

Supplementary Information

Selective Recognition of DNA Defects By Cyclometalated Ir(III) complexes

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Materials and Methods

Synthesis and characterization of [Ir(phpy)₂(L)]PF₆.

A mixture of [(phpy)₂Ir(μ-Cl)]₂ (0.12 g, 0.1 mmol) and Imiphen(L1) or Furphen(L2) or Faqphen(L3) (0.07 g, 0.25 mmol) in MeOH/CH₂Cl₂ (50 mL, 1:1) was heated to reflux with stirring under N₂ for 12h. The reaction mixture was then cooled to room temperature, followed by addition of NH₄PF₆ (0.04 g, 2.5 mmol). The solution was stirred for 30 min. After removal of solvent under reduced pressure, the crude product was purified by column chromatography on silica gel using CH₂Cl₂/CH₃CN (5:1, V:V) as eluent to afford the desired [Ir(phpy)₂(N^N)]PF₆ as orange solid.

Complex Ir-1: ¹H NMR (400 MHz, *d*₆-DMSO), δ(ppm) : 9.4(m,1H), 9.3(s,1H), 8.32(m,1H), 7.9(m,1H), 7.7(m, 2H), 7.5 (s,1H), 7.3(s,1H), 7.1 (m,2H), 6.9(s,1H), 6.4(m,1H). ESI-MS (*m/z*) : 788.16 (M-PF₆)⁺

Complex Ir-2: ¹H NMR (400 MHz, *d*₆-DMSO), δ (ppm): 9.4(d, 1H), 9.0 (dd, 1H), 8.32 (dd, 1H), 8.2 (dd, 1H), 8.1 (d,1H), 7.9(m, 2H), 7.7(m, 2H), 7.1 (m, 1H), 6.9(m, 2H), 6.3(m,1H). ESI-MS (*m/z*) : 839.08 (M+H₂O+Cl-PF₆)

Complex Ir-3: ¹H NMR (400 MHz, *d*₆-DMSO), δ (ppm): 9.24 (dd, 1H), 8.8 (dd, 1H), 8.4 (d, 2H), 8.3 (t,2H), 8.14(dd, 1H), 7.9(m, 5H), 7.6 (d, 1H), 7.1(m, 3H), 6.3(d, 1H) ESI-MS (*m/z*) : 927.18 (M-PF₆)⁺

The molecular mass of the Ir(III) complexes was recorded with Agilent mass spectrometer equipped with an electron spray source. ¹H NMR for the ligands and its corresponding complexes was performed using Bruker 400MHz spectrometer. Electronic absorption spectra of all the three complexes in acetonitrile were carried out using Shimadzu UV-1700 model spectrophotometer. Steady state emission spectra of the complexes were

recorded on a Hitachi F-7000 spectrofluorimeter at 25°C. Steady-state luminescence spectra of the Ir(III) complexes were recorded using Hitachi F7000 spectrofluorimeter equipped with thermostat. The binding constants for the Ir(III) with different oligonucleotides were calculated using Scatchard plot.¹ The room temperature luminescence lifetimes of the Ir(III) complexes with and without oligonucleotides were measured with Time Correlated Single Photon Counting Fluorescence Spectrophotometer (TCSPC-FS) (Edinburgh model-FLS980), UK. The lifetimes of the complexes were calculated using the software provided along with the TCSPC instrument.

Fluorescence experiments:

With Oligonucleotides:

Duplex DNA were prepared by annealing the respective primer and complementary sequence in Tris buffer (10mM)/50mM slowly after heating to 90°C for five minutes followed by slow cooling to room temperature over a period of 2-3 h. The sample were incubated at 4°C for overnight before experiments. Fluorescence experiments were carried out by incubating at iridium (III) complexes (1µM) and varying the duplex concentration (0-2µM) in Tris buffer (pH-7.4). The complex were excited between 370-400nm and the emission intensity was integrated from 500-700nm.

