Electronic Supplementary Material (ESI) for Analyst

Effect of pH on the photophysical properties of two new carboxylic-substituted iridium (III) complexes

Jiena Weng,[a] *Qunbo Mei,**[a] *Weiwei Jiang,*[a] *Quli Fan,*[a] *Bihai Tong,*[b] *Qidan Ling,*[a] *and Wei Huang**[a]

[a] Key Laboratory for Organic Electronics & Information Displays (KLOEID), Institute of Advanced Materials (IAM), Nanjing University of Posts and Telecommunications (NUPT), Nanjing 210046, P. R. China.
[b] Institute of Molecular Engineering and Applied Chemistry, College of Metallurgy and Resources, Anhui University of Technology, Ma'anshan, Anhui 243002, P. R. China.

Fax: +86 25 8586 6999; Tel: +86 25 8586 6008;

E-mail: iamqbmei@njupt.edu.cn (Q. Mei), iamwhuang@njupt.edu.cn, iamdirector@fudan.edu.cn (W.Huang)

Contents:

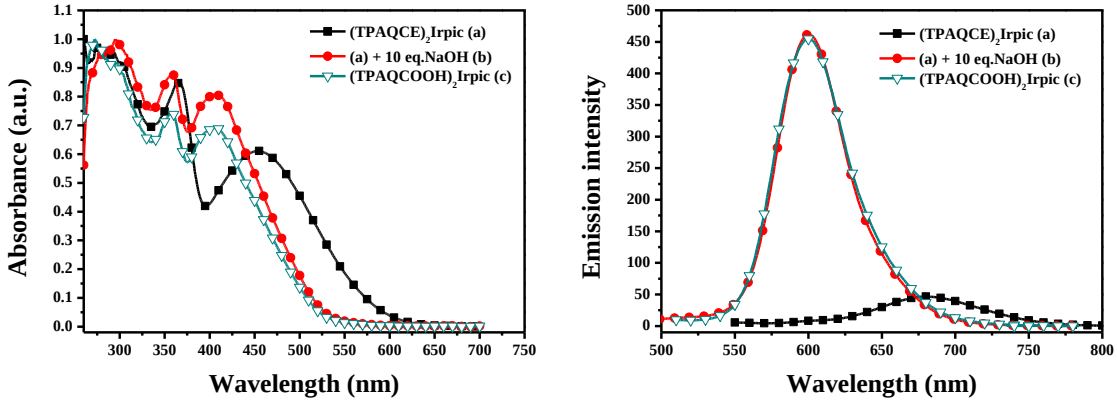

Figure S1. UV-vis absorption (normalized) and emission (excited at 400nm) spectra of: (a, ■), DMSO solution of **(TPAQCE)$_2$Irpic**; (b, ●), solution (a) in presence of 10 equiv of aqueous NaOH; (c, ▽), DMSO solution of **(TPAQCOOH)$_2$Irpic**.

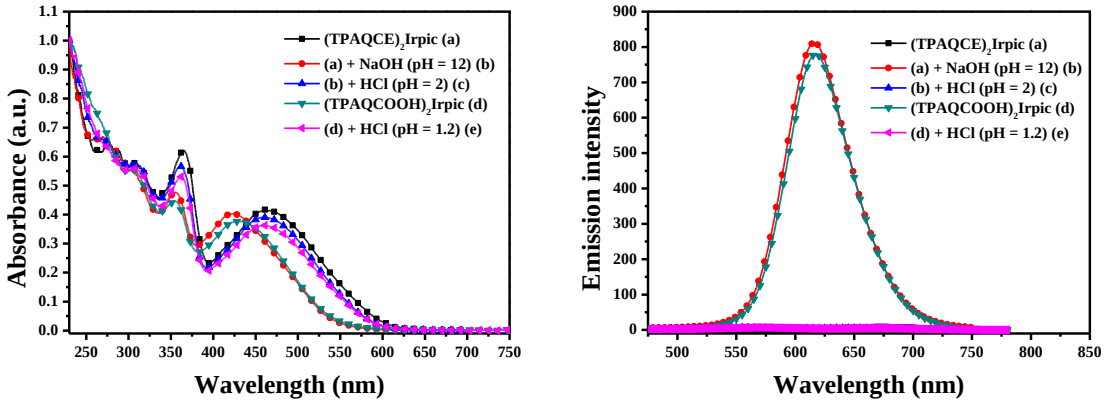

Figure S2. UV-vis absorption (normalized) and emission spectra of: (a, ■), ethanol solution of **(TPAQCE)$_2$Irpic**; (b, ●), solution (a) in presence aqueous NaOH, (c, ▲), solution (b) in presence of HCl; (d, ▽), ethanol solution of **(TPAQCOOH)$_2$Irpic**; (e, ◇), solution (d) in presence of HCl. Exicited at 400nm.

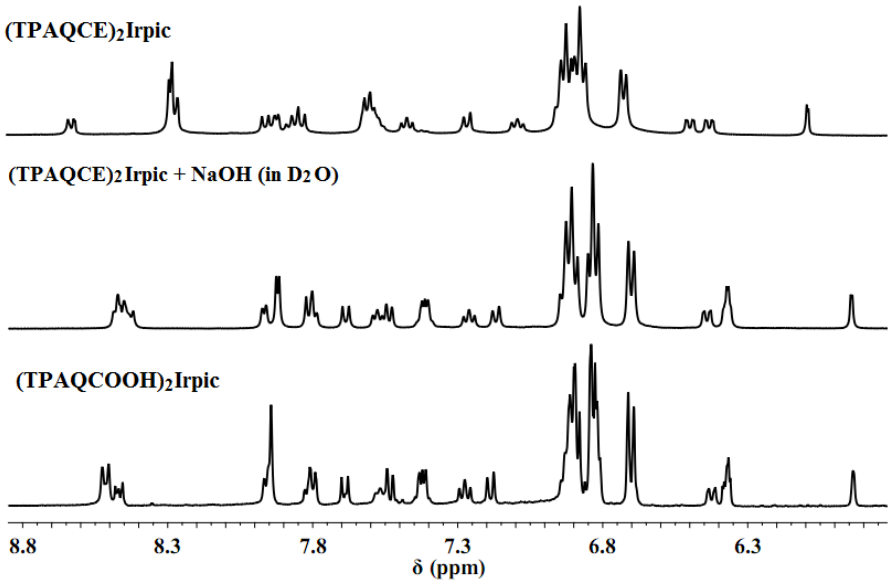

Figure S3. Aromatic part of the ^{1}H NMR in DMSO-d_6 (from top to bottom): **(TPAQCE)$_2$Irpic**; **(TPAQCE)$_2$Irpic** containing 10 equiv of NaOH; and **(TPAQCOOH)$_2$Irpic**.

