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Overcome energy loss of thermally activated delayed fluorescence sensitized-OLEDs by developing fluorescence dopant with a small singlet-triplet energy splitting

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Electronic Supplementary Information

Contents

Section 1:Computational details

Molecular geometry optimizations were performed for the ground (S0) and excited (S1) states at the level of (TD)B3LYP/M062X. Based on the S1-geometry, the excitation energies and natural transition orbitals (NTO) of the low-lying excited states were evaluated at the TD-B3LYP/ M062X level. All calculations were performed by using Gaussian 09 program1. The spin-orbit coupling matrix elements of singlet and triplet excited states were carried out based on the first-order Douglas−Kroll−Hess-like spin−orbit operator derived from the exact two-component (X2C) Hamiltonian by using Beijing Density Function (BDF) program.[2-5]

Section 2:

Synthesis of materials

All reagents were used without further purification. The 1HNMR spectra were recorded on Bruker Avance 400MHz spectrometers and HRMS experiments were carried out on a Thermo Scientific LTQ Orbitrap Discovery (Bremen, Germany).

Synthesis of intermediate (1a and 1b)

6,7-dibromo-2,3-dichloroquinoxaline (0.6 g, 1.68 mmol) was dissolved in MeCN (20 mL), then Pd(PPh3)2Cl2 (5 mol-%) and CuI (5 mol-%) were added. The reaction flask was then sealed and flushed with nitrogen. Then, Et3N (2.5 equiv.) and ethynylbenzene (0.18 g, 1.75 mmol)/4-ethynyl-N,N-diphenylaniline (0.29g, 1.75 mmol) were added. The reaction mixture was stirred at 60 °C for 8 h. After the first coupling reaction was complete, TFA (35 mL) was added. The reaction mixture was then stirred at 60 °C until TLC revealed complete conversion of the intermediate into the final product. The mixture was then cooled, diluted with H2O and filtered. The residue was purified by silica gel column chromatography (CH2Cl2 / petroleum ether) to give the corresponding product.

1a (0.6g, 88%): 1HNMR (400MHz, CDCl3) δ(ppm): 1H NMR (400 MHz, DMSO-d6) δ(ppm): 8.56 (s, 1H), 8.50 (s, 1H), 8.17-8.10 (m, 2H), 7.93 (s, 1H), 7.64-7.58 (m, 3H).

1b(0.8g, 83%): 1HNMR (400MHz, CDCl3) δ(ppm): 1H NMR (400 MHz, DMSO-d6) δ(ppm) : 8.49 (s, 1H), 8.43 (s, 1H), 8.01-7.94 (m, 2H), 7.64 (s, 1H), 7.43-7.35 (m, 4H), 7.22-7.13 (m, 6H), 7.01-6.95 (m, 2H).

Synthesis of 67dTPA-FQ and 267tTPA-FQ

The compound 1a (0.6 g, 1.49 mmol)/1b (0.85 g, 1.49 mmol), (4-(diphenylamino)phenyl)boronic acid (1.07 g, 3.71 mmol), K_2CO_3 (1.23 g, 8.91 mmol) and $Pd(PPh_3)_4$ (0.086 g, 0.074 mmol) were added to 100 ml dioxane/H2O (4:1) mixed solvent. Then the reaction mixture was stirred at 120 ℃ under a nitrogen atmosphere until TLC revealed complete conversion of the starting material. The mixture was cooled, diluted with H2O and filtered. The residue was purified by silica gel column chromatography (CH_2Cl_2/petroleum ether) to gain the product.