Reference

1. C. V. Kumar and E. H. Asuncion, *J. Am. Chem.Soc.*, 1993, **115**, 8547-8553.

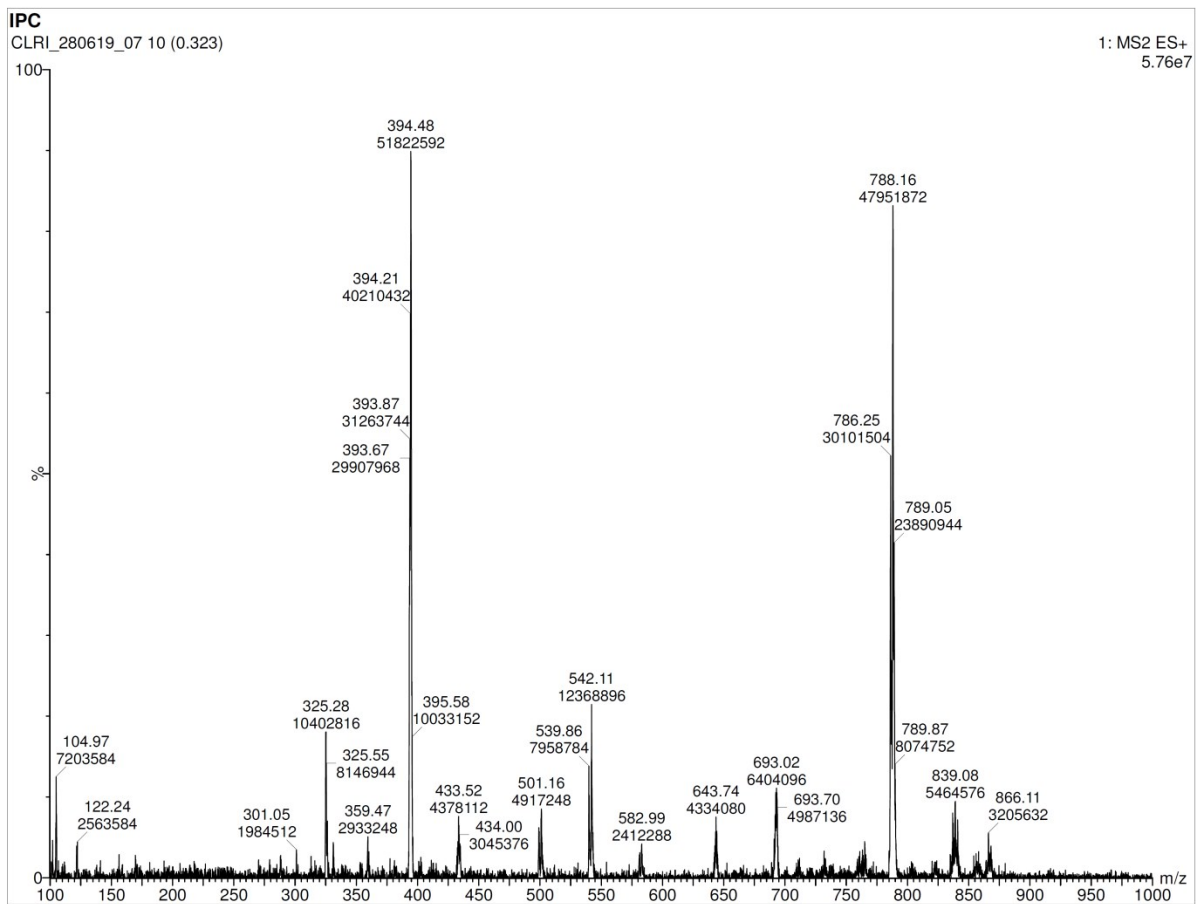