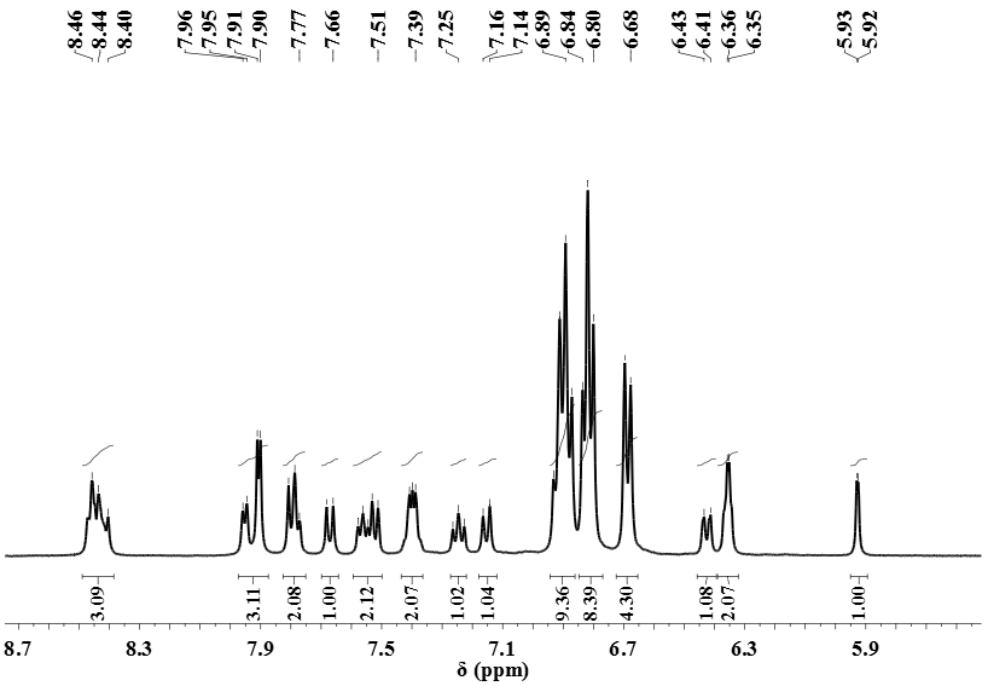

Figure S4. Aromatic part of the ^{1}H NMR in DMSO-d_6: **(TPAQCE)$_2$Irpic** containing 10 equiv of NaOH.

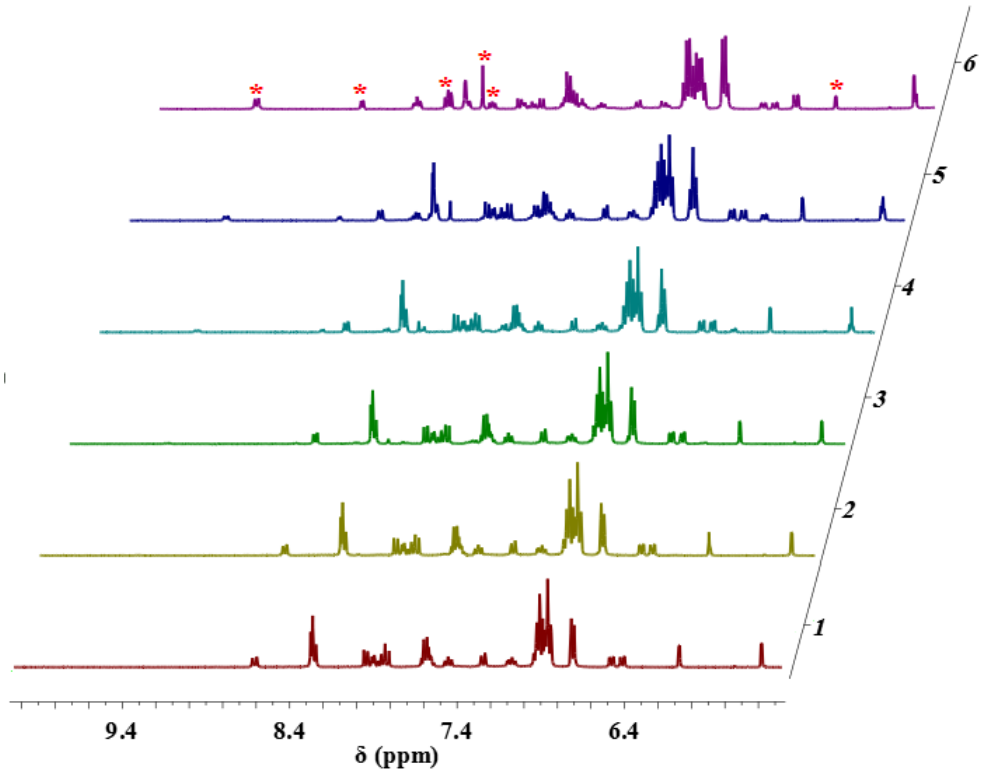

Figure S5. Aromatic part of the ^{1}H NMR in DMSO-d_6: **(TPAQCE)$_2$Irpic** (1) and gradual addition of HCl (ca. 2%-3% in methanol / DMSO-d_6) (2-6); The six new peaks are marked with *.

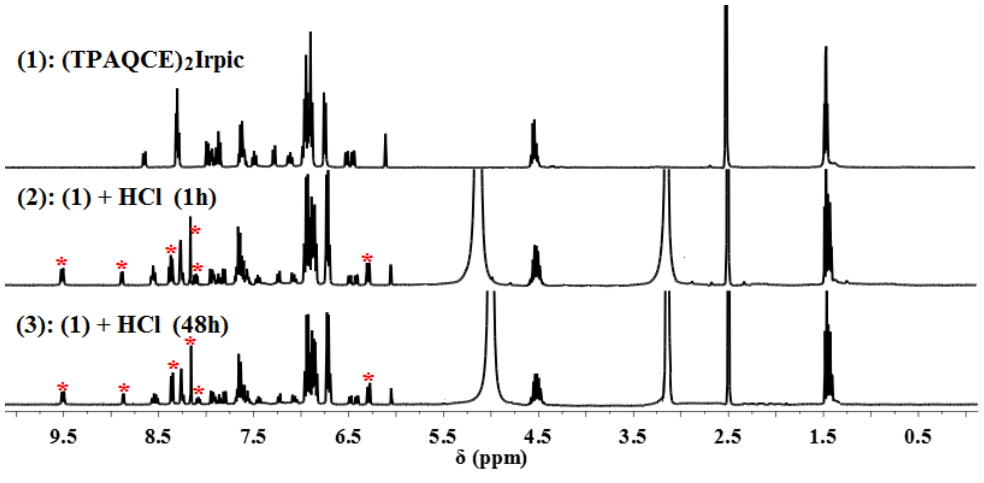

Figure S6. Aromatic part of the ^{1}H NMR in DMSO-d_6: **(TPAQCE)$_2$Irpic** (1); addition of ca. 20-30 equiv of HCl (ca. 2-3% in methanol / DMSO-d_6) to the **(TPAQCE)$_2$Irpic** solution for 2h (2); addition of ca. 20-30 equiv of HCl (ca. 2-3% in methanol / DMSO-d_6) to the **(TPAQCE)$_2$Irpic** solution for 48h (3). The six new peaks appeared by addition HCl to the solution of **(TPAQCE)$_2$Irpic** are marked with *.

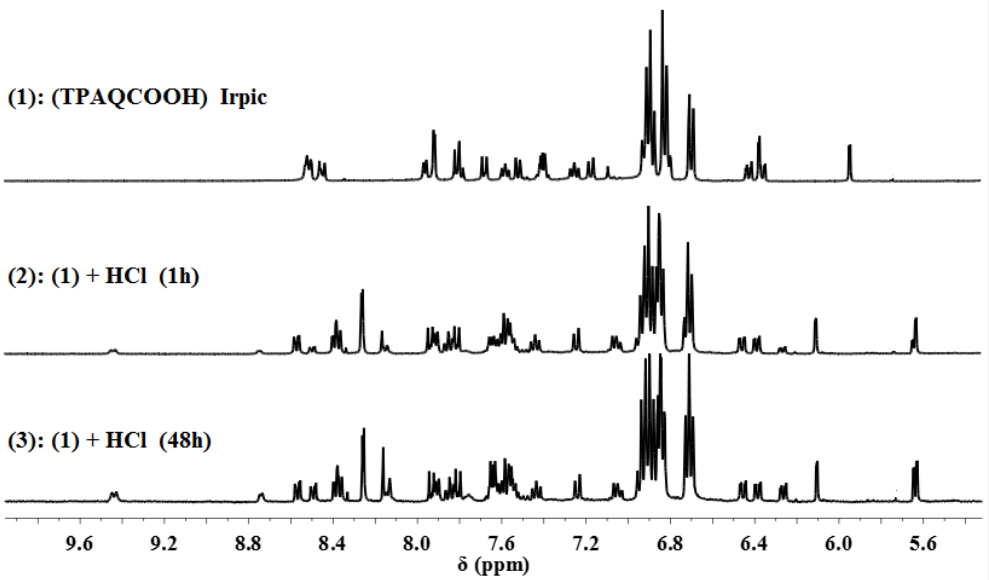

Figure S7. Aromatic part of the ^{1}H NMR in DMSO-d_6: **(TPAQCOOH)$_2$Irpic** (1); addition of ca. 20-30 equiv of HCl (ca. 2-3% in methanol / DMSO-d_6) to the **(TPAQCOOH)$_2$Irpic** solution for 2h (2); addition of ca. 20-30 equiv of HCl (ca. 2-3% in methanol / DMSO-d_6) to the **(TPAQCOOH)$_2$Irpic** solution for 48h (3).

