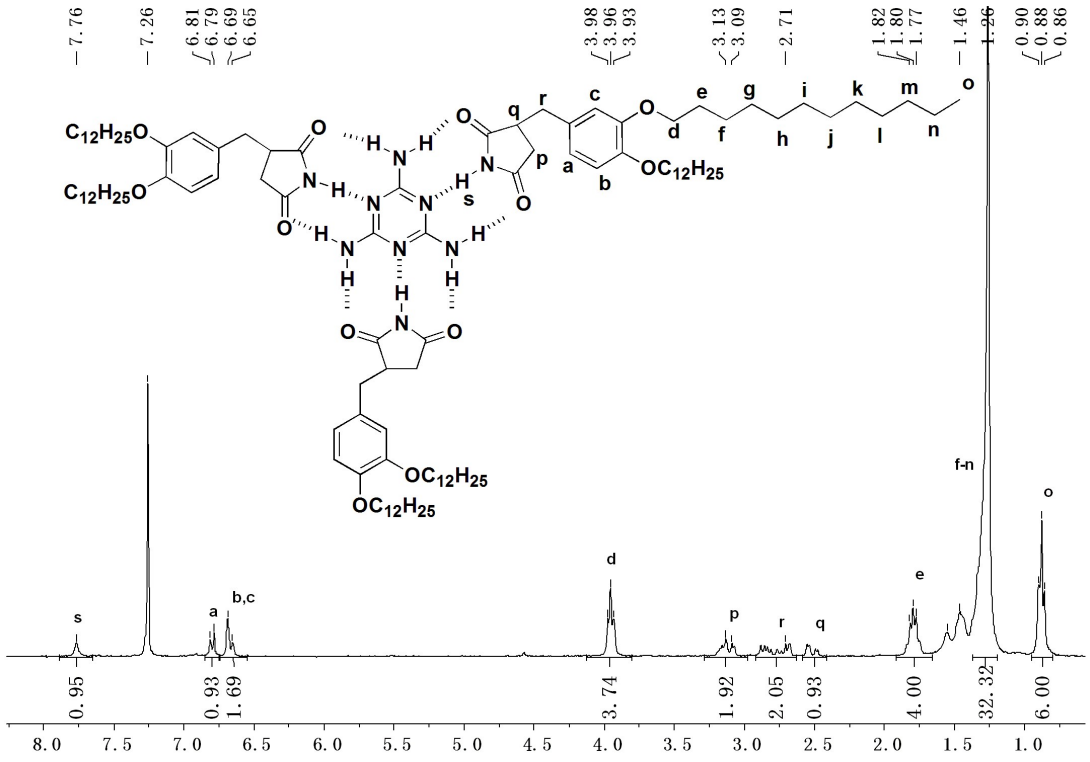
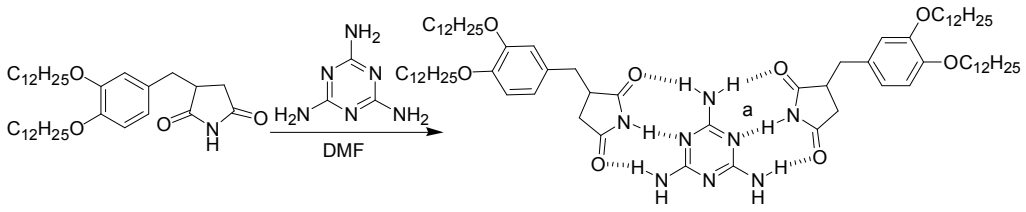


Figure S24. ^{1}H NMR spectrum of Complex **Mel-X6-3**.



X6 **Mel-X6-2**

Complex Mel-X6-2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, 1H), 6.80 (d, J = 8.1 Hz,1H), 6.69 – 6.66 (m, 2H), 3.96 (m,4H), 3.18 – 3.07 (m, 2H), 2.77 (m, 2H), 2.52 (m, 1H), 1.82 – 1.77 (m, 4H), 1.46 (s, 4H), 1.34 – 1.27 (m, 32H), 0.88 (t, J = 6.9 Hz, 6H).

