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Supporting Information

[12]aneN$_3$-Conjugated AIEgens with Two-Photon Imaging Property for Synergistic Gene/Photodynamic Therapy *in Vitro* and *in Vivo*

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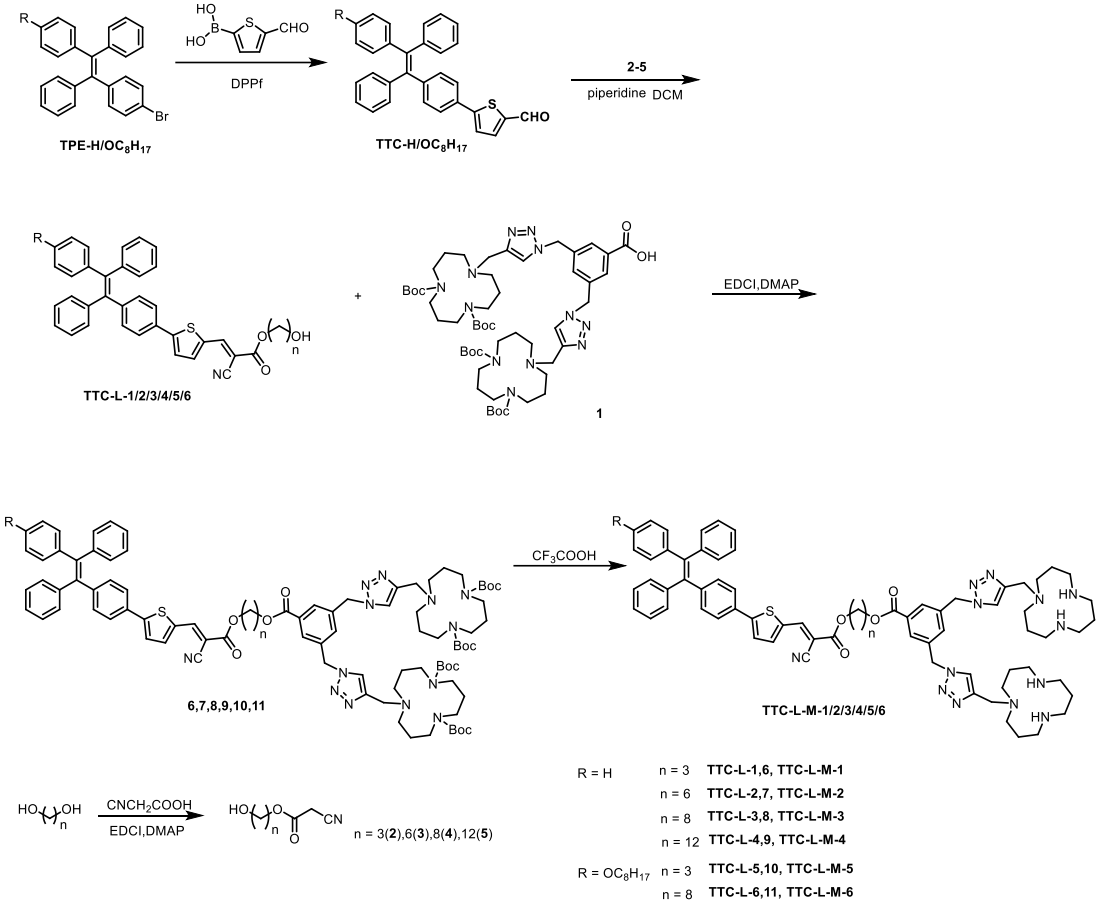
Content

1. Experimental Section

Materials and Instrumentation. Unless otherwise specified, all the analytical pure solvents and chemicals were purchased from Macklin (Shanghai, China), and used without further purification. Anhydrous dichloromethane (DCM) and *N*,*N*-dimethyl formamide (DMF) were dried and purified under nitrogen by using standard methods. Electrophoresis-grade agarose, pUC-18 DNA, Gold View II, ethidium bromide (EB), lipase, ctDNA (calf thymus DNA), the luciferase assay kit, Hochest 33342, Lyso-Tracker Blue and Annexin V-FITC Apoptosis Detection Kit were obtained from Solarbio Company (Beijing, China). pGL-3, EGFP and Cy5-DNA were obtained from Ruibiotech Co., Ltd. (Beijing, China). DOPE (Dioleoylphosphatidyl ethanolamine) and 3-(4,5-dimethylthiazol-2-yl)-2,5- diphenyl tetrazolium bromide (MTT) was purchased from Santa Cruz Biotechnology. Lipofectamine 2000 was purchased from Invitrogen (Life technologies, Mauricio Minotta). DCFH-DA was supplied by Beyotime Biotechnology (China). Plasmid expressing p53 and siLuc were supplied by Shanghai GenePharma Co. Ltd. (China). The concentrations of ctDNA were measured by recording absorptions at 260 nm and applying Lambert-Beer's Law (molar absorption coefficient $\varepsilon = 6600\ M^{-1}cm^{-1}$).

^{1}H and ^{13}C-NMR spectra were obtained on a JOEL spectrometer (400 and 600 MHz) and Bruker Avance III spectrometer (400 MHz) using $CDCl_3$ and DMSO-d_6 as solvent and calibrated using tetramethyl silane (TMS) as internal reference at 25 °C. High resolution mass spectra (HRMS) were recorded on a Waters LCT premier XE spectrometer (USA). Fluorescence spectra were measured on F-4600 FLSPECTOROPHOTOMET. Agarose electrophoresis was performed using a BG-subMIDI submarine system (BayGene Biotech Company Limited, Beijing, China) and the electrophoresis images were obtained on a UVP EC3 visible imaging system using 254 nm UV light for visualization. Scanning electron microscopy (SEM) images were performed on a Hitachi S-4800 (Japan). Confocal fluorescence imaging was obtained with Nikon A1R MP multiphoton microscopy (Japan) with a 60× oil-immersion objective lens. Flow cytometry assays were obtained on a CytoFLEX (Beckmancoulter, USA).

1.1 Synthesis of TTC-L-M-1/2/3/4/5/6



Scheme S1. Schematic Synthetic Route for **TTC-L-M-1/2/3/4/5/6**

Synthesis of 2-5

Under argon atmosphere, malonic mononitrile (2.85 mmol, 1 equiv.) and diol (3.42 mmol, 1.2 equiv.) was added to 30 mL dry DCM, and EDCI (3.42 mmol, 1.2 equiv.) was added slowly at 0 °C, after that, DMAP (3.42 mmol, 1.2 equiv.) was added and the reaction was stirred at room temperature for overnight. After completion, washed with saturated $NaCO_3$ aqueous solution, and combined the organic layer, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Crude residue was purified by silica gel column was eluted with PE/EtOAc (v/v = 3:1 ~ 1:1), to give **2-5** as colorless oil or white solid in 40−52% yields.

Compound 2: 0.163 g, 1.14 mmol; Yield: 40%. ^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm.) 4.37 (t, *J* = 6.2 Hz, 2H), 3.74 (t, *J* = 5.8 Hz, 2H), 3.62 (s, 2H), 3.46 (s, 1H), 2.01 – 1.86 (m, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ (ppm.) 163.23, 113.10, 64.03, 58.92, 31.27, 24.83. ESI-MS: *m/z* calcd. $[M+H]^+$ for $C_6H_9NO_3$, 143.06; found, 144.07

Compound 3: 0.248 g, 1.34 mmol; Yield: 47%. ^{1}H NMR ($CDCl_3$, 600 MHz) δ(ppm.) 4.20 (t, *J* = 6.9 Hz, 2H), 3.63 (t, *J* = 6.8 Hz, 2H), 3.44 (s, 2H), 1.69 (m, 2H), 1.57 (m, 2H), 1.40 (m, 4H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ (ppm.) 163.04, 113.13, 67.08, 62.79, 32.57, 28.35, 25.64, 25.41, 24.83, 24.79. ESI-MS: *m/z* calcd. $[M+H]^+$ for $C_9H_{15}NO_3$, 185.11; found, 186.10.

Compound 4: 0.256 g, 1.20 mmol; Yield: 42%. ^{1}H NMR ($CDCl_3$, 600 MHz) δ(ppm.) 4.17 (t, *J* = 6.8 Hz, 2H), 3.60 (t, *J* = 6.8 Hz, 2H), 3.43 (s, 2H), 1.64 (m, 2H), 1.57 – 1.50 (m, 2H), 1.31 (m, 8H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ (ppm.) 163.06, 113.15, 67.17, 63.02, 32.76, 29.26, 29.12, 28.36, 25.67, 24.83. ESI-MS: *m/z* calcd. $[M+H]^+$ for $C_{11}H_{19}NO_3$, 213.14; found, 214.13.

Compound 5: 0.399 g, 1.48 mmol; Yield: 52%. ^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm.) 4.20 (t, *J* = 5.7 Hz, 2H), 3.63 (t, *J* = 5.9 Hz, 2H), 3.44 (s, 2H), 1.73 – 1.62 (m, 2H), 1.56 (m, 1H), 1.27 (m, 16H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ (ppm.) 163.04, 113.10, 67.24, 63.17, 32.87, 29.56, 29.20, 25.78, 24.83. ESI-MS: *m/z* calcd. $[M+H]^+$ for $C_{16}H_{27}NO_3$, 269.20; found, 270.20.

Synthesis of TTC Derivatives

Compound **TPE-H/OC$_8$H$_{17}$** were obtained according to literature method[1],2.

Under argon atmosphere, compound **TPE** (1.2 mmol, 1 equiv.), (5-formylthiophen-2-yl) boronic acid (2.4 mmol, 2 equiv.) and Dppf (2.4 mmol, 2 equiv.) was added to a solution of dimethyloxyethane (DME): 2 M Na_2CO_3 (3:1, 100 mL). And the resultant mixture was heated to reflux for 24 h. After completion, reaction was quenched with water and extracted with DCM. The combined organic layer was washed with water, dried over anhydrous sodium sulfate, and evaporated. Crude residue was purified by silica gel column was eluted with PE/EtOAc (v/v =40:1 ~ 10:1), to give **TTC** as a yellow solid in 75-87% yield.

Compound TTC-H: 0.398 g, 0.9 mmol; Yield: 75%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm.) 9.85 (s, 1H), 7.69 (d, *J* = 3.9 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 4.0 Hz, 1H), 7.17 – 6.98 (m, 17H).

Compound TTC-OC$_8$H$_{17}$: 0.593 g, 1.04 mmol; Yield: 87%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm.) 9.85 (s, 1H), 7.69 (d, *J* = 4.0 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 3.9 Hz, 1H), 7.08 (m, 8H), 7.00 (m, 4H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.64 (d, *J* = 8.7 Hz, 2H), 3.87 (t, *J* = 6.6 Hz, 2H), 1.77 – 1.67 (m, 2H), 1.41 (m, 2H), 1.27 (m, 8H), 0.86 (t, *J* = 6.9 Hz, 3H).

Synthesis of TTC-L Derivatives

Under argon atmosphere, compound **TTC** (0.41 mmol, 1 equiv.), compound **2-5** and piperidine (1.2 mmol, 3 equiv) was added to 20mL CH_3CN. The reaction mixture was heated to reflux for overnight and cooled to room temperature. The pH value of the aqueous phase was adjusted to 2.0−3.0 with HCl (0.1 M). The reaction mixture was extracted with DCM. The extract was then dried over Na_2SO_4 and filtered. After evaporation at a reduced pressure, crude residue was purified by silica gel column was eluted with PE/EtOAc (v/v =5:1 ~ 2:1), to give **TTC-L-1/2/3/4/5/6** as a yellow solid in 42-95% yield.

TTC-L-1: 0.098 g, 0.17 mmol; Yield: 42%.^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm.) 8.26 (s, 1H), 7.71 (d, *J* = 3.8 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 3.7 Hz, 1H), 7.15 – 6.96 (m, 17H), 4.45 (t, *J* = 6.2 Hz, 2H), 3.78 (t, *J* = 6.2 Hz, 2H), 2.01 – 1.96 (m, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ (ppm.) 163.45, 154.93, 146.93, 145.70, 143.45, 143.28, 142.23, 139.97, 139.51, 134.71, 132.30, 131.45, 131.38, 130.58, 128.03, 127.95, 127.79, 126.99, 126.83, 125.84, 124.32, 116.13, 97.34, 77.49, 77.17, 76.85, 63.38, 59.04, 31.65. ESI-MS: *m/z* calcd. $[M+H]^+$ for $C_{37}H_{29}NO_3S$, 567.19; found, 568.22

TTC-L-2: 0.150 g, 0.25 mmol; Yield: 60%. ^{1}H NMR ($CDCl_3$, 600 MHz) δ(ppm.) 8.25 (s, 1H), 7.70 (d, *J* = 4.7 Hz, 2H), 7.42 (d, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 4.5 Hz, 1H), 7.16 – 7.08 (m, 10H), 7.07 – 7.00 (m, 7H), 4.29 (t, *J* = 6.5 Hz, 2H), 3.65 (t, *J* = 6.0 Hz, 2H), 1.76 (m, 2H), 1.59 (m, 2H), 1.53 – 1.31 (m, 4H). ^{13}C NMR ($CDCl_3$, 151 MHz) δ (ppm.) 163.17, 154.69, 146.62, 145.64, 143.47, 143.44, 143.30, 142.22, 139.99, 139.13, 134.80, 132.28, 132.22, 131.44, 131.37, 130.64, 128.01, 127.98, 127.92, 127.77, 126.96, 126.92, 126.81, 126.75, 125.82, 124.26, 116.13, 97.81, 66.50, 62.90, 32.67, 28.57, 25.80, 25.47, 0.07. ESI-MS: *m/z* calcd. [M+H]+ for $C_{40}H_{35}NO_3S$, 609.23; found, 610.23

TTC-L-3: 0.212 g, 0.33 mmol; Yield: 81%. ^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm.) 8.25 (s, 1H), 7.70 (d, *J* = 3.8 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 3.8 Hz, 1H), 7.16 – 6.98 (m, 17H), 4.28 (t, *J* = 6.8 Hz, 2H), 3.64 (t, *J* = 6.6 Hz, 2H), 1.73 (m, 2H), 1.62 (m, 2H), 1.42 (m, 2H), 1.35 (m, 6H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ (ppm.) 163.18, 154.64, 146.65, 145.62, 143.47, 143.30, 142.20, 139.99, 139.29, 134.78, 132.29, 131.46, 131.39, 130.63, 128.03, 127.95, 127.79, 126.98, 126.83, 125.82, 124.28, 116.13, 97.78, 77.53, 77.23, 76.90, 66.61, 63.01, 32.81, 29.30, 29.19, 28.58, 25.79, 25.72. ESI-MS: *m/z* calcd. $[M+H]^+$ for $C_{42}H_{39}NO_3S$, 637.27; found, 638.26

TTC-L-4: 0.270 g, 0.39 mmol; Yield: 95%.^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm.) 8.25 (s, 1H), 7.70 (d, *J* = 3.9 Hz, 1H), 7.53 (d, *J* = 4.1 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.33 (d, *J* = 4.0 Hz, 1H), 7.14 – 7.07 (m, 10H), 7.07 – 6.97 (m, 7H), 4.27 (t, *J* = 6.6 Hz, 2H), 3.63 (t, *J* = 6.6 Hz, 2H), 1.73 (m, 2H), 1.55 (m, 2H), 1.40 (m, 2H), 1.33 (m, 2H), 1.27 (s, 12H). ^{13}C NMR ($CDCl_3$, 151 MHz) δ (ppm.) 163.18, 154.60, 146.54, 145.61, 143.48, 143.30, 143.12, 142.21, 140.00, 139.05, 134.82, 132.27, 132.21, 131.45, 131.37, 130.99, 130.66, 128.93, 127.98, 127.92, 127.77, 126.96, 126.92, 126.80, 126.75, 125.81, 124.25, 116.10, 97.94, 66.65, 63.19, 32.90, 29.79, 29.59, 29.49, 29.26, 28.63, 25.87, 22.78, 19.27, 14.20, 0.07. ESI-MS: *m/z* calcd. $[M+H]^+$ for $C_{46}H_{47}NO_3S$, 693.33; found, 694.68

TTC-L-5: 0.142 g, 0.21 mmol; Yield: 50%.^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm.) 8.28 (s, 1H), 7.73 (d, *J* = 4.0 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 3.9 Hz, 1H), 7.14 – 7.07 (m, 8H), 7.06 – 7.00 (m, 4H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.66 (d, *J* = 7.9 Hz, 2H), 4.47 (t, *J* = 5.9 Hz, 2H), 3.88 (t, *J* = 6.6 Hz, 2H), 3.79 (t, *J* = 5.8 Hz, 2H), 2.03 – 1.97 (m, 2H), 1.79 – 1.70 (m, 2H), 1.41 (m, 2H), 1.36 – 1.28 (m, 8H), 0.87 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ (ppm.) 163.47, 157.99, 155.07, 146.94, 146.16, 146.08, 143.76, 143.67, 143.58, 141.94, 139.50, 138.93, 135.58, 135.54, 134.63, 132.62, 132.33, 131.50, 131.49, 131.47, 131.03, 130.35, 130.34, 128.94, 128.01, 127.96, 127.72, 126.91, 126.63, 125.78, 124.25, 116.13, 113.68, 97.24, 67.92, 63.34, 59.05, 31.90, 29.47, 29.32, 26.15, 22.75, 14.21. ESI-MS: *m/z* calcd. $[M+H]^+$ for $C_{45}H_{45}NO_4S$, 695.31; found, 696.41

TTC-L-6: 0.263 g, 0.34 mmol; Yield: 84%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm.) δ 8.25 (s, 1H), 7.71 (d, *J* = 4.0 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 4.1 Hz, 1H), 7.11 – 7.06 (m, 8H), 7.04 – 6.98 (m, 4H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.65 (d, *J* = 8.7 Hz, 2H), 4.28 (t, *J* = 6.7 Hz, 2H), 3.87 (t, *J* = 6.6 Hz, 2H), 3.63 (t, *J* = 6.6 Hz, 2H), 1.79 – 1.67 (m, 2H), 1.56 (m, 2H), 1.43 – 1.36 (m, 8H), 1.28 (m, 10H), 0.86 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ (ppm.) 163.20, 158.14, 154.79, 146.63, 146.06,

145.99, 143.75, 143.67, 143.58, 141.93, 139.19, 138.94, 135.58, 134.70, 132.61, 132.31, 131.50, 131.48, 131.46, 130.40, 130.39, 127.99, 127.94, 127.87, 127.70, 126.89, 126.61, 125.87, 125.75, 124.18, 116.16, 116.14, 113.67, 97.71, 67.91, 66.58, 63.09, 33.99, 32.82, 31.89, 29.47, 29.37, 29.26, 29.17, 28.57, 26.14, 25.01, 22.74, 14.20. ESI-MS: *m/z* calcd. $[M-H]^-$ for $C_{50}H_{55}NO_4S$, 765.39; found, 764.24

***Synthesis of target compound* TTC-L-M-1/2/3/4/5/6[2].**

Under argon atmosphere, compound **1** (0.13 mmol, 1 equiv.) and EDCI (0.16 mmol, 1.2 equiv.) was added to 15mL dry DCM, and compounds **TTC-L** derivatives (3.42 mmol, 1.2 equiv.) was added slowly at 0 °C, after that, DMAP (0.16 mmol, 1.2 equiv.) was added and the reaction was stirred at room temperature for overnight. After completion, washed with saturated $NaCO_3$ aqueous solution, and combined the organic layer, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Crude residue was purified by silica gel column was eluted with DCM/MeOH (v/v =40:1 ~ 15:1), to give **6-11** as a yellow solid in 40-56% yield. The obtained compounds **6-11** were subsequently dissolved in 5 mL anhydrous DCM then CF_3COOH was added dropwise to the mixture solution. After stirring for 30 min at room temperature, a large amount of yellow precipitates was obtained. The solid collected by filtering and then washed with ether for several times, and then the solid were dried in vacuo to give the target compounds **TTC-L-M-1/2/3/4/5/6** as yellow solid in 75–90% yields.

Compound 6: 0.117 g, 0.07 mmol; Yield: 56%.^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm.) 8.25 (s, 1H), 7.90 (s, 2H), 7.71 (d, *J* = 4.0 Hz, 1H), 7.47 – 7.32 (m, 6H), 7.17 – 7.08 (m, 11H), 7.06 – 7.00 (m, 6H), 5.53 (s, 4H), 4.45 (dt, *J* = 12.0, 6.0 Hz, 4H), 3.77 (s, 4H), 3.31 (m, 16H), 2.43 (s, 8H), 2.27 – 2.17 (m, 2H), 1.85 (dd, *J* = 13.0, 6.1 Hz, 12H), 1.44 (s, 36H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ (ppm.)171.22, 165.11, 163.01, 156.40, 146.99, 144.44, 143.42, 139.92, 136.70, 134.61, 132.30, 131.36, 130.51, 129.23, 128.00, 127.76, 126.81, 125.82, 124.35, 122.60, 116.02, 97.15, 79.36, 60.47, 53.28, 49.77, 46.80, 45.50, 43.90, 28.58, 26.20, 21.14. HRMS-ESI: *m/z* calcd. $[M+2H]^{2+}$ for $C_{90}H_{113}N_{13}O_{12}S$, 1601.8498; found, 1601.8506

Compound 7: 0.105 g, 0.06 mmol; Yield: 49%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm.) 8.26 (s, 1H), 7.91 (s, 2H), 7.72 (d, *J* = 4.1 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 3H), 7.38 (s, 1H), 7.34 (s, 2H), 7.16 – 7.08 (m, 10H), 7.07 – 7.00 (m, 7H), 5.54 (s, 4H), 4.31 (q, *J* = 6.5 Hz, 4H), 3.78 (s, 2H), 3.32 (m, 18H), 2.43 (m, 6H), 1.83 (m, 18H), 1.48 (m, 4H), 1.44 (s, 36H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ (ppm.) 165.31, 163.17, 156.44, 154.75, 146.70, 145.67, 143.45, 143.28, 142.22, 139.96, 139.32, 136.60, 134.74, 132.29, 131.44, 131.38, 130.60, 129.24, 128.01, 127.93, 127.78, 126.96, 126.82, 125.81, 124.30, 122.61, 116.13, 97.65, 79.41, 77.44, 77.33, 77.12, 76.81, 66.30, 65.58, 53.36, 49.76, 46.83, 45.50, 43.92, 31.68, 29.78, 28.59, 26.18, 25.65, 25.57, 22.74, 14.22, 0.09. HRMS-ESI: *m/z* calcd. $[M+2H]^{2+}$ for $C_{93}H_{119}N_{13}O_{12}S$, 1643.8968; found, 1643.8966

Compound 8: 0.084 g, 0.05 mmol; Yield: 40%. ^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm.) 8.24 (s,1H), 7.89 (s, 2H), 7.70 (d, *J* = 4.1 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.35 (s, 2H), 7.33 (d, *J* = 4.0 Hz, 1H), 7.31 (s, 1H), 7.13 – 7.00 (m, 17H), 5.53 (s, 4H), 4.28 (q, *J* = 6.7 Hz, 4H), 3.77 (s, 2H), 3.76 (s, 2H), 3.30 (m, 16H), 2.42 (m, 8H), 1.86 (d, *J* = 6.6 Hz, 2H), 1.83 – 1.80 (m, 10H), 1.73 (d, *J* = 6.9 Hz, 2H), 1.43 (m, 46H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ (ppm.) 172.46, 166.60, 157.68, 155.92, 147.87, 145.80, 144.74,

144.58, 143.52, 141.28, 140.46, 137.94, 136.06, 133.57, 132.72, 132.65, 130.45, 129.29, 129.22, 129.06, 128.25, 128.10, 127.09, 125.59, 123.84, 80.64, 67.06, 61.74, 54.63, 51.20, 48.16, 46.84, 45.24, 30.43, 29.90, 28.54, 27.59, 27.20, 27.11, 22.41, 15.58. HRMS-ESI: *m/z* calcd. $[M+2H]^{2+}$ for $C_{95}H_{123}N_{13}O_{12}S$, 1671.9281; found, 1671.9280

Compound 9: 0.110 g, 0.06 mmol; Yield: 49%. ^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm.) 8.24 (s, 1H), 7.88 (s, 2H), 7.70 (d, *J* = 4.0 Hz, 1H), 7.42 (d, *J* = 8.2 Hz,2H), 7.35 (s, 1H), 7.33 (d, *J* = 4.1 Hz, 2H), 7.14 – 6.97 (m, 17H), 5.53 (s, 4H), 4.27 (dt, *J* = 6.9, 3.4 Hz, 4H), 3.77 (s, 2H), 3.44 – 3.09 (m, 18H), 2.42 (m, 6H), 1.84 (m, 12H), 1.73 (t, *J* = 7.0 Hz, 6H), 1.43 (s, 40H), 1.28 (m, 12H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ (ppm.) 165.34, 163.15, 156.47, 154.58, 146.53, 145.60, 143.45, 143.29, 142.21, 139.99, 139.09, 136.53, 134.79, 132.26, 132.21, 131.43, 131.36, 130.96, 130.64, 129.57, 129.35, 128.88, 127.99, 127.91, 127.76, 126.95, 126.80, 126.75, 125.79, 124.26, 116.10, 97.91, 79.61, 68.23, 67.85, 66.63, 65.83, 53.51, 49.15, 47.18, 45.52, 44.31, 39.00, 34.02, 32.00, 30.65, 29.76, 29.61, 29.34, 29.06, 28.73, 28.57, 25.02, 24.07, 23.05, 14.19, 11.17, 1.09. HRMS-ESI: *m/z* calcd. $[M+2H]^{2+}$ for $C_{99}H_{131}N_{13}O_{12}S$, 1727.9907; found, 1727.9906

Compound 10: 0.103 g, 0.06 mmol; Yield: 46%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm.) 8.25 (d, *J* = 4.9 Hz, 1H), 7.90 (s, 2H), 7.71 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.49 – 7.32 (m, 6H), 7.16 – 7.08 (m, 7H), 7.07 – 7.00 (m, 5H), 6.92 (dd, *J* = 15.8, 8.6 Hz, 2H), 6.63 (dd, *J* = 12.4, 8.7 Hz, 2H), 5.54 (s, 4H), 4.45 (m, 4H), 3.87 (m, 2H), 3.78 (s, 4H), 3.31 (s, 16H), 2.44 (s, 7H), 2.26 – 2.18 (m, 2H), 1.84 (m, 12H), 1.77 – 1.68 (m,2H), 1.43 (s, 38H), 1.27 (m, 8H), 0.87 (t, *J* = 5.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ (ppm.) 171.13, 165.01, 162.93, 157.89, 156.31, 146.90, 144.25, 143.63, 141.88, 136.57, 135.43, 134.44, 132.50, 132.23, 131.81, 131.63, 131.37, 129.14, 127.83, 126.78, 126.51, 125.78, 125.66, 124.19, 122.58, 113.76, 113.57, 96.96, 79.30, 67.81, 62.92, 60.37, 53.19, 49.57, 45.39, 43.85, 31.78, 29.35, 29.26, 29.19, 28.48, 26.03, 22.63, 21.03, 14.18. HRMS-ESI: *m/z* calcd. $[M+2H]^{2+}$ for $C_{98}H_{129}N_{13}O_{13}S$, 1729.9700; found, 1729.9698

Compound 11: 0.105 g, 0.06 mmol; Yield: 45%.^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm.) 8.24 (d, *J* = 4.0 Hz, 1H), 7.88 (s, 2H), 7.70 (dd, *J* = 7.2, 4.2 Hz, 1H), 7.42 (dd, *J* = 15.5, 8.4 Hz, 2H), 7.36 – 7.30 (m, 4H), 7.10 (m, 7H), 7.03 (m, 5H), 6.91 (dd, *J* = 15.0, 8.7 Hz, 2H), 6.63 (dd, *J* = 12.1, 8.8 Hz, 2H), 5.53 (s, 4H), 4.28 (dd, *J* = 11.7, 6.4 Hz, 4H), 3.86 (t, *J* = 5.5 Hz, 2H), 3.76 (s, 4H), 3.30 (s, 16H), 2.42 (t, *J* = 5.9 Hz, 8H), 1.92 (d, *J* = 9.0 Hz, 6H), 1.86 – 1.79 (m, 10H), 1.71 (d, *J* = 7.2 Hz, 6H), 1.57 (s, 3H), 1.43 (s, 40H), 1.38 (m, 4H), 1.32 (m, 2H), 1.27 (m, 6H), 0.87 (t, *J* = 4.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 151 MHz) δ (ppm.) 171.17, 165.29, 163.14, 156.89, 156.36, 146.58, 144.48, 143.73, 141.92, 139.16, 136.60, 135.55, 134.66, 132.57, 132.28, 131.43, 130.36, 129.14, 127.97, 127.68, 126.86, 126.59, 125.72, 124.19, 122.51, 116.10, 113.67, 97.69, 79.33, 65.75, 60.43, 53.31, 49.87, 46.82, 45.51, 43.90, 34.04, 31.86, 30.98, 29.35, 28.72, 28.67, 28.63, 28.61, 28.60, 28.57, 28.54, 28.53, 26.11, 25.72, 25.02, 22.70, 21.10, 14.26. HRMS-ESI: *m/z* calcd. $[M+2H]^{2+}$ for $C_{103}H_{139}N_{13}O_{13}S$, 1800.0496; found, 1800.0480

Compound TTC-L-M-1: 0.063 g, 0.05 mmol; Yield: 75%. ^{1}H NMR (CD_3OD, 600 MHz) δ (ppm.) 9.41 (s, 4H), 8.50 (s, 1H), 8.15 (s, 2H), 7.99 (d, *J* = 4.4 Hz, 1H), 7.81 (s, 2H), 7.70 (d, *J* = 4.4 Hz, 1H), 7.55 (s, 2H), 7.16 – 6.91 (m, 18H), 5.64 (s, 4H), 4.36 (t, *J* = 4.9 Hz, 4H), 3.73 (m, 4H), 3.13 (m, 4H), 3.04 (s, 12H), 2.10 (m, 2H), 2.04 (m,

5H), 1.99 (m, 2H), 1.97 (m, 1H), 1.93 (s, 6H), 1.89 (m, 7H). ^{13}C NMR (DMSO, 151 MHz) δ (ppm.) 179.79, 172.50, 165.53, 162.77, 153.66, 147.79, 145.43, 143.47, 143.45, 143.25, 142.74, 142.11, 140.24, 138.16, 134.90, 132.29, 131.27, 131.21, 131.15, 131.12, 130.75, 128.74, 128.56, 128.52, 128.39, 127.46, 127.33, 127.27, 126.28, 125.92, 125.38, 116.52, 97.29, 63.45, 62.52, 52.51, 36.15, 31.84, 28.13, 24.41, 24.14, 21.64. HRMS-ESI: *m/z* calcd. $[M+2H]^{2+}$ for $C_{70}H_{81}N_{13}O_4S$, 1201.6401; found, 1201.6400

Compound TTC-L-M-2: 0.062 g, 0.05 mmol; Yield: 83%.^{1}H NMR (DMSO, 600 MHz) δ (ppm.) 8.88 (s, 5H), 8.49 (s, 1H), 8.17 (s, 2H), 8.00 (s, 1H), 7.71 (m, 3H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.50 (s, 1H), 7.19 – 7.08 (m, 9H), 7.04 (d, *J* = 8.1 Hz, 2H), 7.02 – 6.89 (m, 6H), 5.65 (s, 4H), 4.22 (t, *J* = 6.6 Hz, 4H), 3.69 (s, 4H), 3.49 – 3.16 (m, 11H), 3.08 (m, 12H), 2.03 (s, 2H), 1.80 (s, 7H), 1.66 (s, 6H), 1.38 (s, 4H). ^{13}C NMR (DMSO, 151 MHz) δ (ppm.) 165.55, 162.82, 158.88, 158.67, 153.60, 147.73, 145.45, 143.46, 143.25, 142.70, 142.13, 140.22, 138.09, 134.91, 132.31, 131.38, 131.27, 131.22, 131.15, 130.74, 128.56, 128.52, 128.40, 127.45, 127.34, 126.26, 125.90, 125.41, 116.54, 97.35, 66.40, 65.47, 52.55, 43.97, 40.49, 40.35, 40.21, 40.07, 39.93, 39.79, 39.66, 28.55, 28.42, 25.46, 25.41, 21.67. HRMS-ESI: *m/z* calcd. $[M+2H]^{2+}$ for $C_{73}H_{87}N_{13}O_4S$, 1243.6871; found, 1243.6870

Compound TTC-L-M-3: 0.050 g, 0.04 mmol; Yield: 79%. ^{1}H NMR (CD_3OD, 400 MHz) δ (ppm.) 8.36 (s, 1H), 8.09 (s, 1H), 7.90 (d, *J* = 8.5 Hz, 2H), 7.80 (d, *J* = 3.8 Hz, 1H), 7.56 (s, 1H), 7.47 (m, 3H), 7.16 – 6.91 (m, 18H), 5.68 (s, 4H), 4.27 (m, 4H), 3.84 (s, 2H), 3.43 (s, 2H), 3.36 (s, 8H), 3.26 (s, 6H), 3.12 (t, *J* = 6.7 Hz, 1H), 2.81 (s, 4H), 2.30 (s, 3H), 2.15 (m, 4H), 2.10 – 2.03 (m, 9H), 1.73 (m, 2H). ^{13}C NMR (CD_3OD, 151 MHz) δ (ppm.) 165.55, 162.87, 154.14, 146.71, 145.59, 143.46, 143.26, 142.27, 140.49, 140.10, 137.09, 134.70, 132.08, 131.78, 131.10, 131.05, 130.98, 130.70, 128.70, 127.71, 127.66, 127.48, 126.67, 126.52, 125.41, 124.55, 115.80, 97.24, 66.16, 65.39, 52.97, 51.52, 48.34, 48.13, 47.91, 47.70, 47.49, 47.27, 47.06, 45.38, 44.71, 43.28, 28.70, 28.34, 28.21, 27.38, 25.56, 22.18, 21.33, 20.04. HRMS-ESI: *m/z* calcd. $[M+2H]^{2+}$ for $C_{75}H_{91}N_{13}O_4S$, 1271.7146; found, 1271.7182

Compound TTC-L-M-4: 0.072 g, 0.05 mmol; Yield: 90%. ^{1}H NMR (DMSO, 600 MHz) δ (ppm.) 8.86 (s, 5H), 8.50 (s, 1H), 8.17 (s, 2H), 8.01 (s, 1H), 7.70 (m, 3H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.51 (s, 1H), 7.12 (m, 10H), 7.03 (d, *J* = 7.8 Hz, 2H), 7.02 – 6.85 (m, 5H), 5.66 (s, 4H), 4.19 (q, *J* = 6.9 Hz, 4H), 3.69 (s, 4H), 3.35 (m, 6H), 3.08 (m, 14H), 2.51 (m, 6H) ,2.03 (m, 2H), 1.80 (m, 10H), 1.62 (m, 6H), 1.29 (m, 4H), 1.22 (m, 12H). ^{13}C NMR (DMSO, 151 MHz) δ (ppm.) 165.54, 162.81, 158.83, 158.62, 153.58, 147.71, 145.43, 143.46, 143.25, 142.68, 142.11, 140.23, 134.92, 132.30, 131.27, 131.22, 131.16, 128.55, 128.52, 128.47, 128.39, 127.45, 127.33, 126.25, 125.88, 116.52, 97.39, 66.48, 65.55, 65.45, 52.55, 44.00, 42.76, 42.37, 40.50, 40.36, 40.22, 40.08, 39.94, 39.80, 39.66, 29.51, 29.48, 29.44, 29.18, 29.11, 28.67, 28.52, 25.86, 25.76, 15.70. HRMS-ESI: *m/z* calcd. $[M+2H]^{2+}$ for $C_{79}H_{99}N_{13}O_4S$,1327.7810; found, 1327.7808

Compound TTC-L-M-5: 0.064 g, 0.05 mmol; Yield: 80%. ^{1}H NMR (DMSO, 600 MHz) δ (ppm.) 8.54 (d, J = 6.8 Hz, 1H), 8.18 (s, 2H), 8.03 (dd, J = 9.1, 4.2 Hz, 1H), 7.84 (s, 2H), 7.74 (dd, J = 13.0, 4.0 Hz, 1H), 7.59 (dd, J = 25.4, 8.1 Hz, 2H), 7.45 (s,

1H), 7.20 – 7.11 (m, 6H), 7.08 (d, J = 8.2 Hz, 1H), 7.06 – 7.01 (m, 3H), 7.00 – 6.95 (m, 2H), 6.90 (d, J = 8.6 Hz, 1H), 6.85 (d, J = 8.6 Hz, 1H), 6.72 (d, J = 8.7 Hz, 1H), 6.68 (d, J = 8.7 Hz, 1H), 5.69 (s, 4H), 5.29 (s, 2H), 4.40 (d, J = 6.0 Hz, 4H), 3.86 (t, J = 6.4 Hz, 2H), 3.77 (s, 4H), 2.93 (dt, J = 144.8, 42.8 Hz, 14H), 2.13 (t, J = 6.2 Hz, 2H), 2.05 (s, 3H), 2.03 (d, J = 5.2 Hz, 1H), 1.97 (d, J = 2.4 Hz, 1H), 1.91 (s, 4H), 1.64 (q, J = 6.8 Hz, 3H), 1.38 – 1.33 (m, 2H), 1.31 – 1.21 (m, 12H), 0.85 (dt, J = 13.2, 6.9 Hz, 3H). ^{13}C NMR (DMSO, 151 MHz) δ (ppm.) 179.80, 172.50, 165.52, 162.78, 153.75, 147.79, 143.79, 142.75, 141.85, 138.17, 135.50, 134.84, 132.49, 132.34, 131.32, 131.13, 130.58, 128.73, 128.58, 128.50, 128.32, 127.20, 126.34, 126.24, 125.85, 116.52, 114.45, 114.26, 97.21, 67.82, 63.43, 62.50, 52.51, 36.15, 31.75, 29.25, 29.16, 28.13, 26.03, 24.40, 24.13, 22.60, 21.62, 14.48. HRMS-ESI: *m/z* calcd. $[M+2H]^{2+}$ for $C_{78}H_{97}N_{13}O_5S$,1329.7602; found, 1329.7600

Compound TTC-L-M-6: 0.073 g, 0.05 mmol; Yield: 87%. ^{1}H NMR (CD_3OD, 400 MHz) δ(ppm.) 8.33 (s, 1H), 8.08 (s, 1H), 7.87 (s, 2H), 7.77 (d, *J* = 9.3 Hz, 1H), 7.58 (s, 1H), 7.52 (d, *J* = 11.1 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.19 – 6.96 (m, 13H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.67 (d, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 9.1 Hz, 1H), 5.67 (s, 4H), 4.58 – 4.33 (m, 4H), 3.86 (m, 4H), 3.36 (m, 12H), 3.28 – 3.15 (m, 6H), 2.94 – 2.72 (m, 4H), 2.37 – 2.25 (m, 4H), 2.20 (m, 4H), 2.16 (m, 2H), 2.14 – 2.09 (m, 6H), 2.07 – 2.03 (m, 12H), 1.69 (q, *J* = 7.1 Hz, 2H), 1.41 (m, 4H), 1.29 (m, 13H), 0.90 – 0.85 (m, 3H). ^{13}C NMR (DMSO, 151 MHz) δ (ppm.) 179.78, 179.59, 172.49, 165.56, 162.82, 158.04, 157.92, 157.27, 153.67, 153.62, 147.69, 145.77, 143.78, 143.65, 142.70, 141.83, 139.25, 138.19, 135.50, 134.86, 132.54, 132.48, 132.33, 132.10, 131.31, 131.26, 130.56, 128.57, 128.49, 128.32, 127.40, 127.18, 126.30, 126.21, 125.82, 125.37, 116.53, 114.45, 114.25, 97.34, 67.81, 66.49, 65.55, 52.52, 48.00, 33.87, 31.74, 29.24, 29.16, 29.04, 28.65, 28.52, 26.04, 25.89, 25.80, 25.71, 24.97, 24.14, 22.59, 21.64, 14.48. HRMS-ESI: *m/z* calcd. $[M+2H]^{2+}$ for $C_{83}H_{107}N_{13}O_5S$,1399.8385; found, 1399.8384

1.2 *In Vitro* and *in Vivo* Experiments

Fluorescence Measurements: TTC-L-M-1/2/3/4/5/6 were dissolved in DMSO to obtain the stock solutions (1 mM). Solutions of different concentrations were obtained by transferring appropriate aliquots of stock solutions to volumetric flasks and then diluting them to certain volumes using deionised Milli-Q water and organic solvent. All of the samples were vortex mixed and allowed to stand for 6 - 10 min before testing.