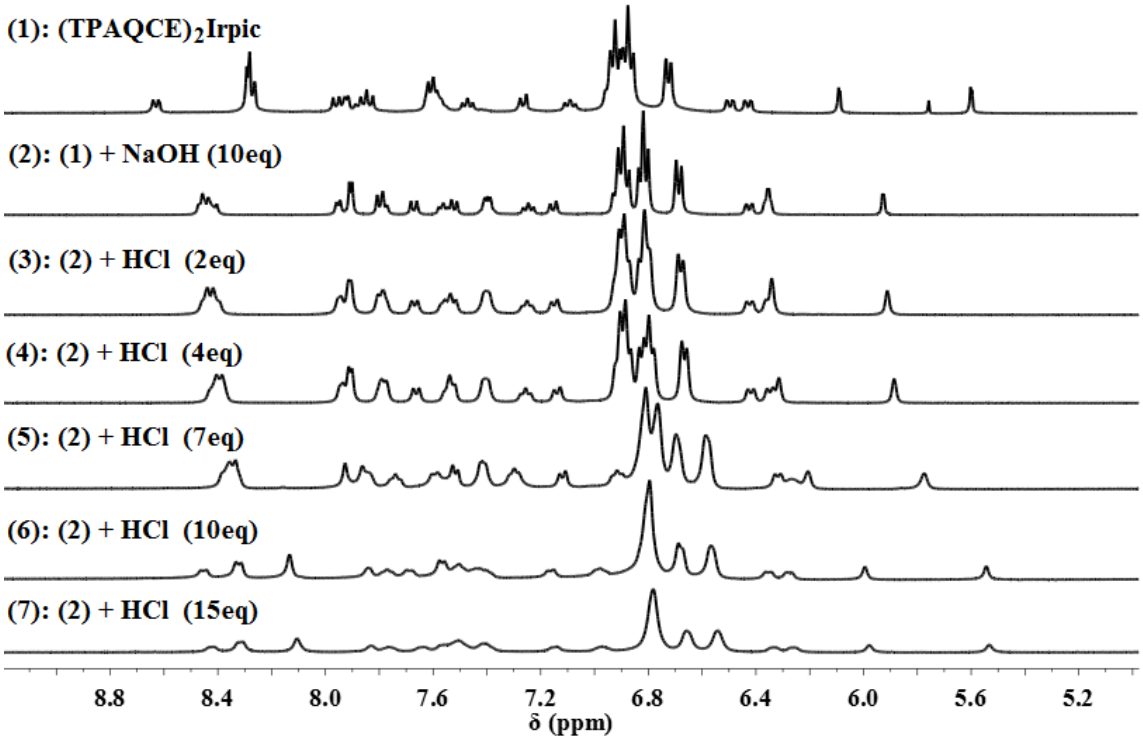

Figure S8. Aromatic part of the ^{1}H NMR in DMSO-d_6: **(TPAQCE)$_2$Irpic** (1); **(TPAQCE)$_2$Irpic** containing 10 equiv of NaOH (2); gradual addition of HCl to the solution of **(TPAQCE)$_2$Irpic** containing 10 equiv of NaOH (3-7).

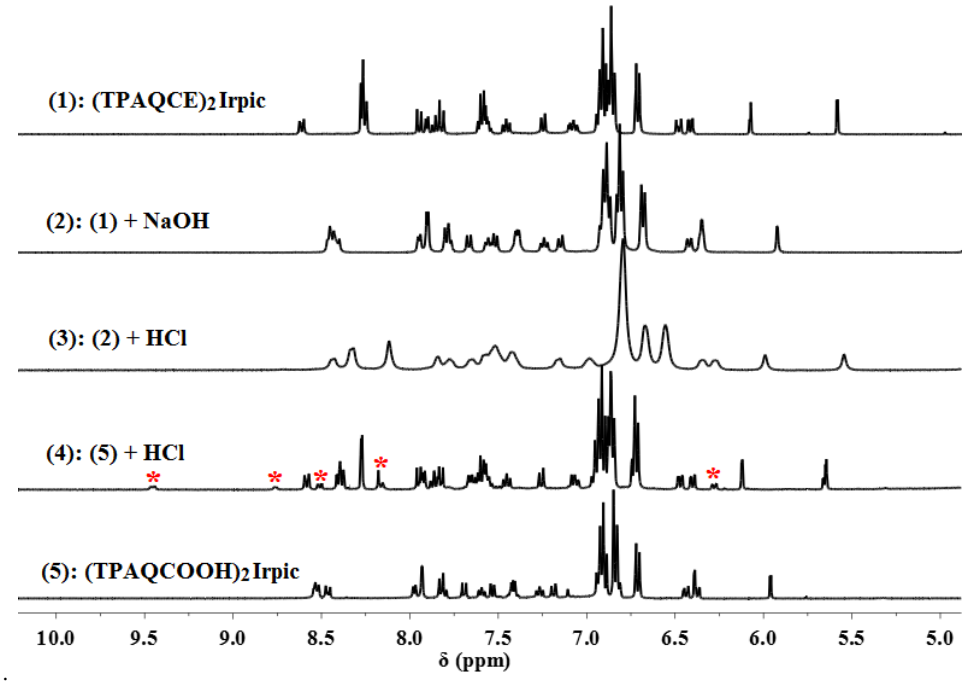

Figure S9. Aromatic part of the ^{1}H NMR in DMSO-d_6: **(TPAQCE)$_2$Irpic** (1); **(TPAQCE)$_2$Irpic** containing aqueous NaOH (10 eqiuve, in D_2O) (2); addition of HCl (ca. 2-3% in methanol / DMSO-d_6) to the **(TPAQCE)$_2$Irpic** solution containing NaOH (3); **(TPAQCOOH)$_2$Irpic** containing HCl (20-30% in methanol) (4); **(TPAQCOOH)$_2$Irpic** (5). The five new peaks appeared by addition HCl to the solution of **(TPAQCOOH)$_2$Irpic** are marked with *.