67dTPA-FQ(0.88g, 81%): 1H NMR (400MHz, CDCl3) δ(ppm): 8.16-8.12 (m, 2H), 8.12 (s, 1H), 8.04 (s, 1H), 7.92 (s, 1H), 7.66-7.54 (m, 3H), 7.30-7.20 (m, 7H), 7.14 (dd, J = 8.4, 2.0 Hz, 4H), 7.02 (dd, J = 15.2, 7.6 Hz, 13H), 6.90 (dd, J = 8.6, 2.6 Hz, 4H); 13CNMR (101 MHz, Chloroform-d) δ(ppm) : 163.93, 154.96, 147.68, 147.07, 147.02, 144.45, 142.30, 141.86, 141.46, 138.24, 134.47, 134.40, 131.39, 130.93, 129.42, 129.31, 129.17, 129.13, 128.66, 126.29, 124.68, 123.16, 123.13, 122.84, 122.78, 100.99.HRMS (ESI) calcd for C46H32N4O $[M+H]^+$ 733.29601, found 733.29594.

267tTPA-FQ(1.0g, 79%): 1H NMR (400 MHz, DMSO-d6) δ(ppm) : 8.05 (s, 1H), 7.99-7.92 (m, 3H), 7.61 (s, 1H), 7.41-7.34 (m, 4H), 7.25 (t, J = 7.6 Hz, 8H), 7.20-7.07 (m, 10H), 7.06-6.96 (m, 14H), 6.89 (dd, J = 8.7, 2.3 Hz, 4H); 13C NMR (101 MHz, Chloroform-d) δ(ppm) : 147.68, 146.96, 146.58, 141.74, 134.53, 130.94, 129.77, 129.42, 129.11, 127.57, 125.92, 124.72, 124.65, 123.13, 123.10, 122.85, 122.78, 121.12.HRMS (ESI) calcd for C46H32N4O $[M+H]^+$ 900.36969, found 900.36915.

Section 3:

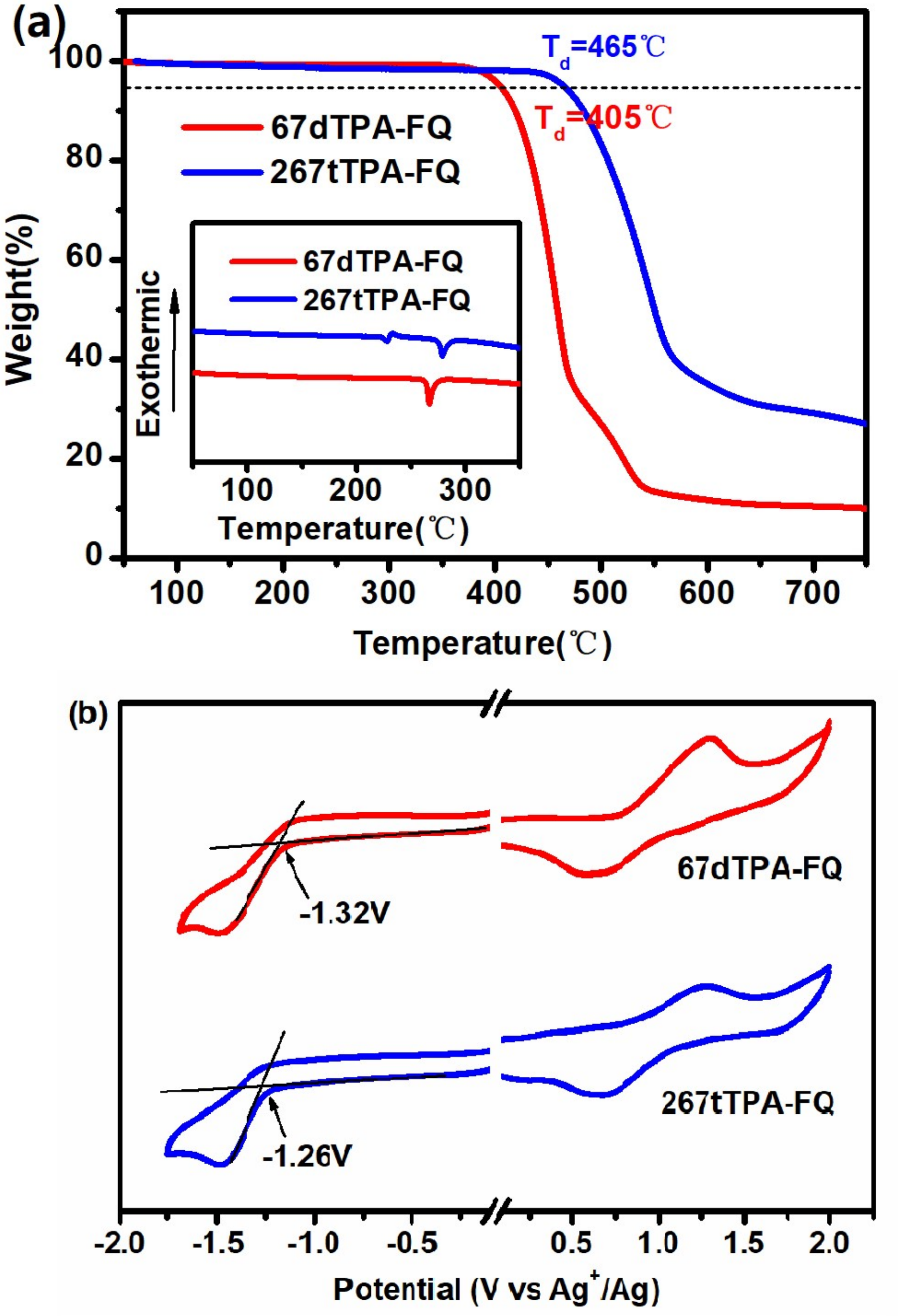

Figure S1(a) TGA and DSC (inset) curves, and (b) CV curves of the 67dTPA-FQ, and 267tTPA-FQ.