Figure S1. ESI-MS of complex Ir-1

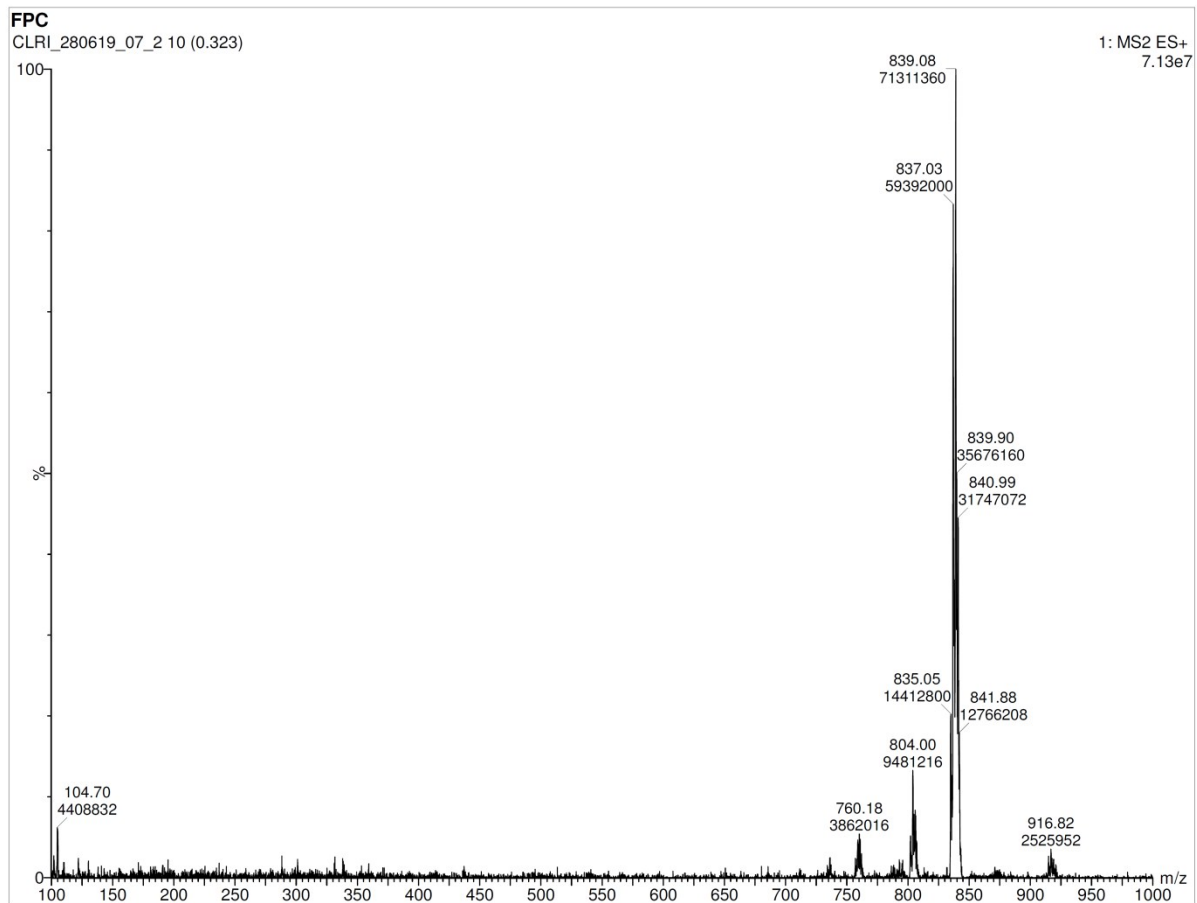


Figure S2. ESI-MS of complex Ir-2

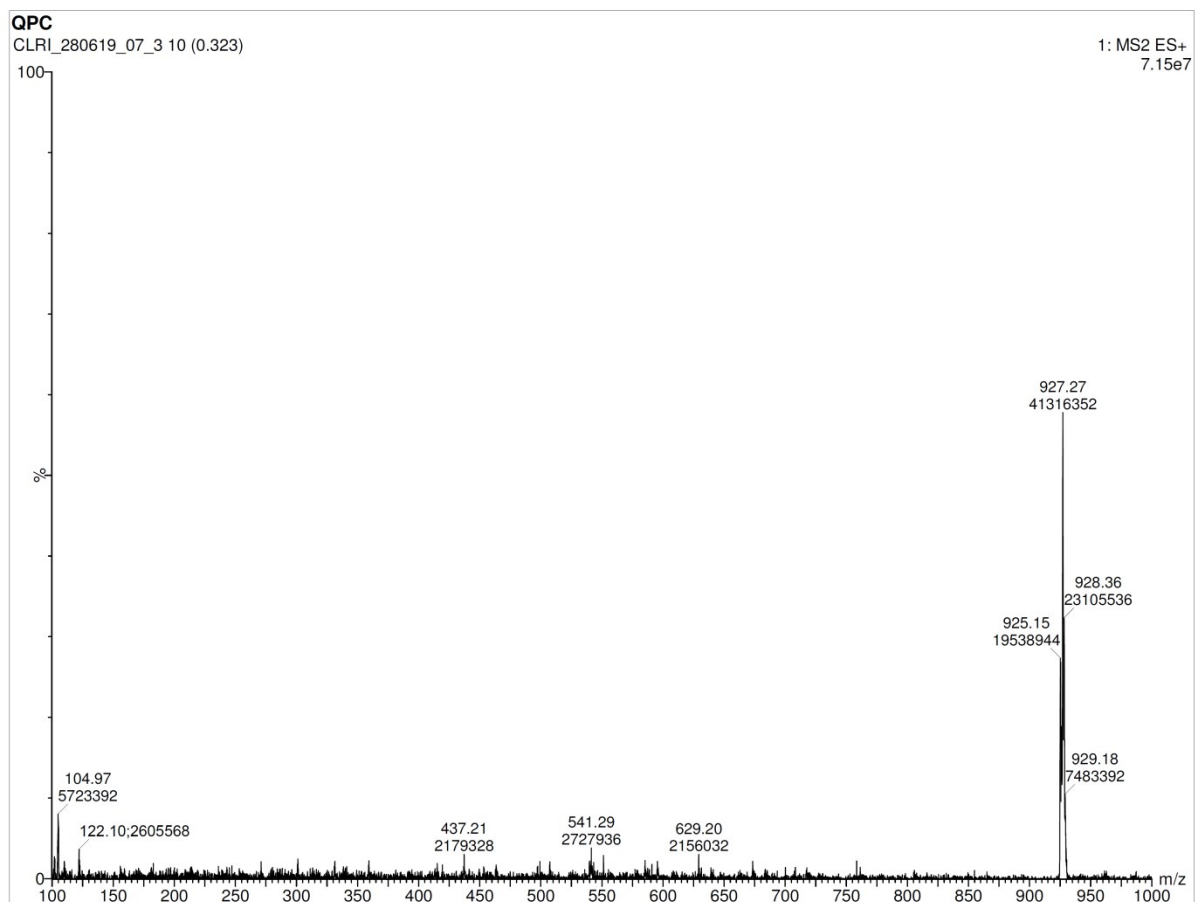