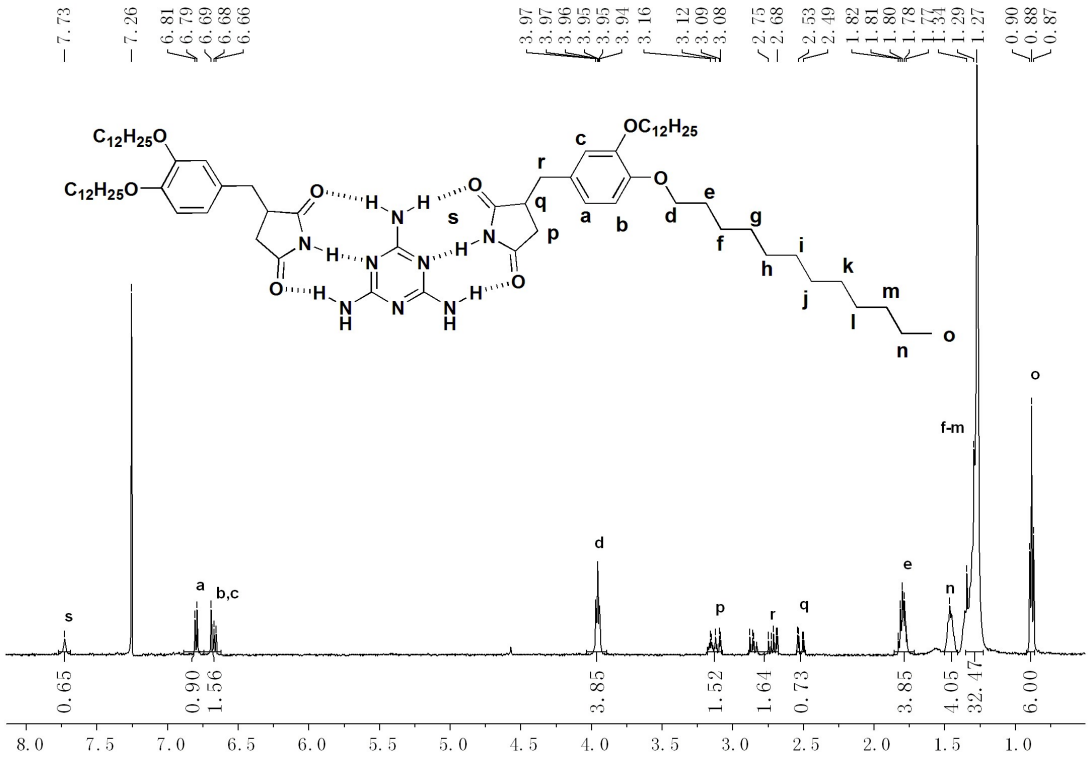
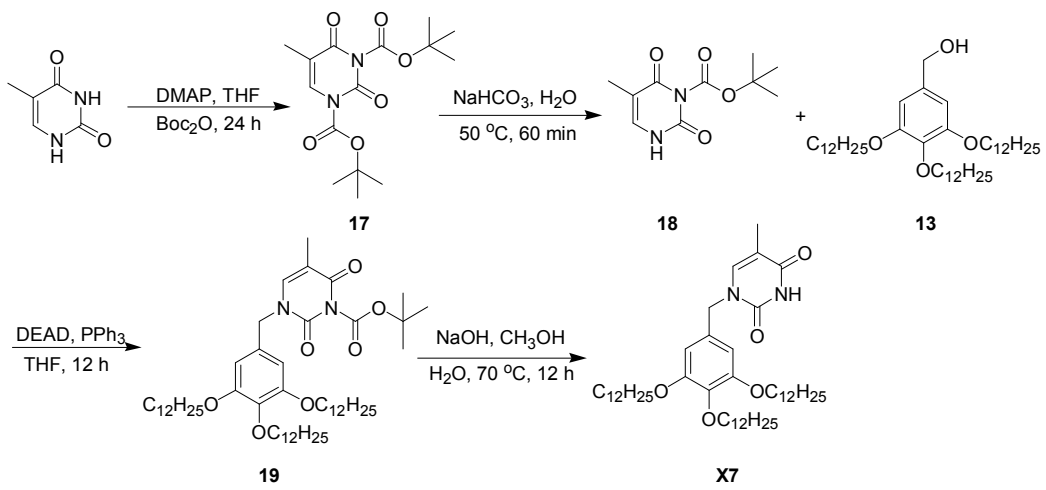
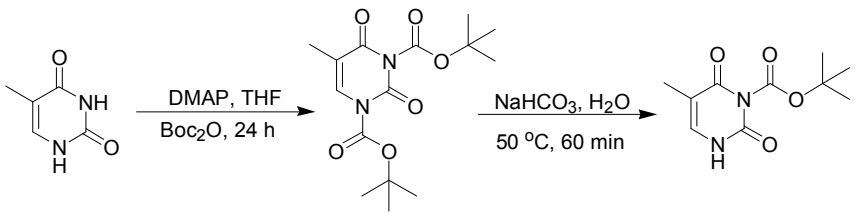