Section 4: ^{1}H NMR spectra

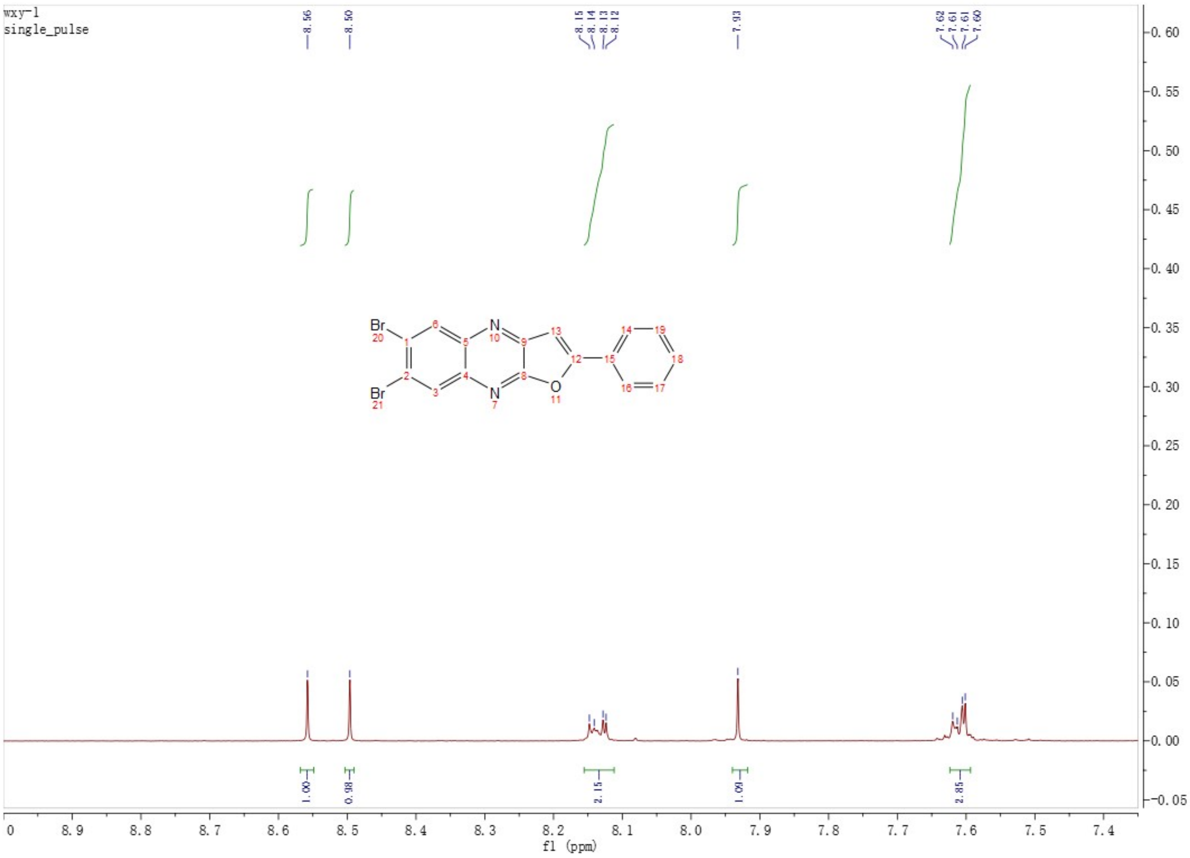

Figure S_2 ^{1}H NMR spectrum of **1a**

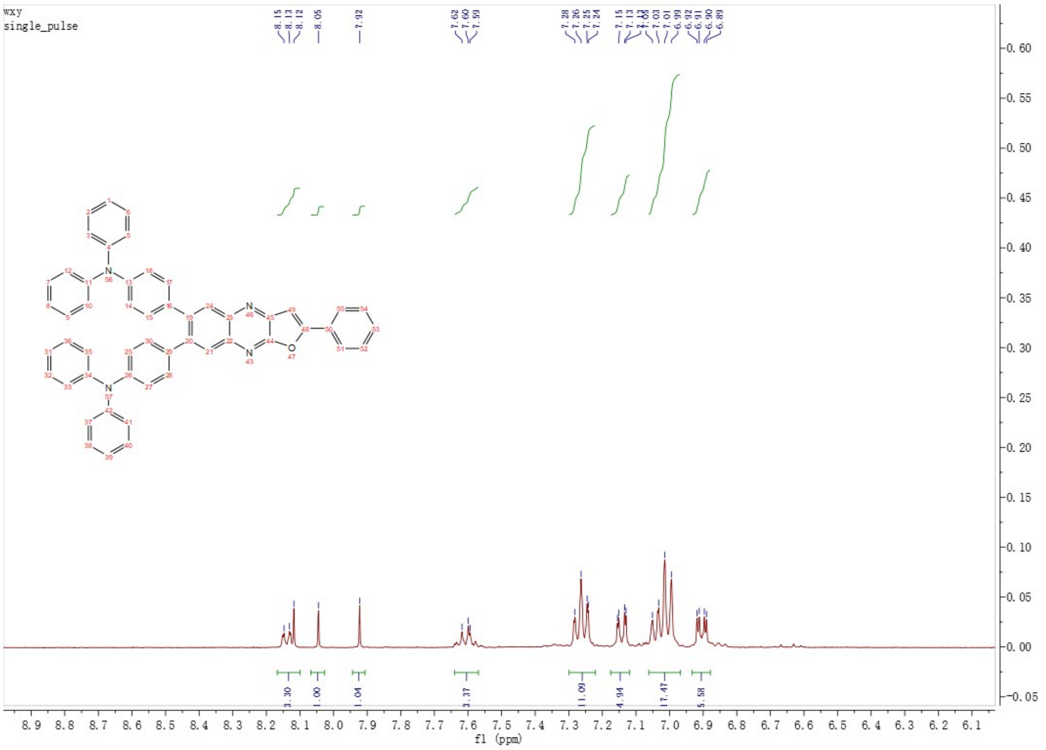