Figure S3. ESI-MS of complex Ir-3

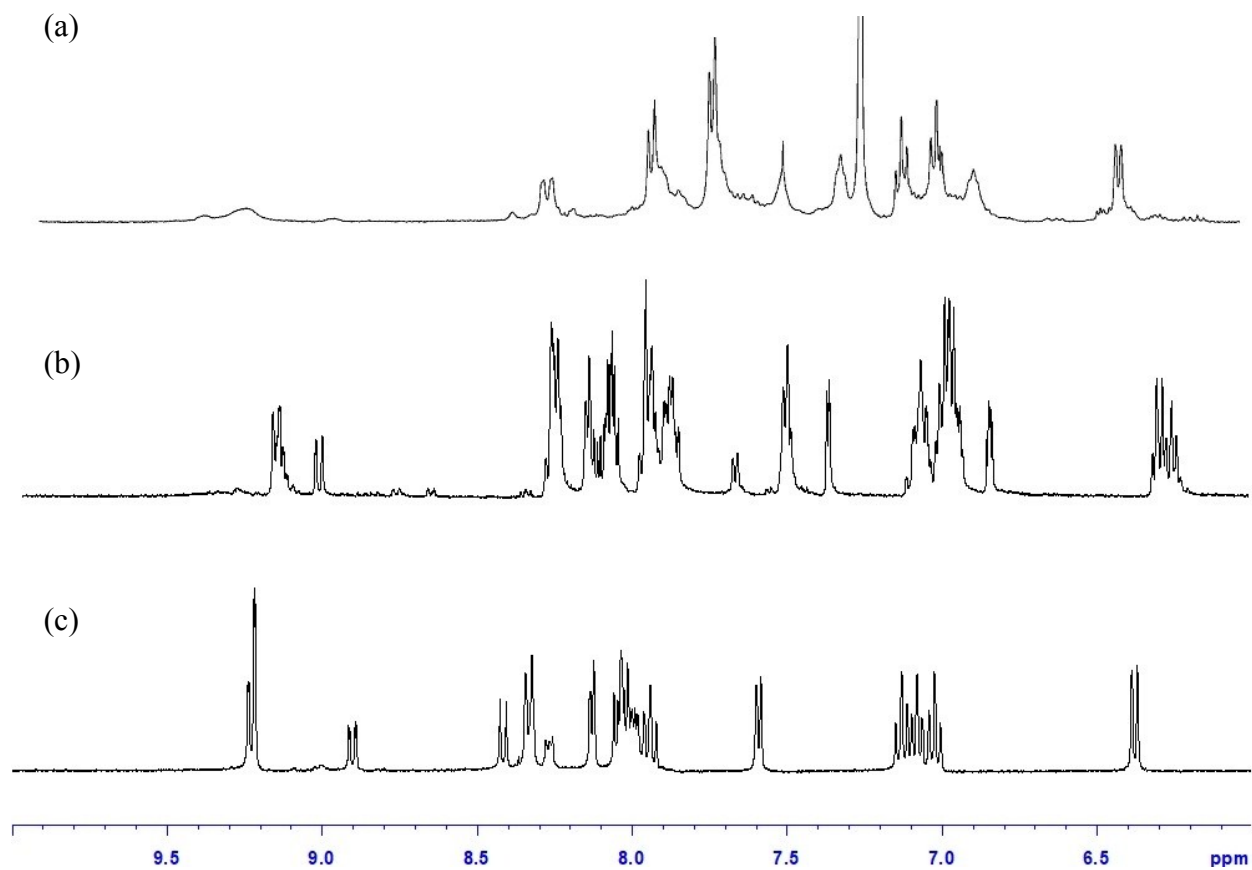


Fig. S4. ^1H NMR spectra of (a) **Ir-1** (b) **Ir-2** and (c) **Ir-3**