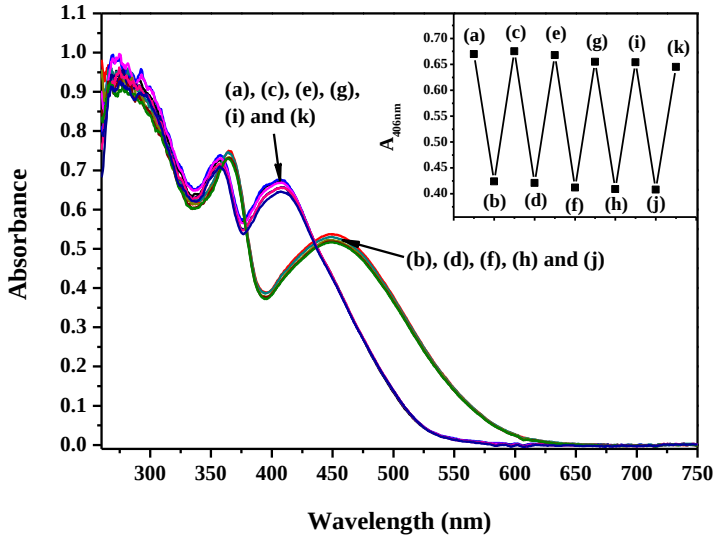

Figure S10. Change in absorption spectra of **(TPAQCOOH)$_2$Irpic** (c = 1.34×10^{-4} M) in DMSO upon the repeated addition of HCl (0.2 M) and aqueous NaOH (0.2M). (a) = **(TPAQCOOH)$_2$Irpic** before the addition of HCl; (b): (a) + HCl; (c): (b) + NaOH; (d): (c) + HCl; (e): (d) + NaOH; (f): (e) + HCl; (g): (f) + NaOH. Inset: Change in absorbance at 546nm of **(TPAQCOOH)$_2$Irpic** caused by the repeated addition of HCl (5μL) and NaOH (5μL).

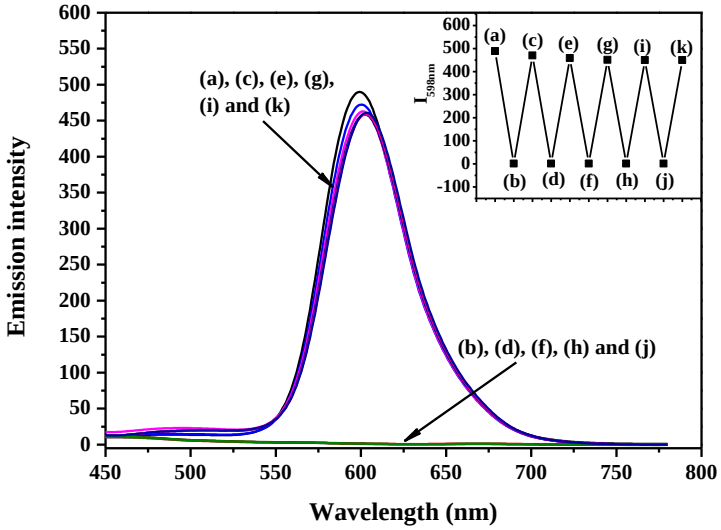

Figure S11. Change in emission spectra of **(TPAQCOOH)$_2$Irpic** (c = 1.34×10^{-4} M) in DMSO (excited at 400nm) upon the repeated addition of HCl (0.2 M) and aqueous NaOH (0.2 M). (a) = **(TPAQCOOH)$_2$Irpic** before the addition of HCl; (b): (a) + HCl; (c): (b) + NaOH; (d): (c) + HCl; (e): (d) + NaOH; (f): (e) + HCl; (g): (f) + NaOH. Inset: Change in emission intensity at 598nm of **(TPAQCOOH)$_2$Irpic** caused by the repeated addition of HCl (5μL) and NaOH (5μL).

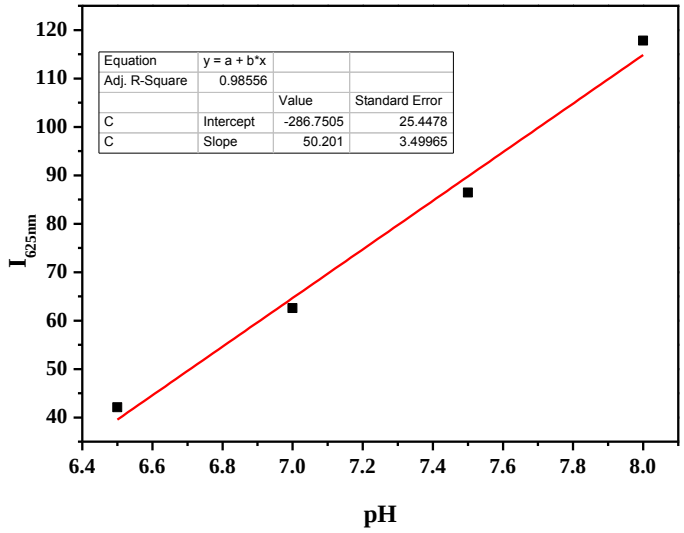

Figure S13. A plot of emission intensity of **(TPAQCOOH)$_2$Irpic** at I_{625nm} *vs* pH (6.50 – 8.00) in aqueous buffer solutions. The red solid curve is fitting line of experimental data with relative coefficient R = 0.985.

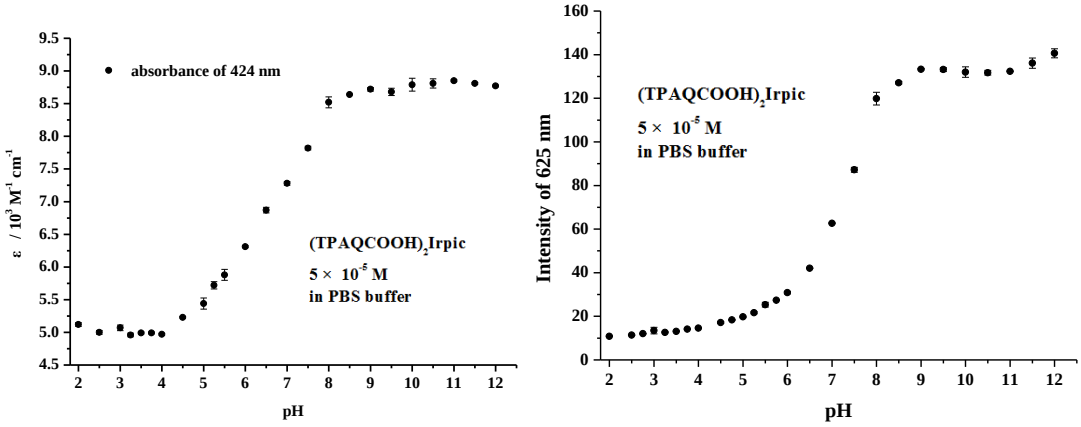

Figure S14. pH-Dependent changes in molar absorption coefficients (424 nm) and emission intensity (625 nm) of the probe **(TPAQCOOH)$_2$Irpic** in aqueous PBS buffers and the corresponding error bars were provided.

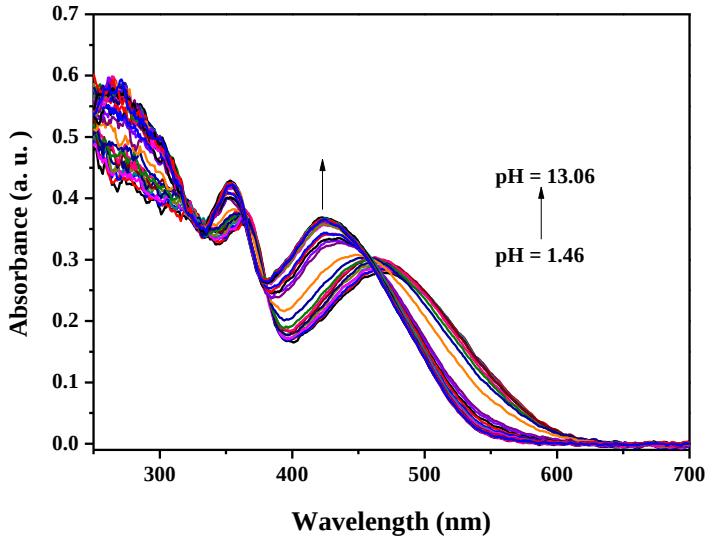

Figure 15. pH-Dependence of the absorption spectra of **(TPAQCOOH)$_2$Irpic** in ethanol:H_2O = 3:7 (containing 0.1 M NaCl) at concentration of 5.0 ×10^{-5} M.

