**Electronic Supplementary Material (ESI) for New Journal of Chemistry.**

# Fluorinated near-infrared fluorescent probes for specific detection of $Hg^{2+}$ in aqueous medium and mitochondria of living cells

Lei Long, Xu Tan, Shenglin Luo *and Chunmeng Shi

Institute of Combined Injury, State Key Laboratory of Trauma, Burns and Combined Injury, Chongqing Engineering Research Center for Nanomedicine, Department of Preventive Medicine, Third Military Medical University, Chongqing, 400038, China.

*Corresponding Author: Shenglin Luo (E-mail: slinluo@126.com)

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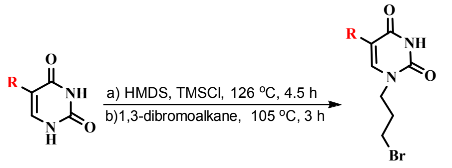
## 1. Synthetic methods and structural characterization

Compounds 3 and IR-D4F were prepared by our previously reported procedures.[1,2]

### 1.1 Synthesis of 1a and 1b



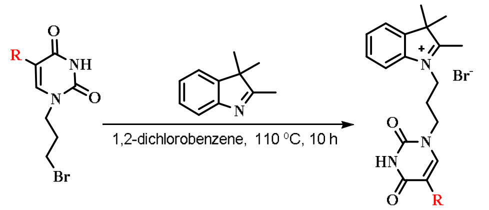
**1a**, R = H; **1b**, R = F

Uracil or 5-Fluorouracil (12.0 mmol) was heated to dissolve in 1,1,1,3,3,3-hexamethyldisilazane (48.0 mmol) under argon. Then chlorotrimethylsilane (250 uL) was added and the solution was stirred for 4.5 h at 126°C. The reaction mixture was cooled and the excess solvent was removed under reduced pressure to yield yellow green oil. This oil was immediately used to react with dried 1, 3-dibromoalkane (10 mL) under 105 °C for 3h. The reaction mixture was cooled to the room temperature, and the dichloromethane was extracted as the organic phase from water, and the organic phase was dried with anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to obtain the crude product. The crude product was then recrystallized from the ethyl acetate/petroleum ether system to give a pale yellow solid.

**1a** (82%): $^1$H NMR (400 MHz, $CDCl_3$ ): δ 11.352(s,1H), 7.47-7.45(d, J=8Hz, 1H), 7.27-7.26(d, J=8Hz, 1H), 7.04-6.98(m, 2H), 6.88-6.85(m, 1H), 5.77-5.75(d, J=8Hz, 1H), 1.63-1.58(m, 2H), 1.42(s, 3H), 1.32-1.28(t, J=6Hz, 1H), 1.24(s,6H);

**1b** (76%): $^1$H NMR (400 MHz, CDC13): δ 8.41(s, 1H), 4.09 (t, J=2.4Hz, 4H), 3.39(t, J=2.4Hz, 2H), 2.86 (m, 2H).

### 1.2 Synthesis of 2a and 2b

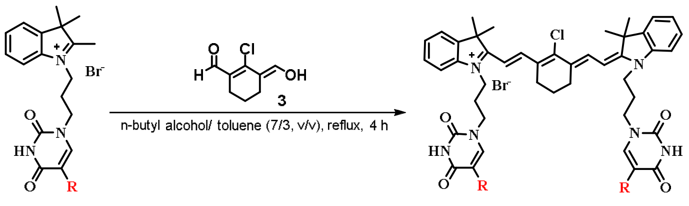


**1a**, R = H; **1b**, R = F

**2a**, R = H; **2b**, R = F

A reaction mixture containing 2,3,3-trimethyl-3H indole (3.67mmol ), 1a or 1b (1.83mmol) was reacted in 1,2-dichlorobenzene at 110°C for 10 h. After the reaction, the reaction mixture was washed with acetone and recrystallized in isopropyl alcohol to obtain the quaternary ammonium salt of indolium. No further purification was required.

### 1.3 Synthesis of IR-DT and IR-DFT



IR-DT, R =H; IR-DFT, R = F

A reaction mixture containing 2a or 2b (0.71mmol) and bisaldehyde 3 (0.31 mmol) in a refluxed solution of toluene and n-butyl alcohol (10mL, 7:3) was allowed to react for 12 h where upon the color of the solution changed from red to green. After the reaction, the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography to achieve the target compounds.