Figure S_3 ^{1}H NMR spectrum of 67dTPA-FQ

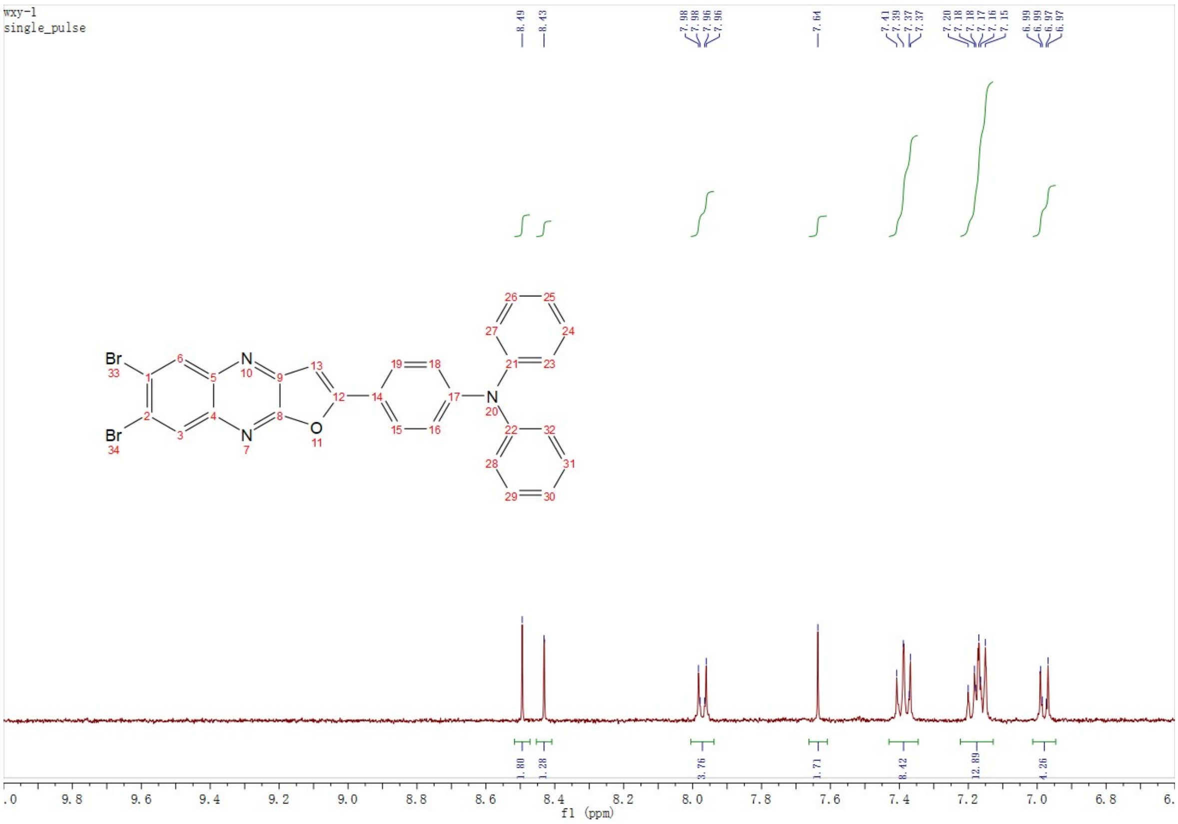

Figure S_4 ^{1}H NMR spectrum of **1b**