Figure S25. ^{1}H NMR spectrum of Complex **Mel-X6-2**.

Synthesis of Compound X7



Scheme S5. The synthetic route of Compound **X7**.



5-Methyl-2,6-dioxo-3,6-dihydro-2H-pyrimidine-1-carboxylic acid tert-butyl ester (18). Thymine (5.00 g, 39.65 mmol), DMAP (0.48 g, 3.93 mmol) and dry THF (200 mL) were added into a 500 mL three-neck flask. Di-tert-butyl dicarbonate (Boc_2O, 26.00 g, 119.13 mmol) was then added into the above solution under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 24 h. Then the solution was concentrated by rotary evaporation to provide the desired yellow oily product **17**, which was used directly in the next step. Compound **17** was dissolved in 200 mL methanol, 100 mL saturated sodium bicarbonate solution was then added into the solution. The reaction mixture was stirred at 50 °C for 30 min. Methanol was concentrated by rotary evaporation after the reaction was completed. The residue was dissolved in H_2O (100 mL) and extracted with CH_2Cl_2 for three times (100 mL × 3). The coalescent organic phase was dried over anhydrous sodium sulfate overnight and the filtrate was concentrated under reduced pressure to give the crude product. The crude mixture was purified by column chromatography (petroleum ether : ethyl acetate = 1 : 2) to give the desired product **18** (3.80 g, Yield: 42.4 %) as a white powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.02 (d, J = 3.5 Hz, 1H), 7.05 (d, J = 5.2 Hz, 1H), 1.89 (d, J = 10.6 Hz, 3H), 1.70 – 1.49 (m, 9H).