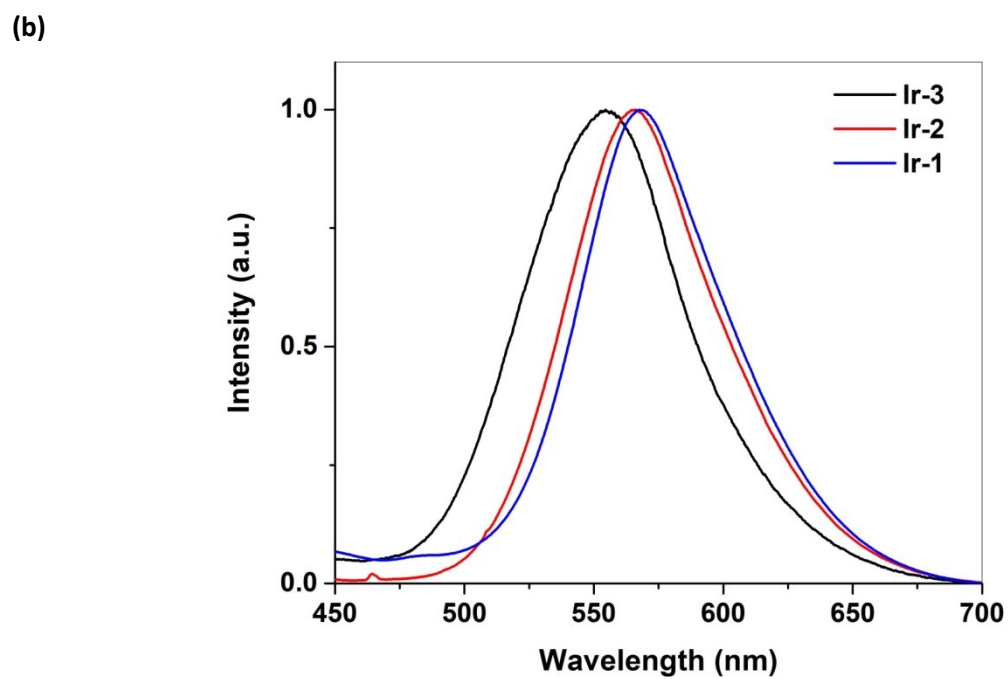
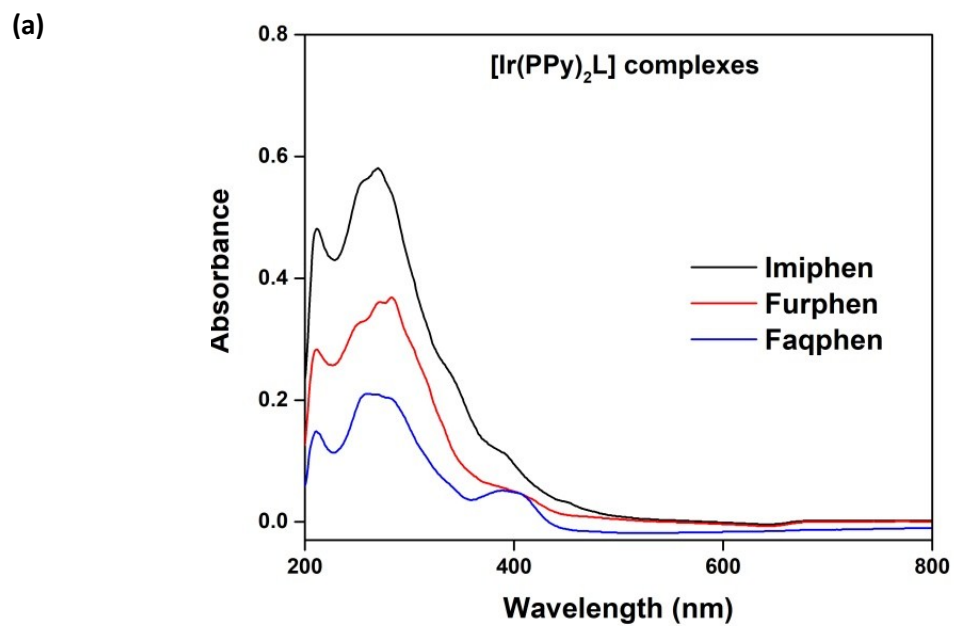
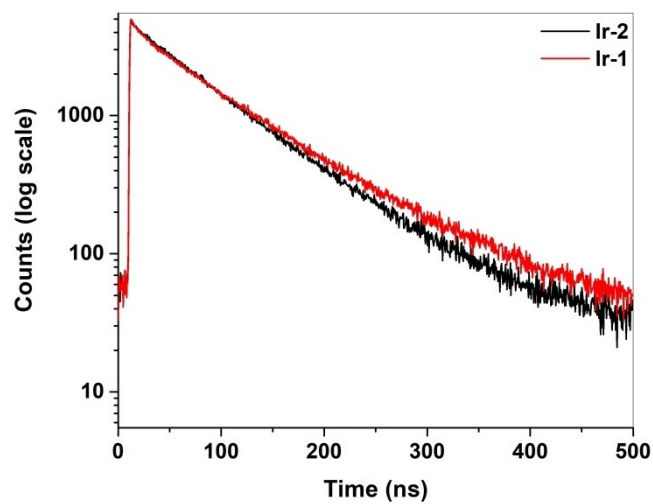