**IR-DT** (38%): $^{1}$H NMR (400 MHz, DMSO-d) δ 11.27(s, 2H), 8.24-8.22(d, J=12Hz, 2H), 7.69-7.68(d, J=6Hz, 2H), 7.62-7.61(d, J=6Hz, 2H), 7.46-7.40(m, 4H), 7.28-7.26(t, J=6Hz, 2H), 6.23-6.21(d, J=12Hz, 2H), 5.57-5.56(s, J-6Hz, 2H), 4.23(m, 4H), 3.82-3.80(t, J=6Hz, 4H), 2.64(m, 4H), 2.03(m, 2H), 1.84-1.82(m, 2H), 1.65(s, 12H). $^{3}$C NMR(400 MHz, DMSO-d6 ): δ 172.611, 164.144, 151.451, 148.630, 145.902, 143.509, 142.374, 141.508, 129.055, 126.807, 125.684, 123.023, 111.820, 101.971, 101.636, 49.495, 45.476, 41.673, 27.861, 27.076, 26.308, and 20.747; MS (ESI+): 759.4(M-Br) calcd exact Mass: 759.3

**IR-DFT** (30%): $^{1}$H NMR (400 MHz, DMSO-d ): δ 8.70-8.66(d, J=16Hz, 2H), 8.58-8.56(d, J=8Hz, 2H), 8.07-8.05(d, J=8Hz,2H), 7.92-7.84(m, 4H), 7.74-7.70(t, J=8Hz, 2H), 6.69-6.66(d, J=12Hz, 2H), 4.70-4.66(m, 4H), 4.24-4.21(t, J=6Hz, 4H), 3.82(s, 2H), 3.09(s, 6H), 2.10(s, 12H). $^{13}$C NMR(400 MHz, DMSO-d6 ): δ 174.223, 172.180, 171.925, 147.948, 147.930, 142.004, 141.021, 128.598, 126.156, 125.134, 122.478, 111.489, 101.573, 48.945, 43.629, 33.402, 27.434, 26.680, 25.788, 25.597, 24.123, 20.971, and 20.339. $^{19}$F NMR(400 MHz, DMSO-d6 ):δ -168.73 ppm. HRMS: 795.32 (M-Br) calcd exact Mass: 795.3.