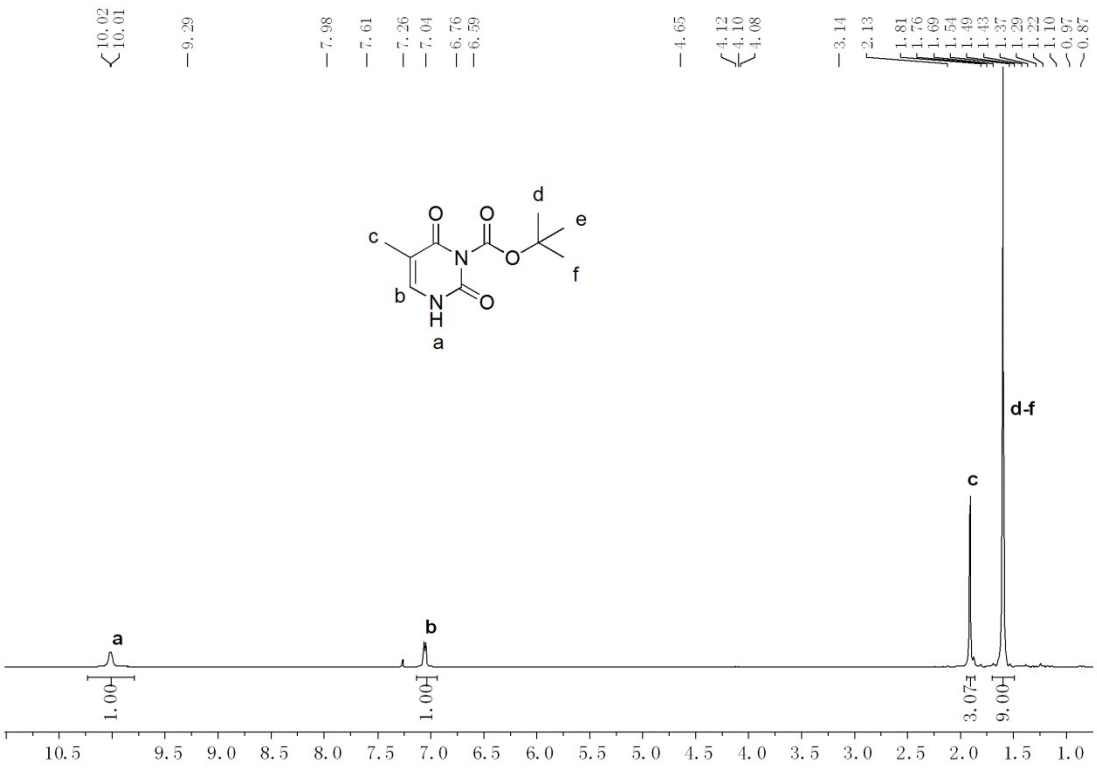
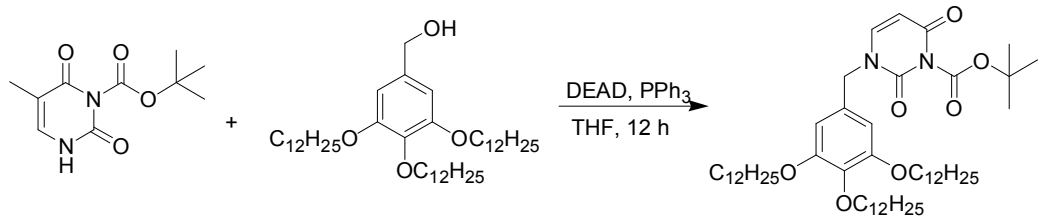


Figure S26. ^{1}H NMR spectrum of compound **18**.



18 **13** **19**

5-Methyl-2,6-dioxo-3-(3,4,5-tris-dodecyloxy-benzyl)-3,6-dihydro-2H-pyrimidine-1-carboxylic acid tert-butyl ester (19). Compound **18** (1.36 g, 6.01 mmol), 3,4,5-tris-dodecyloxy-benzyl alcohol (4.00 g, 6.01 mmol), triphenylphosphine (1.76 g, 6.71 mmol) and dry THF (100 mL) were added into a 200 mL Schlenk flask at 0 °C. Under nitrogen atmosphere, DEAD (1.16 g, 6.71 mmol) was added dropwise into the above solution. The resulting mixture was stirred at room temperature for 12 h. The reaction solution was concentrated by rotary evaporation to give the crude product. The final purification was carried out by column chromatography (petroleum ether : ethyl acetate = 5 : 1) to give the desired product **19** (2.96 g, Yield: 56.7 %) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.90 (s, 1H), 6.46 (s, 2H), 4.76 (s, 2H), 3.96 – 3.82 (m, 6H), 1.88 (s, 3H), 1.82 – 1.70 (m, 6H), 1.62 (s, 9H), 1.50 – 1.41 (m, 6H), 1.30 (m, 54H), 0.88 (t, J = 6.8 Hz, 9H).