Gel Retardation Assay. The samples were prepared by adding liposomes with different concentrations to 1 μL of pUC18 DNA (200 μg/mL) in Tris-HCl buffer (50 mM, pH 7.4) with a total volume of 20 μL at room temperature. After that, the samples were incubated at 37°C for 30 min, and 2 μL of 6× loading buffer were added to the above samples. The samples were electrophoresed at 100 V on a 0.7% agarose gel containing GelRed in Tris-acetate (TAE) running buffer for 30 min. The result was visualized under on a UVP EC3 visible imaging system

Assembly of TTC-L-M-1/2/3/4/5/6: The morphologies of micelles and complexes were studied by scanning electronic microscopy (SEM) and dynamic light scattering (DLS). The DLS sample were prepared similar to gel retardation assay, the solution was

diluted to 200 μL after interaction with negatively supercoiled pUC18 DNA at 37°C for 30 min. The diluted solution 10 μL dropped on the surface of wafer, then completely evaporated to obtain the SEM.

$^1O_2$-Generation Detection: ABDA was applied as the $^1O_2$ monitoring agent. The 25 μL of ABDA stock solution (1mg/mL) was added to 2 mL of **TTC-L-M-4** suspension (10 μM), and LED light (450 nm, 10 mW/cm^{-2}) was employed as the irradiation source. The absorption of ABDA was recorded at 378 nm at various irradiation times to obtain the decay rate of the photosensitizing process.

Cytotoxicity Assay. The cytotoxicity of liposomes was investigated in HeLa, A549 and HepG2 cells by MTT assay. All cells were cultured in complete medium in a humidified atmosphere containing 5% CO_2 at 37 ºC. After 24 h of incubation, the cells were seeded in 96-well plate (7000 cells/well) and cultured for another 24 h. The cells were incubated with different concentrations of liposomes for 4 h. Then, 100 μL complete medium were added to each well and cultured for 20 h. The medium was replaced with 20 μL of MTT (5 mg/mL) and incubated for another 4 h. Finally, MTT was replaced with 120 μL of DMSO, and the plates were oscillated for 10 min to fully dissolve the formazan crystals formed by living cells in the wells. The optical density (OD) was recorded at 490 nm using a Thermo Scientific Multiskan GO. The viability of the cells was calculated using the following formula:

Cell viability = [$OD490\ (Sample)$ - $OD490\ (Blank)$] / [$OD490\ (Control)$ - $OD490\ (Blank)$] × 100%

HeLa cells were treated with **TTC-L-M-4**/DOPE for 4 h and then exposed to LED light (450 nm, 10 mW/cm^{-2}) for the exploration of phototoxicity. The cytotoxicity was performed using the MTT assay as described above 24 h later. Cells without any treatments were used as controls.

Cell Imaging. Time dependence of cellular uptakes of **TTC-L-M-4**/DOPE/Cy5-DNA were measured by confocal laser scanning microscopy (CLSM) in HeLa cell lines. The cells were seeded in Glass Bottom Cell Culture Dishes at 5 × 10^4 cells per dish and cultured for 24 h. After washed three times with PBS, the cells were exposure to **TTC-L-M-4**/DOPE/Cy5-DNA for predetermined durations. The Hoechst 33342 (5 μg/mL) was also added to the cells for nuclear staining at 37 ºC for 10 min. Finally, the cells were washed for 5 times with PBS buffer, observed using a confocal laser scanning microscope with a 60× oil-immersion objective.

Cell Migration Study: The cells were incubated for 4 h with **TTC-L-M-4**/DOPE/pGL-3 and **TTC-L-M-4**/DOPE/p53 in a 6-well chamber. Then, a 10 μL tip was then used to scratch a wound gap on the monolayer HeLa cells. The scratched cells were washed away with 1 × PBS buffer, and the wound gaps were imaged by CLSM with a 10× objection and cultured for 20 h. For the PDT-treated group (**TTC-L-M-4**/DOPE/pGL-3 (+L)) and the combination treatment group (**TTC-L-M-4**/DOPE/p53 (+L)), the cells were subjected to light irradiation for 10 min irradiation at 24 h post-internalization. For the gene therapy group (**TTC-L-M-4**/DOPE/p53 (-L)), cells were cultured for another 20 h. Finally, the wound gaps were imaged.

***In Vitro* Apoptosis Assay:** HeLa cells were cultured as described above, incubated with **TTC-L-M-4**/DOPE/pGL-3 and **TTC-L-M-4**/DOPE/p53 for 4 h. After changing the

medium to fresh ones, cells were cultured for 20 h. For the PDT-treated group (**TTC-L-M-4**/DOPE/pGL-3 (+L)) and the combination treatment group (**TTC-L-M-4**/DOPE/p53 (+L)), the cells were subjected to light irradiation for 10 min irradiation at 24 h post-internalization. For the gene therapy group (**TTC-L-M-4**/DOPE/p53 (-L)), cells were cultured for another 24 h. The cell viability was determined at 48 h post transfection using the MTT assay. Furthermore, the Annexin V-FITC Apoptosis Detection Kit were used for detecting the apoptosis of HeLa cells treated with different formulations via flow cytometry following the manufacturer's instructions.

In Vivo **Antitumor Assay:** BALB/c nude mice (five weeks, female) were subcutaneously injected with 1×10^6 HeLa cells in the right flank to establish a HeLa tumor model. When the tumors reached 50-100 mm^3, the mice were randomly divided into four groups (n = 5 per group) and subcutaneously injected around the tumor every other day with 100 μL of lipoplexes (7 μg DNA and 140 μM liposomes). Group 1 treated injection of PBS. Group 2 treated **TTC-L-M-4**/DOPE/pGL-3 and light irradiation (LED light, 450 nm, 10 mW/cm^{-2}) for 30 min at 24 h post injection. Group 3 treated **TTC-L-M-4**/DOPE/p53 but without light irradiation. Group 4 treated **TTC-L-M-4**/DOPE/p53 and light irradiation (LED light, 450 nm, 10 mW/cm^{-2}) for 30 min at 24 h post injection. Tumor sizes of each group were monitored every other day by a caliper (tumor volume = length × width × width/2). Relative tumor volumes were calculated as V/V_0 (V_0 was the tumor volume when the treatment was initiated). On the14th day, all the mice were sacrificed and the tumor tissues were sectioned and collected for hematoxylin-eosin (H&E) staining.

2. Characterizations of TTC-L-M Derivatives

2.1. UV-Visible Spectra of the Compounds in Different Solvents

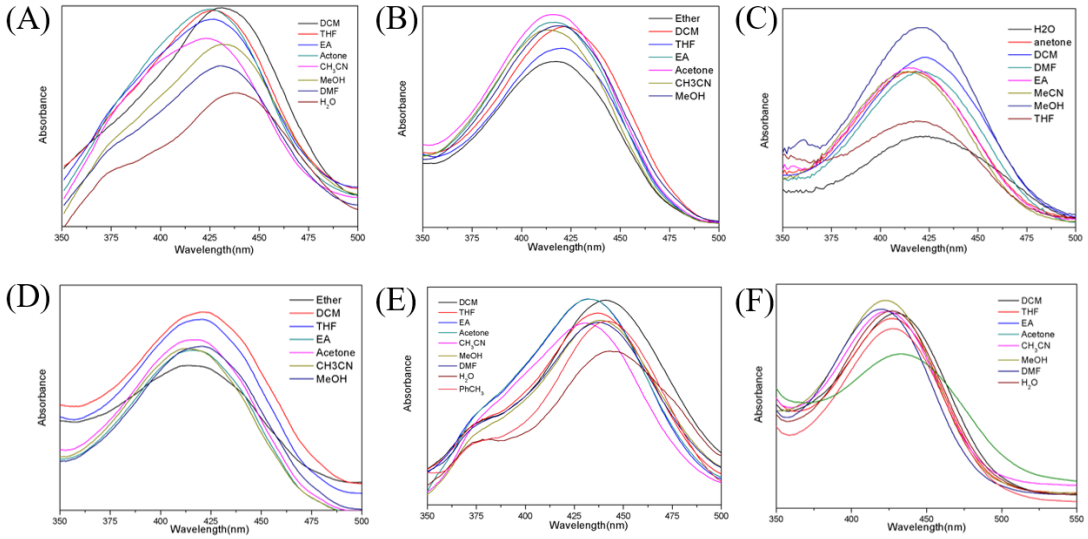


Figure S1. UV-vis spectra of **TTC-L-M-1/2/3/4/5/6** in different solutions. Concentration: 10 μM

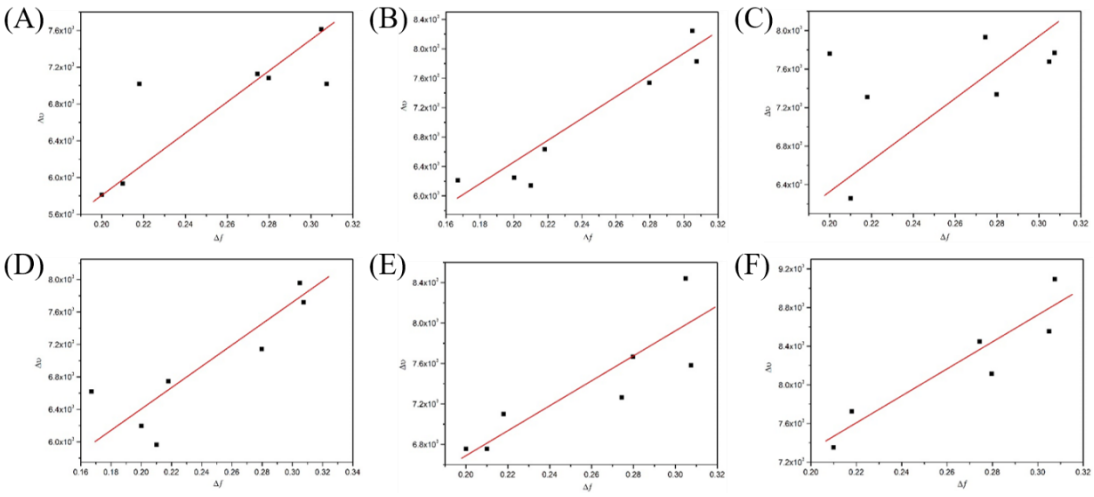


Figure S2. Plot of Stokes shift (Δυ) of **TTC-L-M-1/2/3/4/5/6** versus Δf of their solutions. Concentration: 10 μM; λex = 426 nm

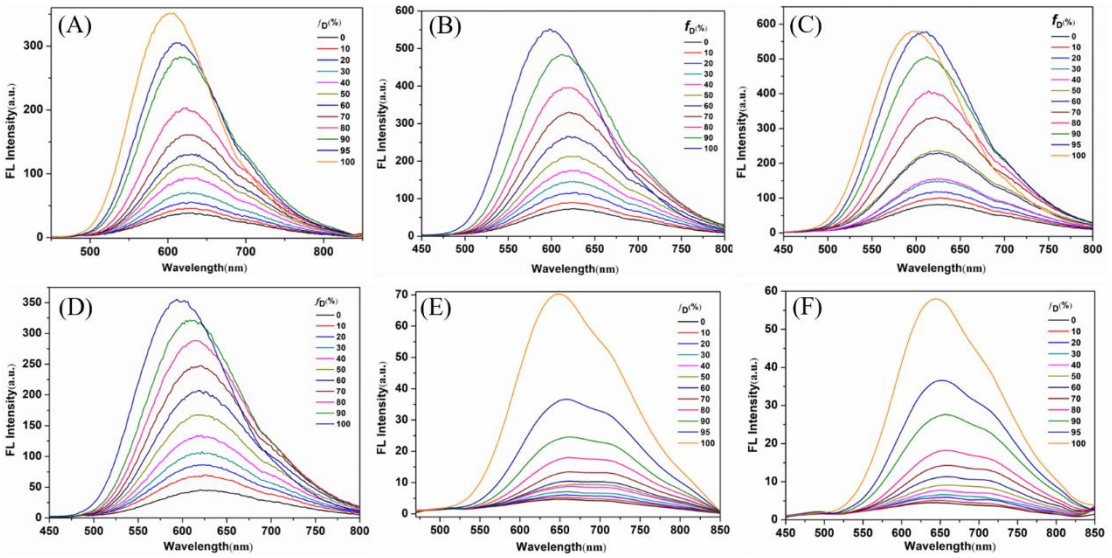


Figure S3. (A-F) Fluorescence spectra of **TTC-L-M-1/2/3/4/5/6** in MeOH/DCM mixtures with different DCM fractions (f_w). Concentration: 10 μM; λex = 426 nm.

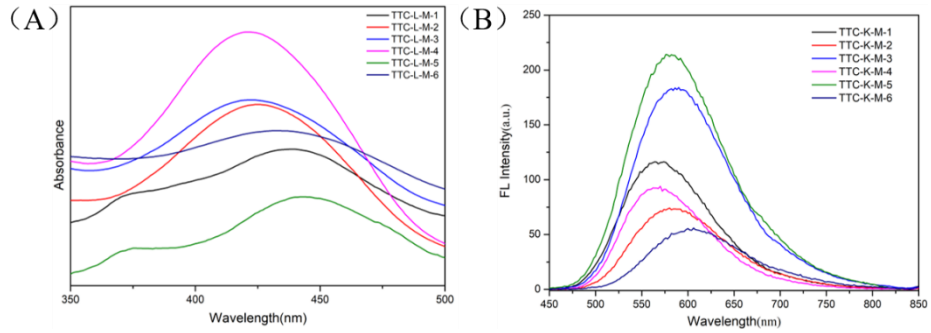


Figure S4. (A) UV-vis spectra of **TTC-L-M** derivatives in H_2O. (B) Fluorescence spectra of **TTC-L-M** derivatives in H_2O. Concentration: 10 μM; λex = 426 nm.

Table S1 Summarized photophysical data of **TTC-L-M** derivatives in Different Solvents

Compound	solvent	λ_{ab}(nm)	λ_{em}(nm)	Stoke's shift (nm)	Φ_F/%
TTC-L-M-1	DCM	431	618	187	19.3
	THF	427	572	145	5.3
	EA	427	568	141	6.1
	Acetone	426	610	184	7.6
	MeCN	423	624	201	8.4
	MeOH	432	620	188	3.6
	DMF	430	620	190	9.3
TTC-L-M-2	Ether	422	572	150	1.8
	DCM	424	590	166	14.1
	THF	420	566	146	8.2
	EA	417	564	147	5.3
	Acetone	416	606	190	8.8
	MeCN	412	624	212	8.1
	MeOH	421	628	207	2.6
TTC-L-M-3	DCM	420	606	186	16.8
	THF	418	566	148	5
	EA	414	610	196	3.7
	Acetone	420	607	187	6.5
	MeCN	421	622	201	6.6
	MeOH	423	630	207	3.7
	DMF	417	623	206	9.6

Compound	solvent	λ_{ab}(nm)	λ_{em}(nm)	Stoke's shift (nm)	Φ_F/%
TTC-L-M-4	Ether	417	576	159	8.0
	DCM	423	592	169	9.5
	THF	422	564	142	4.3
	EA	419	566	147	4.9
	Acetone	419	598	179	7.5
	MeCN	417	624	207	6.7
	MeOH	422	626	204	3.0
TTC-L-M-5	DCM	441	642	201	5.6
	THF	437	620	183	4.8
	EA	432	610	178	7.1
	Acetone	432	646	214	3.3
	MeCN	430	675	245	1.5
	MeOH	439	658	219	1.4
	DMF	447	662	215	1.8
TTC-L-M-6	DCM	430	644	214	5.0
	THF	423	614	191	4.9
	Acetone	423	644	221	2.3
	MeCN	421	658	237	1.1
	MeOH	427	698	271	0.7
	DMF	427	668	241	1.5

Abbreviation: λab = absorption maximum, λem = emission maximum, Φ_F = fluorescence quantum yield, concentration: 10 μM

Table S2 Summarized photophysical data of **TTC-L-M** derivatives in H_2O

	λ_{ab}(nm)	λ_{em}(nm)	Stoke's shift (nm)	Φ_F/%
TTC-L-M-1	439	564	125	7.7
TTC-L-M-2	427	580	153	8.3
TTC-L-M-3	422	590	168	9.0
TTC-L-M-4	421	570	149	10.5
TTC-L-M-5	444	576	132	9.4
TTC-L-M-6	433	600	167	12.0

2.2 Micelle Formation

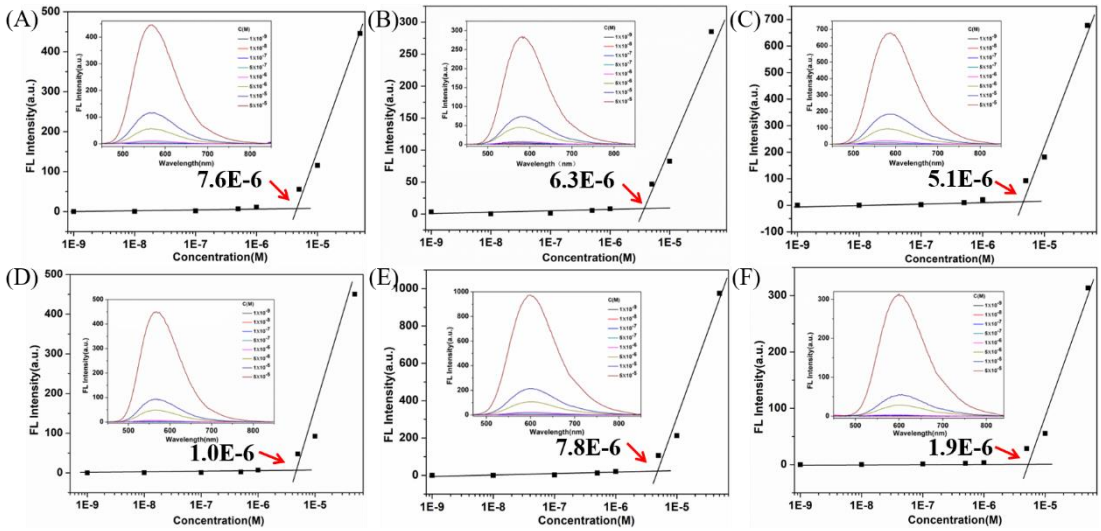


Figure S5. (A-F) Determination of critical micelle concentrations (CMCs) of **TTC-L-M-1/2/3/4/5/6** in water. λex = 426 nm, 25 ℃

2.3 SEM, DLS and Zeta Measurements

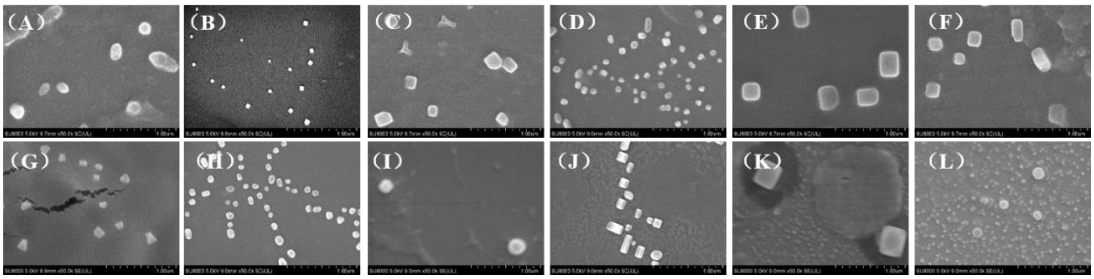


Figure S6. SEM images of **TTC-L-M** derivatives in the absence (A-F) and presence of DOPE (G-L). [**TTC-L-M-1**] = 35 μM, [**TTC-L-M-2**] = 10 μM, [**TTC-L-M-3**] = 15 μM, [**TTC-L-M-4**] = 25 μM, [**TTC-L-M-5**] = 30 μM, [**TTC-L-M-6**] = 20 μM; scale bars: 1 μm.

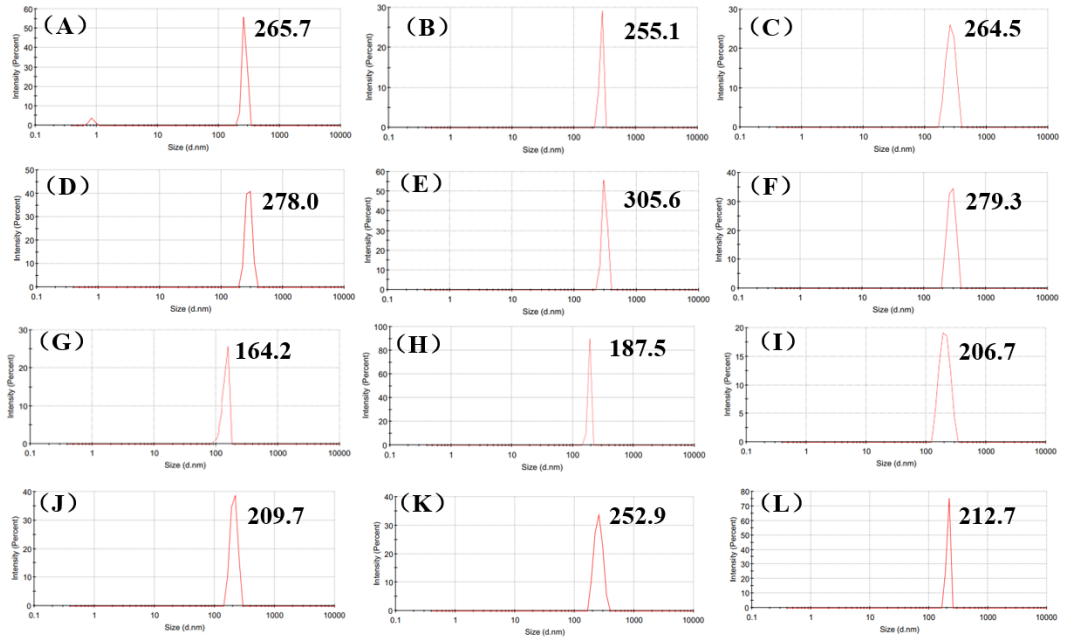


Figure S7. DLS of **TTC-L-M** derivatives in the absence (A-F) and presence of DOPE (G-L). [**TTC-L-M-1**] = 35 μM, [**TTC-L-M-2**] = 10 μM, [**TTC-L-M-3**] = 15 μM, [**TTC-L-M-4**] = 25 μM, [**TTC-L-M-5**] = 30 μM, [**TTC-L-M-6**] = 20 μM

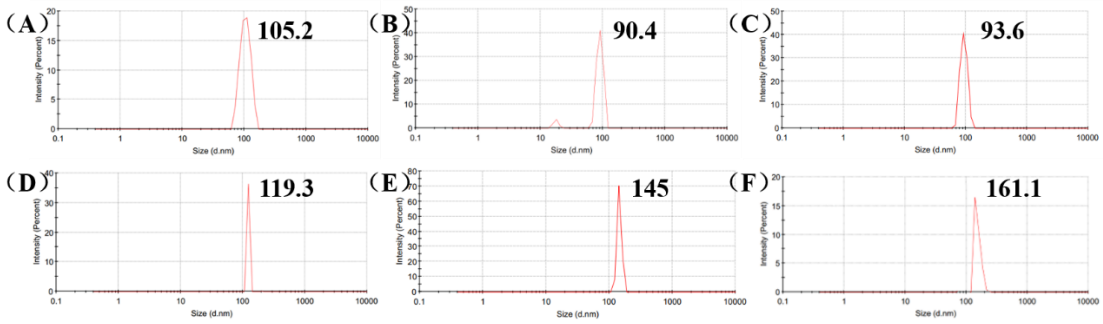


Figure S8. DLS of the lipoplexes of **TTC-L-M** derivatives/DOPE (1:2) with pUC18 DNA in Tris buffer (50 mM, pH 7.4). [**TTC-L-M-1**] = 35 μM, [**TTC-L-M-2**] = 10 μM, [**TTC-L-M-3**] = 15 μM, [**TTC-L-M-4**] = 25 μM, [**TTC-L-M-5**] = 30 μM, [**TTC-L-M-6**] = 30 μM.

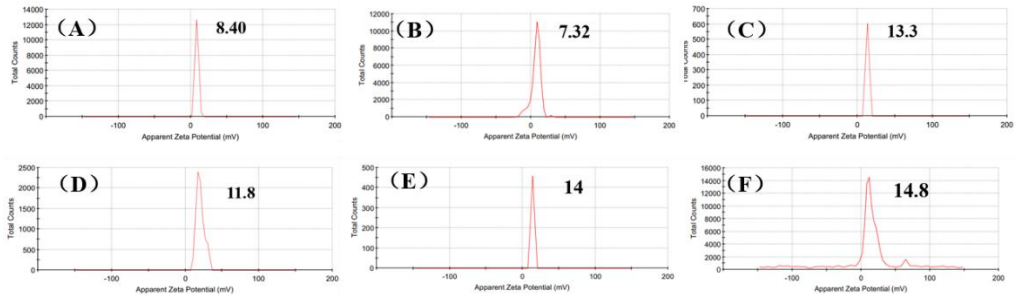


Figure S9. Zeta potentials of pUC18 DNA complexes. [**TTC-L-M-1**] = 35 μM, [**TTC-L-M-2**] = 10 μM, [**TTC-L-M-3**] = 15 μM, [**TTC-L-M-4**] = 25 μM, [**TTC-L-M-5**] = 30 μM, [**TTC-L-M-6**] = 20 μM, [DNA] = 10 μg/mL

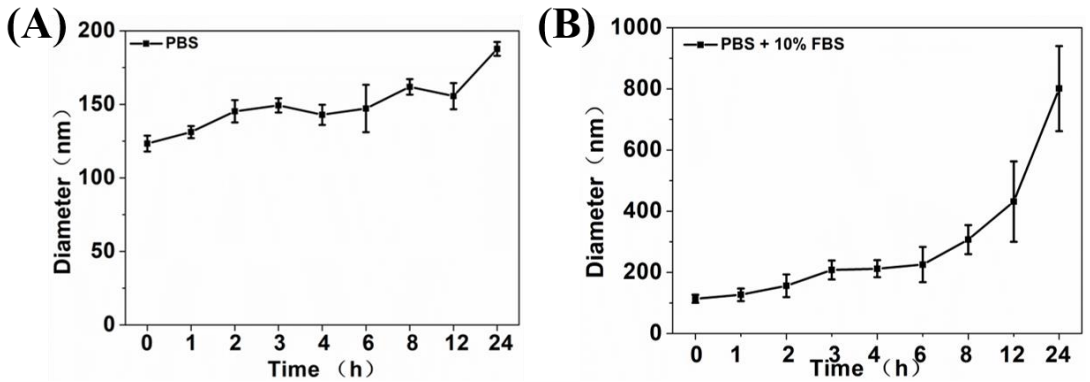


Figure S10. The average diameters of **TTC-L-M-4**/DOPE/DNA in PBS (A) and 10% FBS (B) after incubation for different time. [**TTC-L-M-4**] = 15 μM, [pDNA] = 10 μg/mL, r.t.

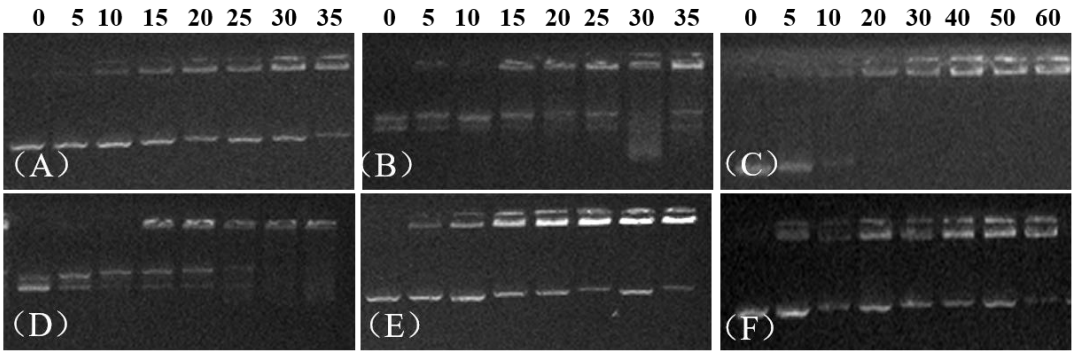


Figure S11. Gel electropherogram assay of the DNA induced by different concentrations of **TTC-L-M-1/2/3/4/5/6** in the absence of DOPE (A-F) in Tris-HCl (50 mM, pH 7.4). [DNA] = 10 μg/mL, r.t.

2.4 EB Assay

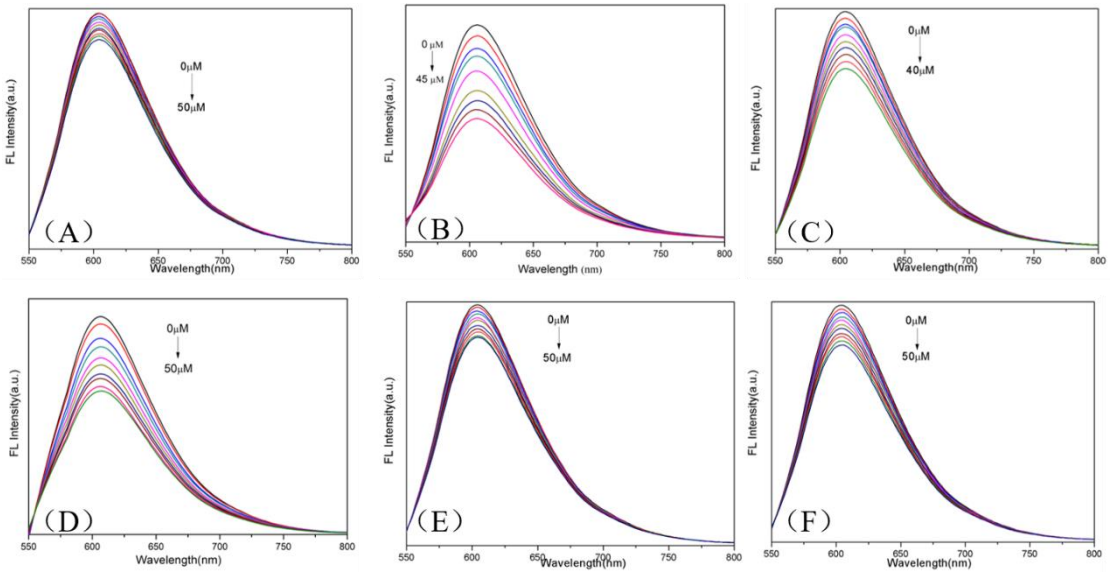


Figure S12. Ethidium bromide exclusion measurements by **TTC-L-M-1/2/3/4/5/6** in the presence of DOPE (1:2 ratio) in 5mM Tris-HCl/50mM NaCl (pH 7.4, 25 °C). [EB] = 20 μM, [DNA] = 100 μM.