## 2. Supplementary Figures

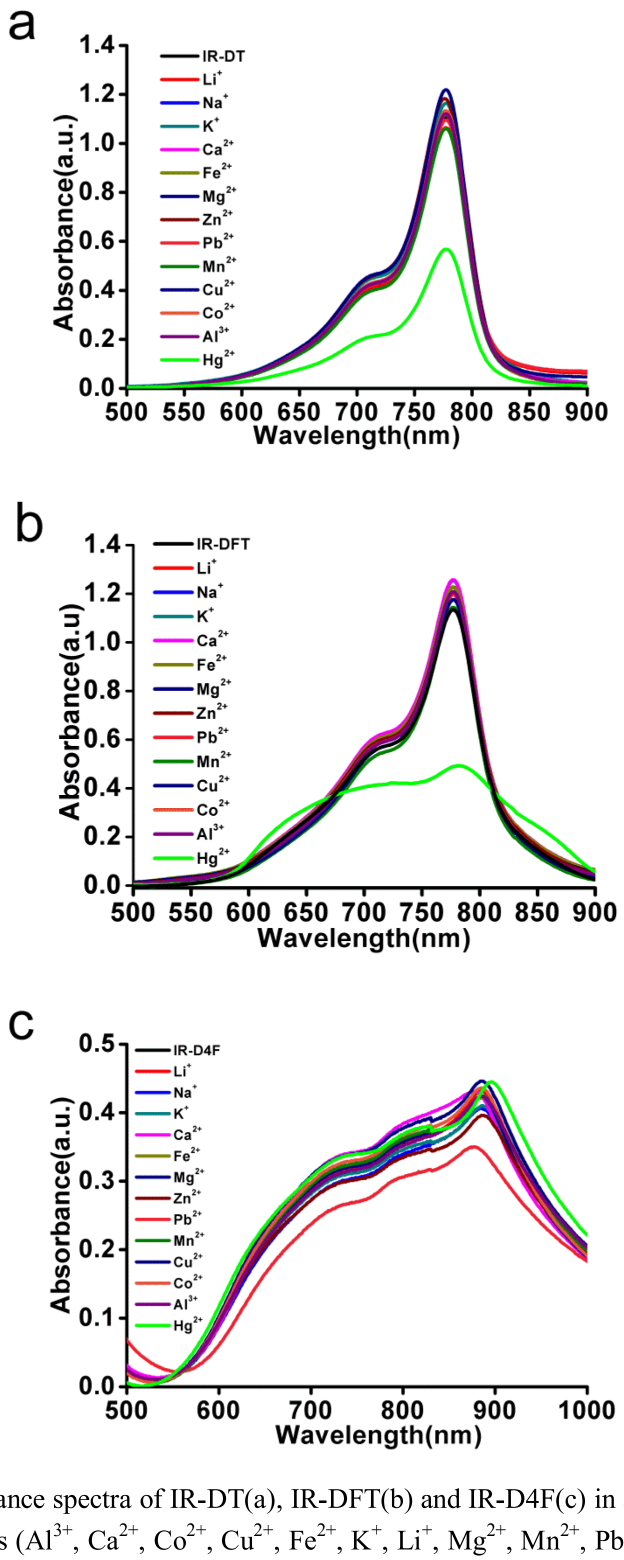


Figure S1. Absorbance spectra of IR-DT(a), IR-DFT(b) and IR-D4F(c) in absence and presence of different metal ions ($Al^{3+}$, $Ca^{2+}$, $Co^{2+}$, $Cu^{2+}$, $Fe^{2+}$, $K^{+}$, $Li^{+}$, $Mg^{2+}$, $Mn^{2+}$, $Pb^{2+}$, $Zn^{2+}$, $Na^{+}$, and $Hg^{2+}$) in buffer (10 μM, pH 6.55).

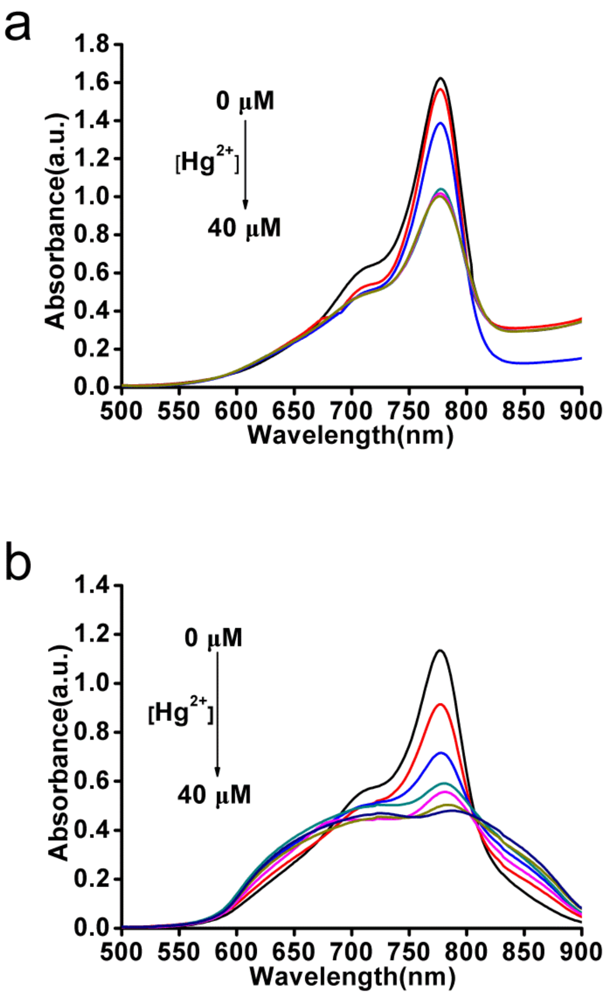
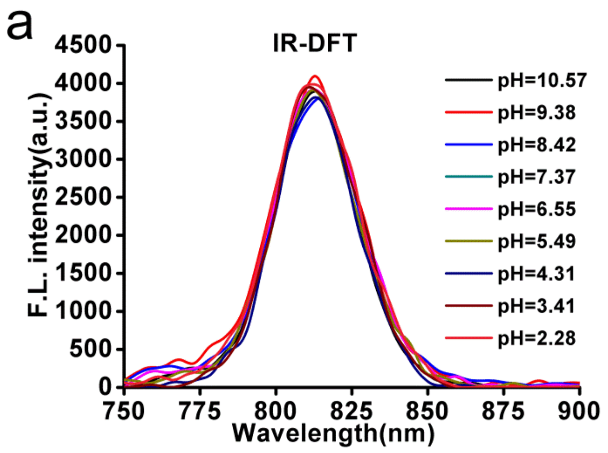


Figure S2. Absorbance spectra of IR-DT(a) and IR-DFT(b) in in various concentrations of $Hg^{2+}$.