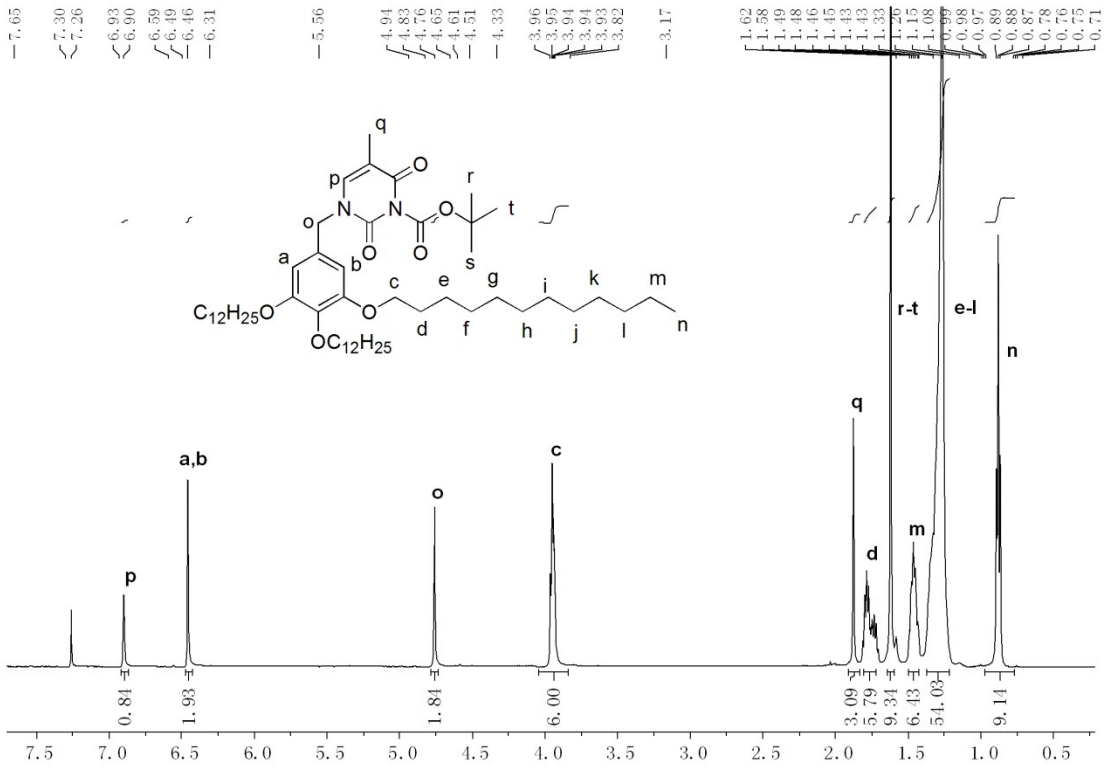
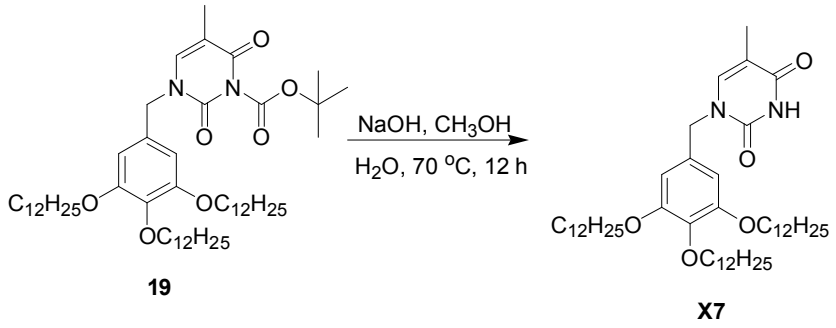


Figure S27. ^{1}H NMR spectrum of compound **19**.



19 **X7**

5-Methyl-1-(3,4,5-tris-dodecyloxy-benzyl)-1H-pyrimidine-2,4-dione (X7).