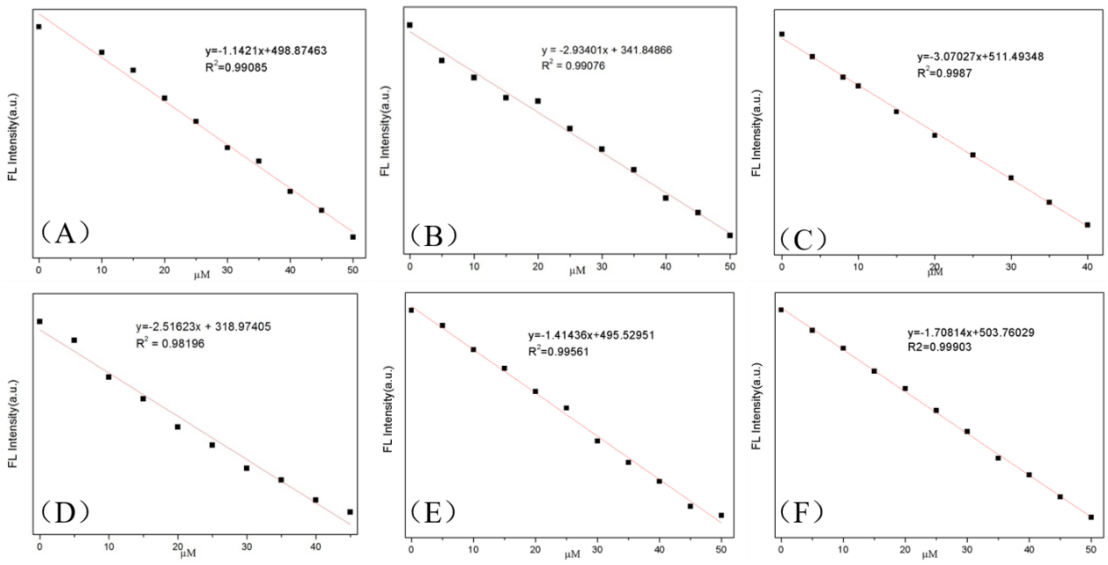
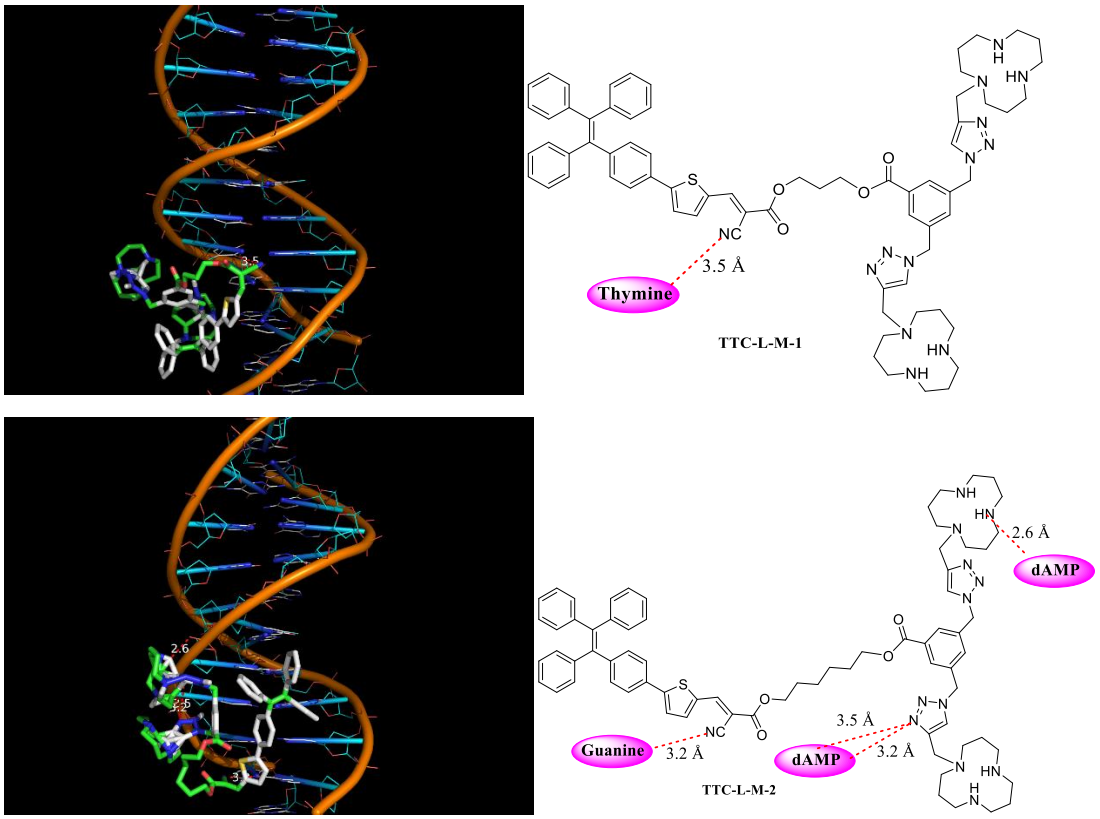


Figure S13. (A-F) Ethidium bromide exclusion measurements by **TTC-L-M-1/2/3/4/5/6** in the presence of DOPE (1:2 ratio) in 5mM Tris-HCl/50mM NaCl (pH 7.4, 25 °C). [EB] = 20 μM, [DNA] = 100 μM.

2.5 Docking Assays and Gel Electrophoresis



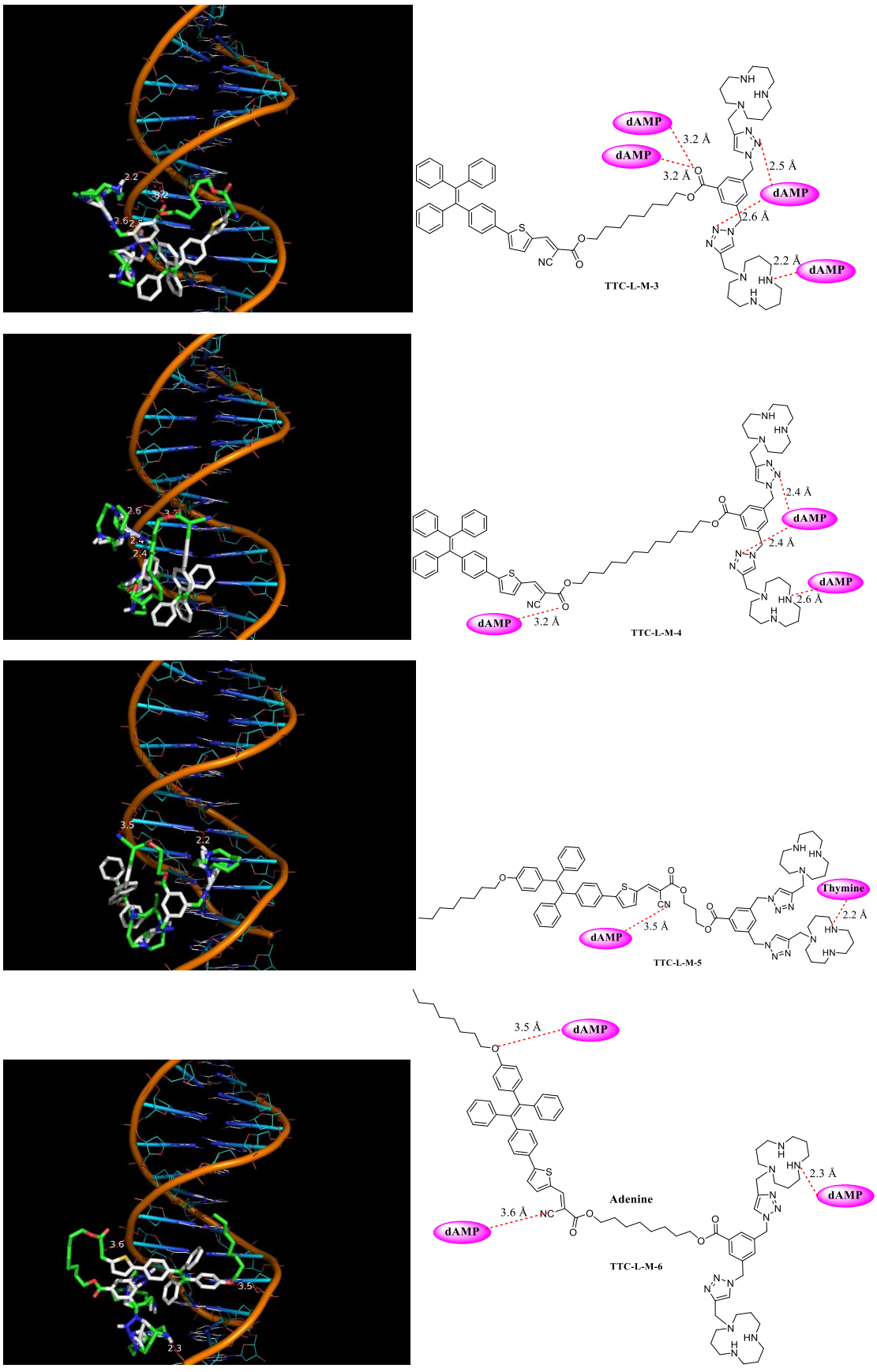


Figure S14. Molecular docking results of compounds and DNA. (PDB code 1BNA)

2.6 DNA Release

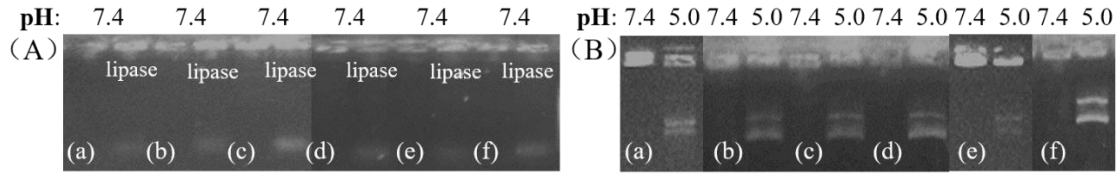


Figure S15. (A) Gel electrophoresis to measure the reversibility of DNA condensations caused by **TTC-L-M** derivatives/DOPE (1:2) in the presence of lipase. (B) Gel electrophoresis experiments at different pH values. [DNA] = 9 μg/mL, [lipase] = 10 μg/mL, [heparin] = 40 μg/mL.

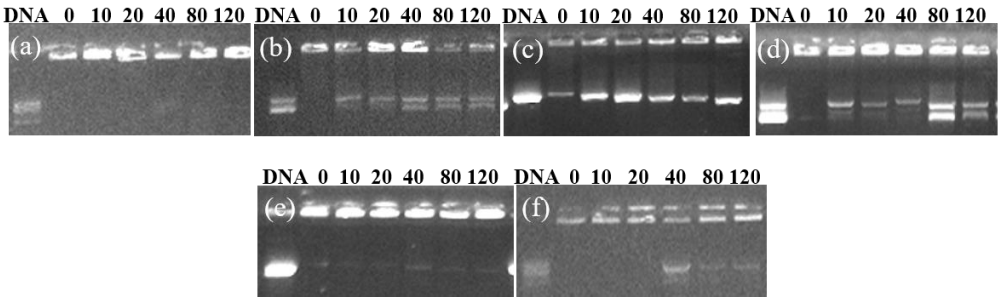


Figure S16. Gel electrophoresis to measure the reversibility of DNA condensations caused by **TTC-L-M-1**/DOPE (35 μM), **TTC-L-M-2**/DOPE (15 μM), **TTC-L-M-3**/DOPE (10 μM), **TTC-L-M-4**/DOPE (15 μM), **TTC-L-M-5**/DOPE (30 μM) and **TTC-L-M-6**/DOPE (20 μM) at heparin. [DNA] = 10 μg/mL, heparin= 0 −120 μg/mL.

2.7 Cell Cytotoxicity

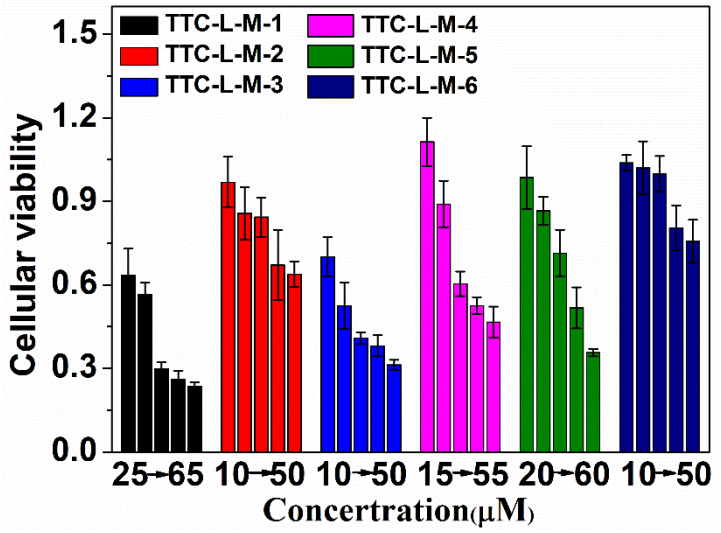


Figure S17. Cytotoxicity of HeLa cell lines cultured with **TTC-L-M** derivatives at different concentrations

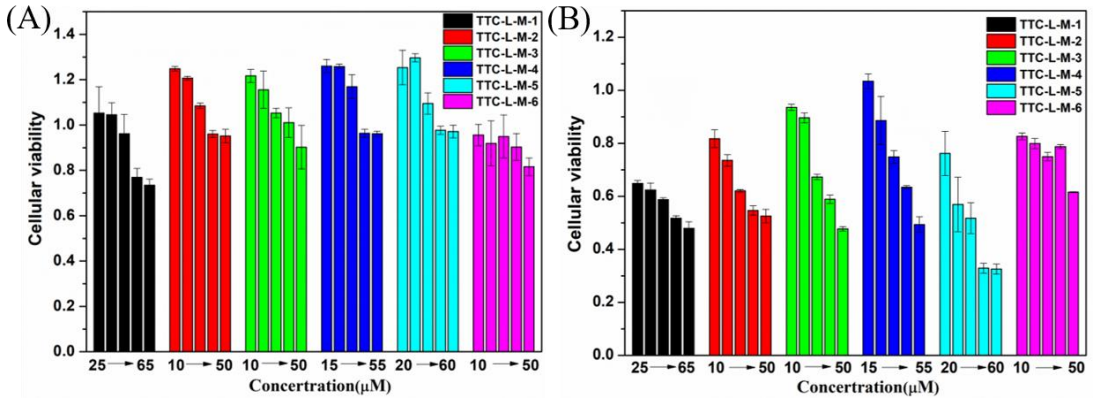


Figure S18. Cytotoxicity of **TTC-L-M** derivatives/DOPE (1:2) at different concentrations cultured with HepG2 cell lines (A) and A549 cell lines (B).

Table S3 The calculated IC_{50} values of **TTC-L-M** derivatives.

	A549	**HeLa**	**HepG2**
TTC-L-M-1	53.02	77.85	77.19
TTC-L-M-2	54.74	73.51	122.69
TTC-L-M-3	55.59	117.96	126.87
TTC-L-M-4	62.95	131.91	>1000
TTC-L-M-5	37.57	101.93	143.09
TTC-L-M-6	201.67	84.32	343.18

2.8 Gene Transfection Assays

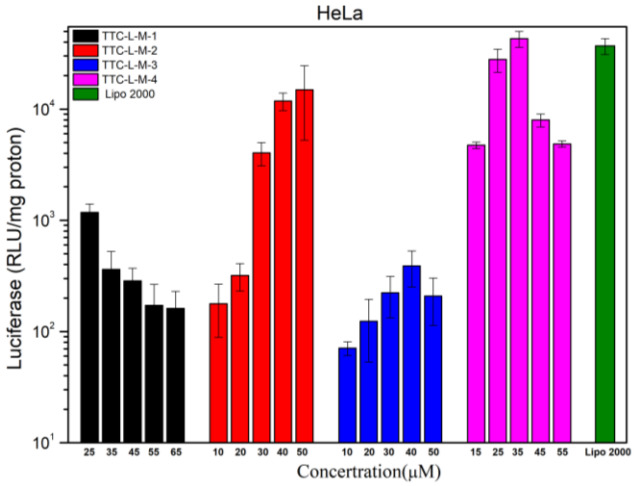


Figure S19. Luciferase gene expressions transfected by **TTC-L-M-1/2/3/4** in HeLa cell lines with Lipo2000 as control. [pGL-3] = 10 μg/mL

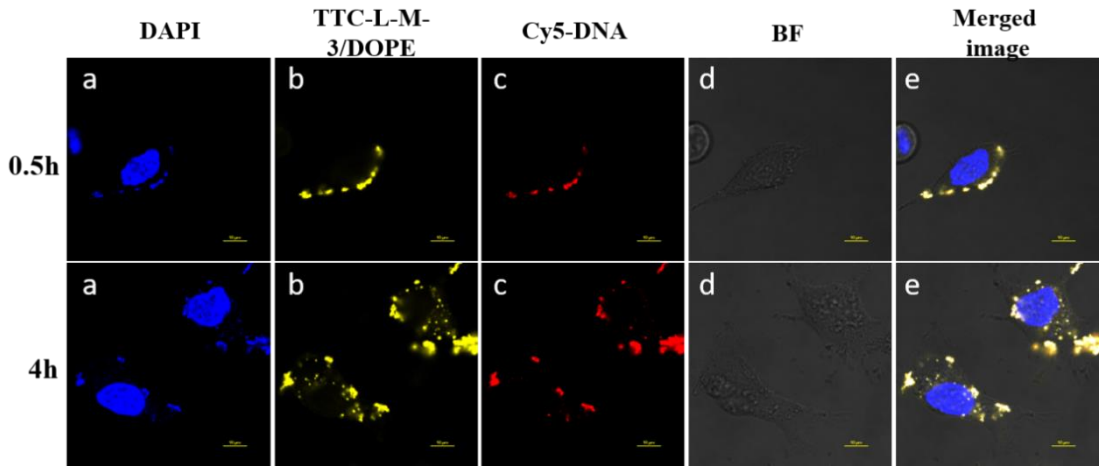


Figure S20. CLSM images of transport process into HeLa cells after treated with **TTC-L-M-3**/DOPE (1:2) and Cy5-labeled DNA for 0.5 and 4h. The nuclei were stained with Hoechst 33342. (a) The nucleus (Blue channel). (b) **TTC-L-M-3**/DOPE (yellow channel). (c) Cy5-labeled DNA (red channel). (d) Bright field. (e) Merge of a, b, c, d. [**TTC-L-M-3**] = 25 μM, [Cy5-DNA] = 10 μg/mL, scale bar: 10 μm.

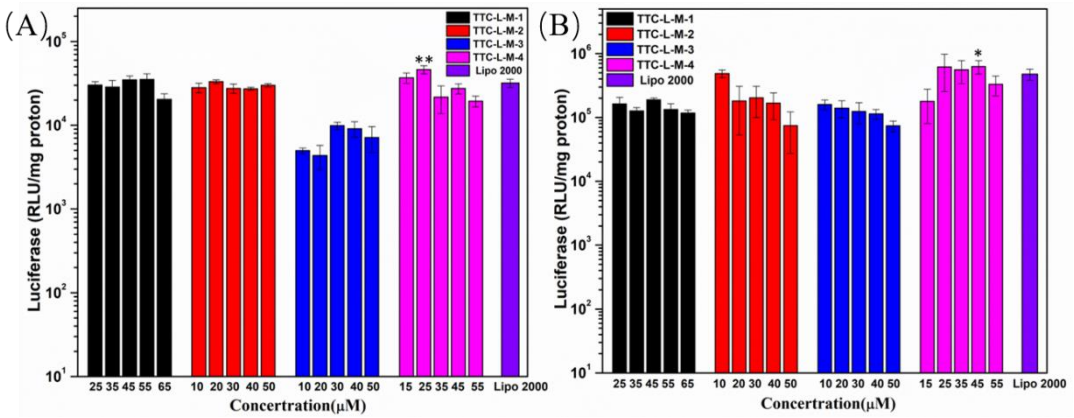


Figure S21. Luciferase expression induced by different concentrations of **TTC-L-M-1/2/3/4-**DOPE (1:2) in HepG2 cell lines (A) and A549 cell lines (B) with Lipo2000 as control. Data represent mean ± SD (n = 3); *0.01 < p < 0.05, **0.001 < p < 0.01, and *** p < 0.001 analyzed by Student's t-test.

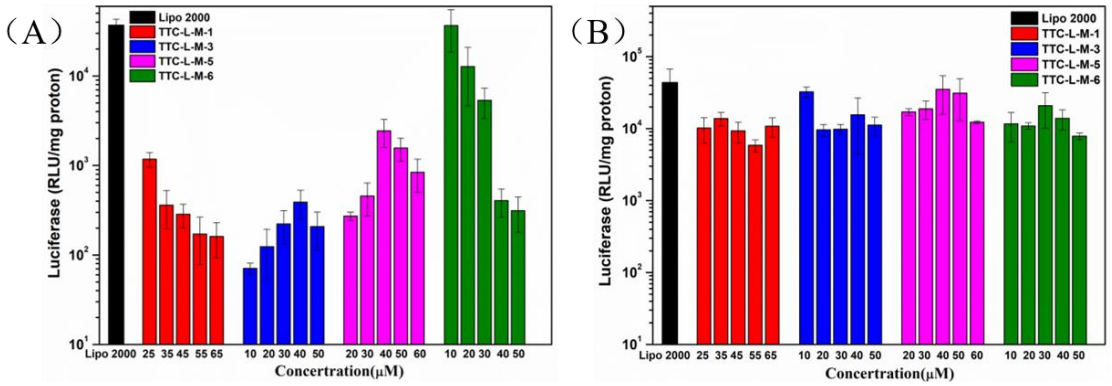


Figure S22. Luciferase expression induced by different concentrations of **TTC-L-M-1/3/5/6** without or with DOPE in Hela cell lines with Lipo2000 as control.

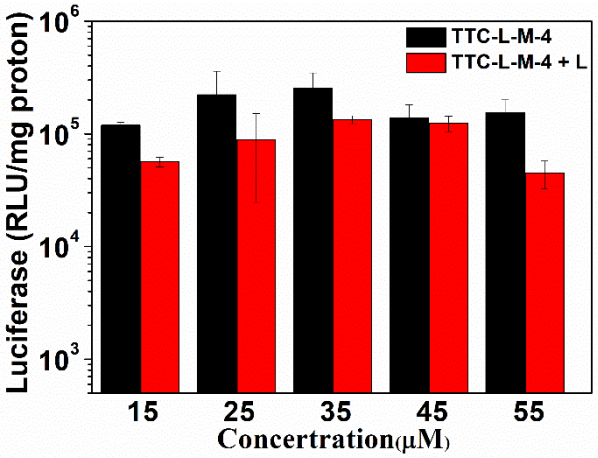


Figure S23. Luciferase expression induced by different concentrations of **TTC-L-M-4-**DOPE (1:2) in HeLa cell lines under dark or LED light irradiation.

Table S4 Optimal luciferase expressions of **TTC-L-M-1/2/3/4** in HeLa cell lines (% of Lipo2000).

	TTC-L-M-1	**TTC-L-M-2**	**TTC-L-M-3**	**TTC-L-M-4**
HeLa	3.2	40.3	1.1	116.5

Table S5 Optimal luciferase expressions of **TTC-L-M-1/3/5/6** in HeLa cell lines (% of Lipo2000).

	TTC-L-M-1	**TTC-L-M-3**	**TTC-L-M-5**	**TTC-L-M-6**
HeLa	3.2	1.1	6.6	99.3

Table S6 Optimal luciferase expressions of **TTC-L-M** derivatives/DOPE in different cell lines (% of Lipo2000). The molar ratio of **TTC-L-M** derivatives and DOPE was 1:2

	A549	**HepG2**	**HeLa**
TTC-L-M-1	40	111	32
TTC-L-M-2	102	104	48
TTC-L-M-3	36	31	74
TTC-L-M-4	131	145	450
TTC-L-M-5	--	--	80
TTC-L-M-6	--	--	47

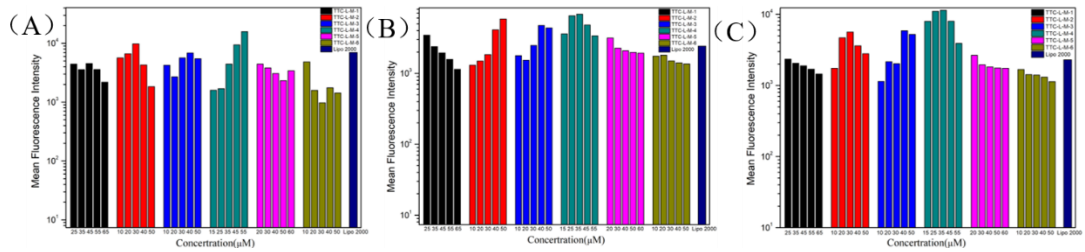


Figure S24. Green Fluorescent protein induced by different concentrations of **TTC-L-M** derivatives/DOPE (1:2) in A549 cell lines, HepG2 cell lines and HeLa cell lines with Lipo2000 as control.

Table S7 Optimal green fluorescent protein expressions of **TTC-L-M** derivatives/DOPE in different cell lines (% of Lipo2000). The molar ratio of **TTC-L-M** derivatives and DOPE was 1:2

	A549	**HepG2**	**HeLa**
TTC-L-M-1	63	140	102
TTC-L-M-2	140	240	246
TTC-L-M-3	98	180	256
TTC-L-M-4	226	280	498
TTC-L-M-5	63	130	115
TTC-L-M-6	69	75	73

Table S8 Optimal luciferase expressions of **TTC-L-M-4**/DOPE in the media containing 10% serum in different cell lines (% of Lipo2000). The molar ratio of **TTC-L-M-4** and DOPE was 1:2

	HeLa	**HepG2**	**A549**
TTC-L-M-4	442	88	143

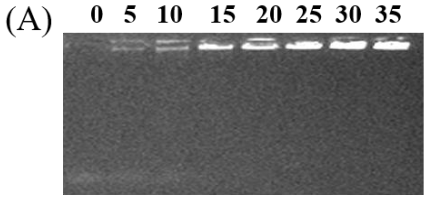


Figure S25. (A) Gel electropherogram assay of the siRNA induced by different concentrations of **TTC-L-M-4**/DOPE in Tris-HCl (50 mM, pH 7.4).

Table S9 Optimal gene silencing of **TTC-L-M**-4/DOPE in different cell lines (% of control). The molar ratio of **TTC-L-M-4** and DOPE was 1:2

	HepG2 -Luc	**A549-Luc**
TTC-L-M-4	60	79
Lipo2000	42	48

2.9 Tracing the Delivery of DNA

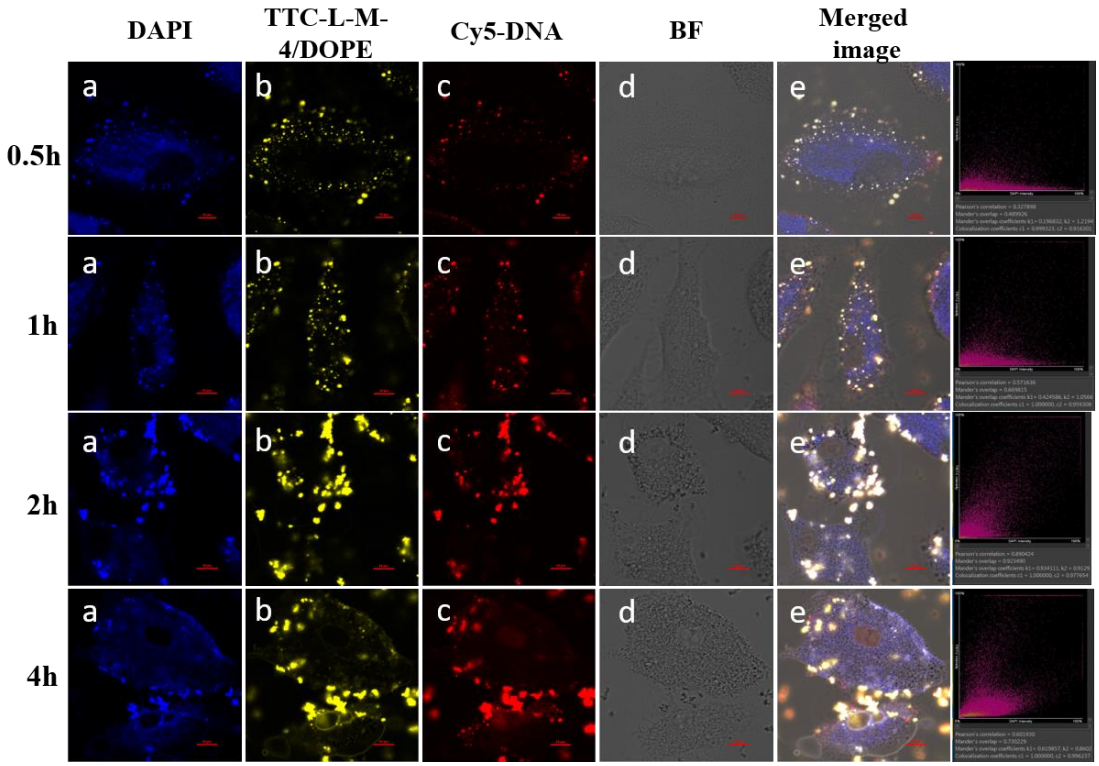


Figure S26. Endo/lysosomal escape of **TTC-L-M-4**/DOPE/Cy5-DNA in HeLa cells for 0.5, 1, 2, and 4 h. The blue channel was LysoTracker-Blue (a). The yellow channel was **TTC-L-M-4**/DOPE (b). The red channel wad Cy5-labeled DNA (c). Bright field (d). Merge of a, b, c, d (e). [**TTC-L-M-4**] = 25 μM, [Cy5-DNA] = 10 μg/mL, scale bar: 10 μm.

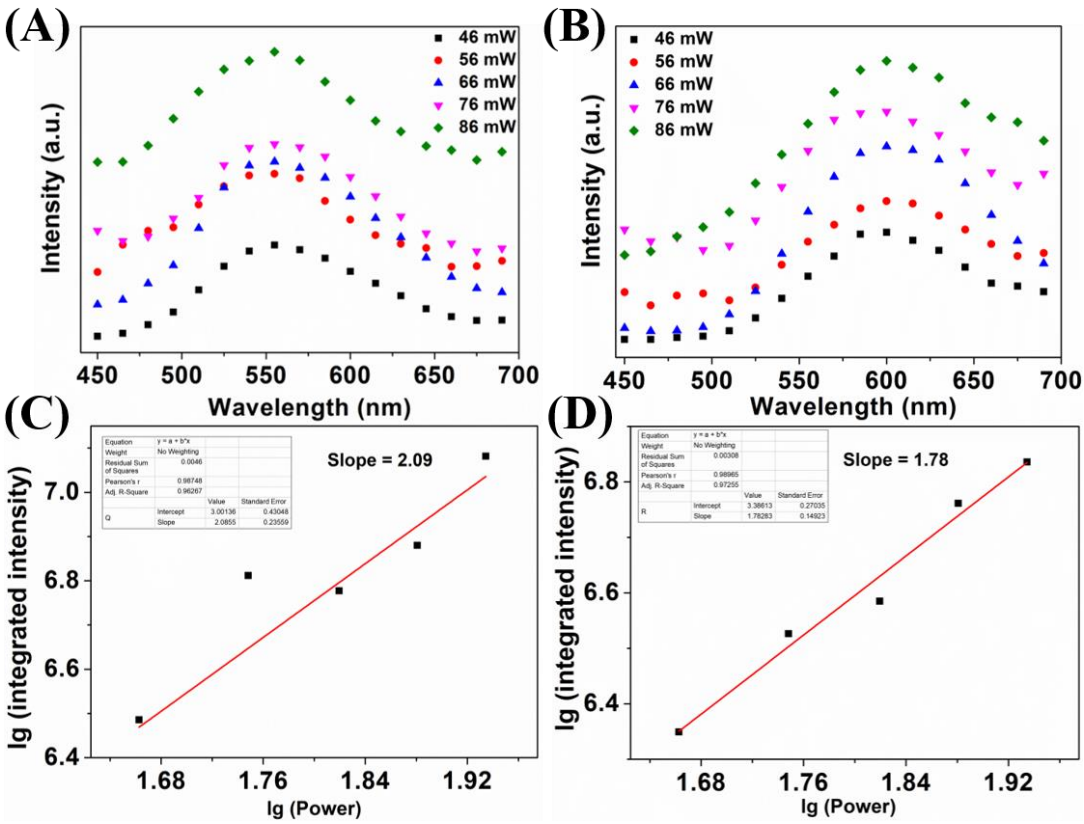


Figure S27 TPEF spectra of **TTC-L-M-4** (A) and **TTC-L-M-5** (B) at different excitation energies at 840 nm. Linear relationship of logarithm laser power and logarithm-integrated intensity for **TTC-L-M-4** (A) and **TTC-L-M-5** (B) in water. Concentration: 10 μM. Rhodamine B was used as the standard. 1 GM = 1 × 10^{-50} $cm^4 \cdot s \cdot molecule^{-1} \cdot photon^{-1}$.

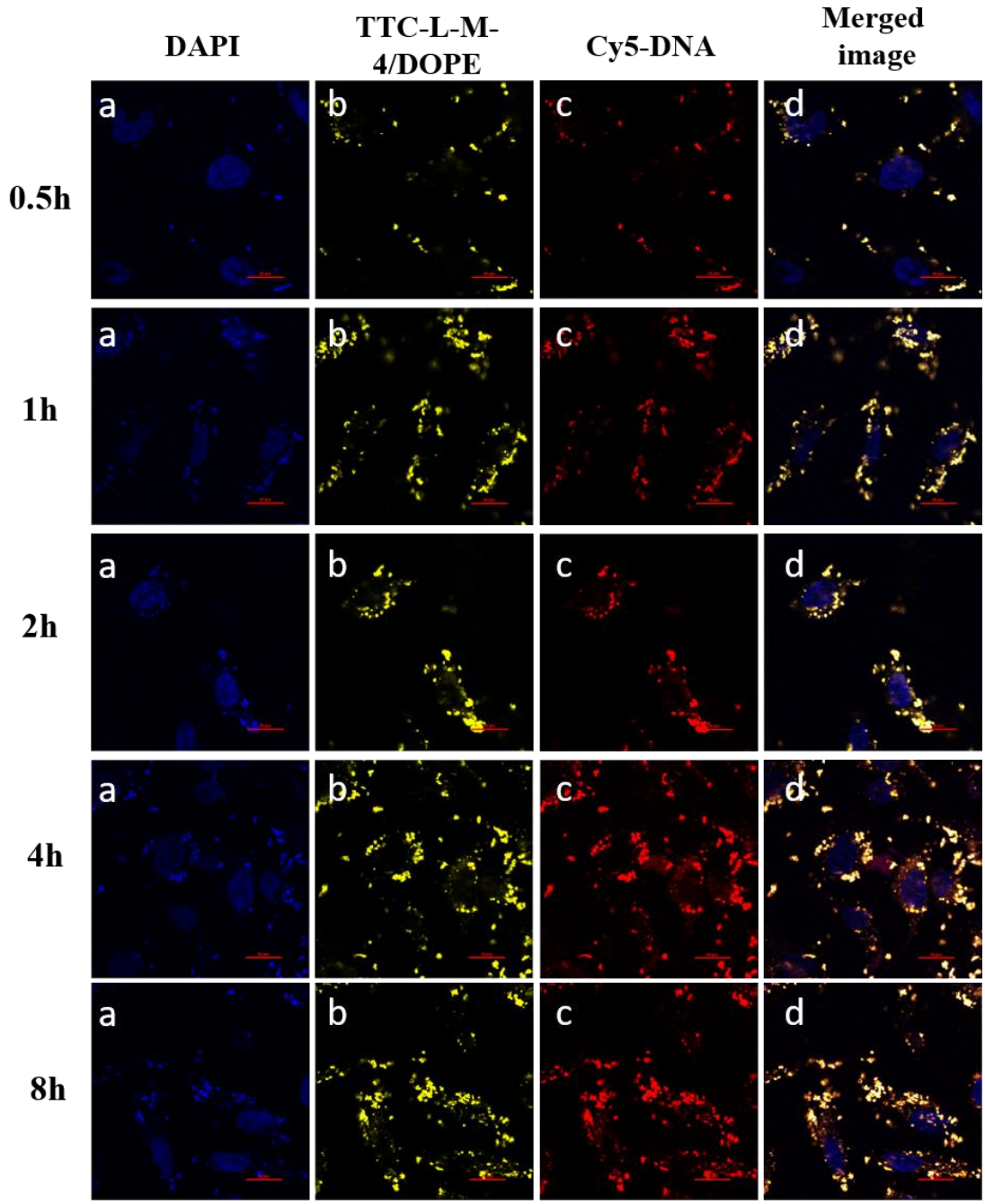


Figure S28. Two-photon CLSM images of transport process into HeLa cells after treated with **TTC-L-M-4**/DOPE (1:2) and Cy5-labeled DNA for 0.5, 1, 2, 4, and 8 h. The nuclei were stained with Hoechst 33342. (a) The nucleus (Blue channel). (b) **TTC-L-M-4**/DOPE (yellow channel). (c) Cy5-labeled DNA (red channel). (d) Merge of a, b, c. [**TTC-L-M-4**] = 25 μM, [Cy5-DNA] = 10 μg/mL, scale bar: 10 μm.