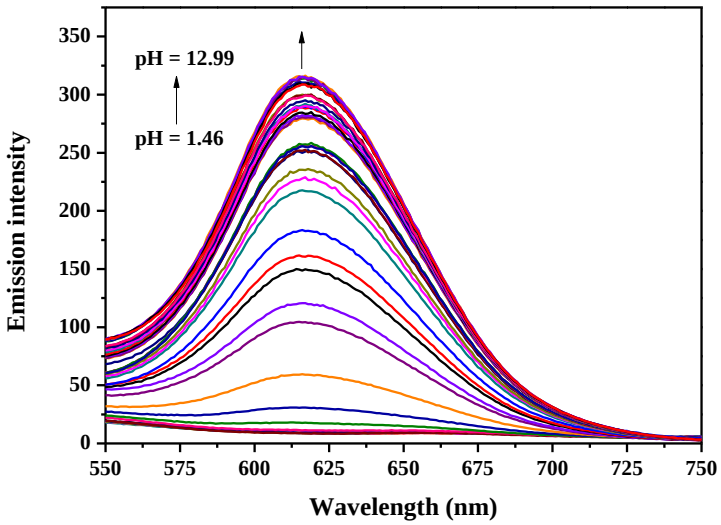

Figure 16. pH-Dependence of the emission spectra of **(TPAQCOOH)$_2$Irpic** in ethanol:H_2O = 3:7 (containing 0.1 M NaCl) at concentration of 5.0 ×10^{-5} M.