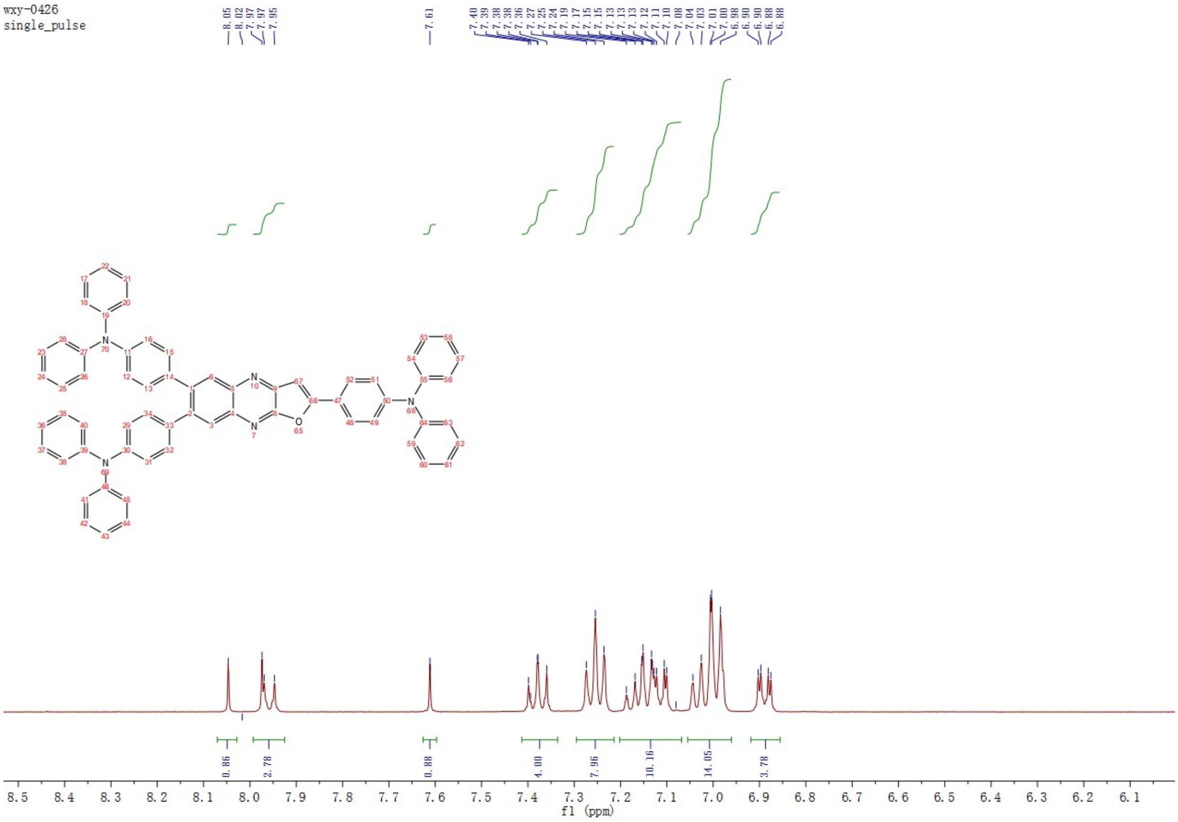

Figure S_5 ^{1}H NMR spectrum of 267tTPA-FQ

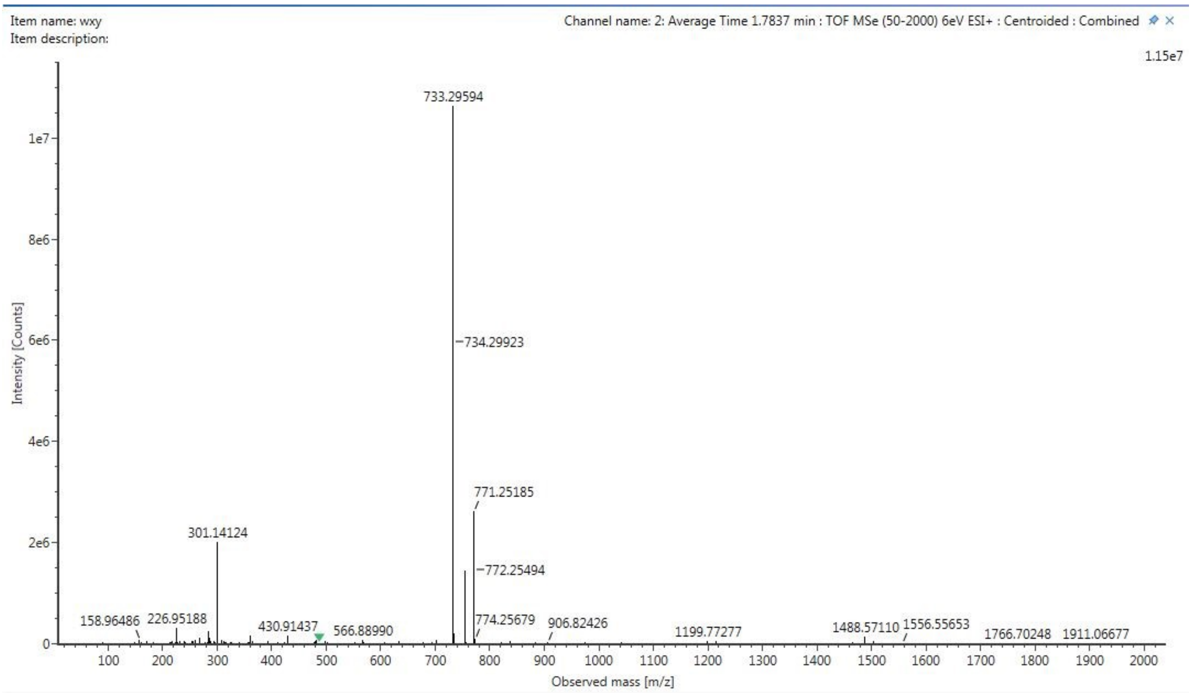

Figure S_6 HRMS spectrum of 67dTPA-FQ