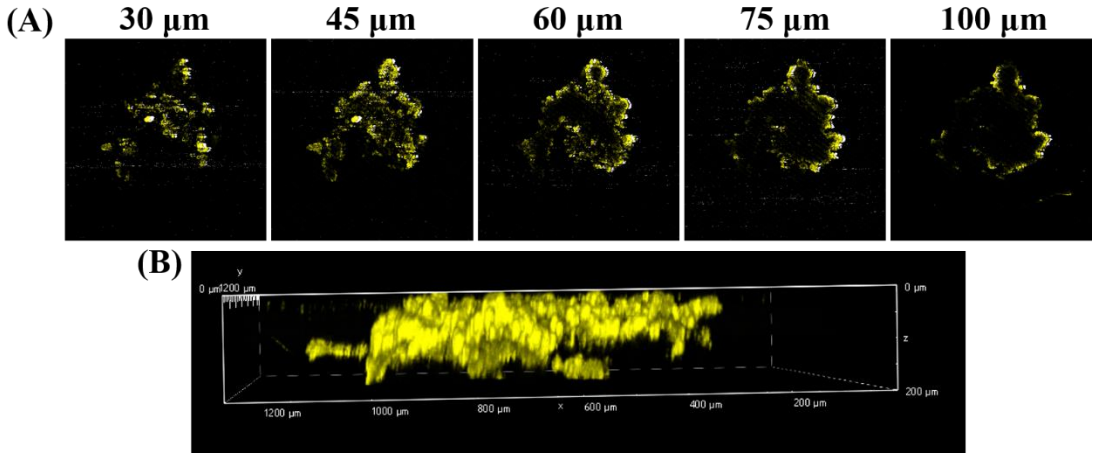


Figure S29. (A) The two-photon CLSM Z-stack scanning of the 3D HeLa-cell-based multicellular spheroids after 2 h of treatment with **TTC-L-M-4**. (B) 3D model showing the corresponding positions of CLSM Z stacking scanning in the tumor. [**TTC-L-M-4**] =10 μM, λ_{ex} = 840 nm.

2.10 ROS and PDT

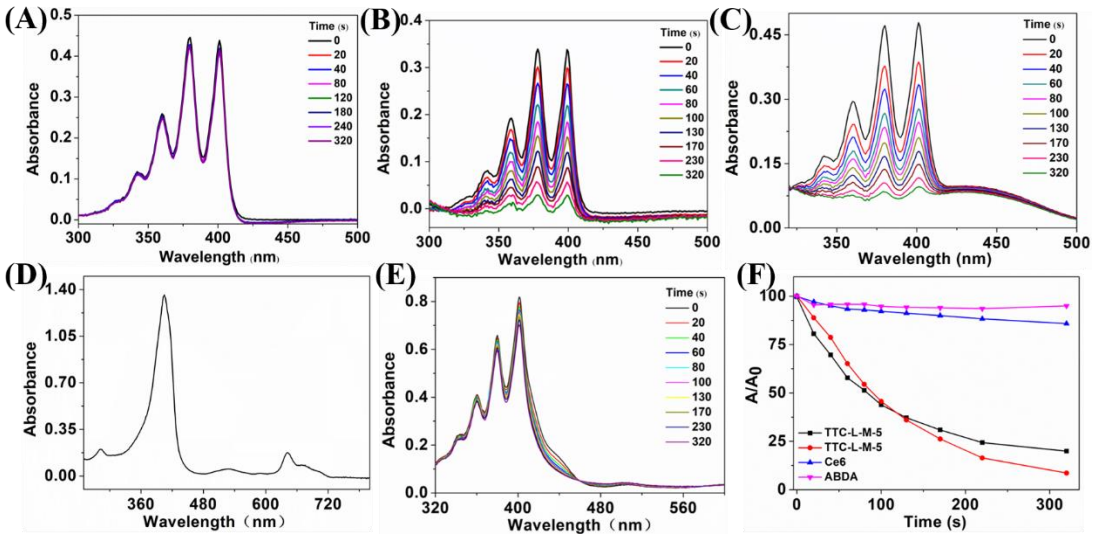


Figure S30. Absorption spectra of ABDA (50 μM) in the absence (A) or presence (B) of **TTC-L-M-4** (B) **/5** (C) and Ce6 (E) under LED light irradiation with different irradiation time. (D) Absorption spectra of Ce6 (10 μM). (F) Decomposition rates of ABDA by **TTC-L-M-4/6** and Ce6 under LED light irradiation at pH 7.4, where A_0 and A are ABDA absorbance at 399 nm.

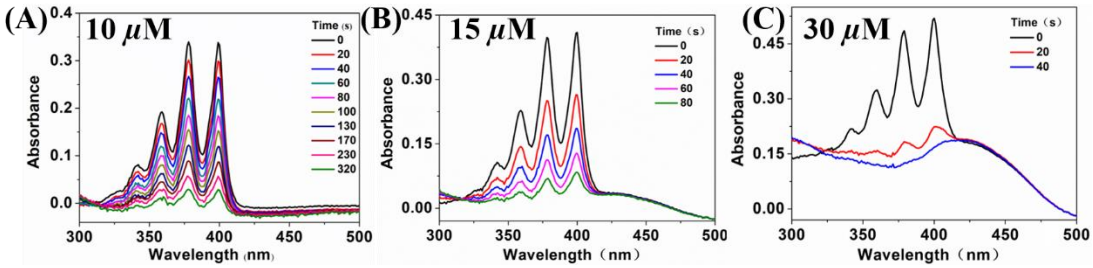


Figure S31. Absorption spectra of ABDA (50 μM) in presence of **TTC-L-M-4** with different concentration under LED light irradiation with different irradiation time.

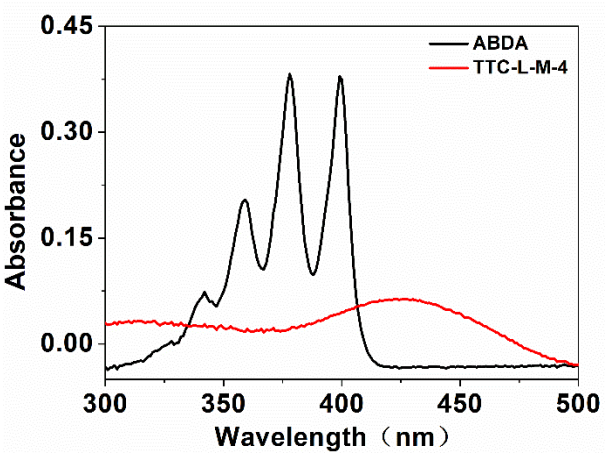


Figure S32. Absorption spectra of ABDA (50 μM) and **TTC-L-M-4** (15 μM).

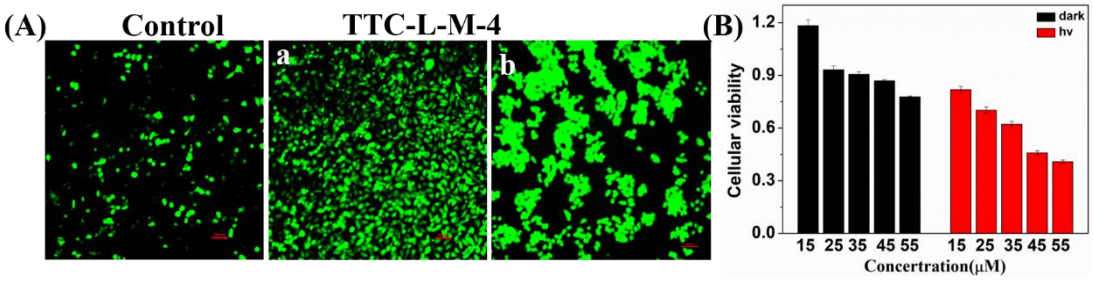


Figure S33. (A) Intracellular ROS detection inside HeLa cells by DCFH-DA after treatment in the absence and presence of **TTC-L-M-4**/DOPE and LED light irradiation (a: λ_{ex} = 450 nm, b: λ_{ex} = 880 nm). (B) Viabilities of HeLa cells after treatment with **TTC-L-M-4**/DOPE for 4 h with and without LED light treatment for 10 min.

Table S10 The calculated IC_{50} values of **TTC-L-M-4**/DOPE with and without LED light treatment for 10 min.

	Dark	LED light irradiation
TTC-L-M-4	131.91	43.5

2.11 Western Blot

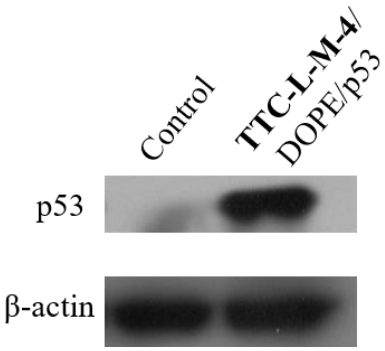


Figure S34. Western blot analysis of p53 in HeLa cells treated with **TTC-L-M-4**/DOPE/p53.

2.12 *In vivo* imaging

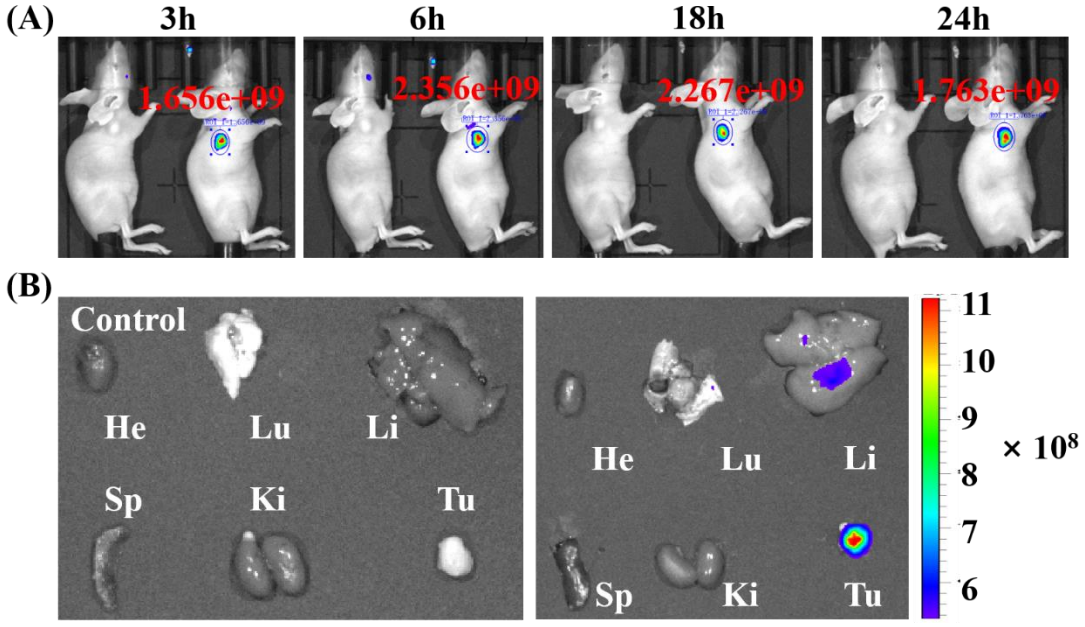


Figure S35. (A) In vivo imaging of HeLa tumor-bearing mice after subcutaneously injection of **TTC-L-M-4**/DOPE/pGL3 at different time points. (B) ex vivo biodistribution of organs and tumor at 24 h post-injection.

2.13 *In vivo* Antitumor Efficacy

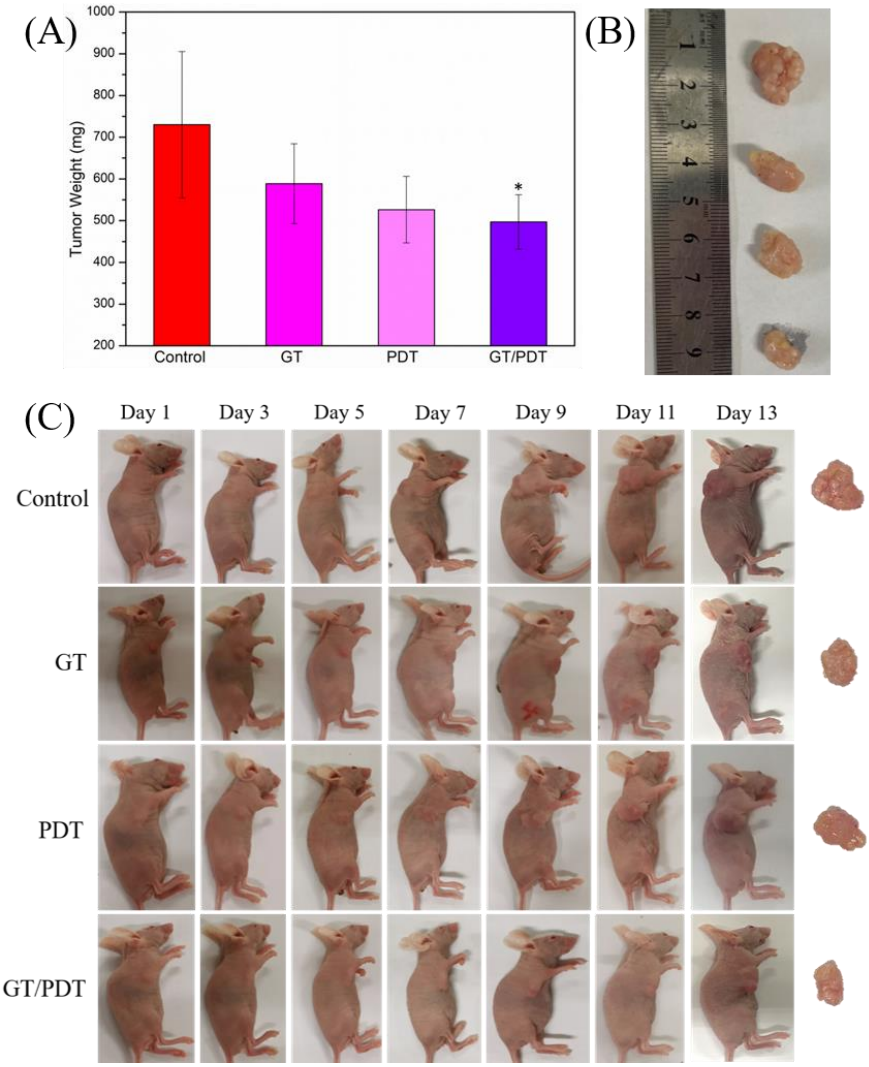


Figure S36. (A) Tumor weight change of mice (n = 5). (B) Images of tumor tissues from different groups of tumors bearing mice on 14th day. (C) Representative photos of mice from different groups from 1th day to14th day.

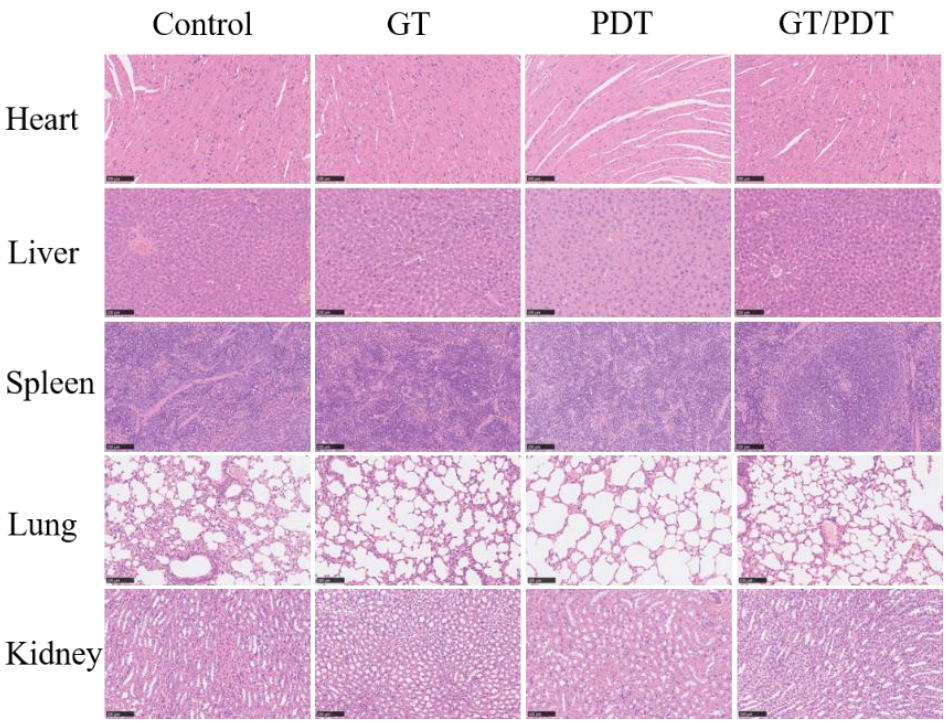


Figure S37. H&E-stained tissues excised from mice. Scale bar: 100 μm.

3. ^{1}H, ^{13}C-NMR Spectra and HR-MS of Synthesized Compounds

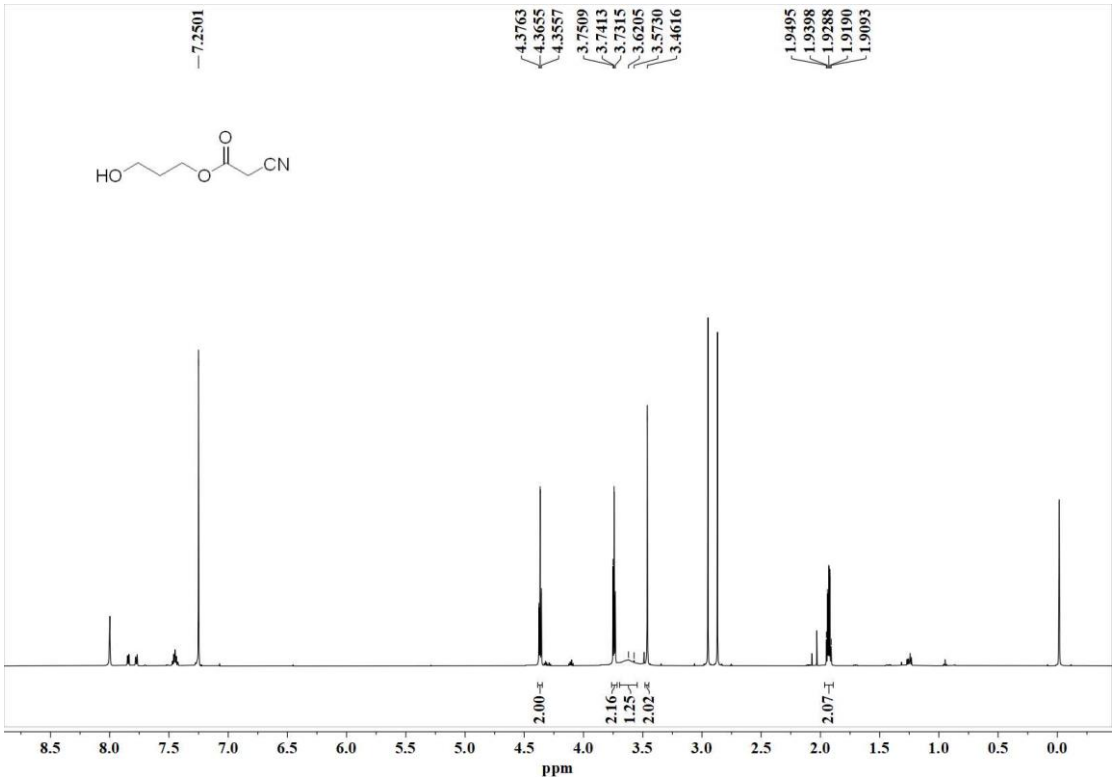


Figure S38 ^{1}H NMR spectrum of **2** (600 MHz, $CDCl_3$)

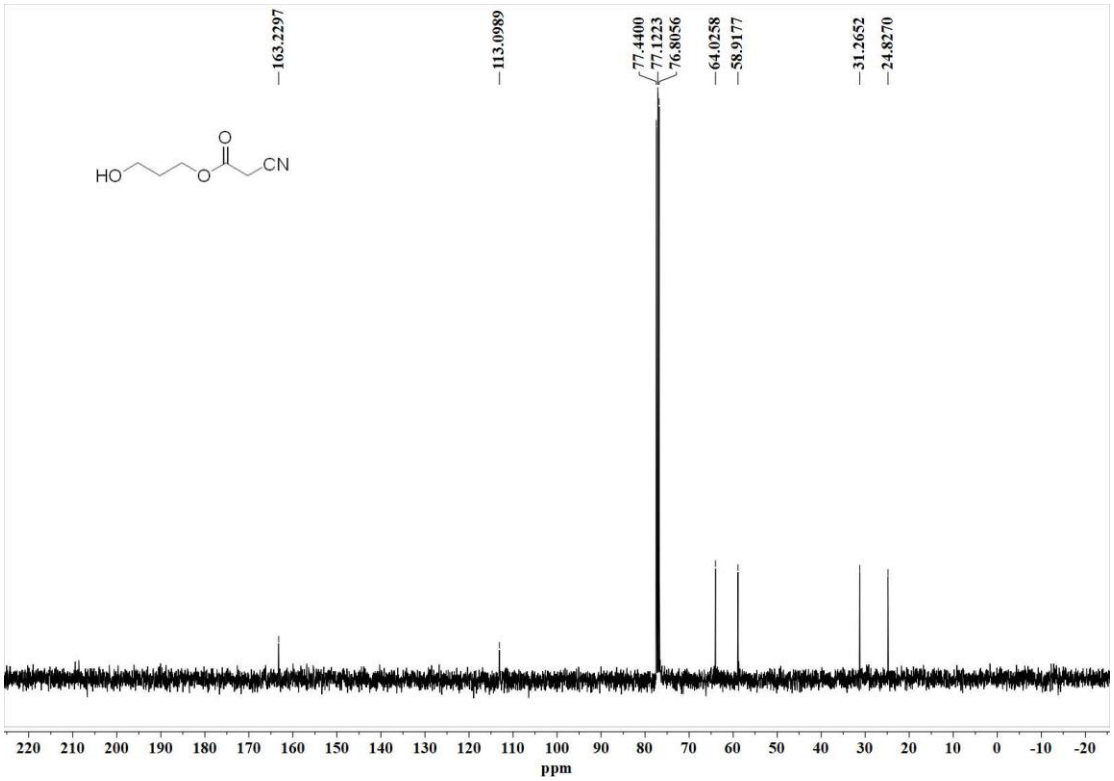


Figure S39 ^{13}C NMR spectrum of **2** (101 MHz, $CDCl_3$).

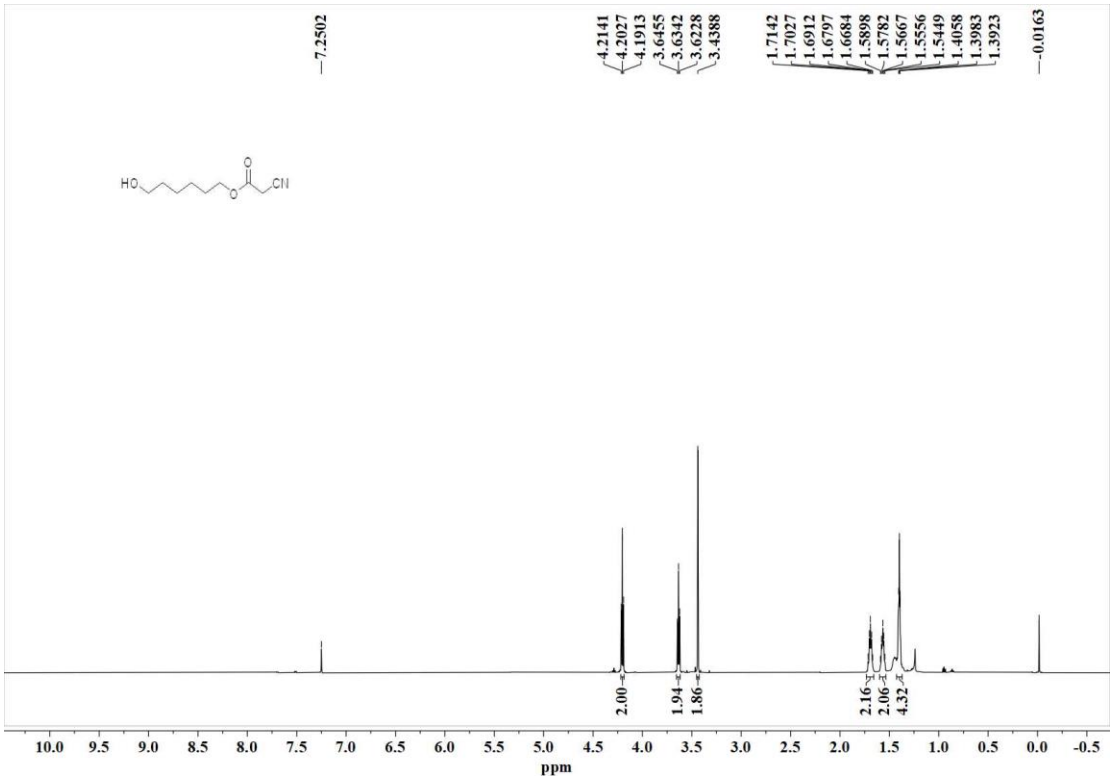


Figure S40 ^{1}H NMR spectrum of **3** (600 MHz, $CDCl_3$)

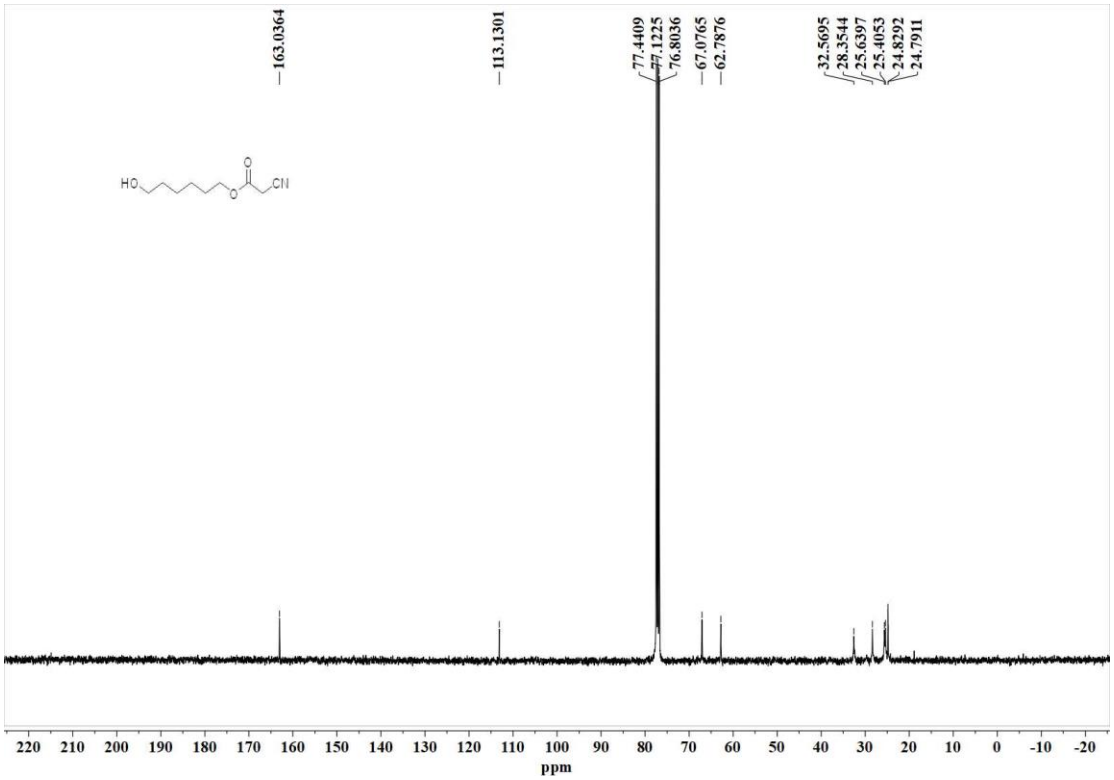


Figure S41 ^{13}C NMR spectrum of **3** (101 MHz, $CDCl_3$).

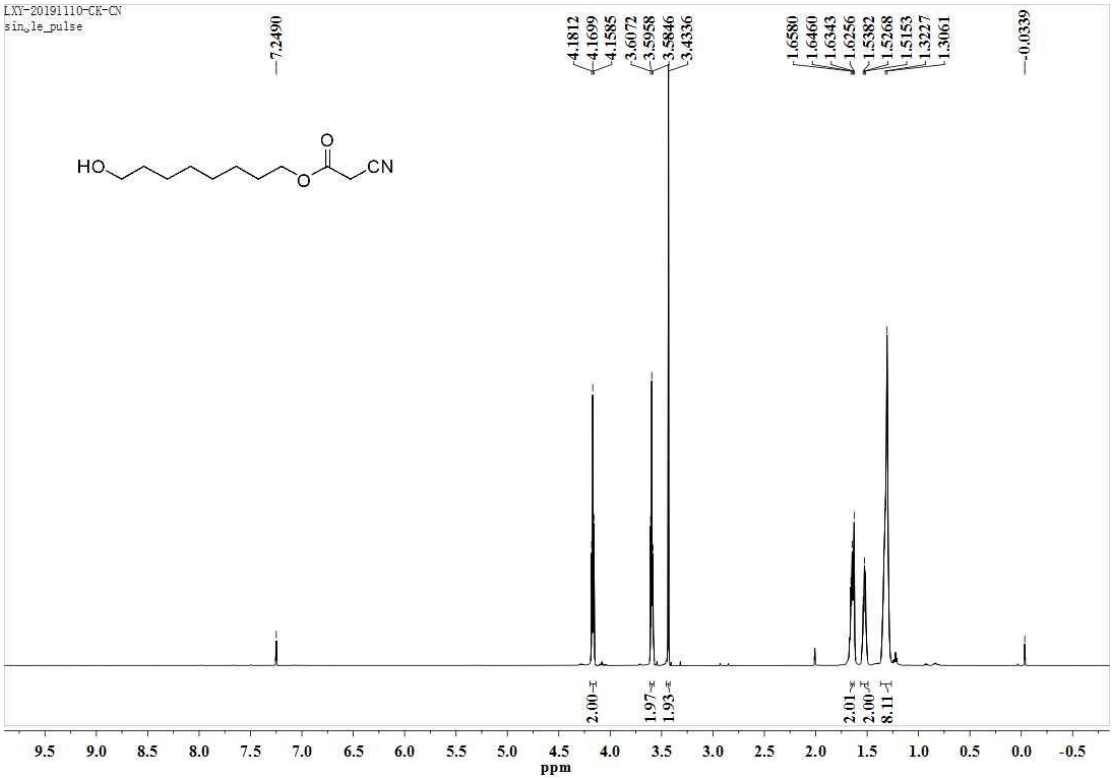


Figure S42 ^{1}H NMR spectrum of **4** (600 MHz, $CDCl_3$)

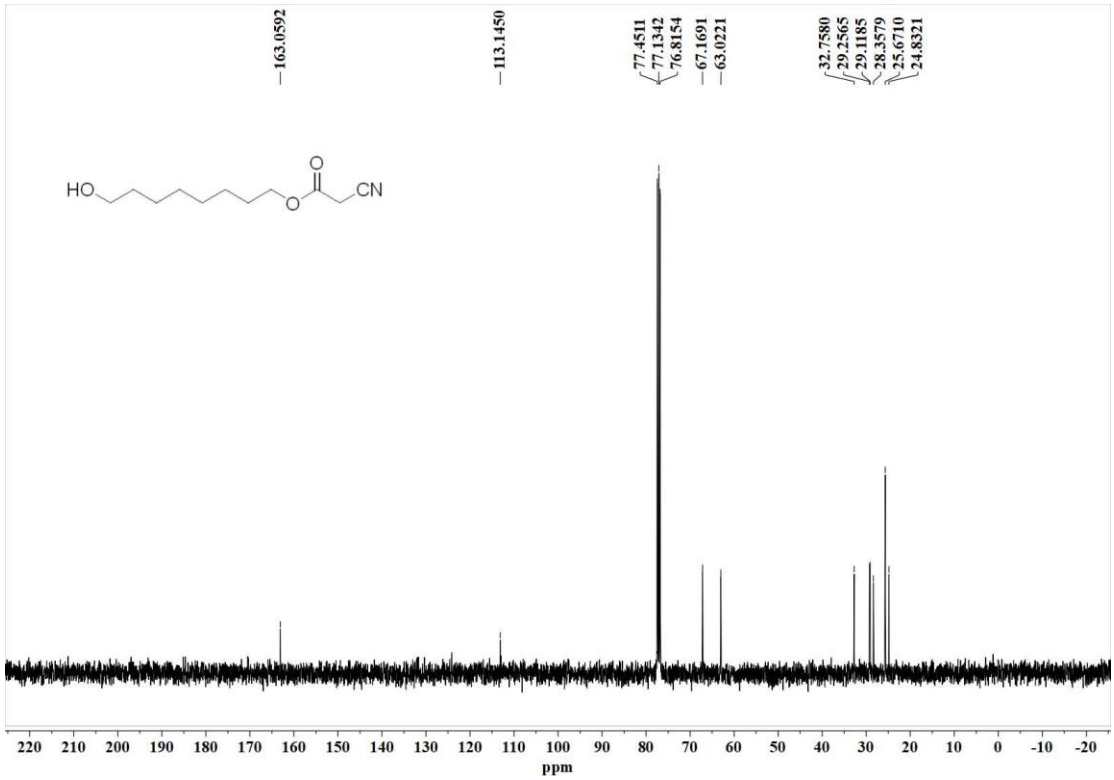


Figure S43 ^{13}C NMR spectrum of **4** (101 MHz, $CDCl_3$).