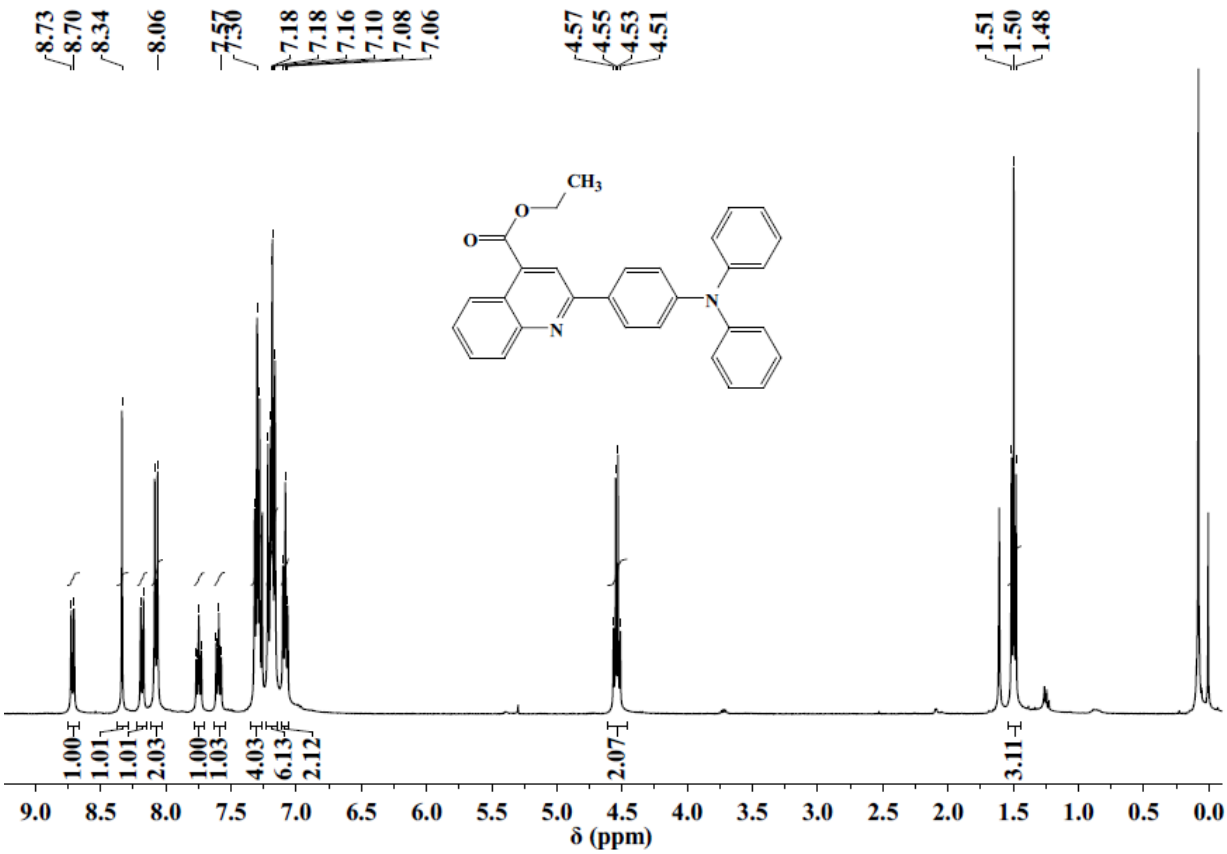

Figure S17. ^{1}H NMR of **TPAQCE** in $CDCl_3$

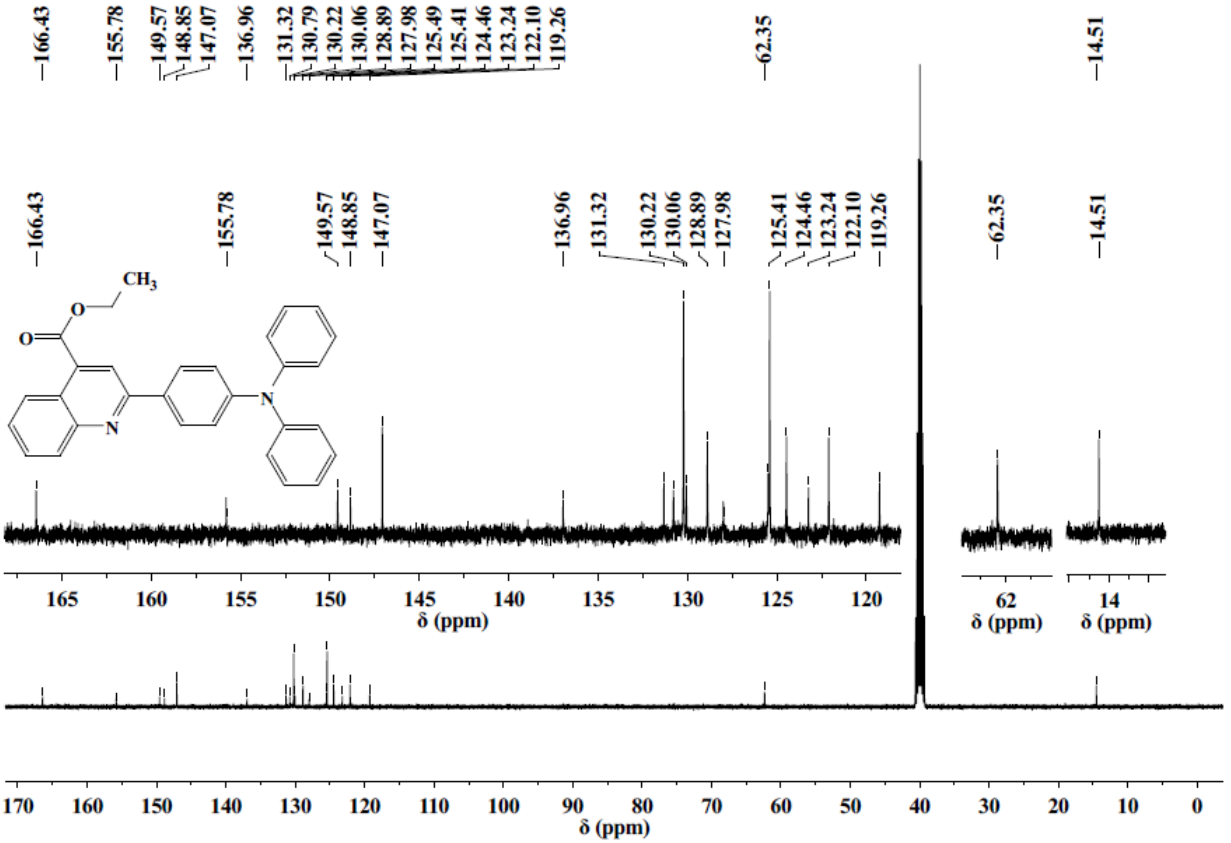

Figure S18. ^{13}C NMR of **TPAQCE** in DMSO-d_6

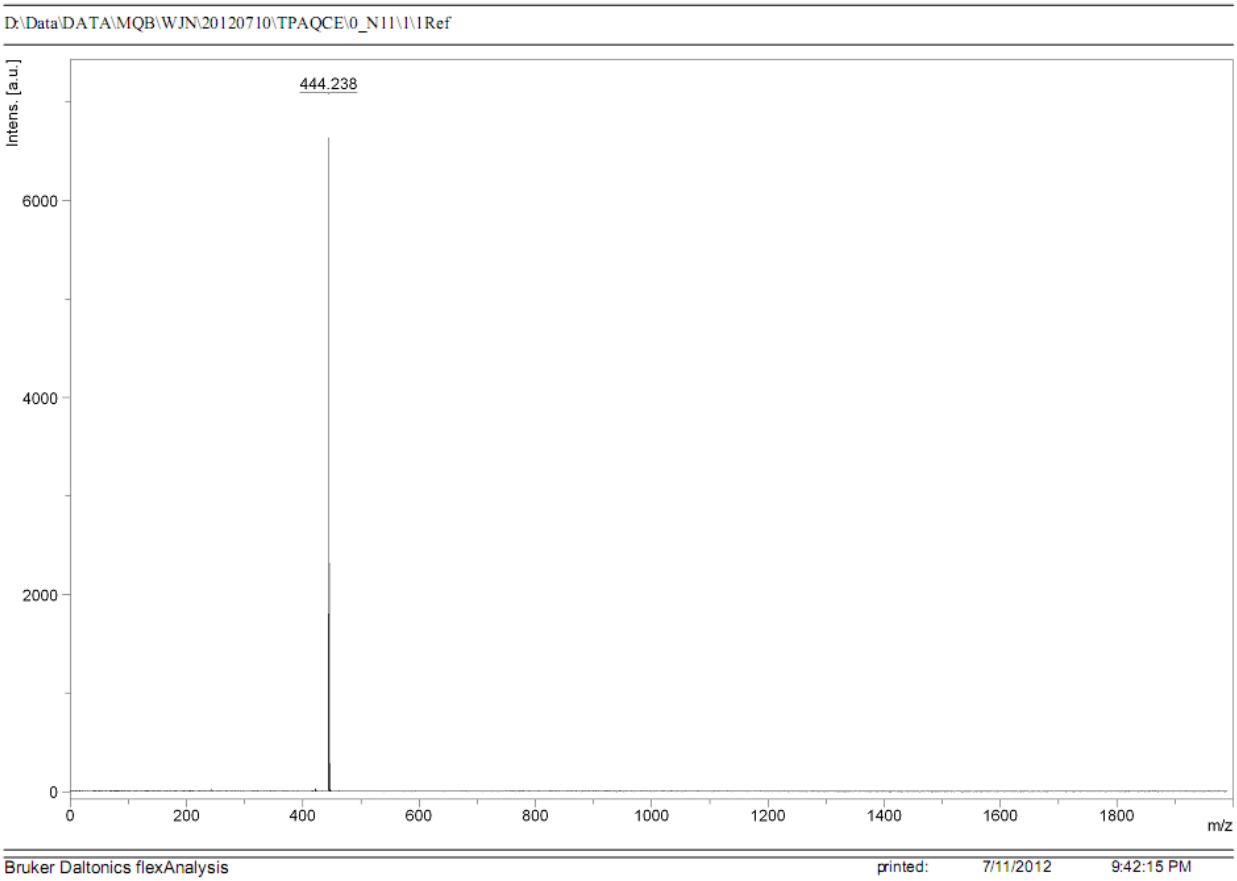

Figure S19. MADIL-TOF MS of **TPAQCE**

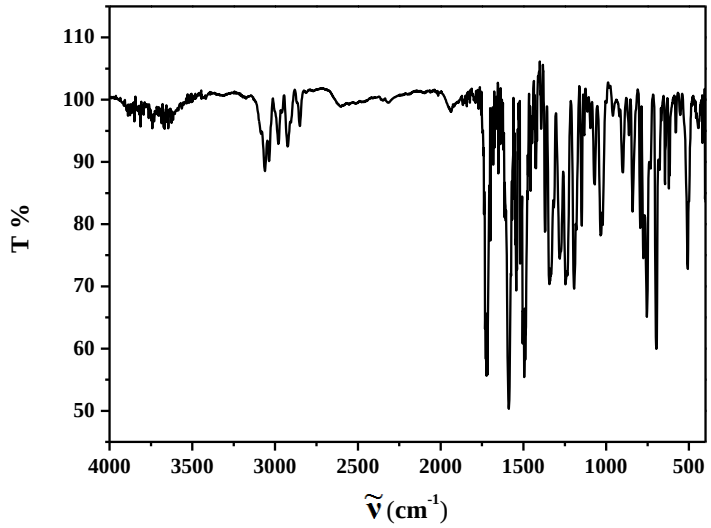