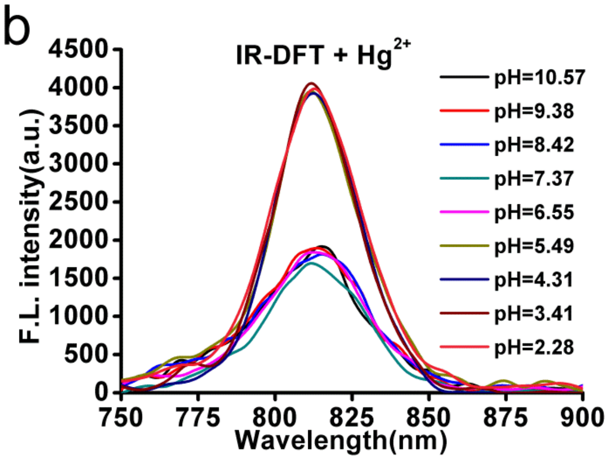


Figure S3. Fluorescencespectra of IR-DFT not containing(a) or containing(b) $Hg^{2+}$ in different pH of buffer solutions.

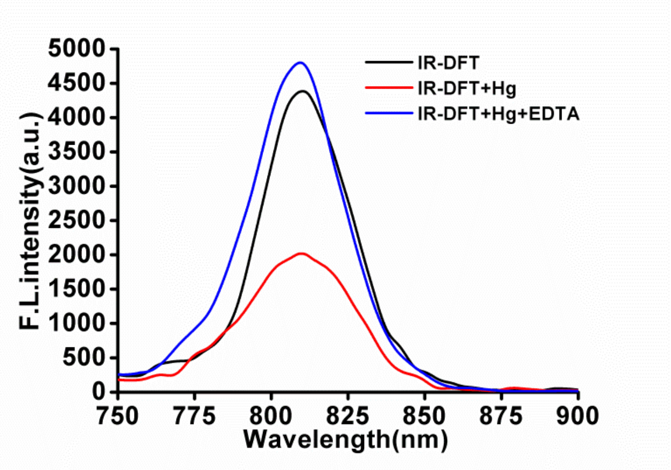


Figure S4. Fluorescence changes of IR-DFT before and after adding $Hg^{2+}$ and excess EDTA.