Compound **19** (2.50 g, 2.88 mmol), sodium hydroxide (4.00 g, 100.01 mmol), methanol (160 mL) and H_2O (40 mL) were added into a 500 mL round-bottom flask. The reaction mixture was stirred at 70 °C for 12 h. The resulting solution was concentrated by rotary evaporation to remove methanol. The residue was dissolved in H_2O (40 mL) and extracted with CH_2Cl_2 for three times (80 mL × 3). The coalescent organic phase was concentrated under reduced pressure to give the crude product. The final purification was carried out by column chromatography (petroleum ether : ethyl acetate = 2 : 1) to give the desired compound **X7** (0.91 g, Yield: 41.1 %) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (s, 1H), 6.94 (s, 1H), 6.45 (s, 2H), 4.76 (s, 2H), 3.96 – 3.91 (m, 6H), 1.88 (s, 3H), 1.82 – 1.70 (m, 6H), 1.46 (m, 6H), 1.39 – 1.18 (m, 54H), 0.88 (t, J = 6.8 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.83, 153.65, 151.03, 139.50, 138.60, 130.24, 111.06, 106.93, 77.24, 76.98, 76.73, 73.45, 69.40, 31.90, 30.32, 29.79 – 29.46, 29.46 – 29.22, 26.08, 22.65, 14.05, 12.33, 0.97.

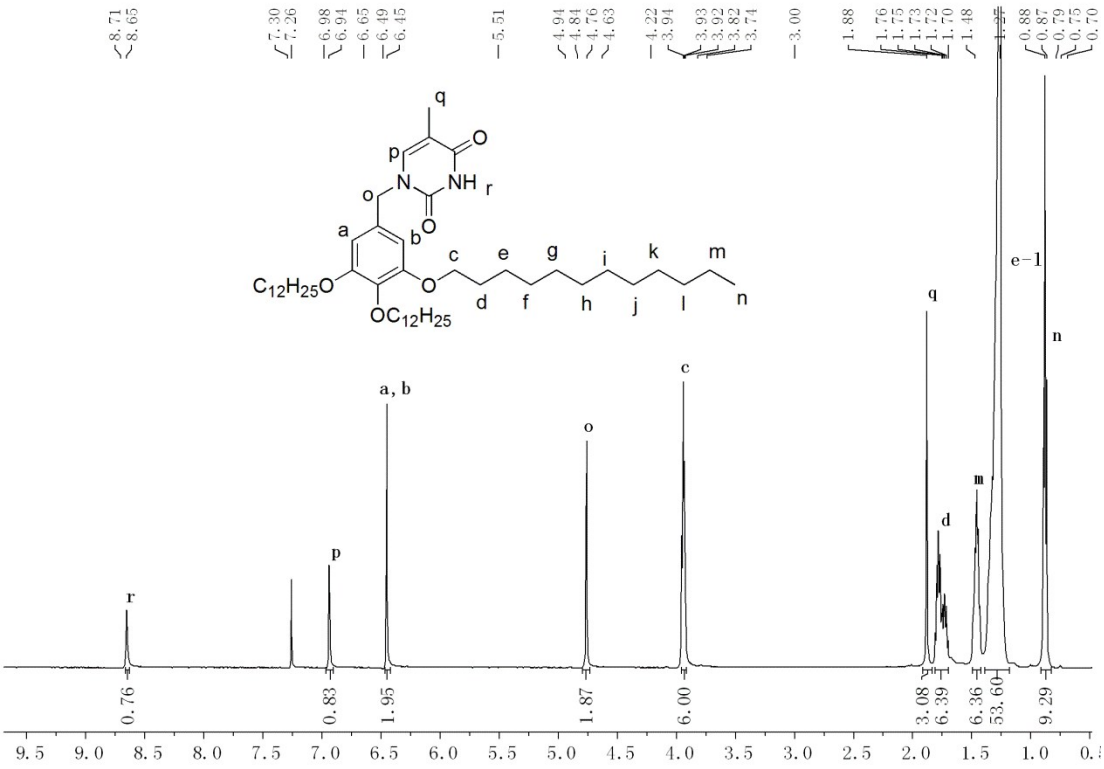


Figure S28. ^{1}H NMR spectrum of Compound **X7**.