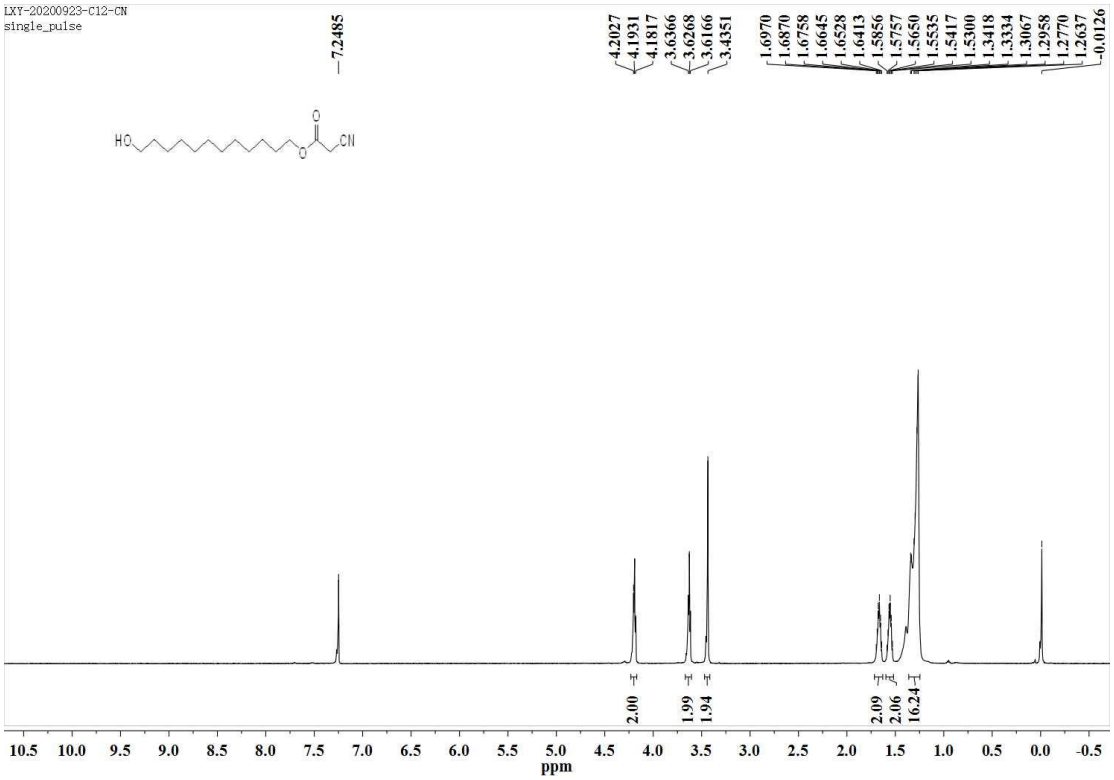


Figure S44 ^{1}H NMR spectrum of **5** (600 MHz, $CDCl_3$)

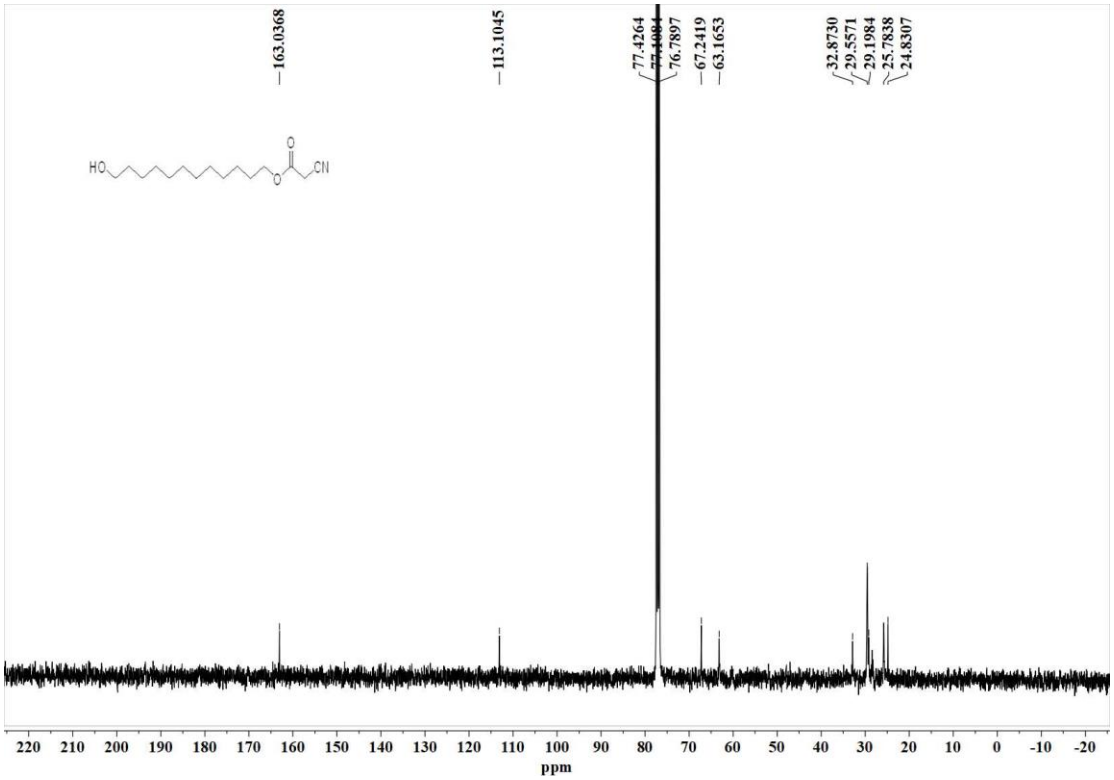


Figure S45 ^{13}C NMR spectrum of **5** (101 MHz, $CDCl_3$).

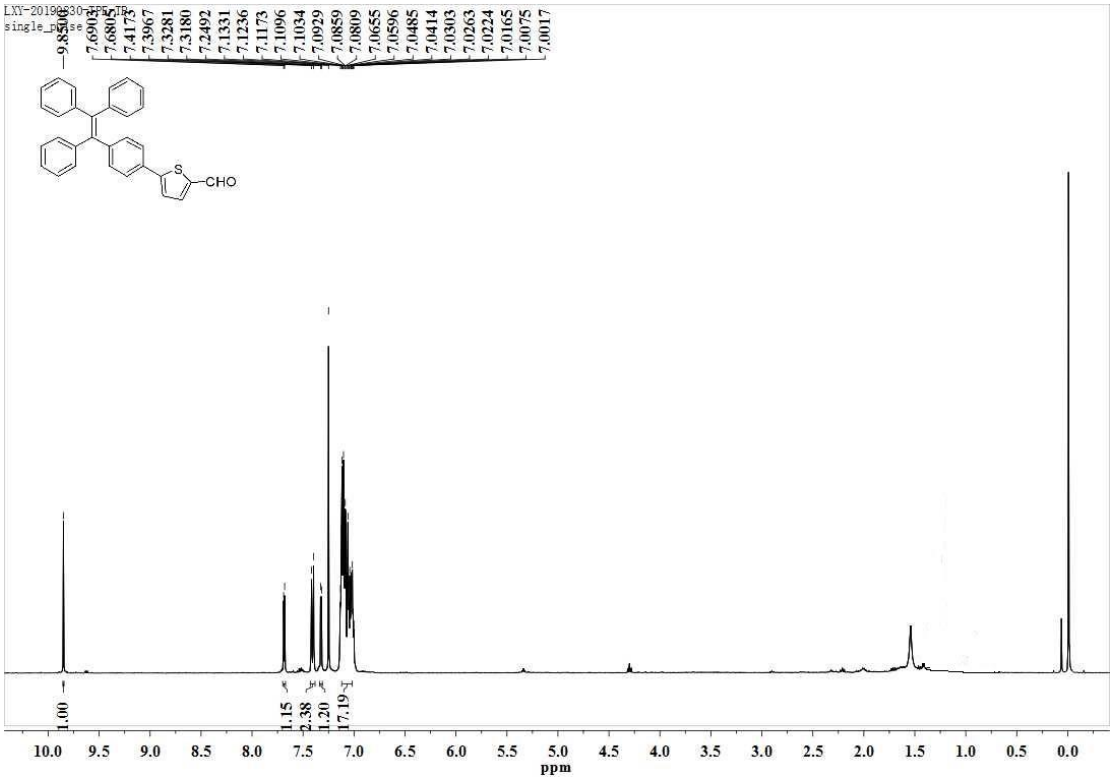


Figure S46 ^{1}H NMR spectrum of **TT-H** (400 MHz, $CDCl_3$)

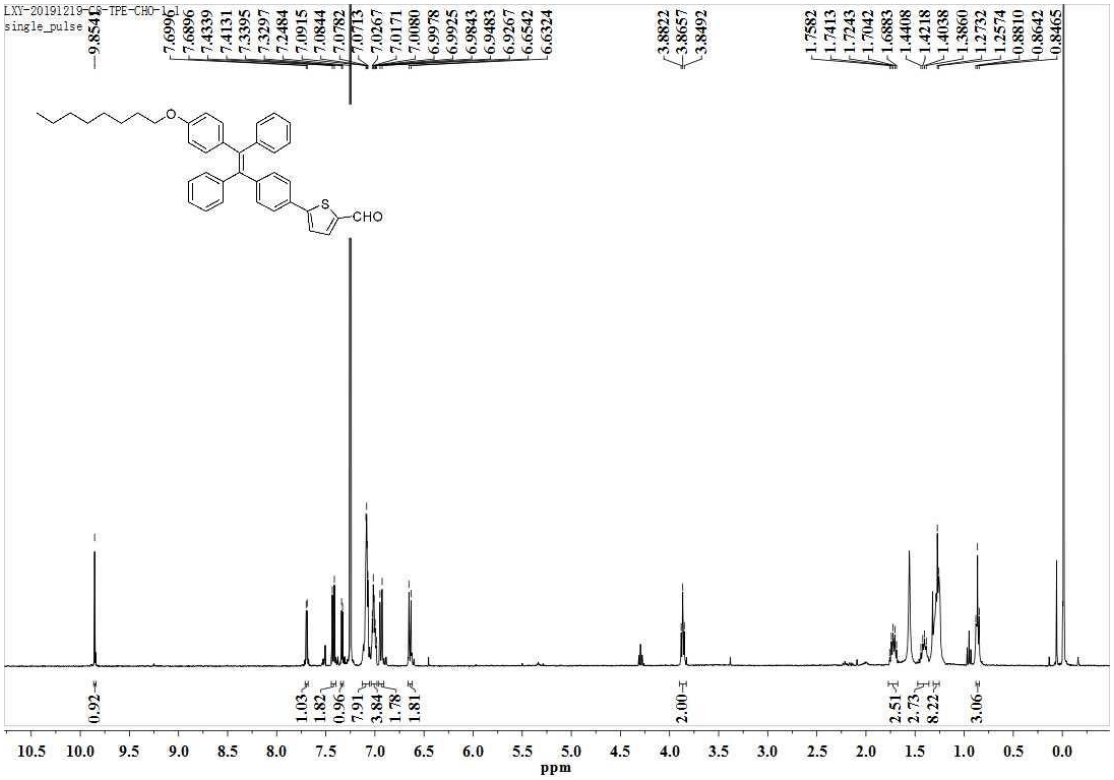


Figure S47 ^{1}H NMR spectrum of **TT-OC$_8$H$_{17}$** (400 MHz, $CDCl_3$)

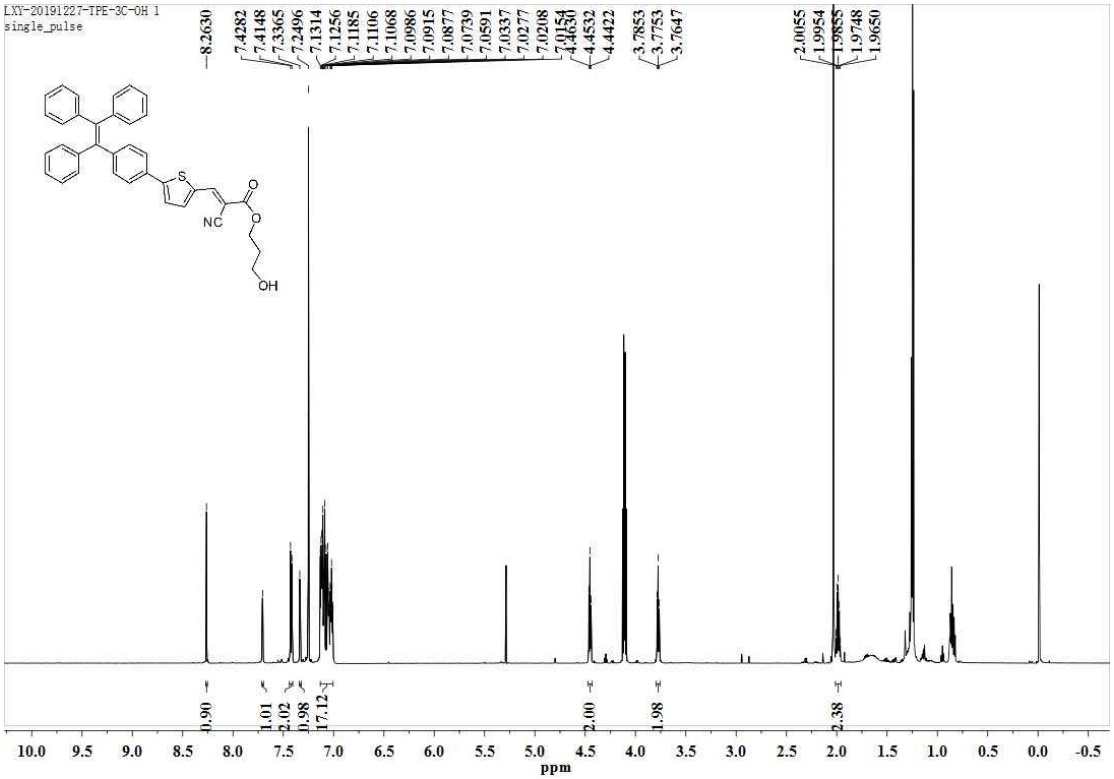


Figure S48 ^{1}H NMR spectrum of **TTC-L-1** (600 MHz, $CDCl_3$)

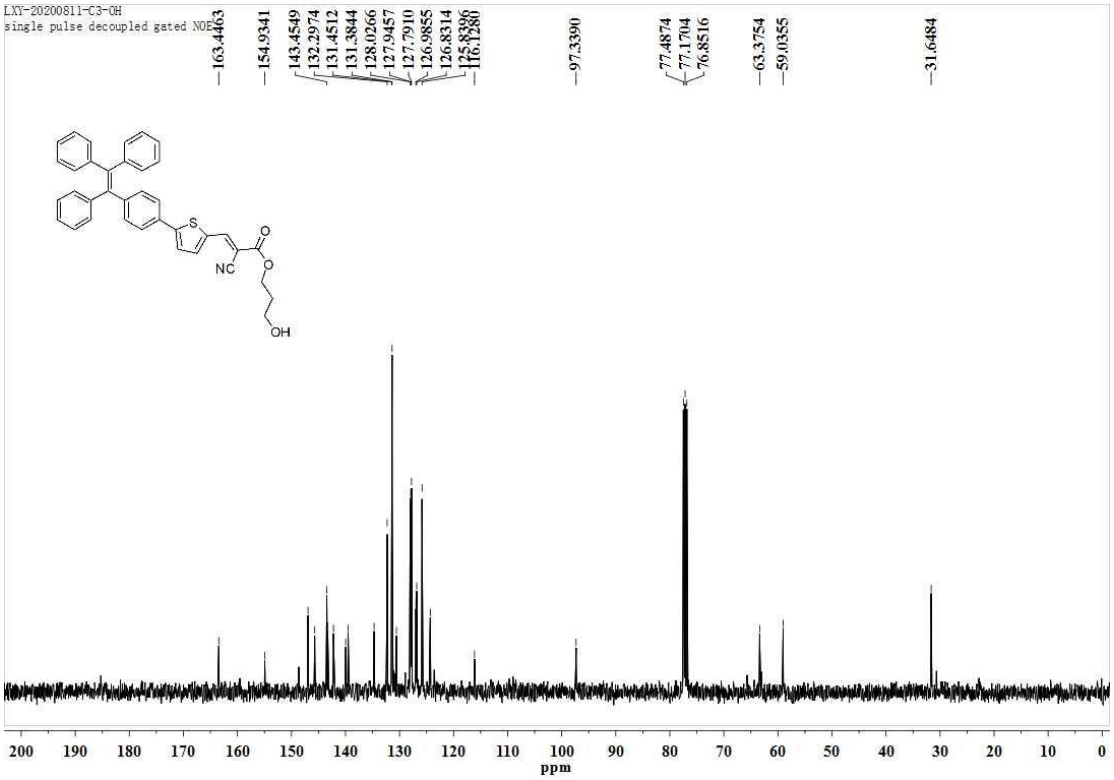


Figure S49 ^{13}C NMR spectrum of **TTC-L-1** (101 MHz, $CDCl_3$).

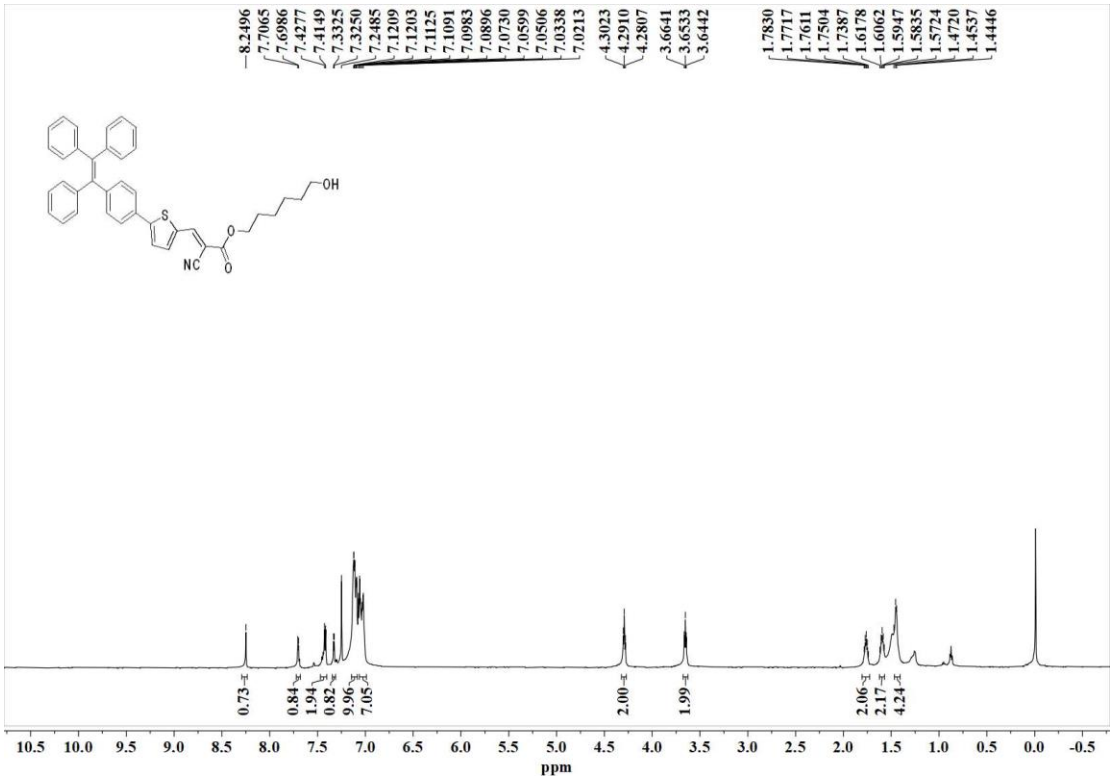


Figure S50 ^{1}H NMR spectrum of **TTC-L-2** (600 MHz, $CDCl_3$)

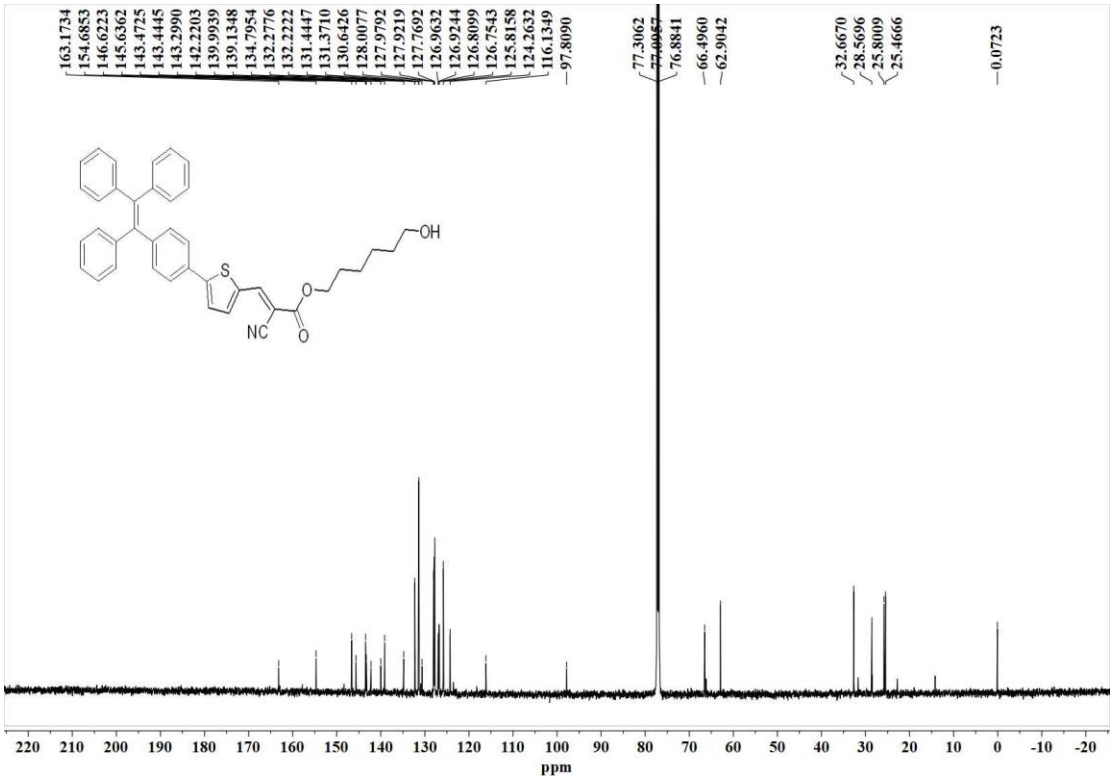


Figure S51 ^{13}C NMR spectrum of **TTC-L-2** (151 MHz, $CDCl_3$).

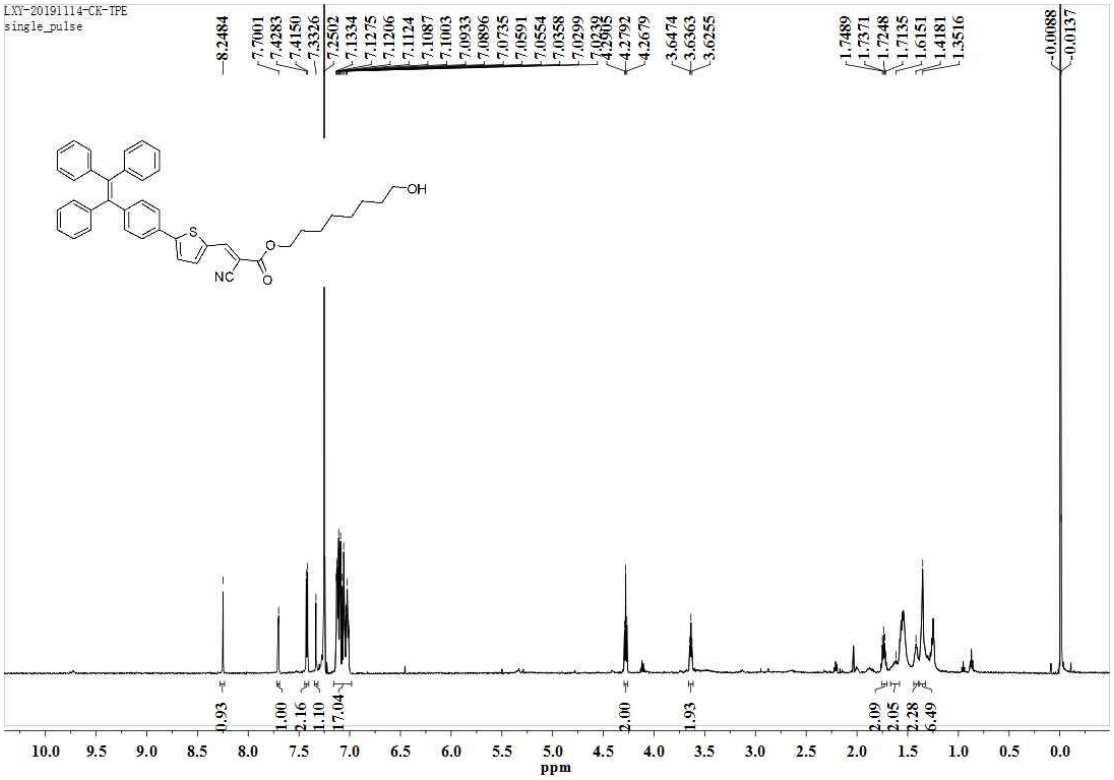


Figure S52 ^{1}H NMR spectrum of **TTC-L-3** (600 MHz, $CDCl_3$)

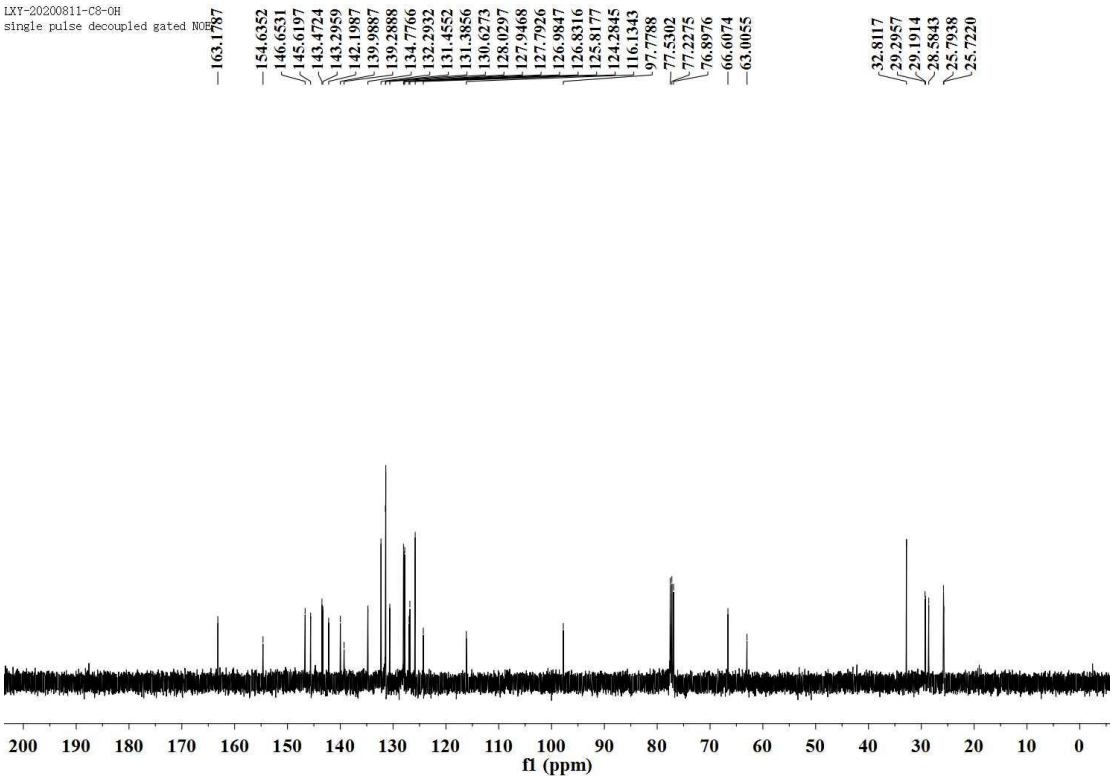


Figure S53 ^{13}C NMR spectrum of **TTC-L-3** (101 MHz, $CDCl_3$).

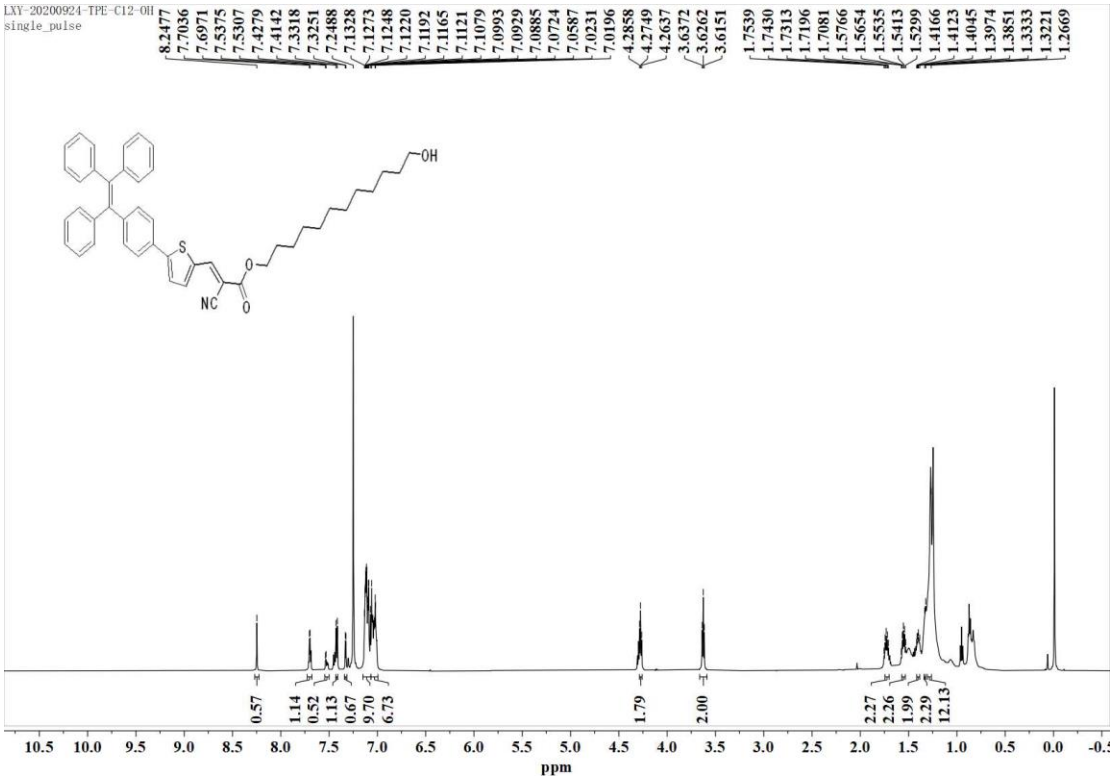


Figure S54 ^{1}H NMR spectrum of **TTC-L-4** (600 MHz, $CDCl_3$)

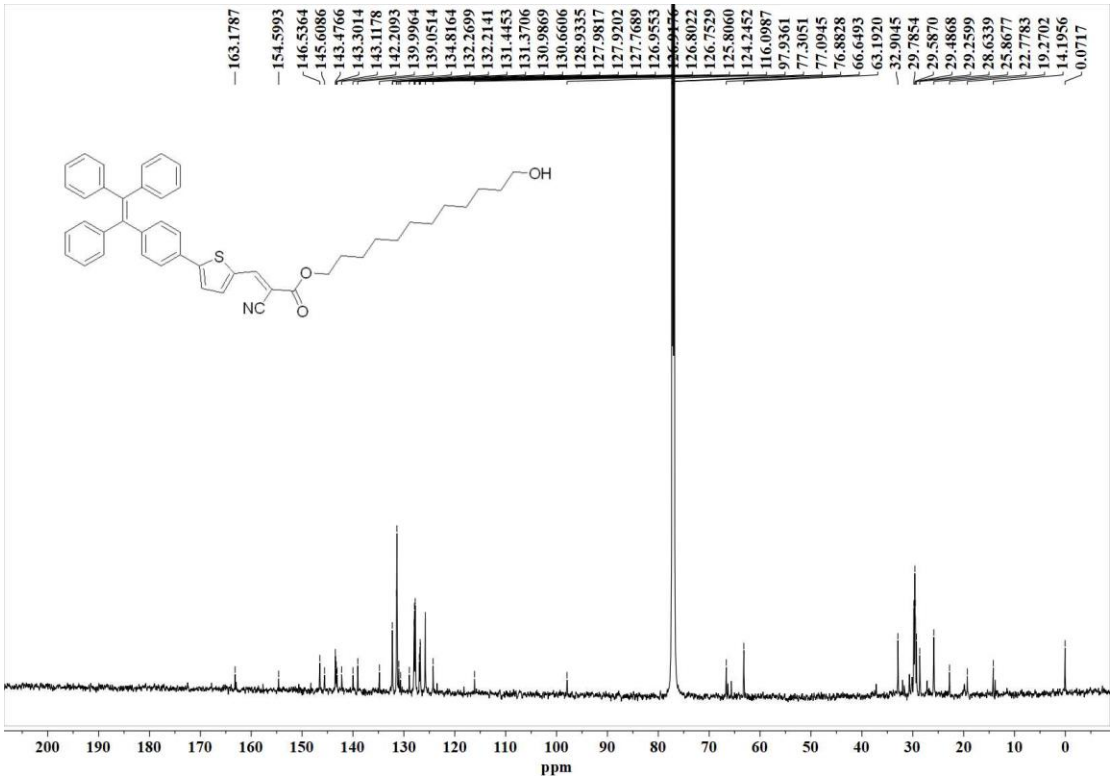


Figure S55 ^{13}C NMR spectrum of **TTC-L-4** (151 MHz, $CDCl_3$).

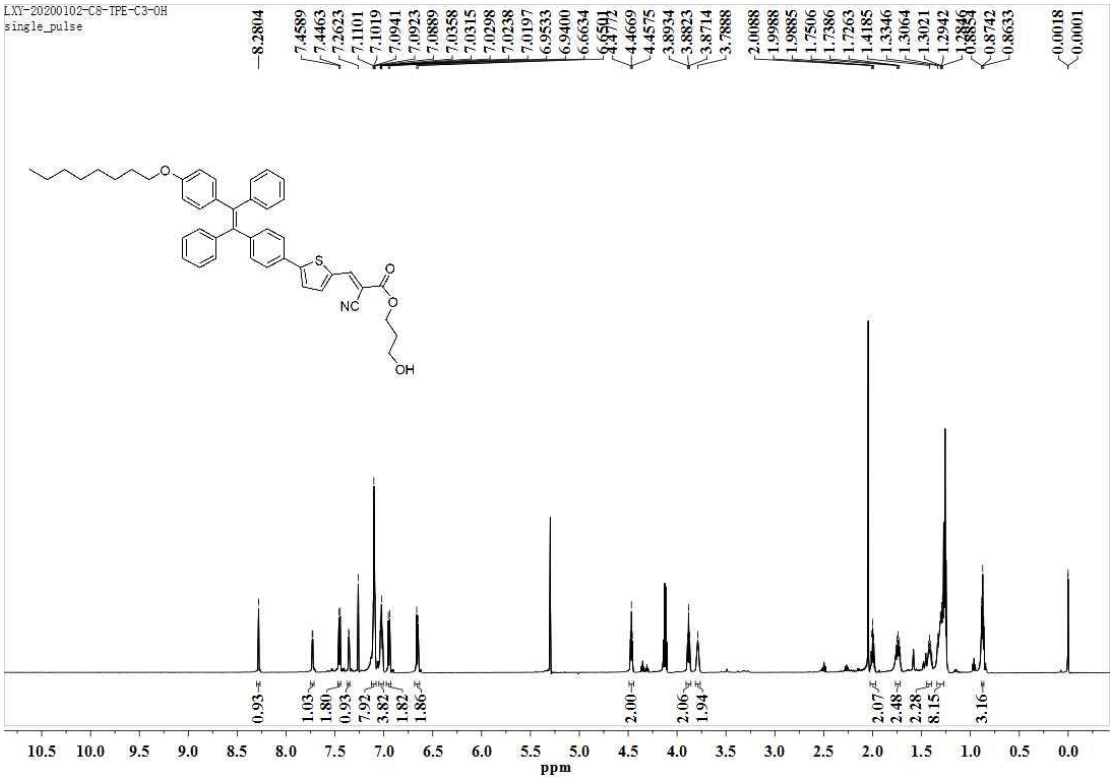


Figure S56 ^{1}H NMR spectrum of **TTC-L-5** (600 MHz, $CDCl_3$)

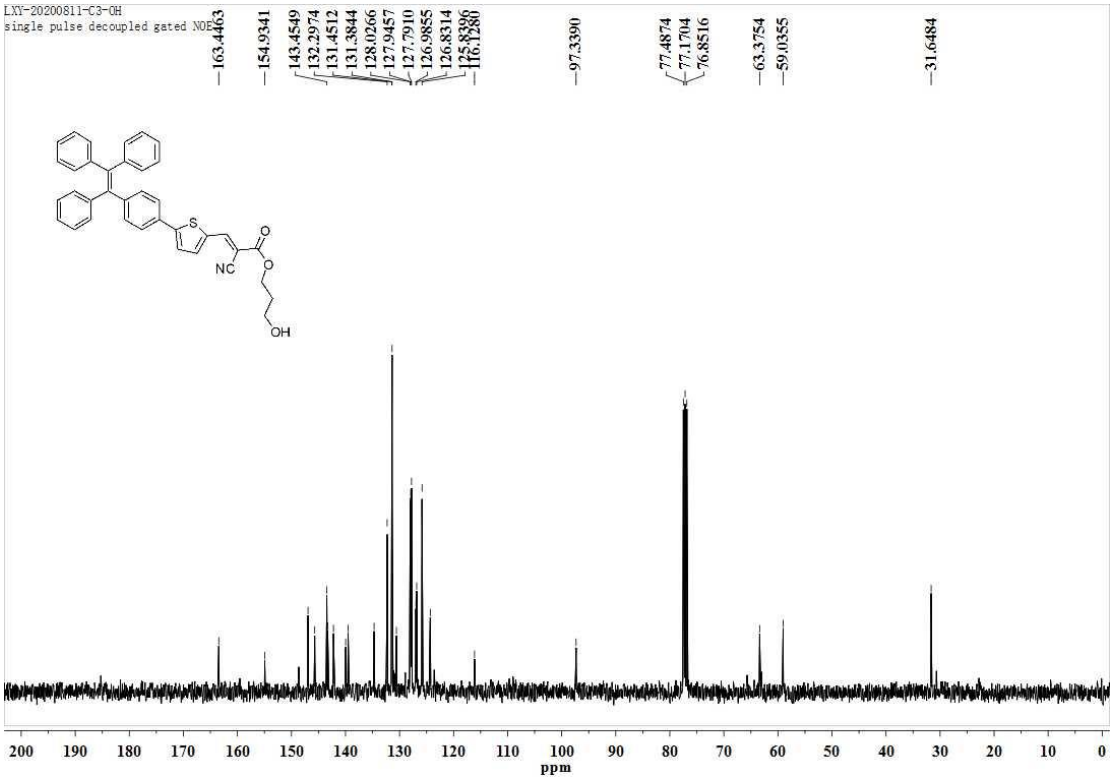


Figure S57 ^{13}C NMR spectrum of **TTC-L-5** (101 MHz, $CDCl_3$).