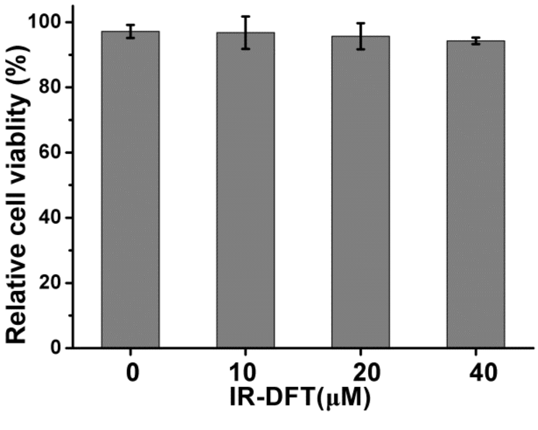
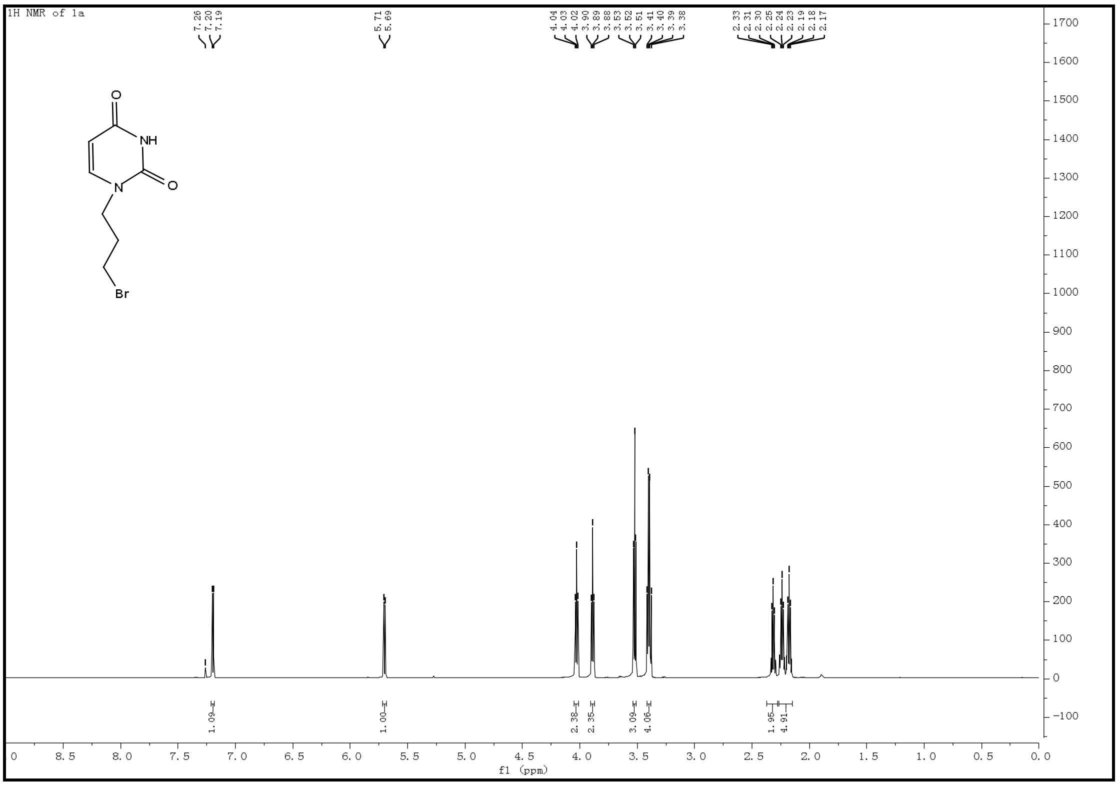
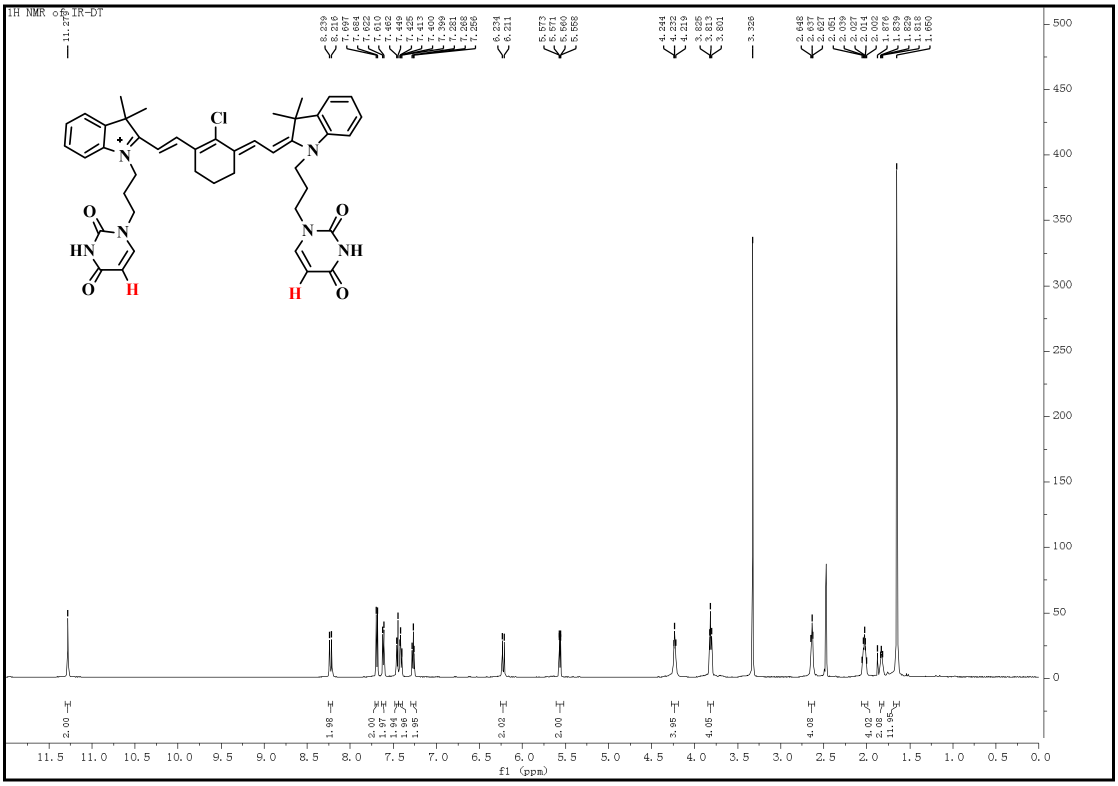


Figure S5. Relative cell viability of living MCF-7 cells was tested by CCK-8 array after 24 h incubation of IR-DFT(0, 10, 20, 40 μM).