Figure S20. IR spectrum of **TPAQCE**

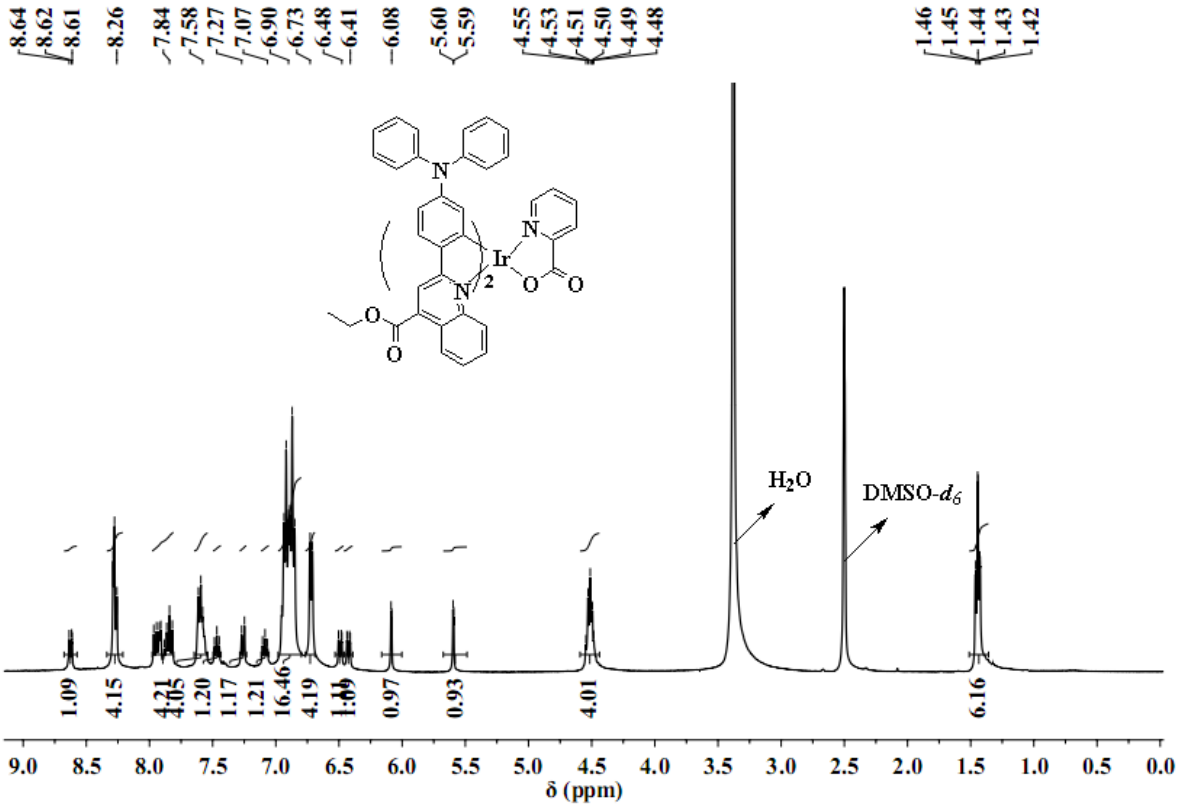

Figure S21. ^{1}H NMR of **(TPAQCE)$_2$Irpic** in DMSO-d_6

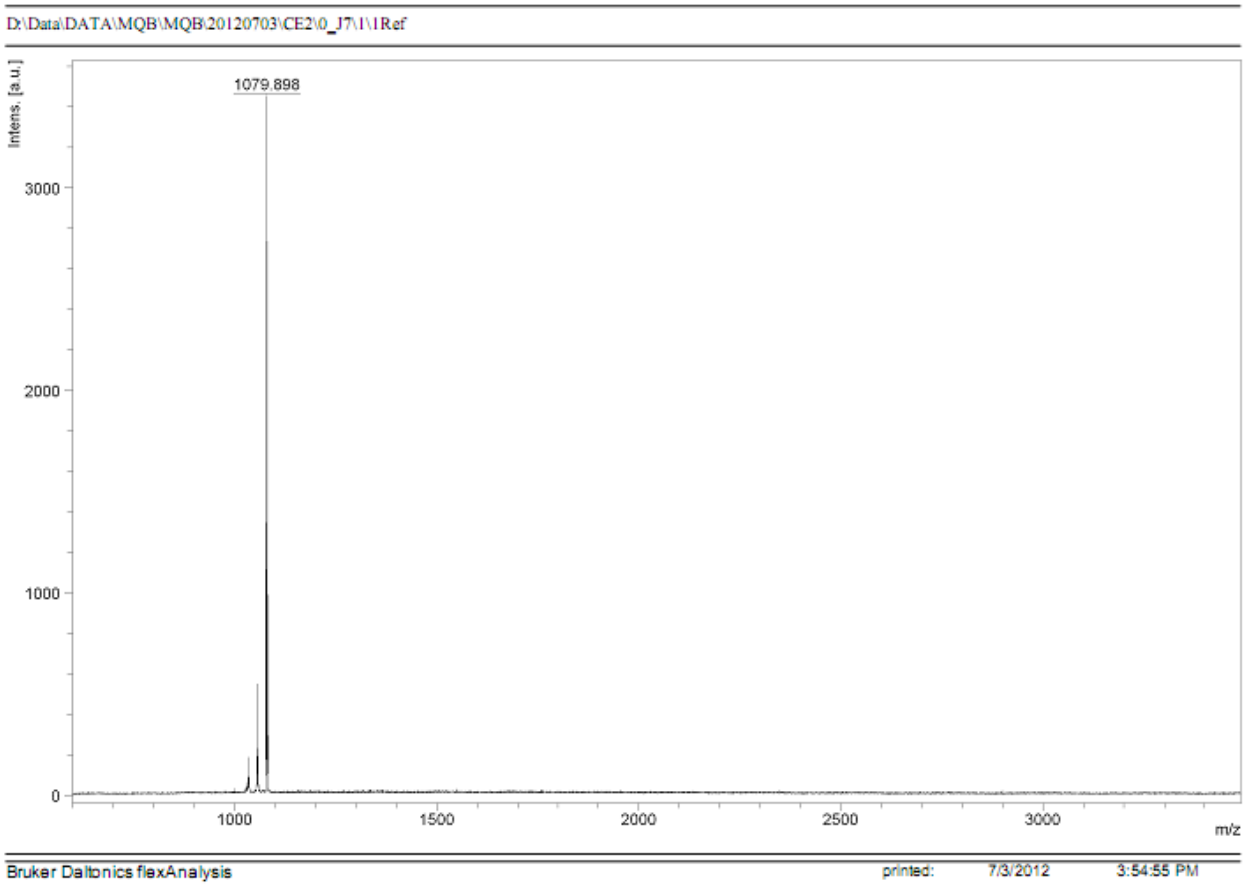

Figure S22. MADIL-TOF MS of **(TPAQCE)$_2$Irpic**

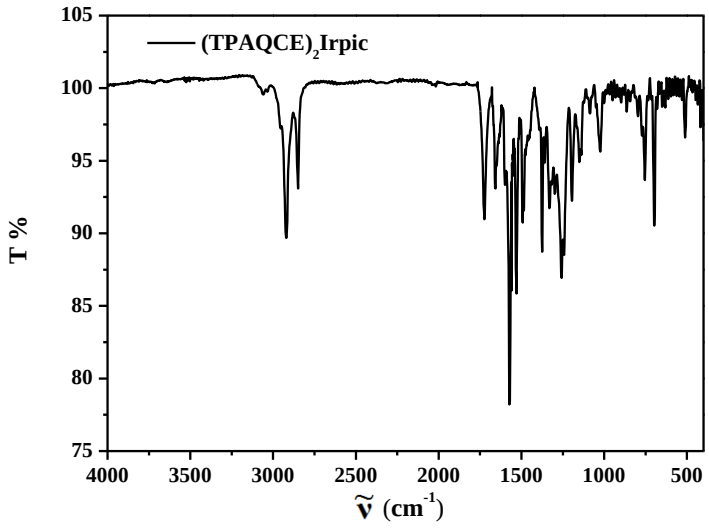

Figure S23. IR spectrum of **(TPAQCE)$_2$Irpic**