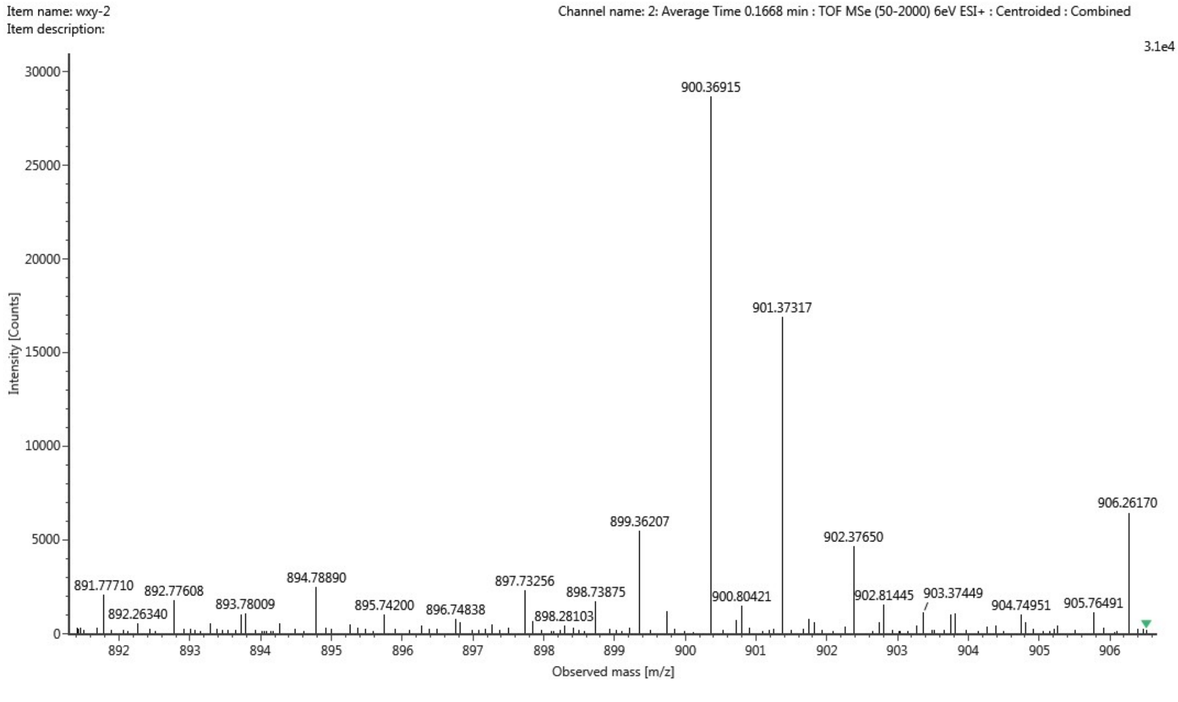

Figure S_7 HRMS spectrum of 267tTPA-FQ

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