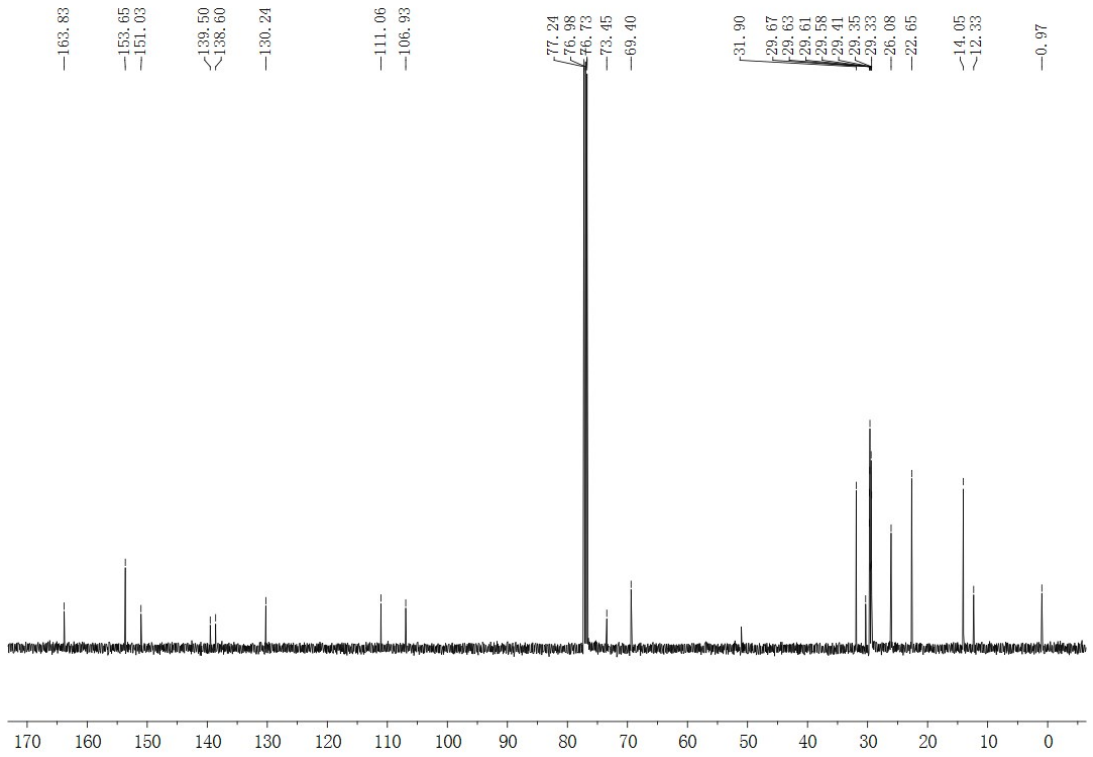
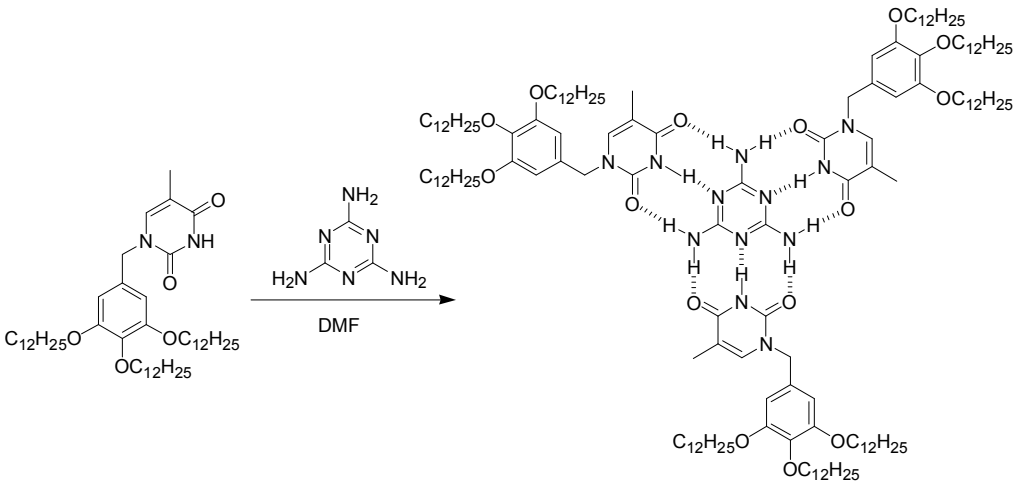