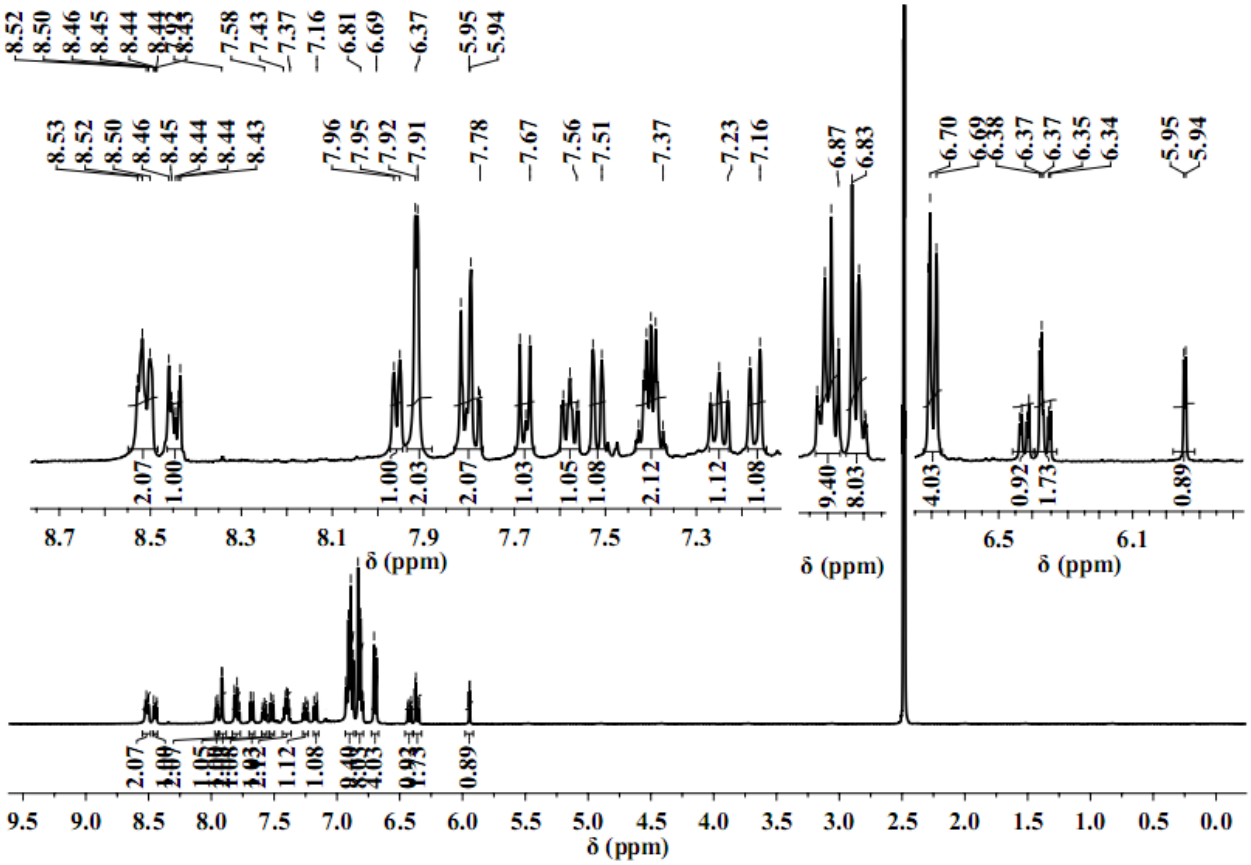

Figure S24. ^{1}H NMR of **(TPAQCOOH)$_2$Irpic** in DMSO-d_6

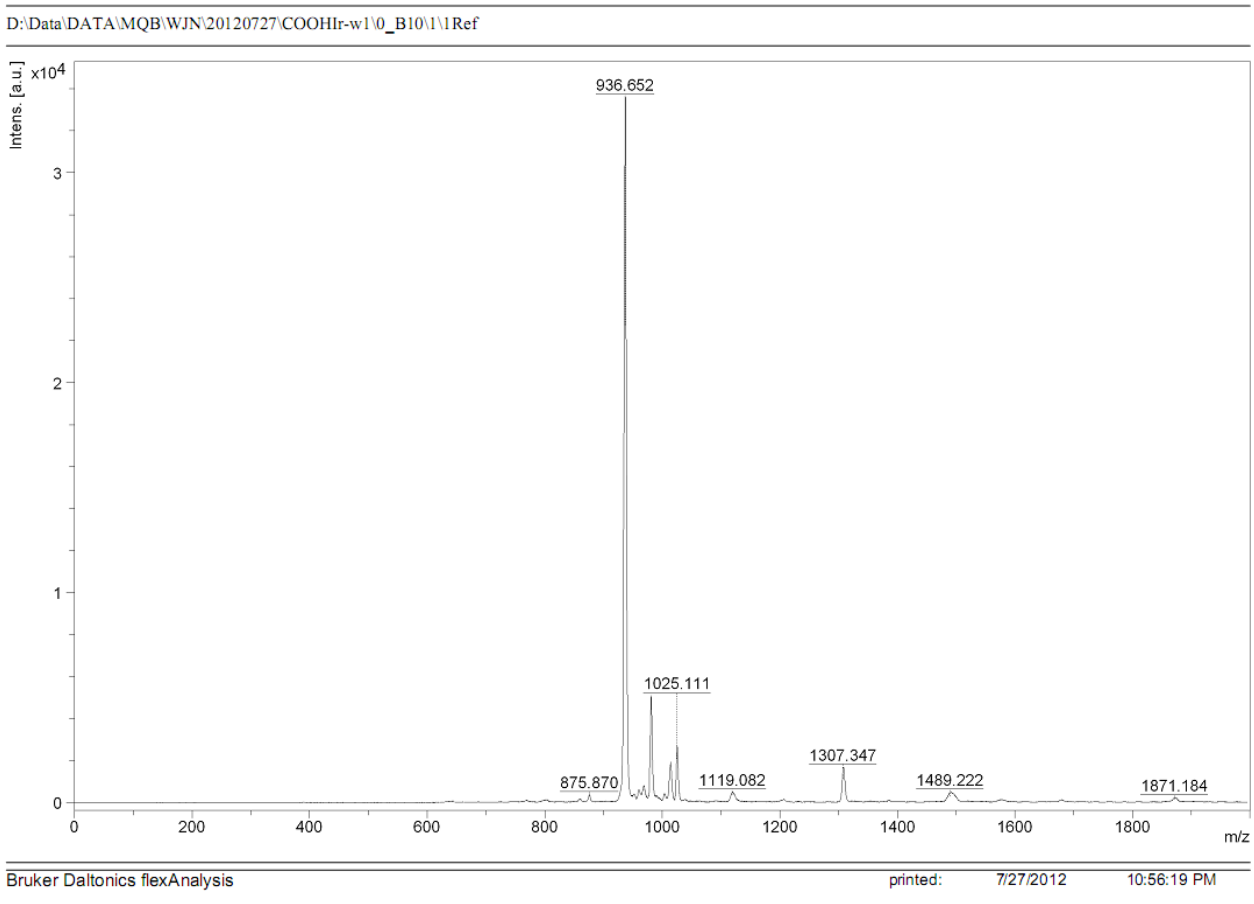

Figure S25. MADIL-TOF MS of **(TPAQCOOH)$_2$Irpic**

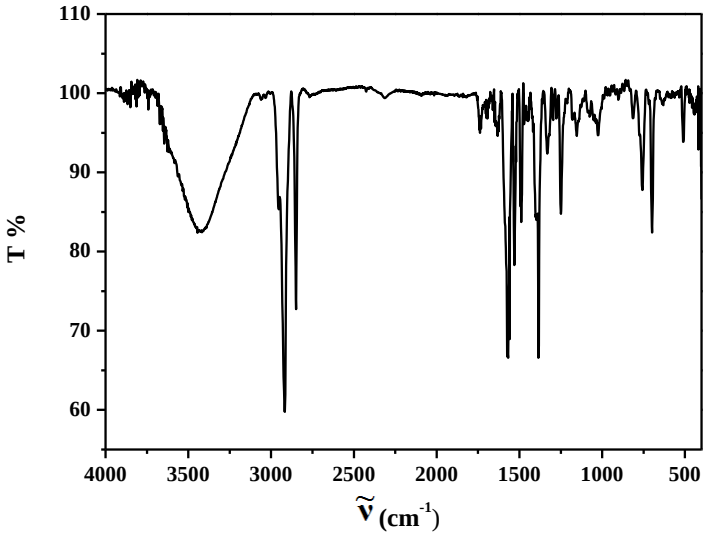

Figure S26. IR spectrum of **(TPAQCOOH)$_2$Irpic**