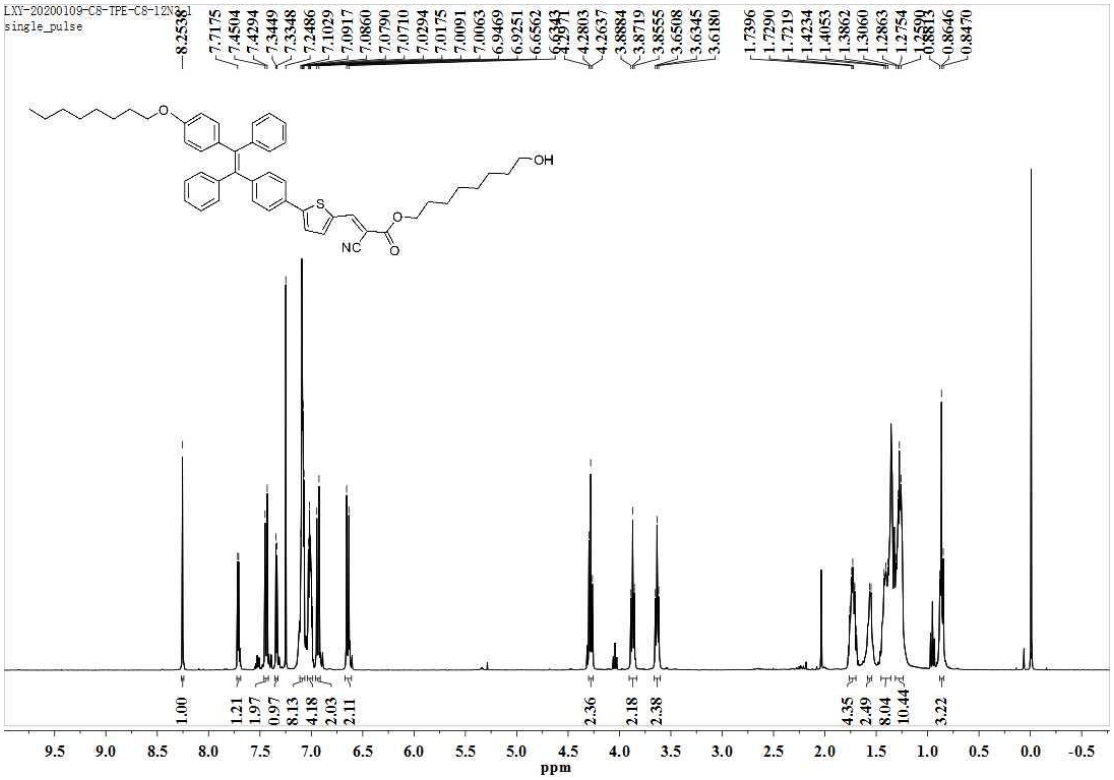


Figure S58 ^{1}H NMR spectrum of **TTC-L-6** (400 MHz, $CDCl_3$)

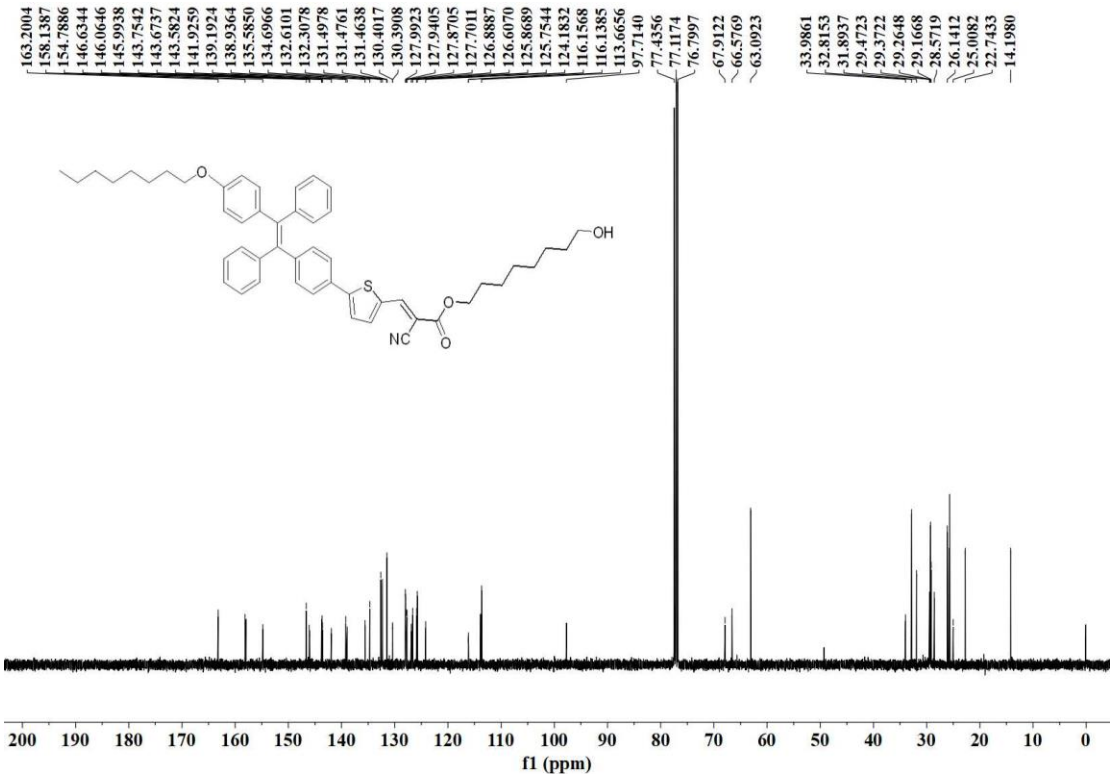


Figure S59 ^{13}C NMR spectrum of **TTC-L-6** (101 MHz, $CDCl_3$).

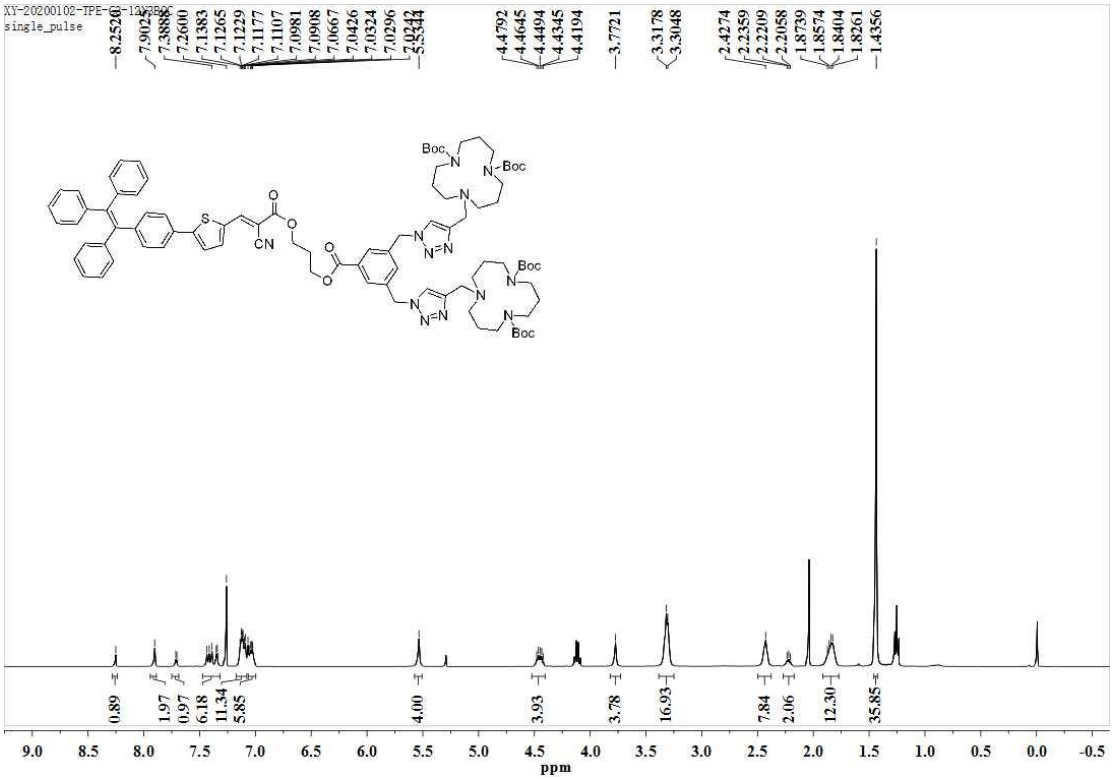


Figure S60 ^{1}H NMR spectrum of **6** (400 MHz, $CDCl_3$)

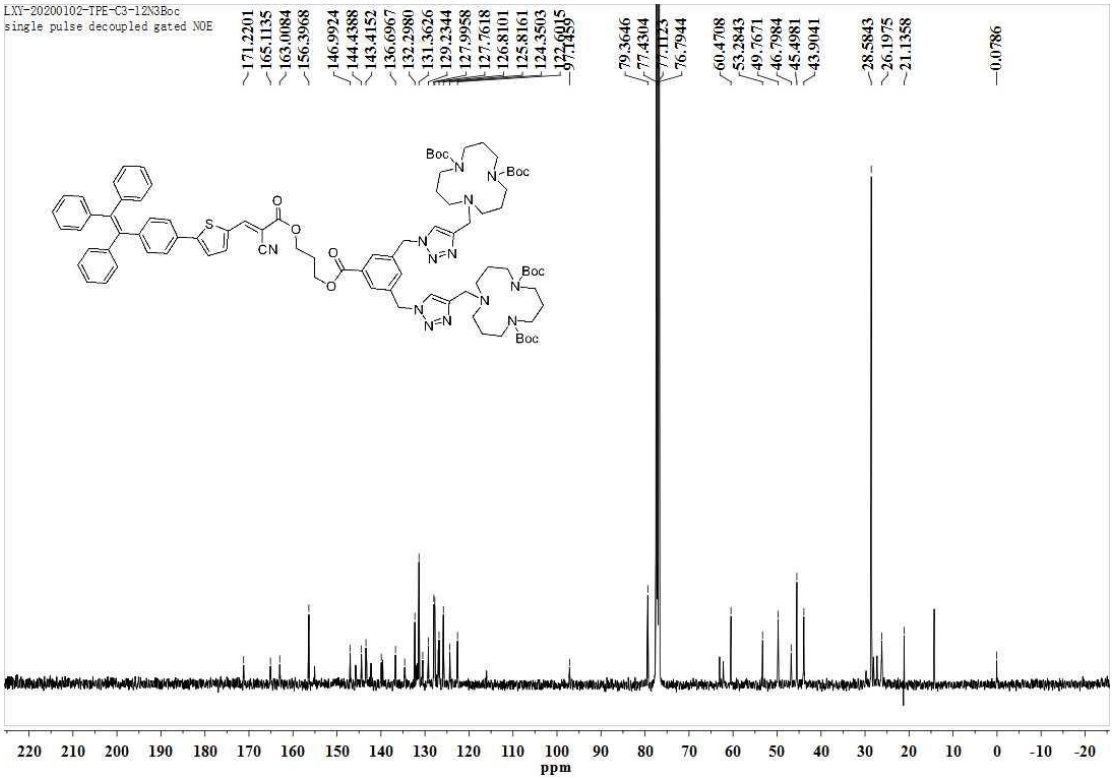
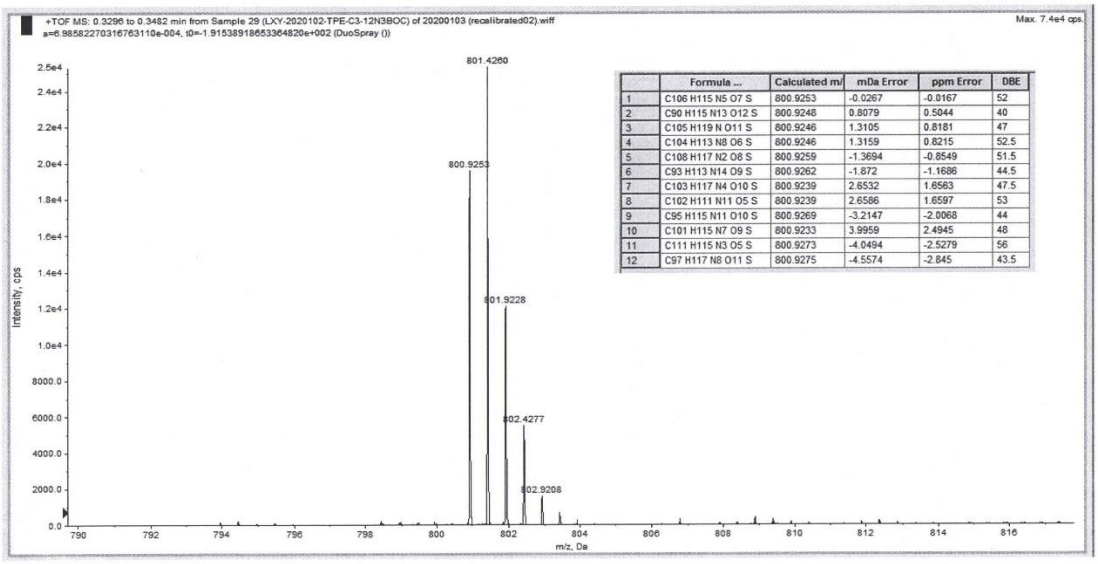


Figure S61 ^{13}C NMR spectrum of **6** (101 MHz, $CDCl_3$).



	Formula ...	Calculated m/	mDa Error	ppm Error	DBE
1	C106 H115 N5 O7 S	800.9253	-0.0267	-0.0167	52
2	C90 H115 N13 O12 S	800.9248	0.8079	0.5044	40
3	C105 H119 N O11 S	800.9246	1.3105	0.8181	47
4	C104 H113 N8 O6 S	800.9246	1.3159	0.8215	52.5
5	C108 H117 N2 O8 S	800.9259	-1.3694	-0.8549	51.5
6	C93 H113 N14 O9 S	800.9262	-1.872	-1.1686	44.5
7	C103 H117 N4 O10 S	800.9239	2.6532	1.6563	47.5
8	C102 H111 N11 O5 S	800.9239	2.6586	1.6597	53
9	C95 H115 N11 O10 S	800.9269	-3.2147	-2.0068	44
10	C101 H115 N7 O9 S	800.9233	3.9959	2.4945	48
11	C111 H115 N3 O5 S	800.9273	-4.0494	-2.5279	56
12	C97 H117 N8 O11 S	800.9275	-4.5574	-2.845	43.5

Figure S62 HR-MS spectrum of **6**.

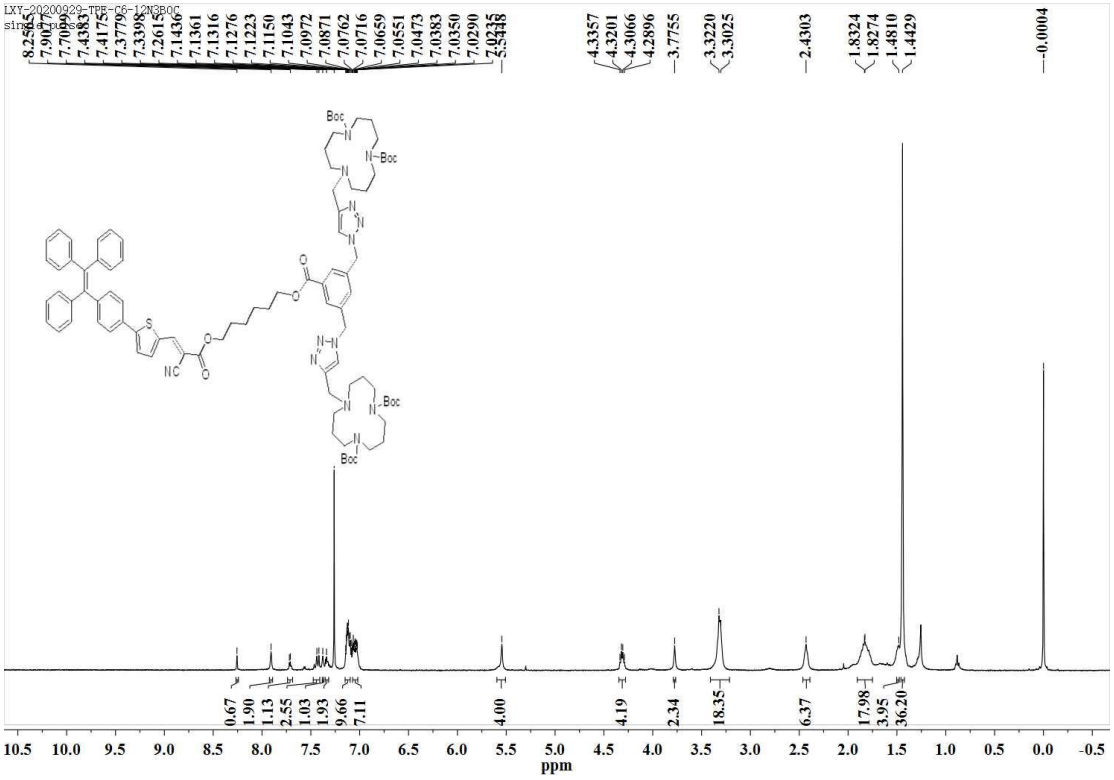


Figure S63 ^{1}H NMR spectrum of **7** (400 MHz, $CDCl_3$)

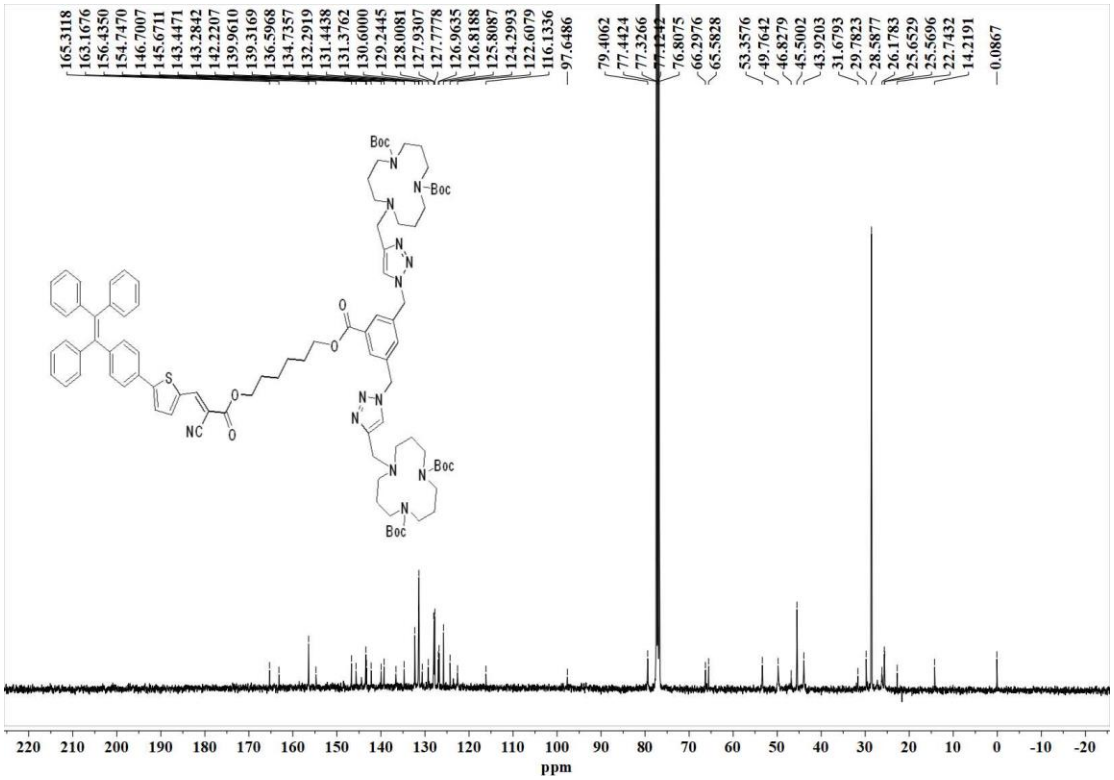


Figure S64 ^{13}C NMR spectrum of **7** (101 MHz, $CDCl_3$).

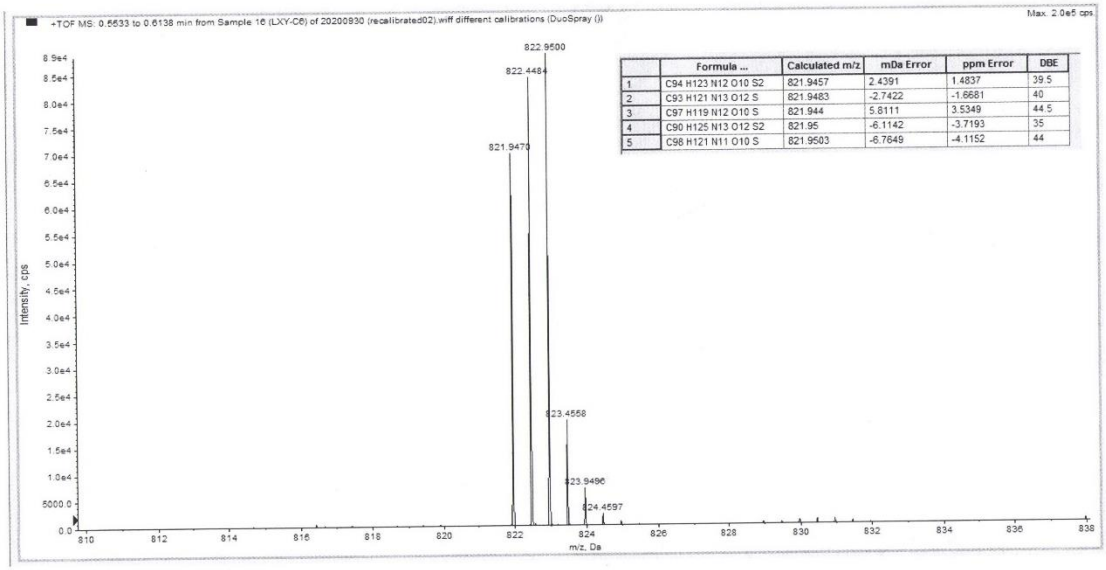


Figure S65 HR-MS spectrum of **7**.

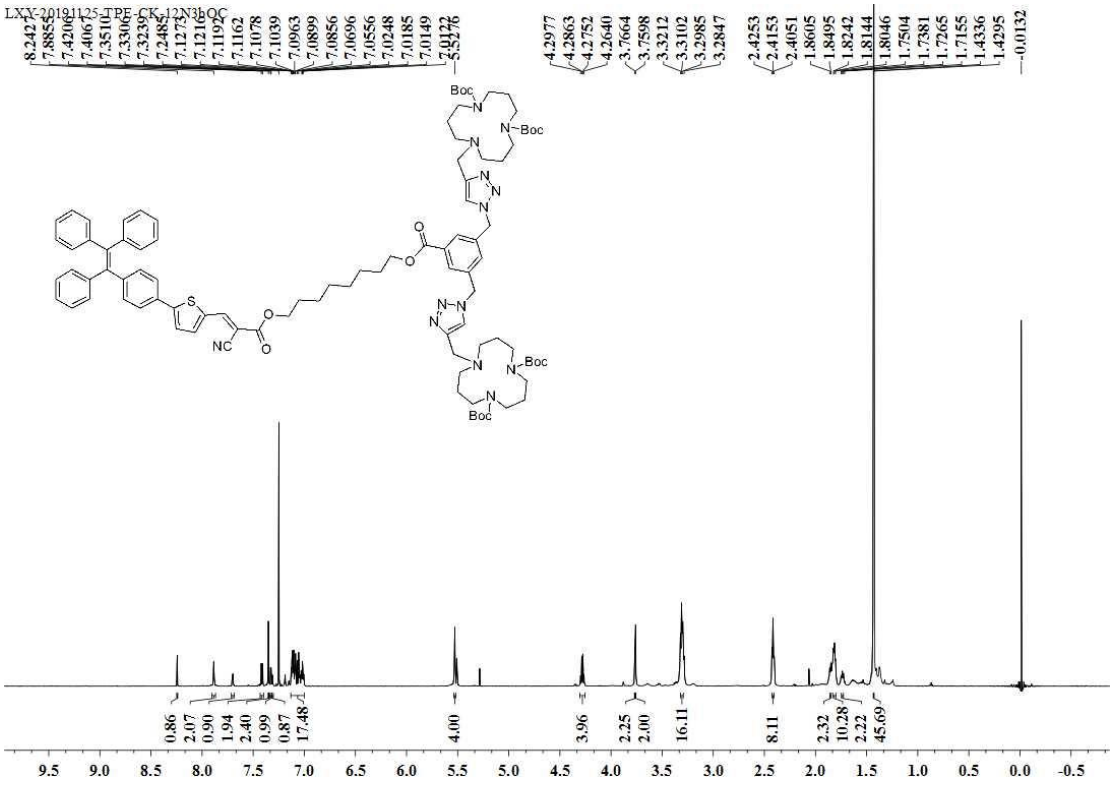


Figure S66 ^{1}H NMR spectrum of **8** (600 MHz, $CDCl_3$)

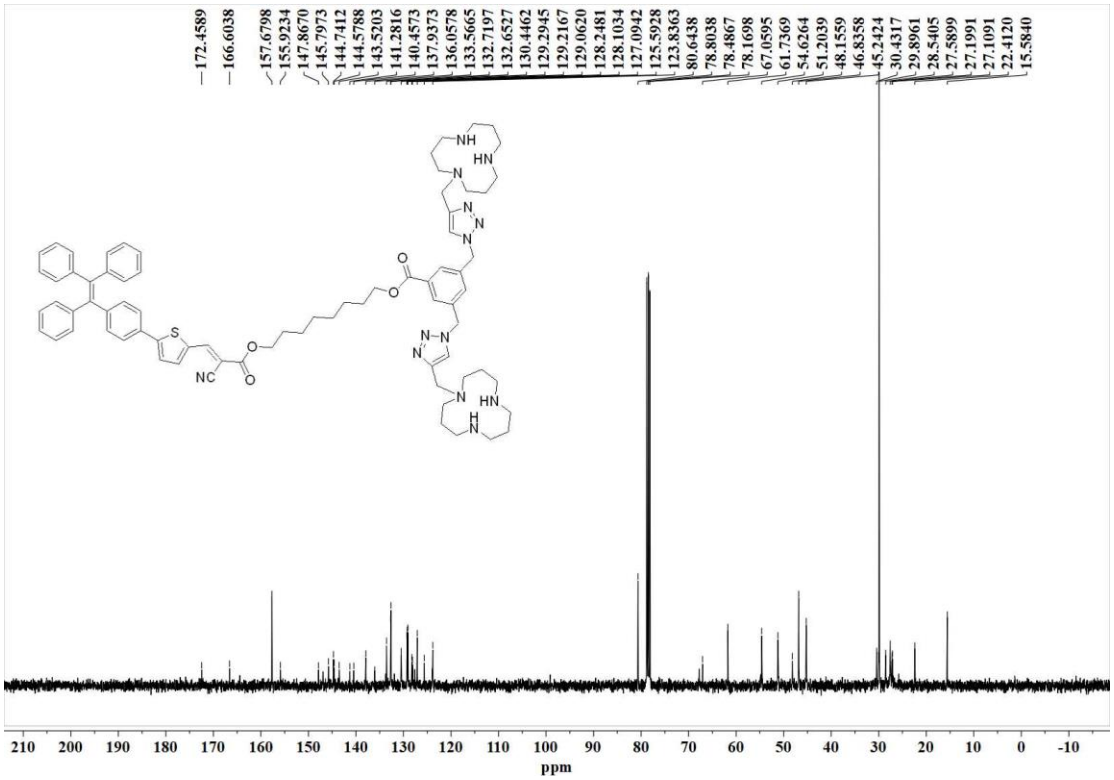
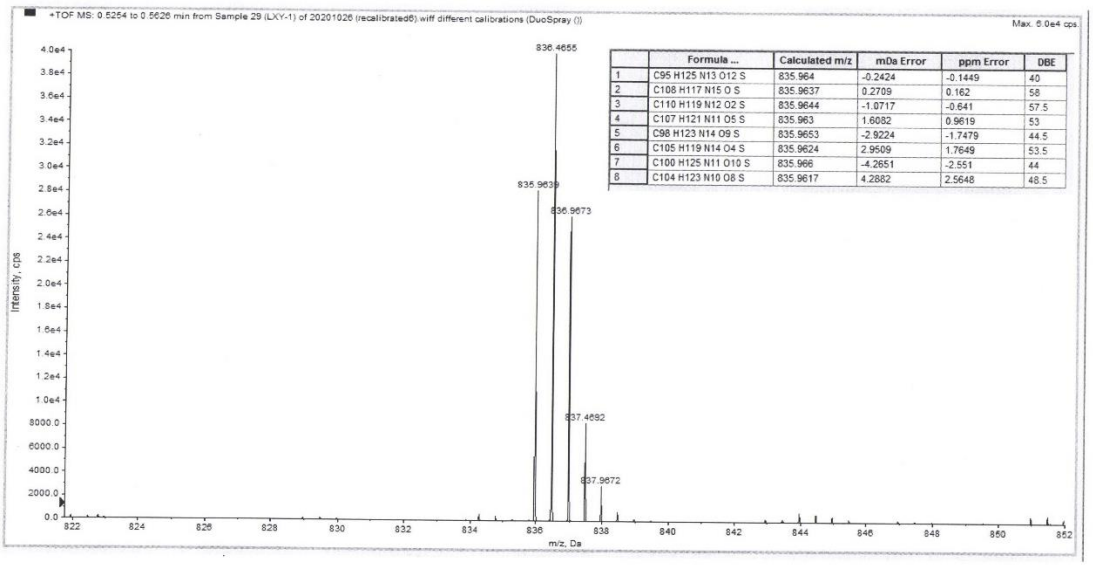


Figure S67 ^{13}C NMR spectrum of **8** (101 MHz, $CDCl_3$).



	Formula ...	Calculated m/z	mDa Error	ppm Error	DBE
1	C95 H125 N13 O12 S	835.964	-0.2424	-0.1449	40
2	C108 H117 N15 O S	835.9637	0.2709	0.162	58
3	C110 H119 N12 O2 S	835.9644	-1.0717	-0.641	57.5
4	C107 H121 N11 O5 S	835.963	1.6082	0.9619	53
5	C98 H123 N14 O9 S	835.9653	-2.9224	-1.7479	44.5
6	C105 H119 N14 O4 S	835.9624	2.9509	1.7649	53.5
7	C100 H125 N11 O10 S	835.966	-4.2651	-2.551	44
8	C104 H123 N10 O8 S	835.9617	4.2882	2.5648	48.5

Figure S68 HR-MS spectrum of **8**.

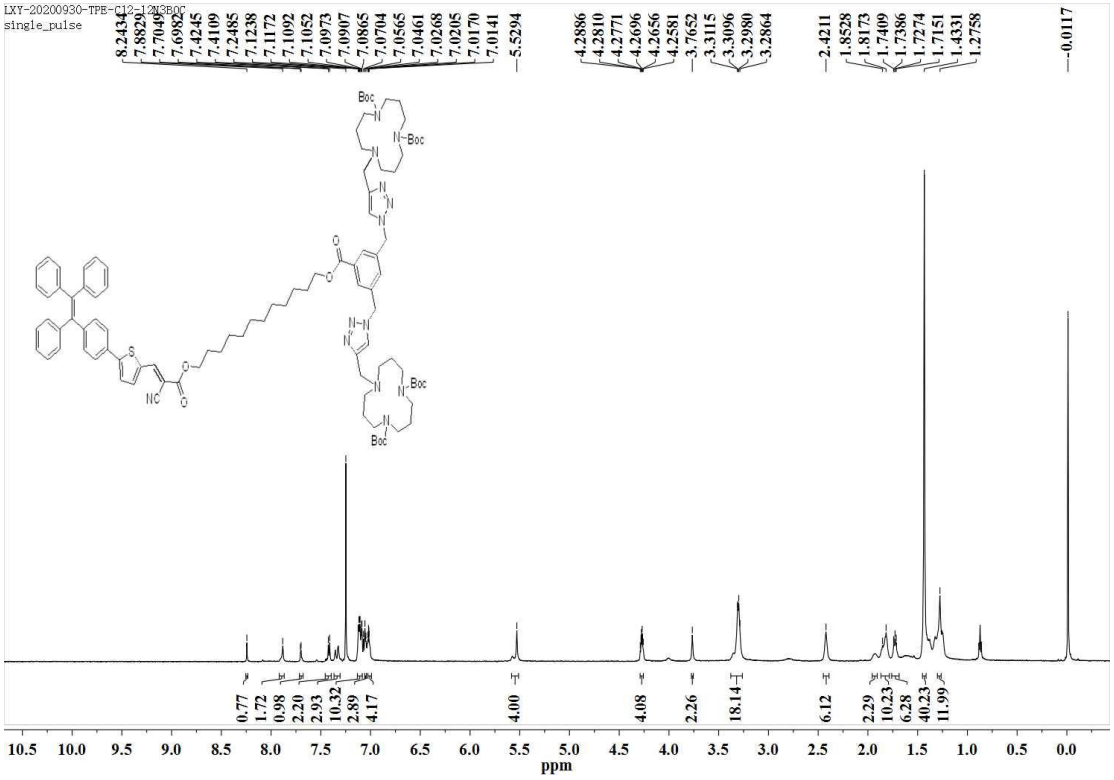


Figure S69 ^{1}H NMR spectrum of **9** (600 MHz, $CDCl_3$)

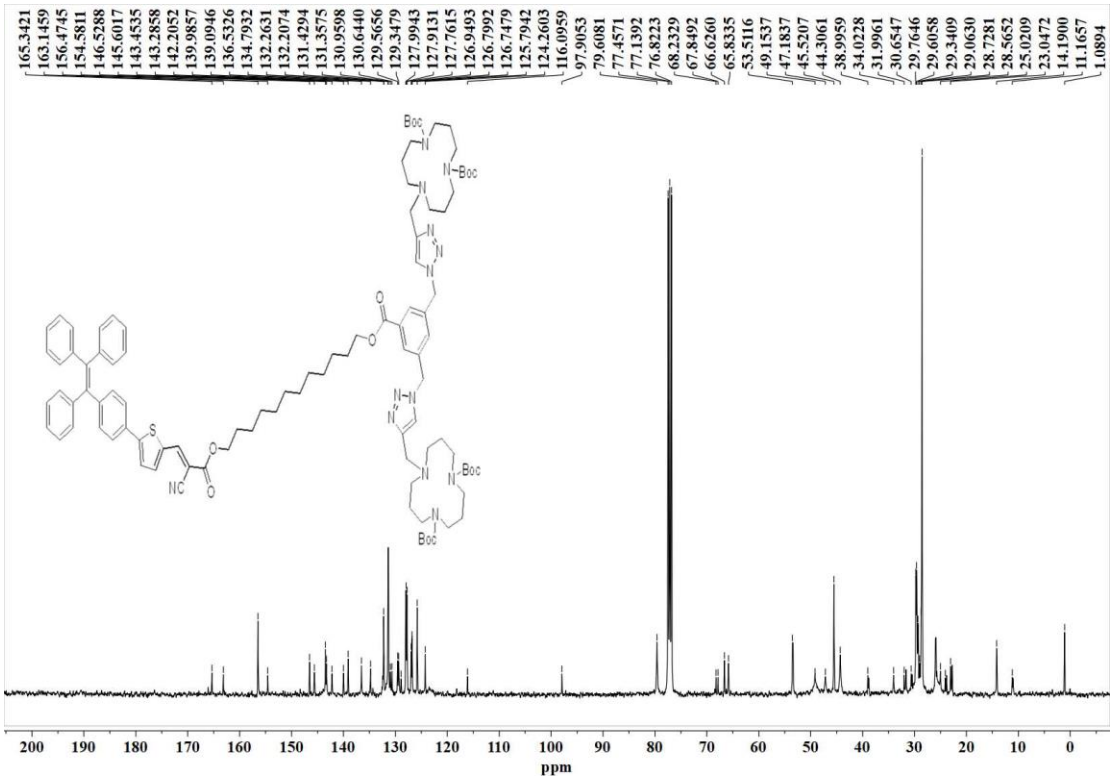


Figure S70 ^{13}C NMR spectrum of **9** (101 MHz, $CDCl_3$).