## 3. Appendixes: $^1$H-NMR, $^{13}$C-NMR, $^{19}$F-NMR and HRMS

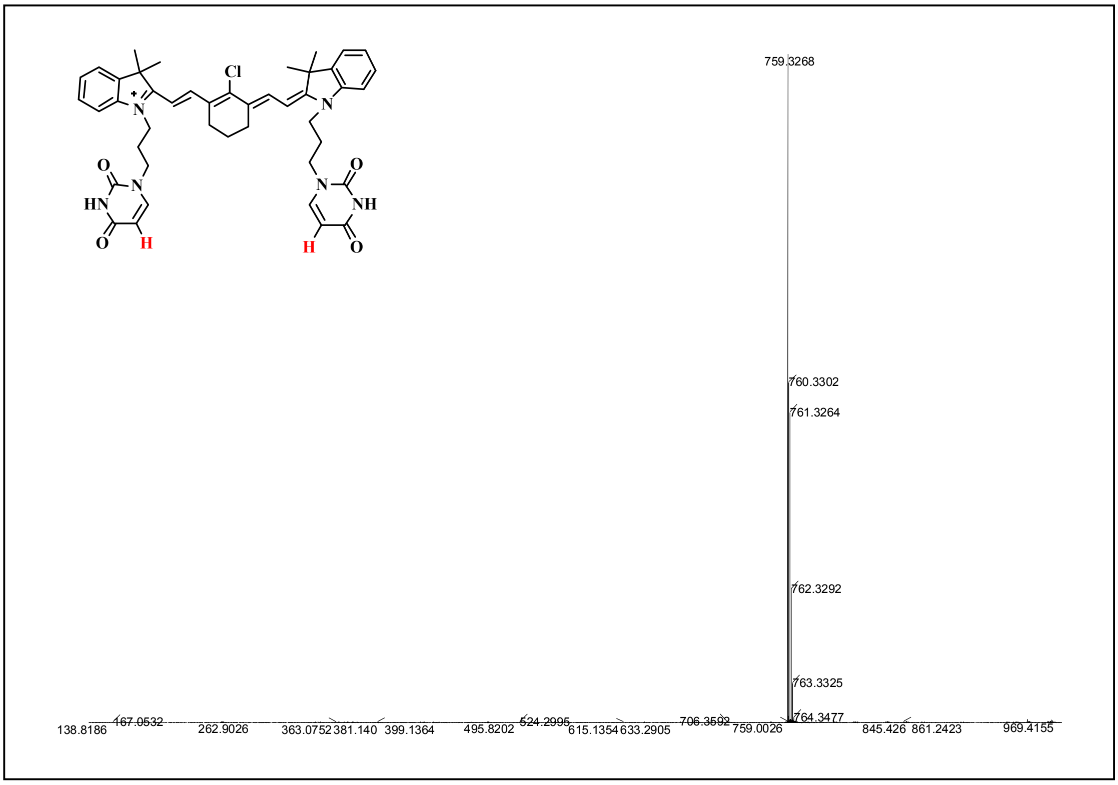


$^1$H NMR of 1a

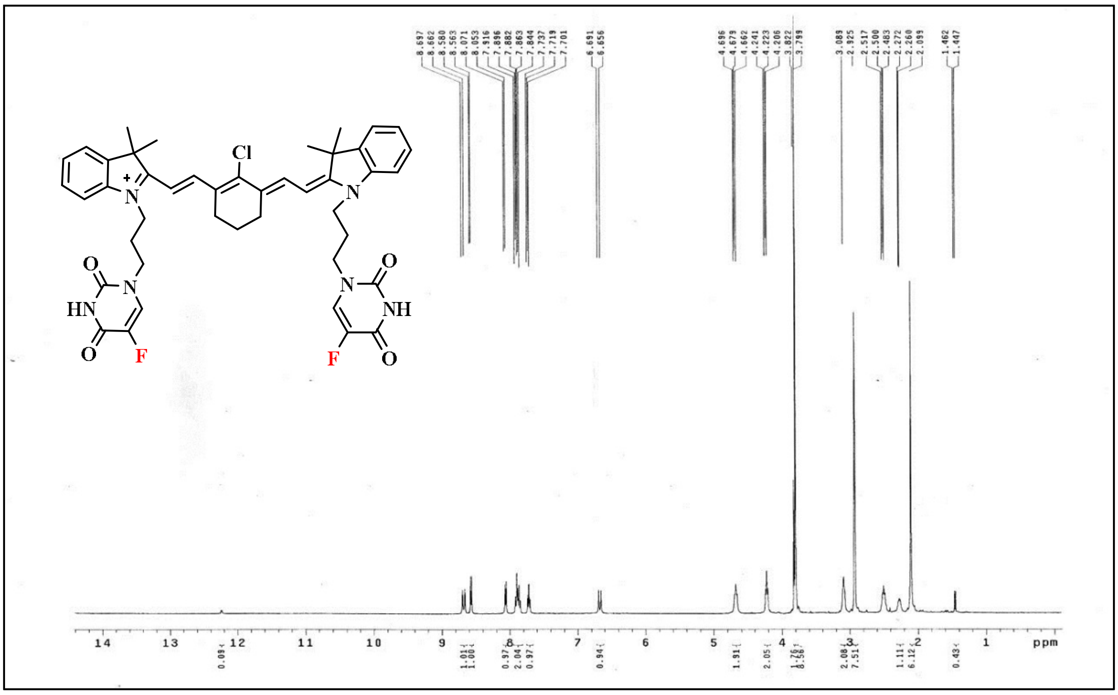


$^1$H NMR of IR-DT

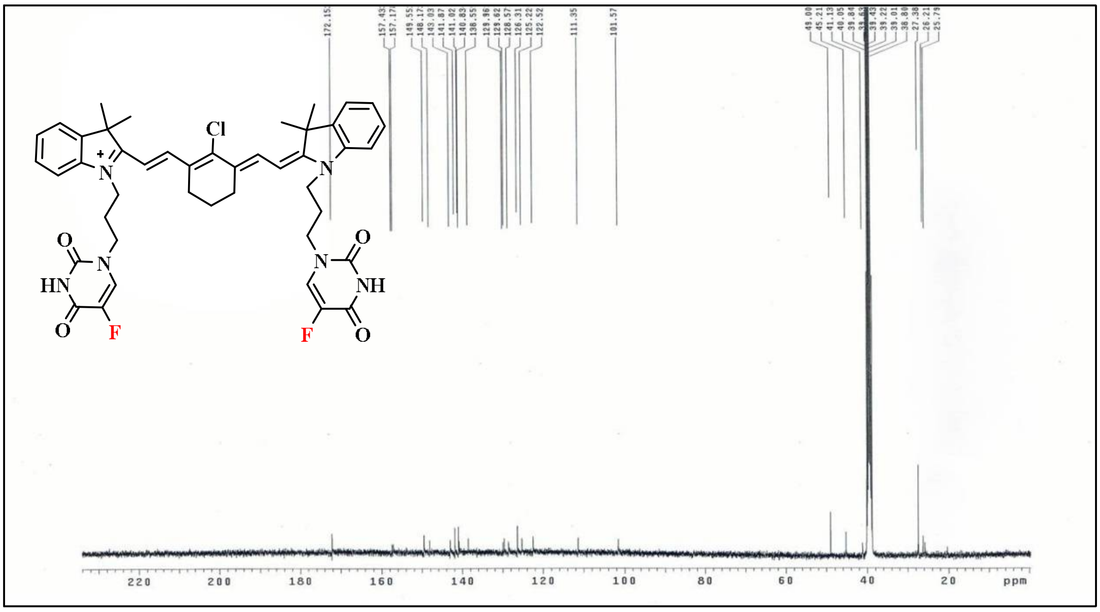
$^{13}$C NMR of IR-DT



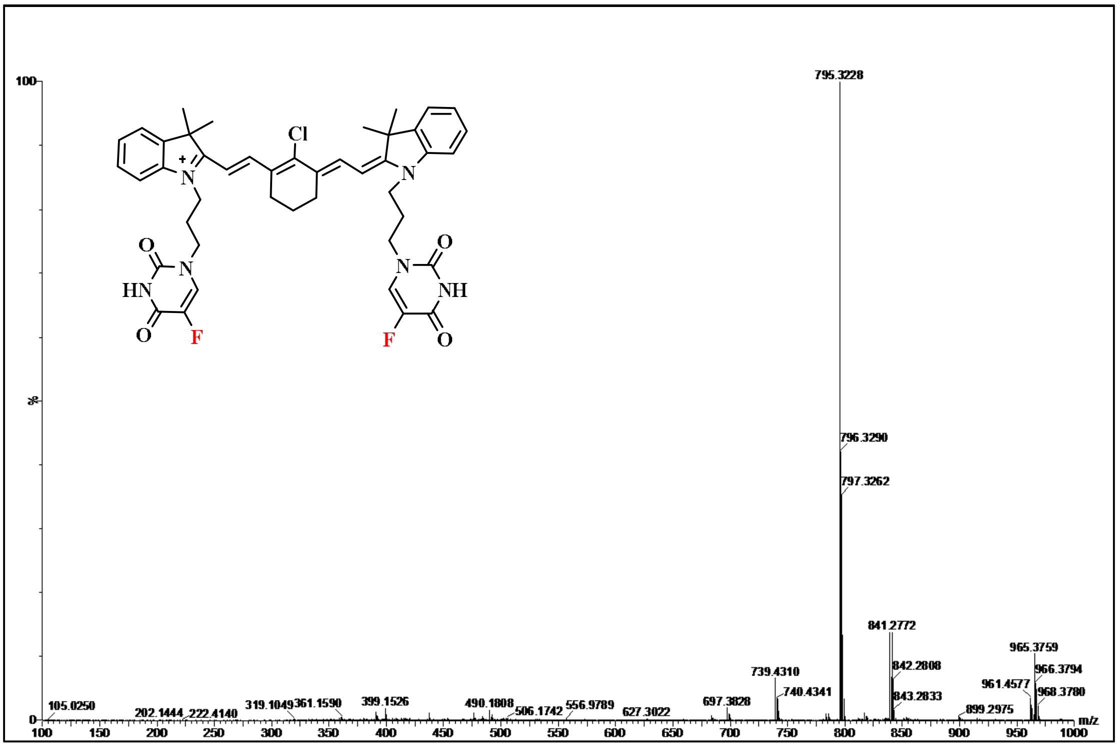