Figure S29. ^{13}C NMR spectrum of Compound **X7**.



Complex Mel-X7. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.94 (s, 1H), 6.81 (s, 1H), 6.45 (s, 2H), 4.76 (s, 2H), 3.94 (q, J = 6.2 Hz, 6H), 1.88 (s, 3H), 1.83 – 1.70 (m, 6H), 1.46 (m, 6H), 1.30 (m, 54H), 0.88 (t, J = 6.8 Hz, 9H).

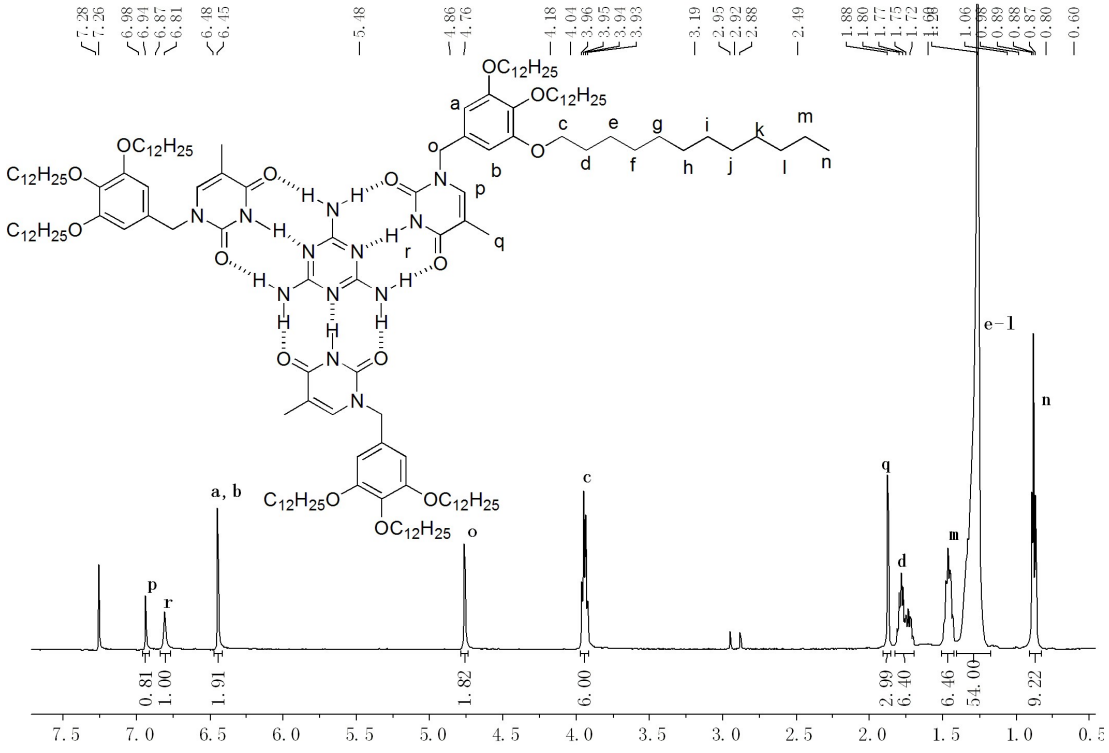


Figure S30. ^{1}H NMR spectrum of Complex **Mel-X7**.