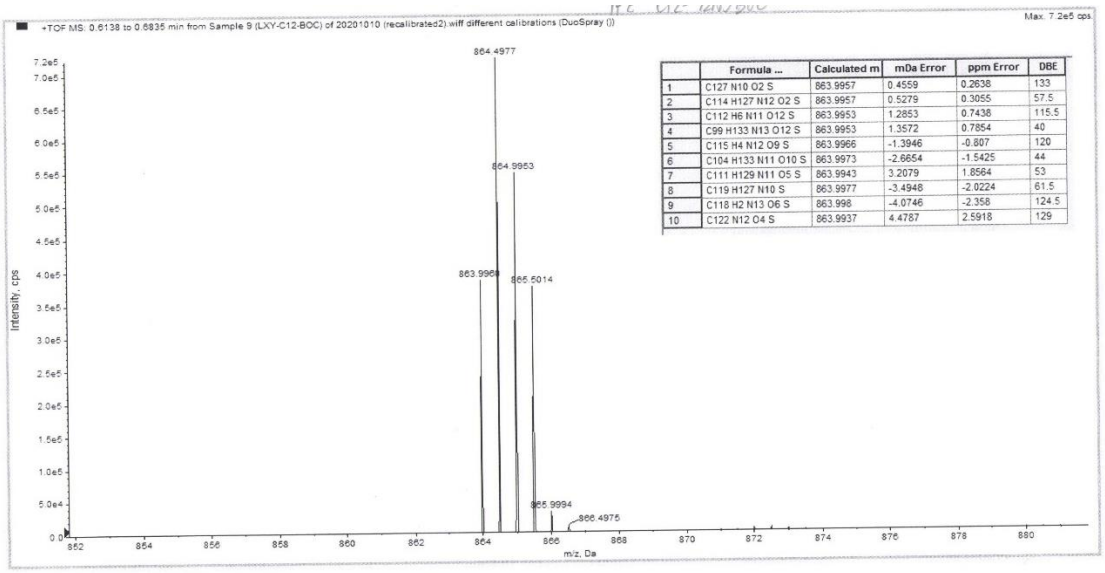


Figure S71 HR-MS spectrum of **9**.

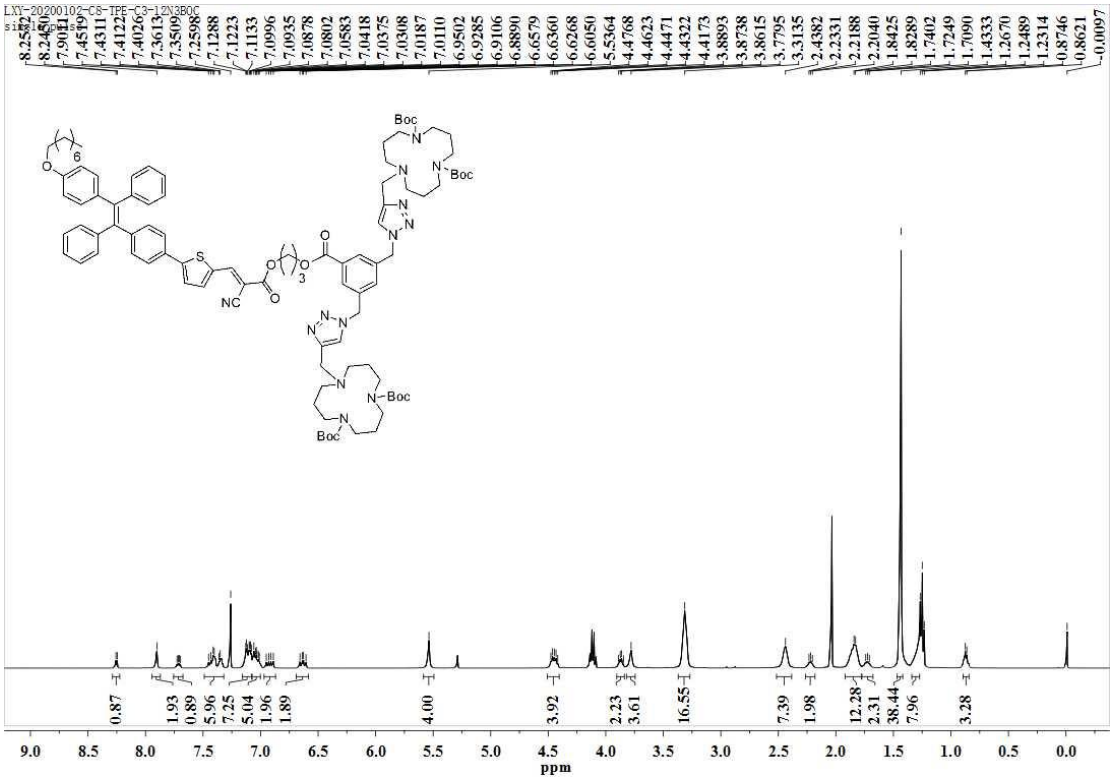


Figure S72 ^{1}H NMR spectrum of **10** (400 MHz, $CDCl_3$)

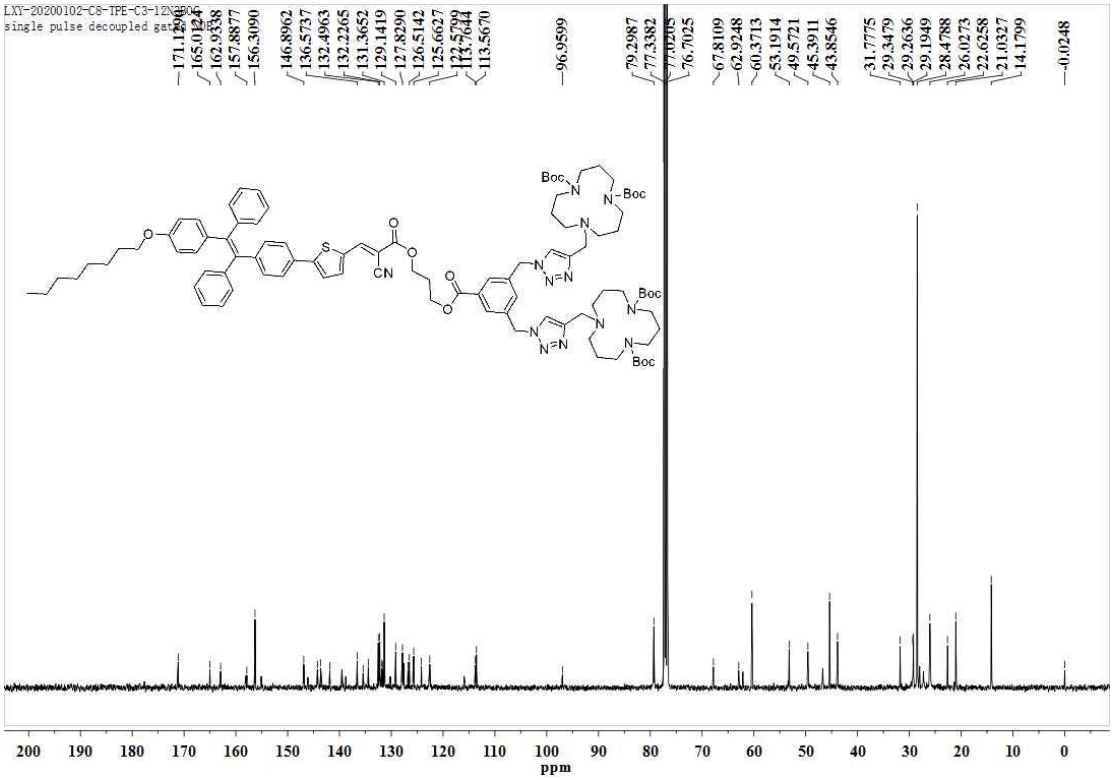


Figure S73 ^{13}C NMR spectrum of **10** (101 MHz, $CDCl_3$).

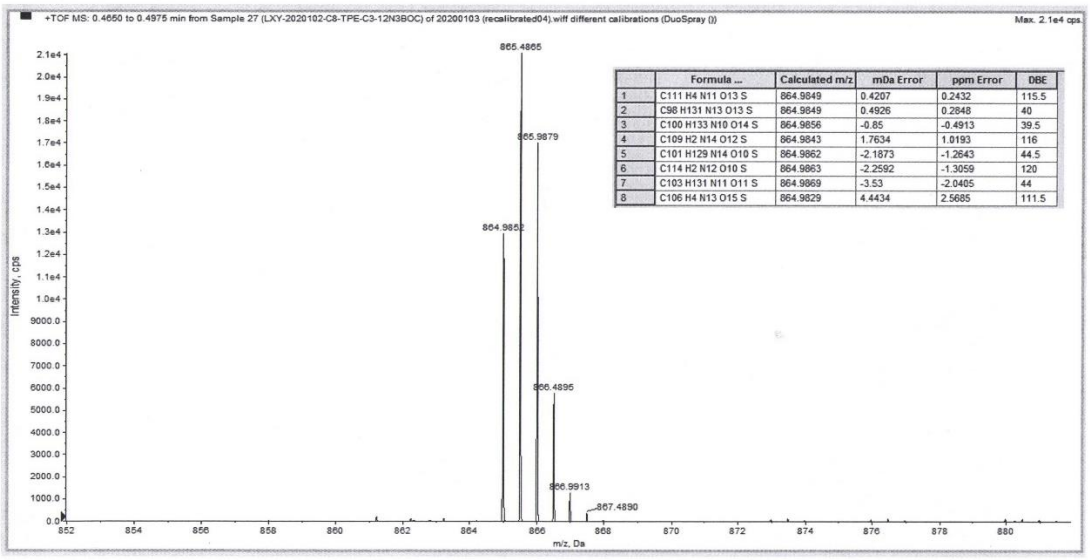


Figure S74 HR-MS spectrum of **10**.

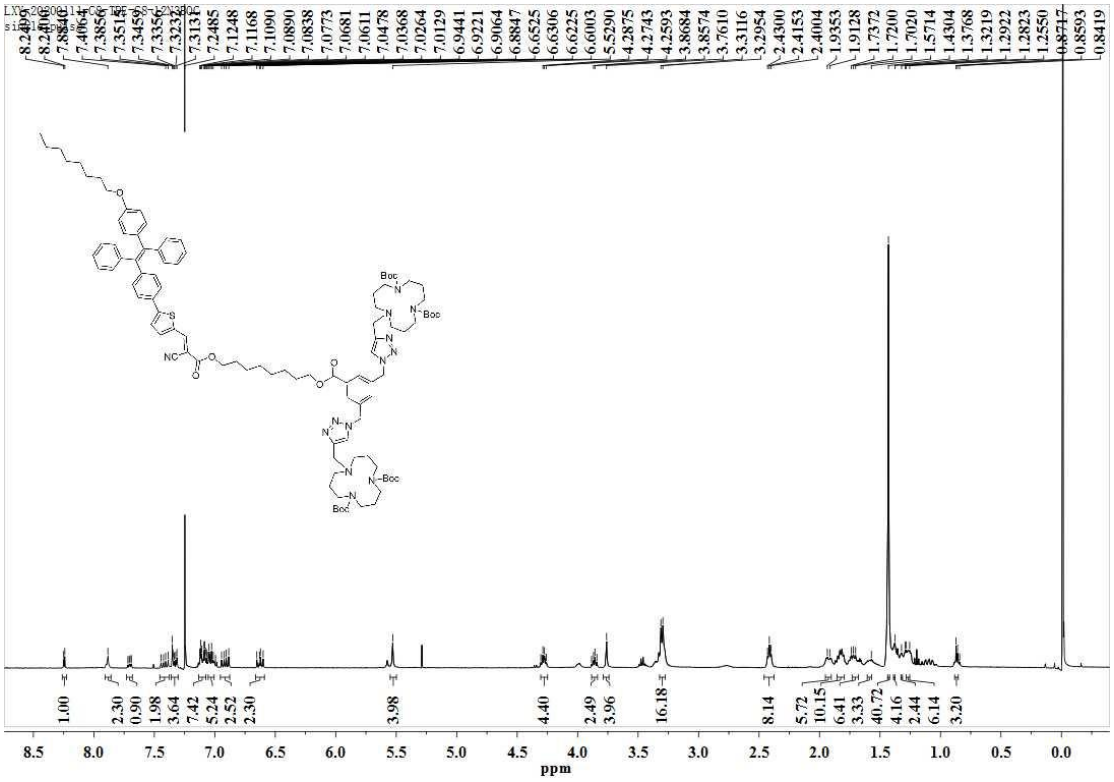


Figure S75 ^{1}H NMR spectrum of **11** (400 MHz, $CDCl_3$)

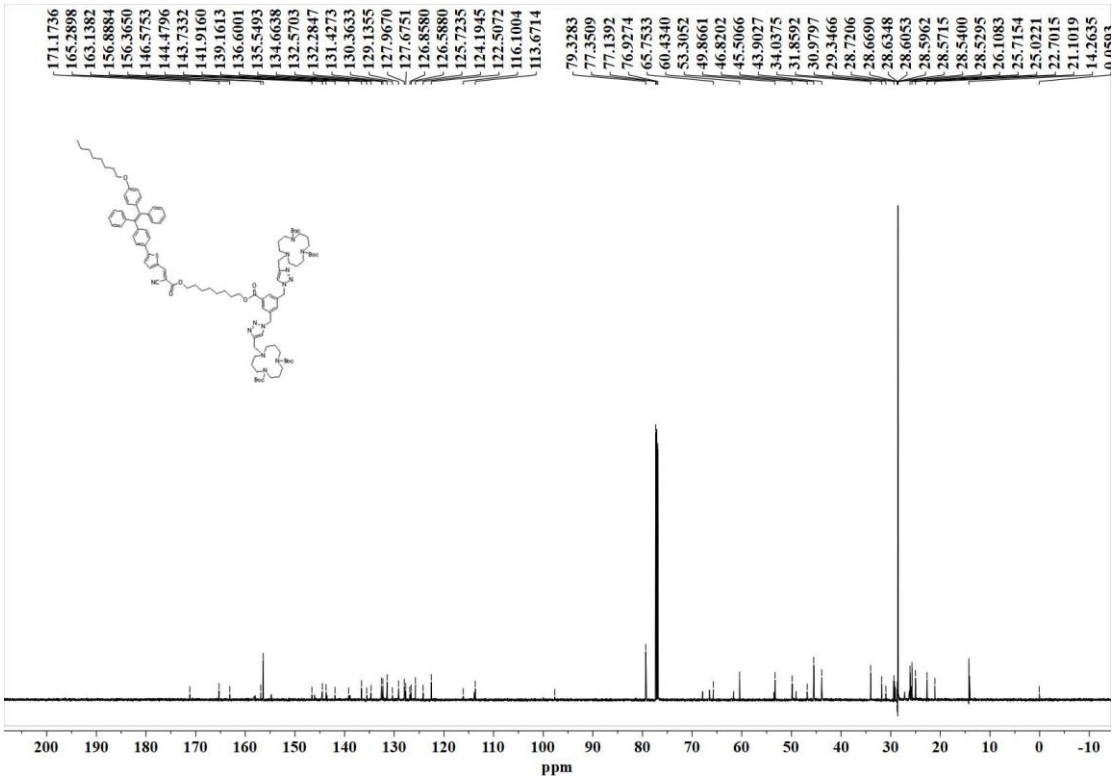
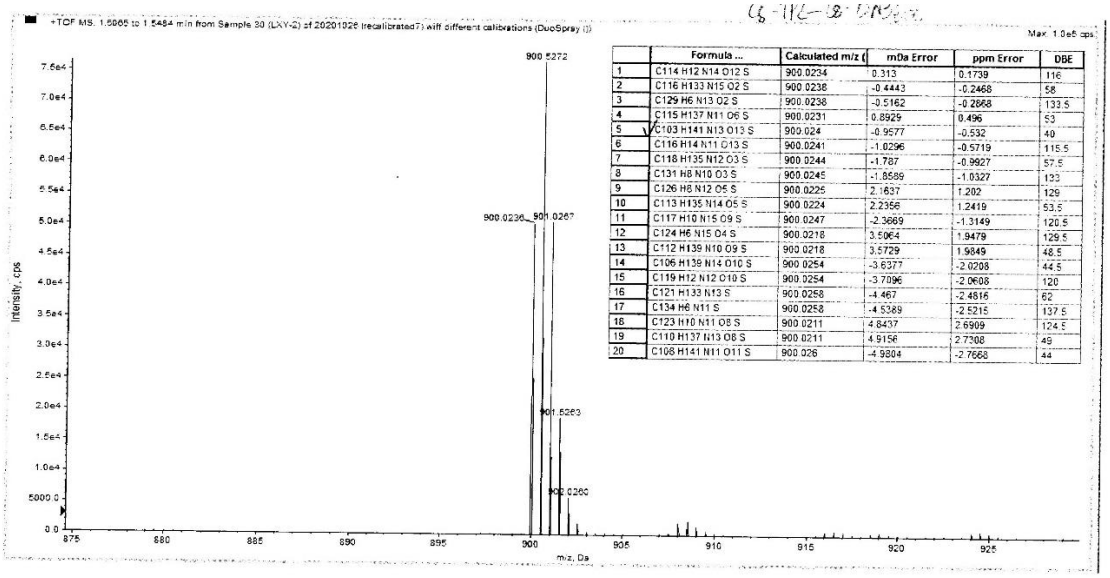


Figure S76 ^{13}C NMR spectrum of **11** (151 MHz, $CDCl_3$).



	Formula ...	Calculated m/z (	mDa Error	ppm Error	DBE
1	C114 H12 N14 O12 S	900.0234	0.313	0.1739	116
2	C116 H133 N15 O2 S	900.0238	-0.4443	-0.2468	58
3	C129 H6 N13 O2 S	900.0238	-0.5162	-0.2868	133.5
4	C115 H137 N11 O6 S	900.0231	0.8929	0.496	53
5	C103 H141 N13 O13 S	900.024	-0.9577	-0.532	40
6	C116 H14 N11 O13 S	900.0241	-1.0296	-0.5719	115.5
7	C118 H135 N12 O3 S	900.0244	-1.787	-0.9927	57.5
8	C131 H8 N10 O3 S	900.0245	-1.8589	-1.0327	123
9	C126 H8 N12 O5 S	900.0225	2.1637	1.202	129
10	C113 H135 N14 O5 S	900.0224	2.2356	1.2419	53.5
11	C117 H10 N15 O9 S	900.0247	-2.3669	-1.3149	120.5
12	C124 H6 N15 O4 S	900.0218	3.5064	1.9479	129.5
13	C112 H139 N10 O9 S	900.0218	3.5729	1.9849	48.5
14	C106 H139 N14 O10 S	900.0254	-3.6377	-2.0208	44.5
15	C119 H12 N12 O10 S	900.0254	-3.7096	-2.0608	120
16	C121 H133 N13 S	900.0258	-4.467	-2.4816	62
17	C134 H6 N11 S	900.0258	-4.5389	-2.5215	137.5
18	C123 H10 N11 O8 S	900.0211	4.8437	2.6909	124.5
19	C110 H137 N13 O8 S	900.0211	4.9156	2.7308	49
20	C108 H141 N11 O11 S	900.026	-4.9804	-2.7668	44

Figure S77 HR-MS spectrum of **11**.

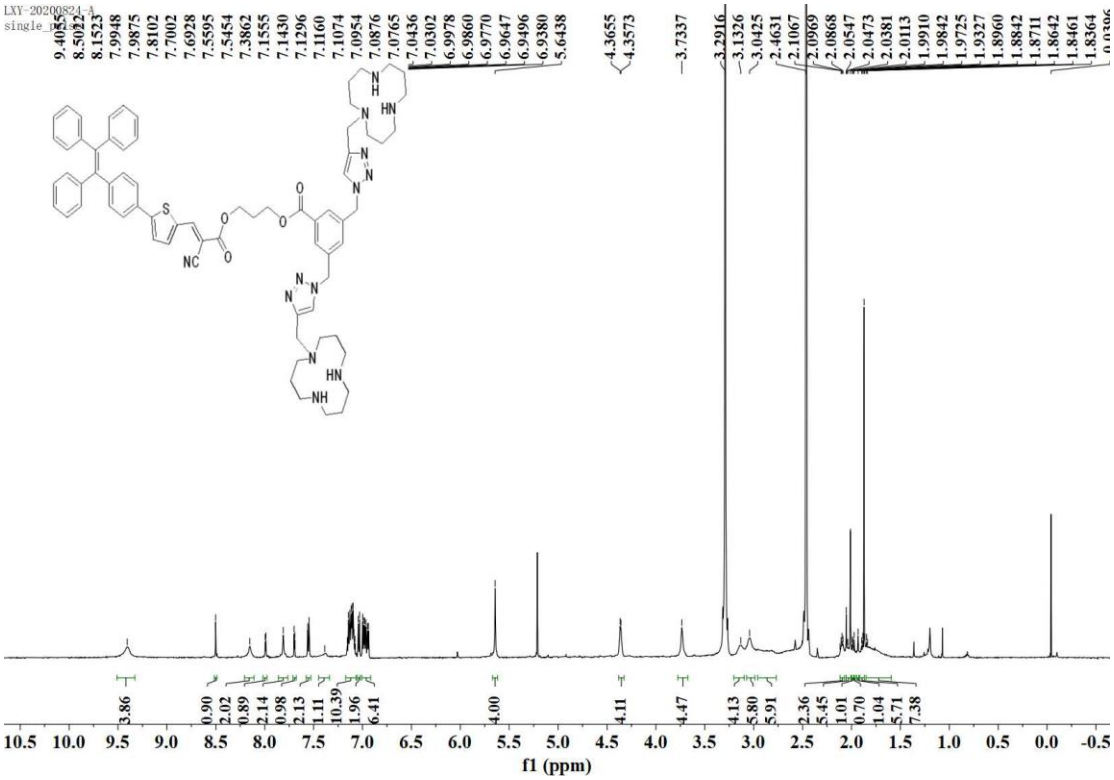


Figure S78 ^{1}H NMR spectrum of **TTC-L-M-1** (600 MHz, DMSO-d_6)

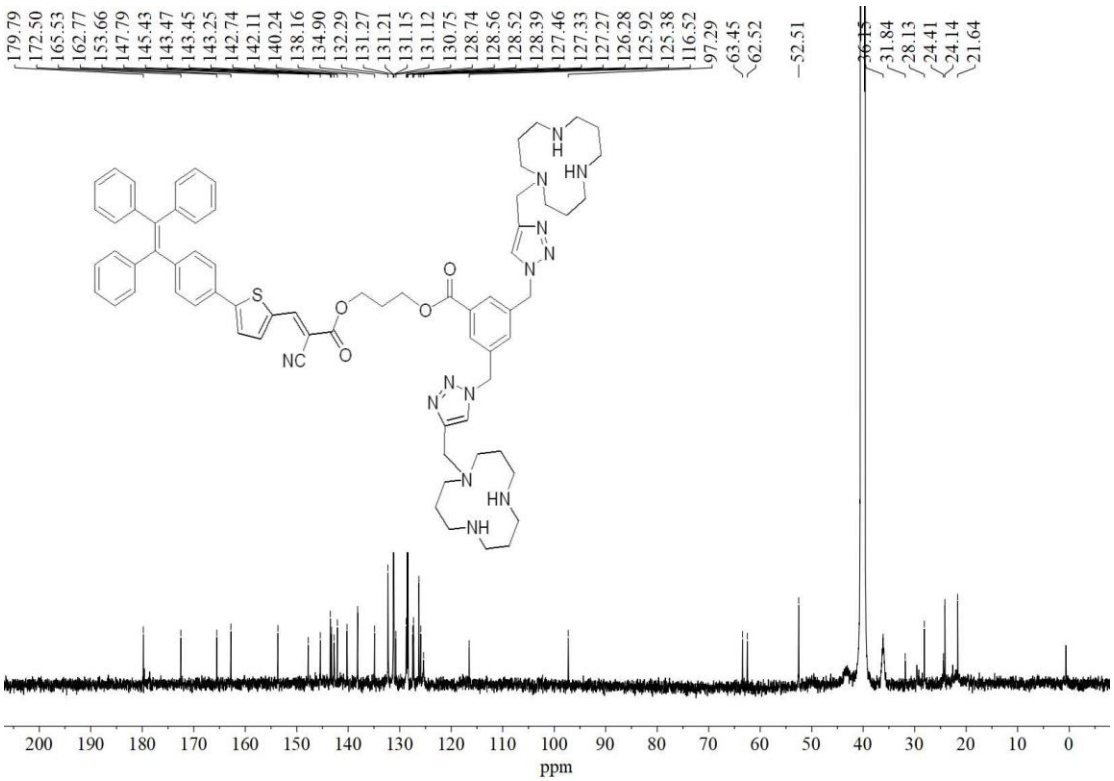
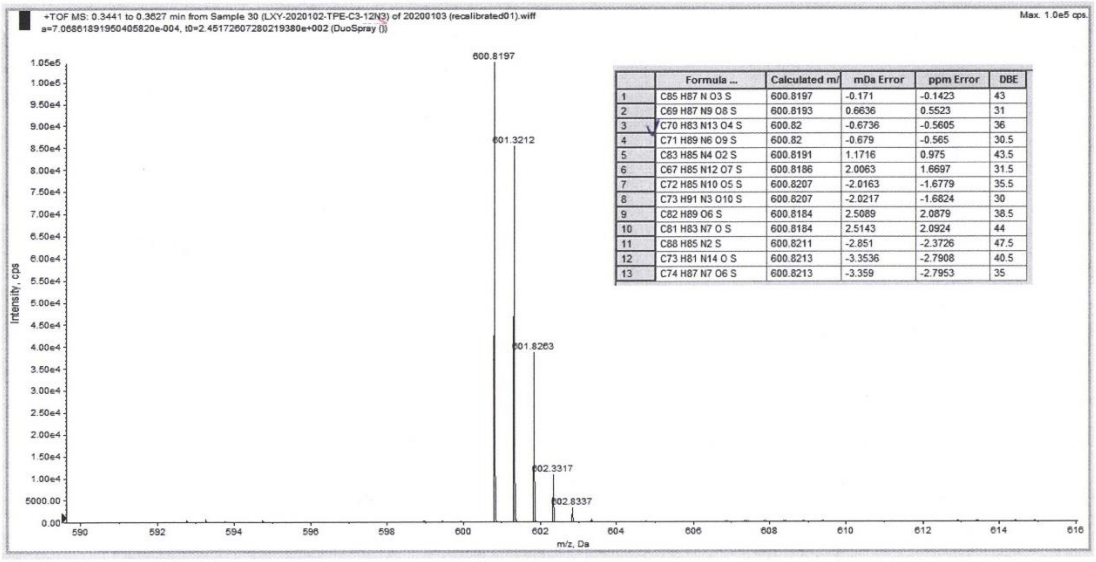


Figure S79 ^{13}C NMR spectrum of **TTC-L-M-1** (151 MHz, DMSO-d_6)



	Formula ...	Calculated m/	mDa Error	ppm Error	DBE
1	C85 H87 N O3 S	600.8197	-0.171	-0.1423	43
2	C69 H87 N9 O8 S	600.8193	0.6636	0.5523	31
3	C70 H83 N13 O4 S	600.82	-0.6736	-0.5605	36
4	C71 H89 N6 O9 S	600.82	-0.679	-0.565	30.5
5	C83 H85 N4 O2 S	600.8191	1.1716	0.975	43.5
6	C67 H85 N12 O7 S	600.8186	2.0063	1.6697	31.5
7	C72 H85 N10 O5 S	600.8207	-2.0163	-1.6779	35.5
8	C73 H91 N3 O10 S	600.8207	-2.0217	-1.6824	30
9	C82 H89 O6 S	600.8184	2.5089	2.0879	38.5
10	C81 H83 N7 O S	600.8184	2.5143	2.0924	44
11	C88 H85 N2 S	600.8211	-2.851	-2.3726	47.5
12	C73 H81 N14 O S	600.8213	-3.3536	-2.7908	40.5
13	C74 H87 N7 O6 S	600.8213	-3.359	-2.7953	35

Figure S80 HR-MS spectrum of **TTC-L-M-1**.

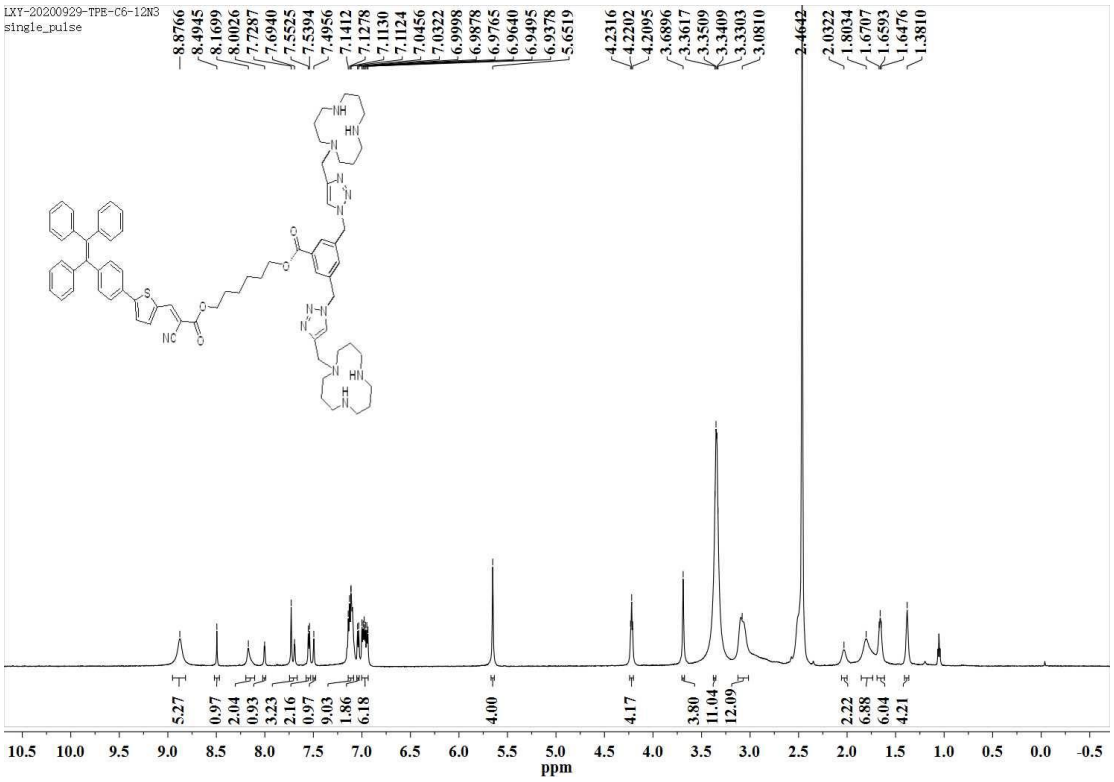


Figure S81 ^{1}H NMR spectrum of **TTC-L-M-2** (600 MHz, DMSO-d_6)

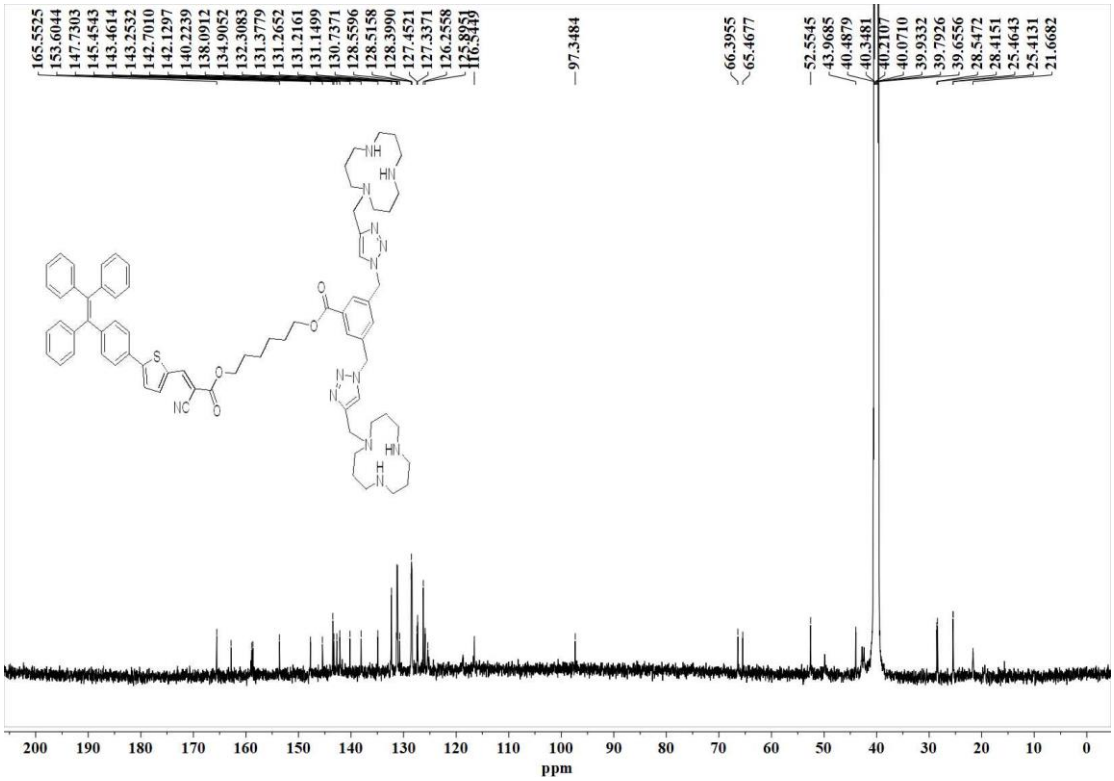
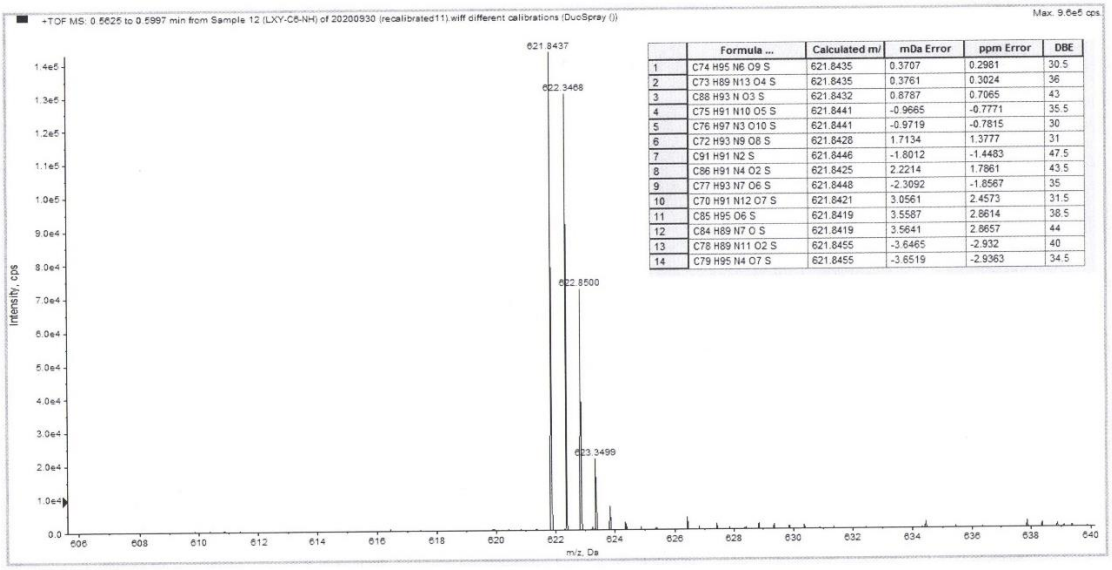


Figure S82 ^{13}C NMR spectrum of **TTC-L-M-2** (151 MHz, DMSO-d_6)



	Formula ...	Calculated m/	mDa Error	ppm Error	DBE
1	C74 H95 N6 O9 S	621.8435	0.3707	0.2981	30.5
2	C73 H89 N13 O4 S	621.8435	0.3761	0.3024	36
3	C88 H93 N O3 S	621.8432	0.8787	0.7065	43
4	C75 H91 N10 O5 S	621.8441	-0.9665	-0.7771	35.5
5	C76 H97 N3 O10 S	621.8441	-0.9719	-0.7815	30
6	C72 H93 N9 O8 S	621.8428	1.7134	1.3777	31
7	C91 H91 N2 S	621.8446	-1.8012	-1.4483	47.5
8	C86 H91 N4 O2 S	621.8425	2.2214	1.7861	43.5
9	C77 H93 N7 O6 S	621.8448	-2.3092	-1.8567	35
10	C70 H91 N12 O7 S	621.8421	3.0561	2.4573	31.5
11	C85 H95 O6 S	621.8419	3.5587	2.8614	38.5
12	C84 H89 N7 O S	621.8419	3.5641	2.8657	44
13	C78 H89 N11 O2 S	621.8455	-3.6465	-2.932	40
14	C79 H95 N4 O7 S	621.8455	-3.6519	-2.9363	34.5

Figure S83 HR-MS spectrum of **TTC-L-M-2**.