Figure S5. (a) UV-Visible in acetonitrile and (b) Emission spectra of Ir(III) complexes in dichloromethane

(a)



(b)

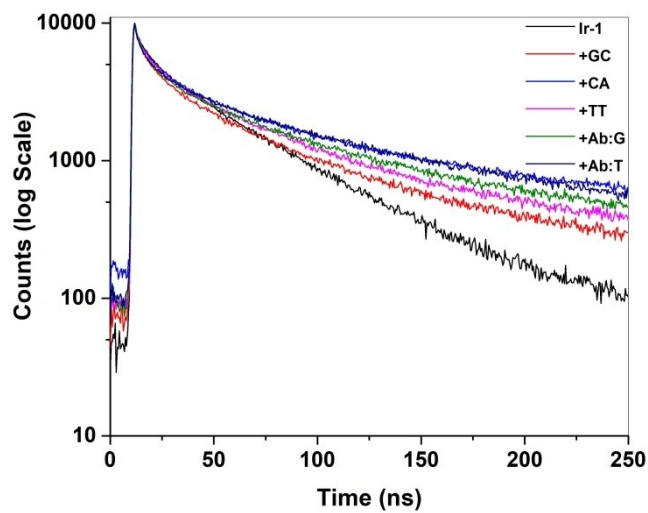


Figure S6. Excited state lifetime decay plots of Ir(III) complexes (a) complexes alone and (b) with control and DNA defects

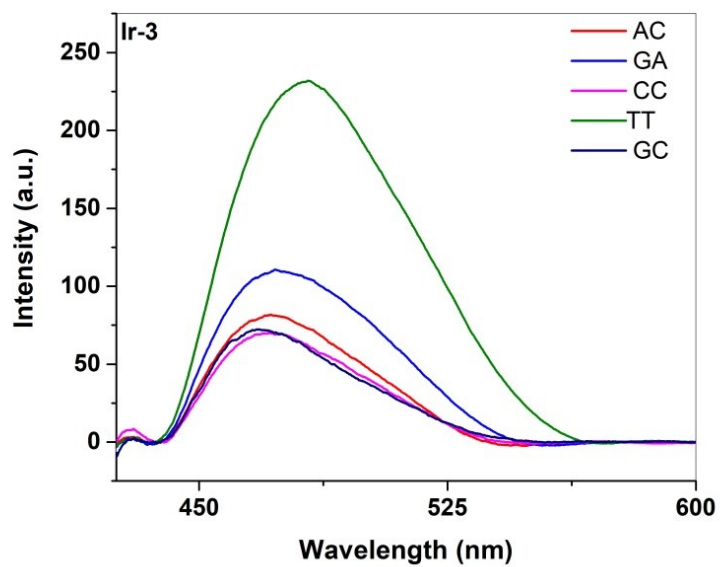


Figure S7. Emission spectra of Ir-3 with match and mismatch oligonucleotide