HRMS of IR-DT



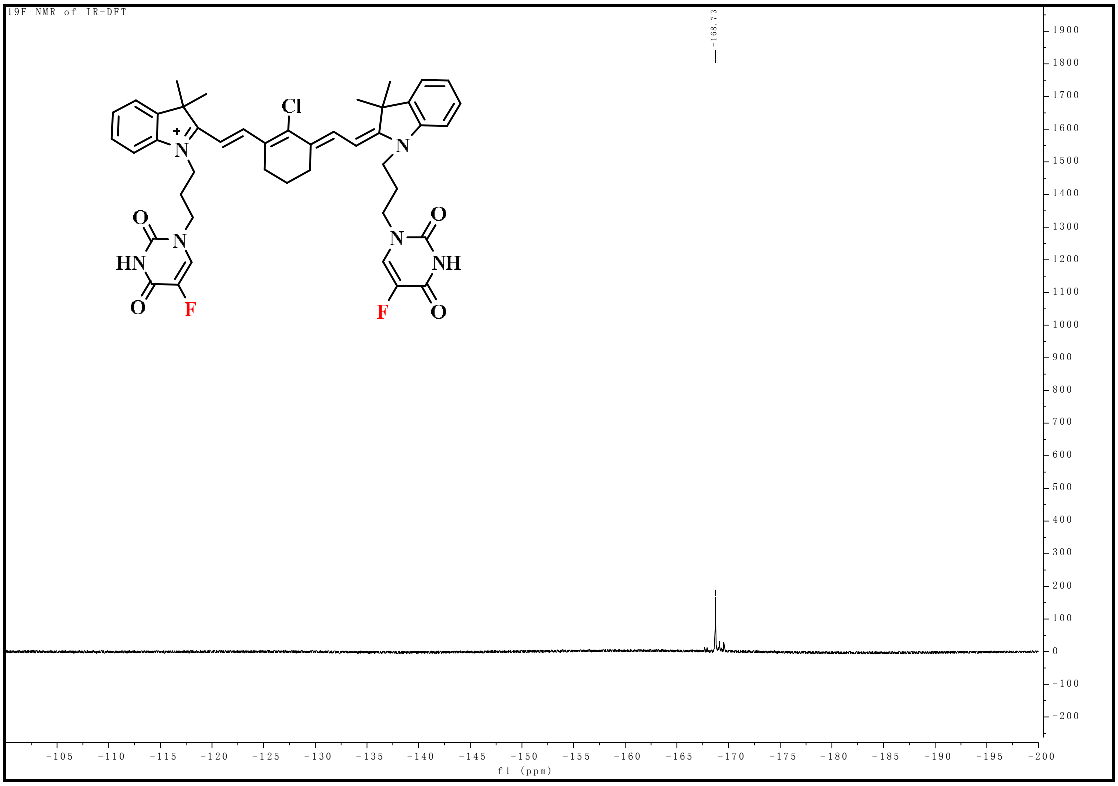
$^1$H NMR of IR-DFT



$^{13}$C NMR of IR-DFT



HRMS of IR-DFT



$^{19}$F NMR of IR-DFT

## 4. References

1. S. Luo, X. Tan, S. Fang, Y. Wang, T. Liu, X. Wang, Y. Yuan, H. Sun, Q. Qi, and C. Shi, *Adv. Funct. Mater.,* 2016, **26**, 2826-2835.

2. (a)S. Luo, X. Tan, Q. Qi, Q. Guo, X. Ran, L. Zhang, E. Zhang, Y. Liang, L. Weng, H. Zheng, T. Cheng, Y. Su, and C. Shi, *Biomaterials,* **2013**, 34, 2244-2251.; (b)X. Tan, S. Luo, D. Wang, Y Su,. T. Cheng, and C. Shi, *Biomaterials,* **2012**, 33, 2230-2239.