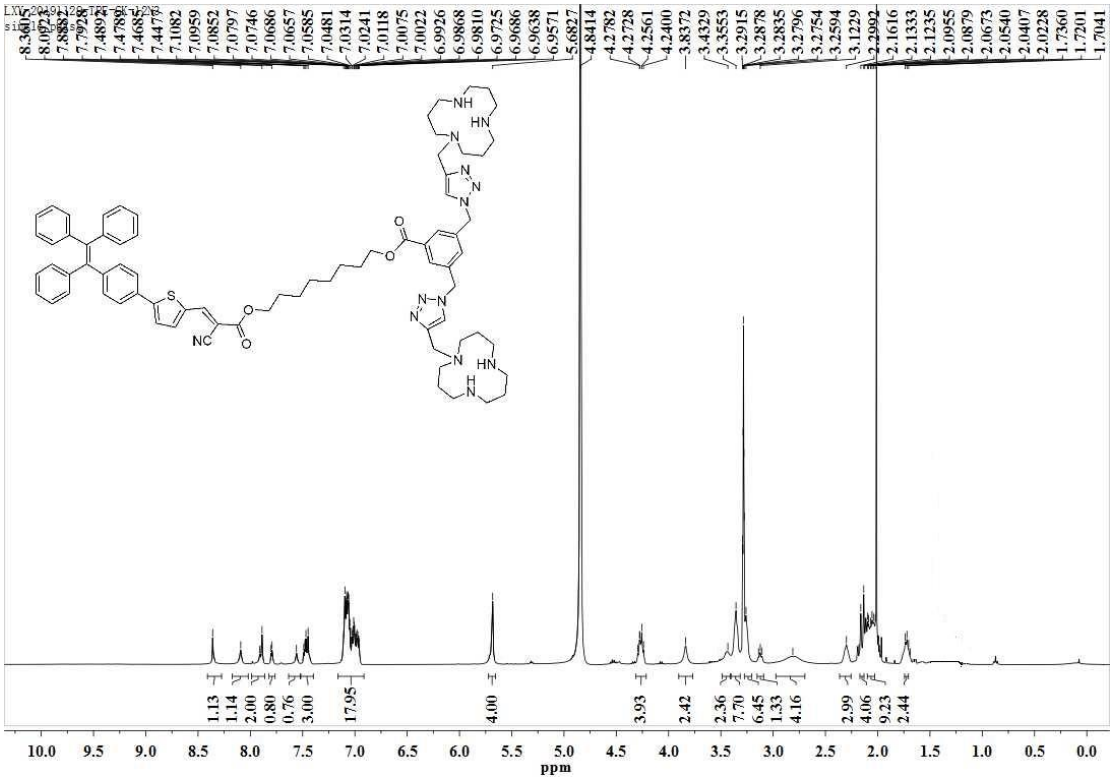


Figure S84 ^{1}H NMR spectrum of **TTC-L-M-3** (400 MHz, CD_3OD)

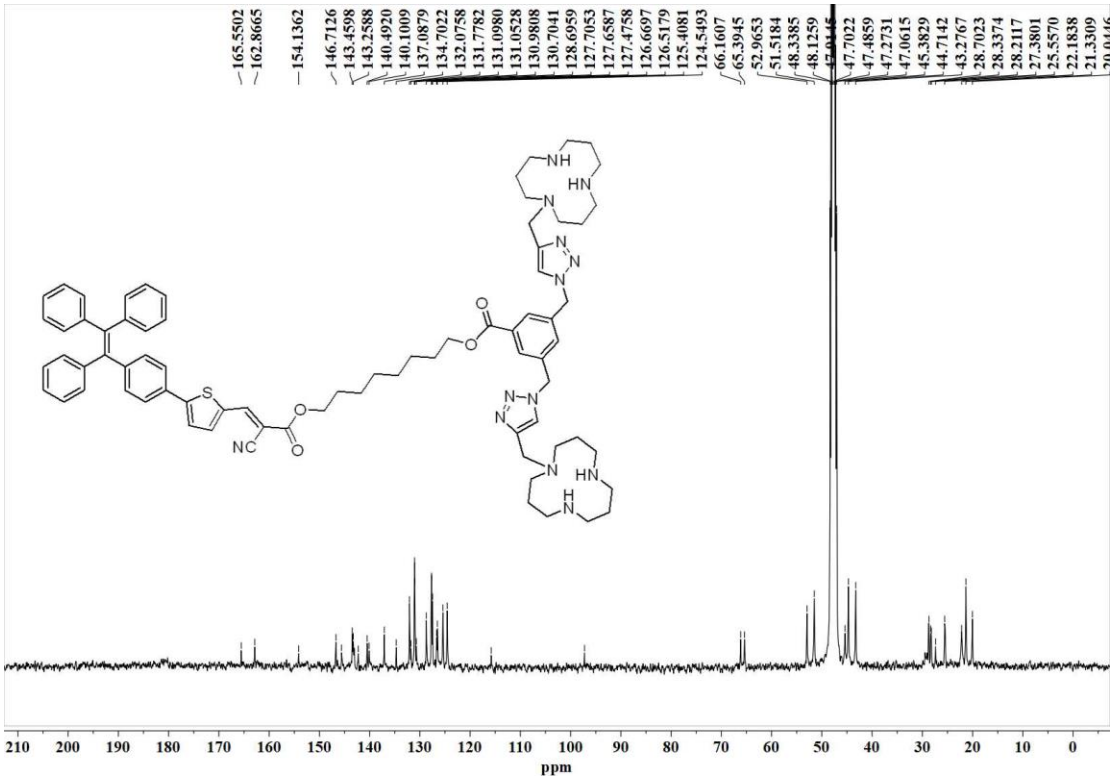


Figure S85 ^{13}C NMR spectrum of **TTC-L-M-2** (151 MHz, CD_3OD)

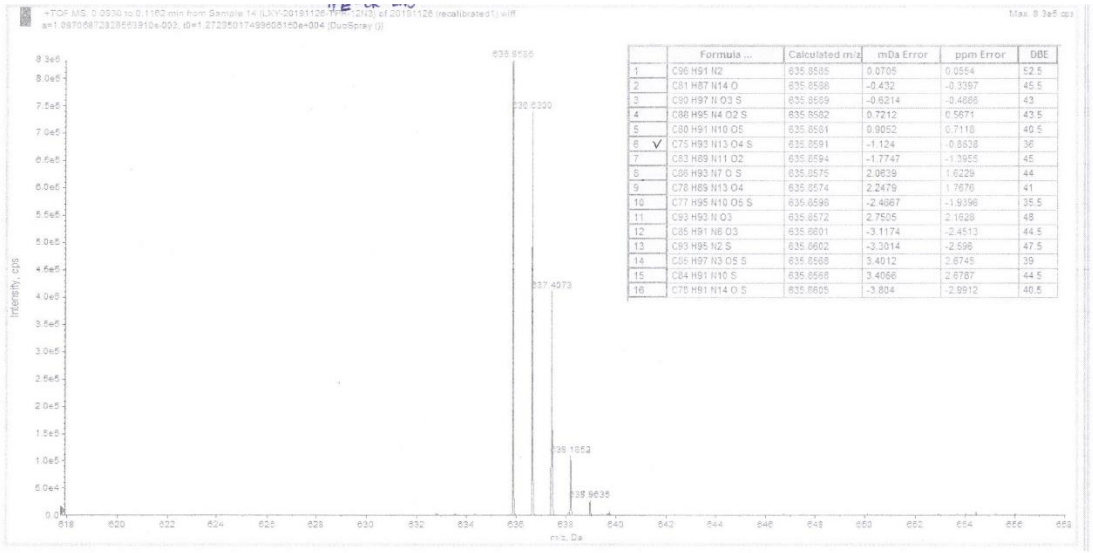


Figure S86 HR-MS spectrum of **TTC-L-M-3**.

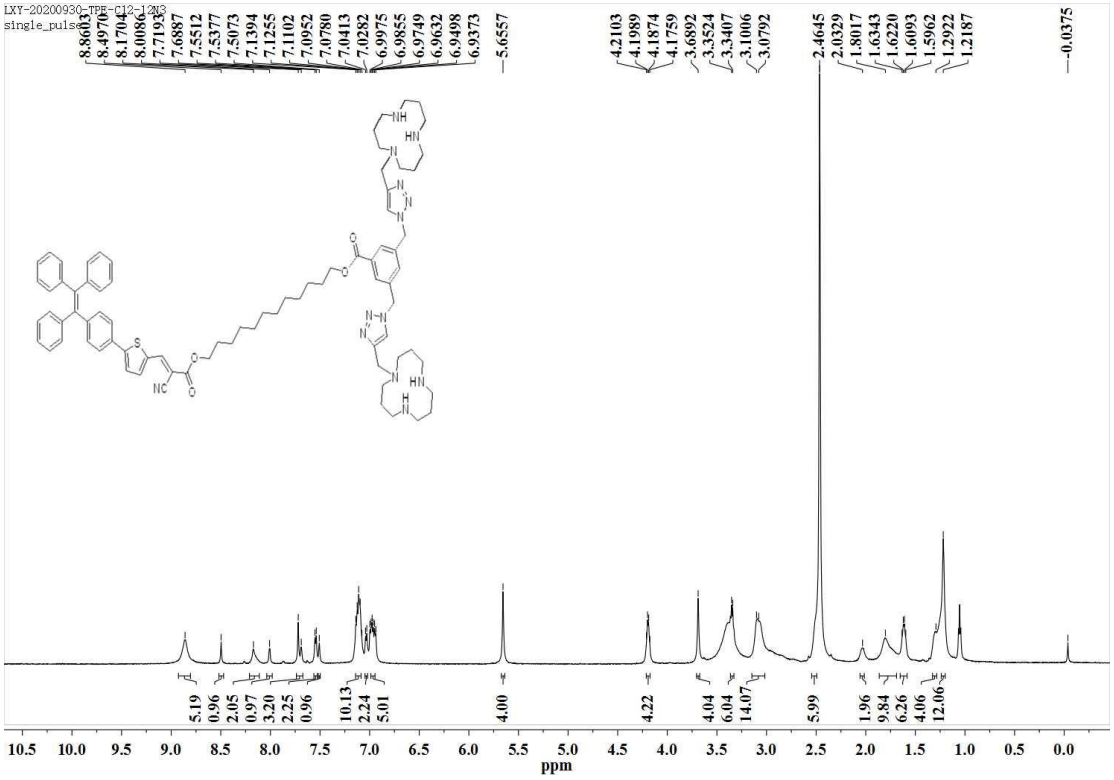


Figure S87 ^{1}H NMR spectrum of **TTC-L-M-4** (600 MHz, DMSO-d_6)

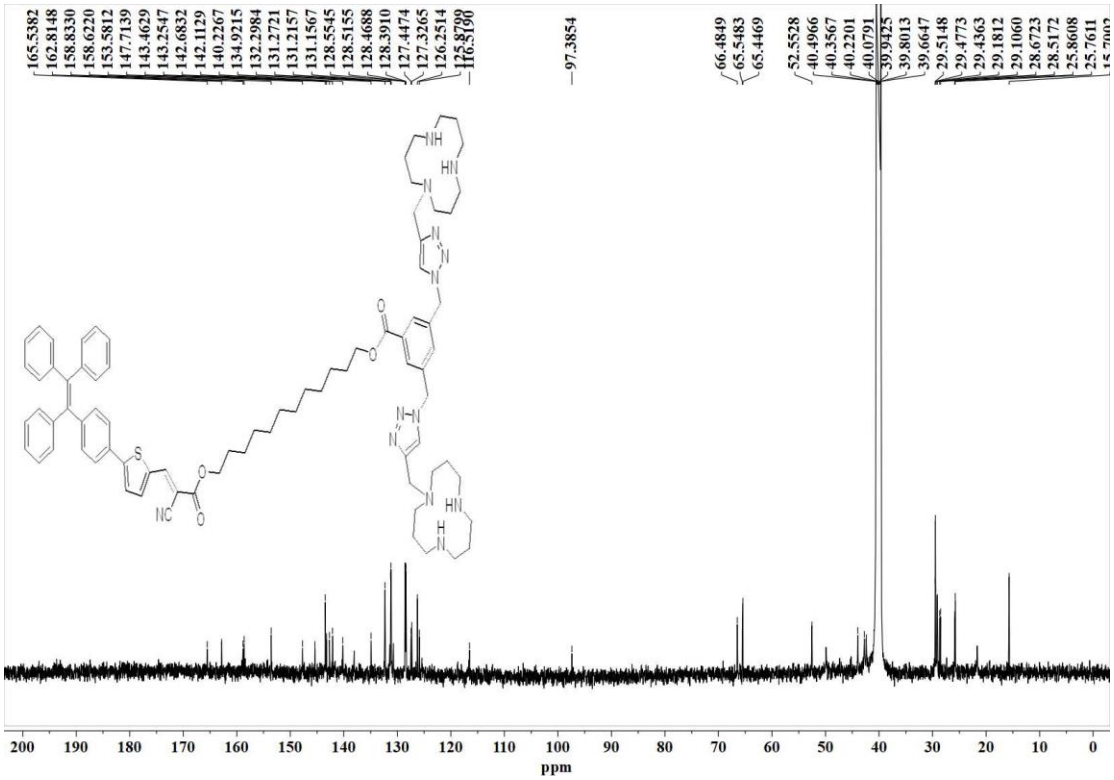
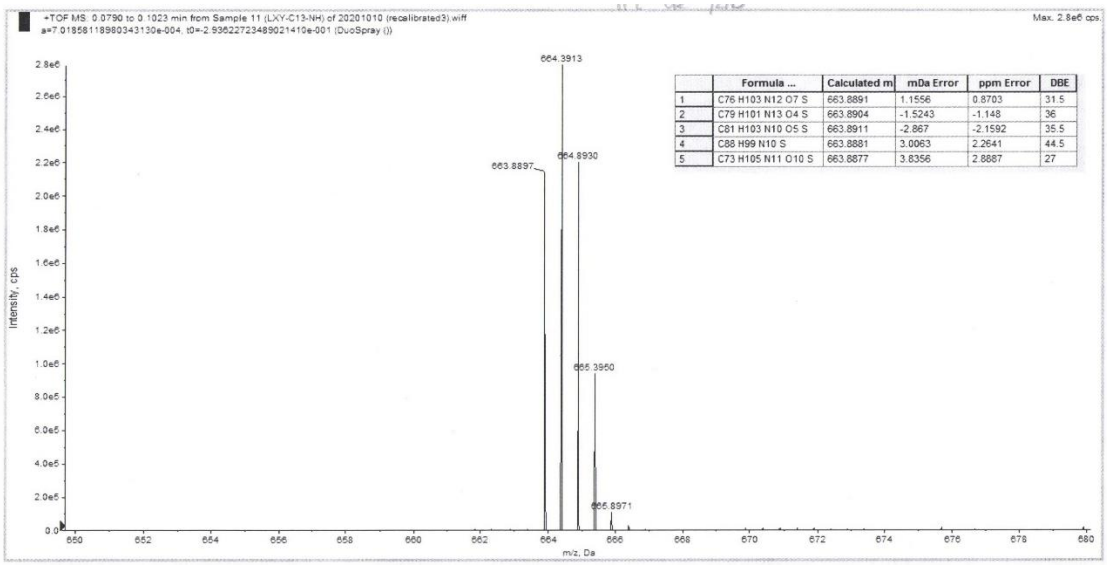


Figure S88 ^{13}C NMR spectrum of **TTC-L-M-4** (151 MHz, DMSO-d_6)



	Formula ...	Calculated m	mDa Error	ppm Error	DBE
1	C76 H103 N12 O7 S	663.8891	1.1556	0.8703	31.5
2	C79 H101 N13 O4 S	663.8904	-1.5243	-1.148	36
3	C81 H103 N10 O5 S	663.8911	-2.867	-2.1592	35.5
4	C88 H99 N10 S	663.8881	3.0063	2.2641	44.5
5	C73 H105 N11 O10 S	663.8877	3.8356	2.8887	27

Figure S89 HR-MS spectrum of **TTC-L-M-4**.

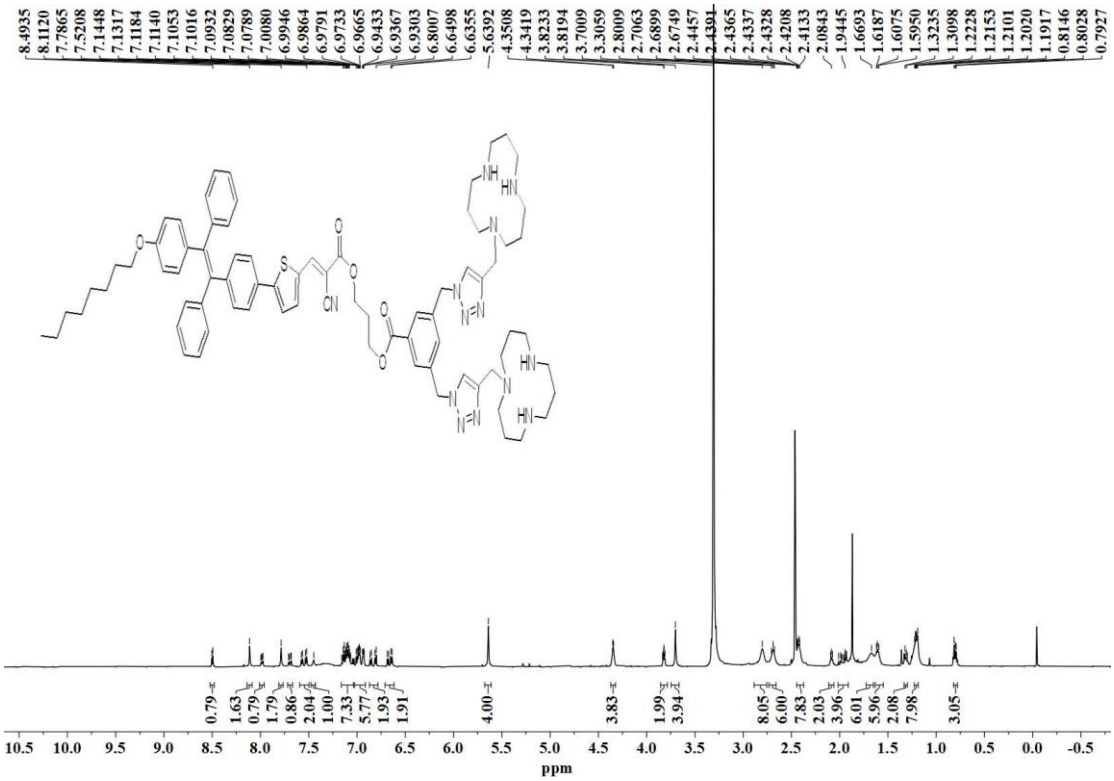


Figure S90 ^{1}H NMR spectrum of **TTC-L-M-5** (600 MHz, DMSO-d_6)

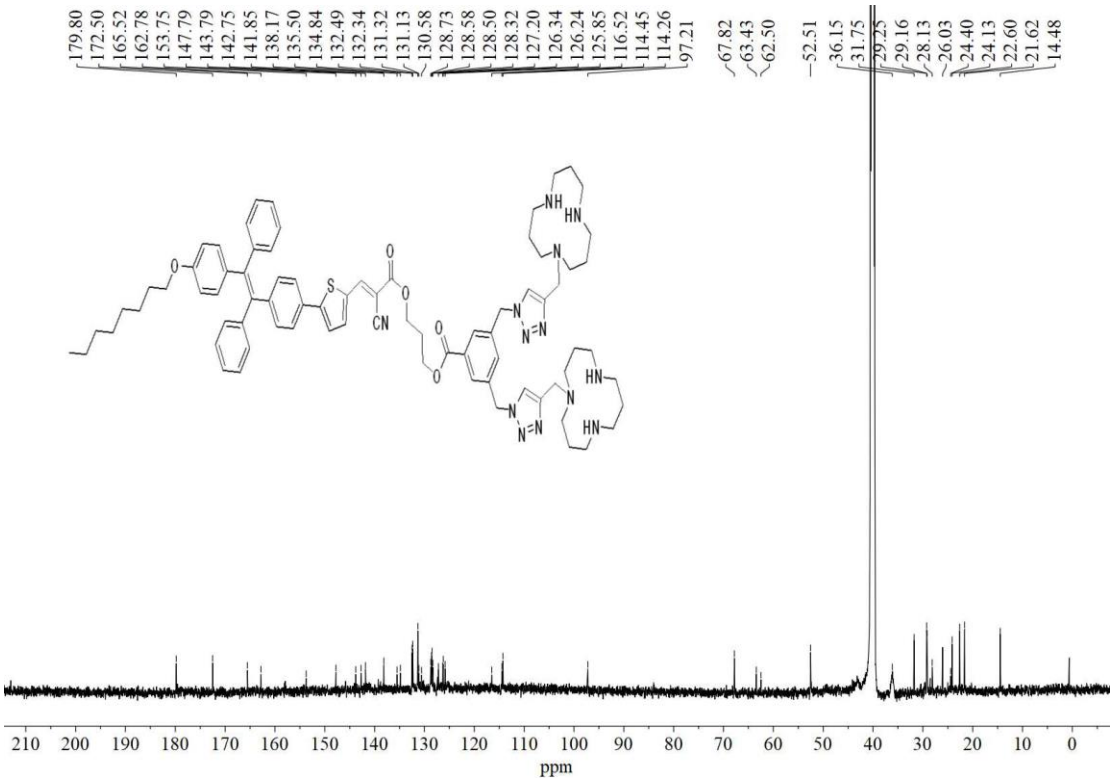


Figure S91 ^{13}C NMR spectrum of **TTC-L-M-5** (151 MHz, DMSO-d_6)

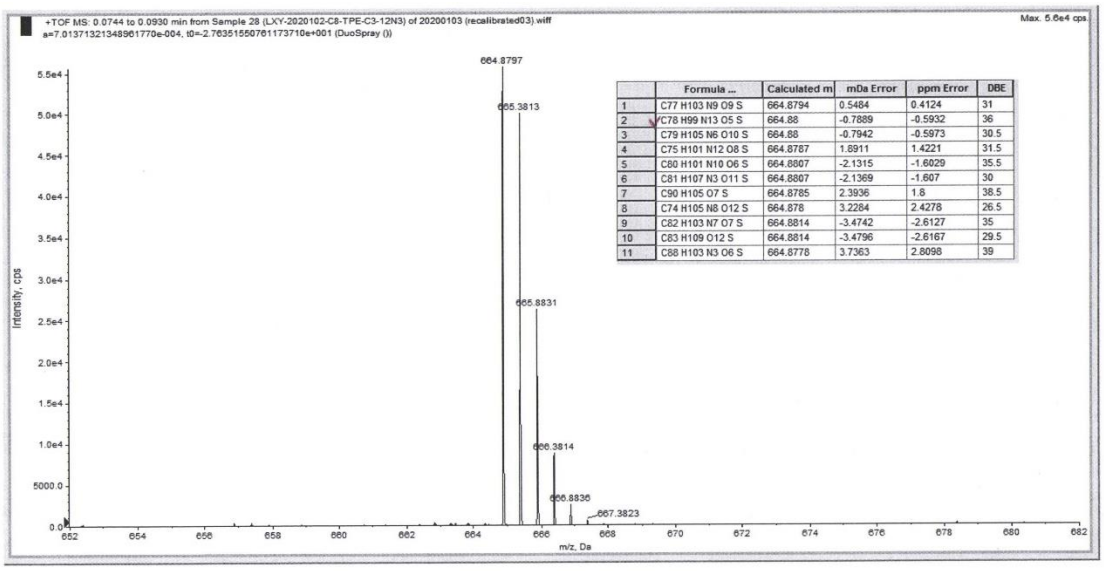


Figure S92 HR-MS spectrum of **TTC-L-M-5**.

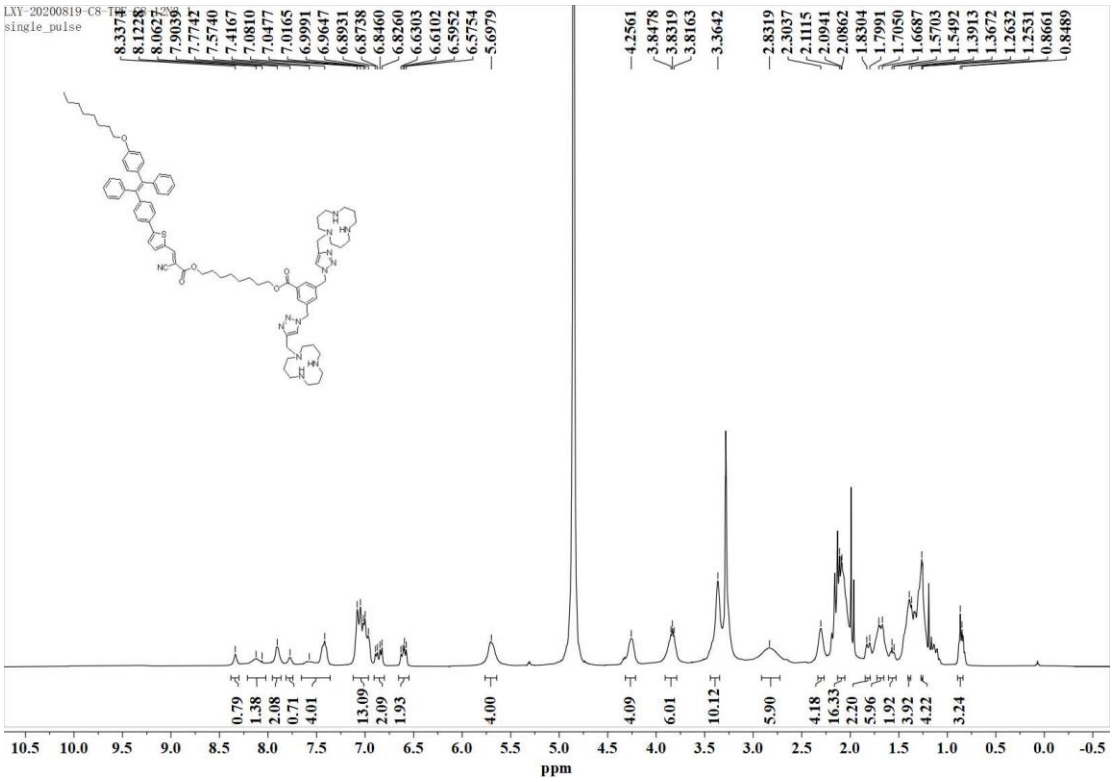


Figure S93 ^{1}H NMR spectrum of **TTC-L-M-6** (400 MHz, CD_3OD)

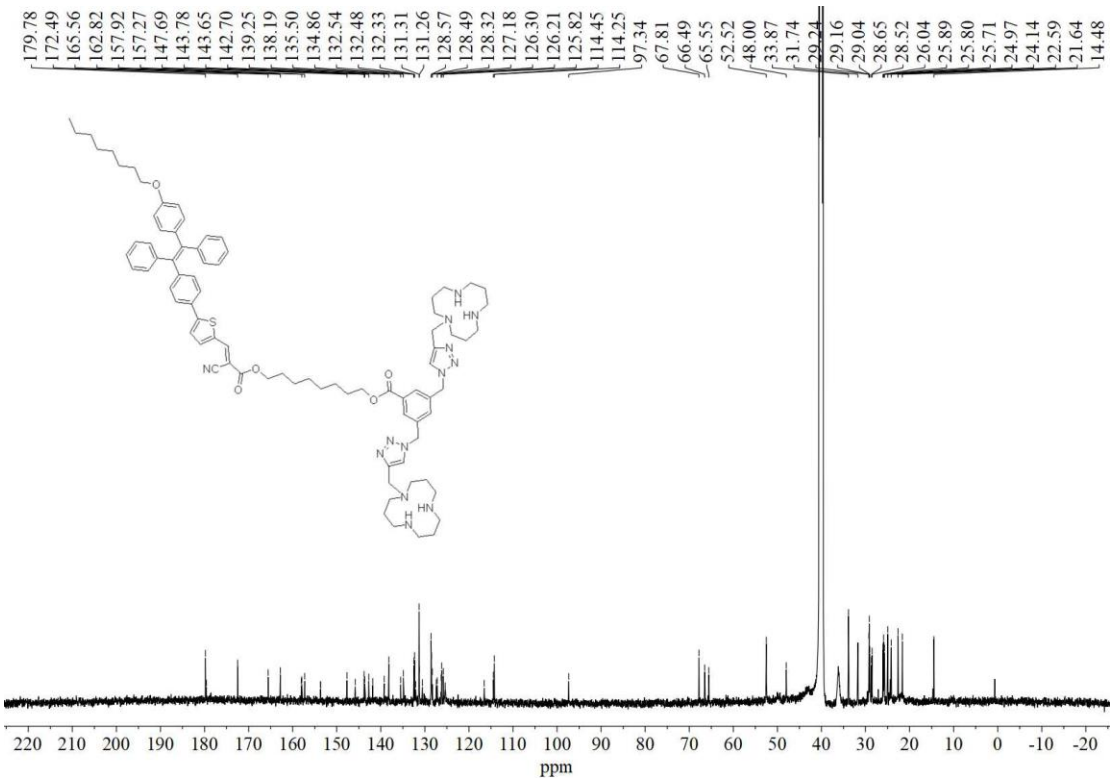
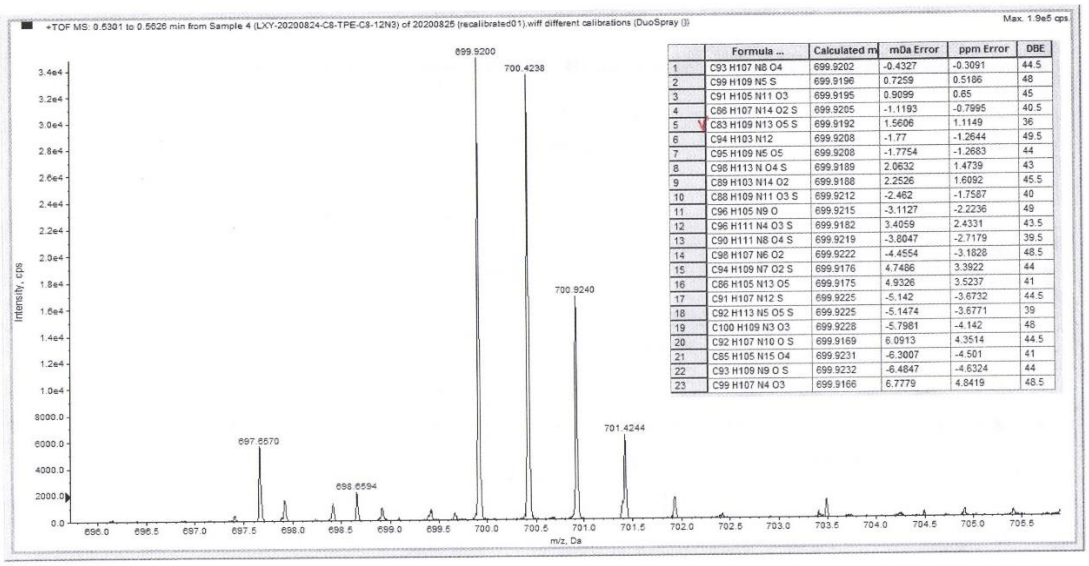


Figure S94 ^{13}C NMR spectrum of TTC-L-M-6 (151 MHz, DMSO-d_6)



	Formula ...	Calculated m	mDa Error	ppm Error	DBE
1	C93 H107 N8 O4	699.9202	-0.4327	-0.3091	44.5
2	C99 H109 N5 S	699.9196	0.7259	0.5186	48
3	C91 H105 N11 O3	699.9195	0.9099	0.65	45
4	C86 H107 N14 O2 S	699.9205	-1.1193	-0.7995	40.5
5	C83 H109 N13 O5 S	699.9192	1.5606	1.1149	36
6	C94 H103 N12	699.9208	-1.77	-1.2644	49.5
7	C95 H109 N5 O5	699.9208	-1.7754	-1.2683	44
8	C98 H113 N O4 S	699.9189	2.0632	1.4739	43
9	C89 H103 N14 O2	699.9188	2.2526	1.6092	45.5
10	C88 H109 N11 O3 S	699.9212	-2.462	-1.7587	40
11	C96 H105 N9 O	699.9215	-3.1127	-2.2236	49
12	C96 H111 N4 O3 S	699.9182	3.4059	2.4331	43.5
13	C90 H111 N8 O4 S	699.9219	-3.8047	-2.7179	39.5
14	C98 H107 N6 O2	699.9222	-4.4554	-3.1828	48.5
15	C94 H109 N7 O2 S	699.9176	4.7486	3.3922	44
16	C86 H105 N13 O5	699.9175	4.9326	3.5237	41
17	C91 H107 N12 S	699.9225	-5.142	-3.6732	44.5
18	C92 H113 N5 O5 S	699.9225	-5.1474	-3.6771	39
19	C100 H109 N3 O3	699.9228	-5.7981	-4.142	48
20	C92 H107 N10 O S	699.9169	6.0913	4.3514	44.5
21	C85 H105 N15 O4	699.9231	-6.3007	-4.501	41
22	C93 H109 N9 O S	699.9232	-6.4847	-4.6324	44
23	C99 H107 N4 O3	699.9166	6.7779	4.8419	48.5

Figure S95 HR-MS spectrum of **TTC-L-M-6**.

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(3) Liu, B.; Liu, J. Methods and compositions for near infrared fluorescent nanodots with aggregation-induced emission characteristics. US2019358350A1, 2019-11-28.