Supporting Information (SI)

Four membered red iridium(III) complexes with Ir-S-P-S structures: rapidly room temperature synthesis and application in OLEDs

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Materials and Measurements.

All reagents and chemicals were purchased from commercial sources and used without further purification. ^{1}H NMR and ^{19}F NMR spectra were measured on a Bruker AM 400 spectrometer. High-resolution electrospray mass spectra (HRMS) was measured on G6500 from Agilent for complexes. TGA measurements were carried out on a DSC 823e analyzer (METTLER). Absorption and photoluminescence spectra were measured on a UV-3100 spectrophotometer and a Hitachi F-4600 photoluminescence spectrophotometer, respectively. The decay lifetimes were measured with an Edinburgh Instruments FLS 980 fluorescence spectrometer in degassed CH_2Cl_2 solution at room temperature. The luminescence quantum efficiencies were calculated by comparison of the emission intensities (integrated areas) of a standard (*fac*-$Ir(ppy)_3$) and the sample.

X-ray Crystallography.

The single crystals of complexes were carried out on a Bruker SMART CCD diffractometer using monochromated Mo Kα radiation (λ = 0.71073 Å) at 173 K. Cell parameters were retrieved using SMART software and refined using SAINT [1] on all observed reflections. Data were collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 10 s/frame. The highly redundant data sets were reduced using SAINT and corrected for Lorentz and polarization effects. Absorption corrections were applied using SADABS [2]

supplied by Bruker. The structures were solved by direct methods with SHELXT-2014/5 and refined by full-matrix least-squares on *F*2 using the program SHELXL-2018/3.[3] The positions of metal atoms and their first coordination spheres were located from direct-methods E-maps; other non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. Hydrogen atoms were placed in calculated position and refined as riding atoms with a uniform value of Uiso.

Details of cyclic voltammetry measurements and theoretical calculations.

Cyclic voltammetry measurements were conducted on a MPI-A multifunctional electrochemical and chemiluminescent system (Xi'an Remex Analytical Instrument Ltd. Co., China) at room temperature, with a polished Pt plate as the working electrode, platinum thread as the counter electrode and Ag-$AgNO_3$ (0.1 M) in CH_2Cl_2 as the reference electrode, *tetra*-n-butylammonium perchlorate (0.1 M) was used as the supporting electrolyte, using Fc^+/Fc as the internal standard, the scan rate was 0.1 V s^{-1}. We perform theoretical calculations employing Gaussian09 software with B3LYP function.[4] The basis set of 6-31G(d, p) was used for C, H, N, O, F, P and S atoms while the LanL2DZ basis set was employed for Ir atoms.[5] The solvent effect of CH_2Cl_2 was taken into consideration using conductor like polarizable continuum model (C-PCM).[6]

OLEDs fabrication and measurement.

All OLEDs were fabricated on the pre-patterned ITO-coated glass substrate with a sheet resistance of 15 Ω sq^{-1}. The deposition rate for organic compounds is 1-2 Å s^{-1}. The phosphor and the host 26DCzppy were co-evaporated to form emitting layer. The cathode consisting of LiF/ Al was deposited by evaporation of LiF with a deposition rate of 0.1 Å s^{-1} and then by evaporation of Al metal with a rate of 3 Å s^{-1}. The characteristic curves of the devices were measured with a computer which controlled KEITHLEY 2400 source meter with a calibrated silicon diode in air without device encapsulation. On the basis of the uncorrected PL and EL spectra, the Commission Internationale de l'Eclairage (CIE) coordinates were calculated using a test program of the Spectra scan PR650 spectrophotometer.

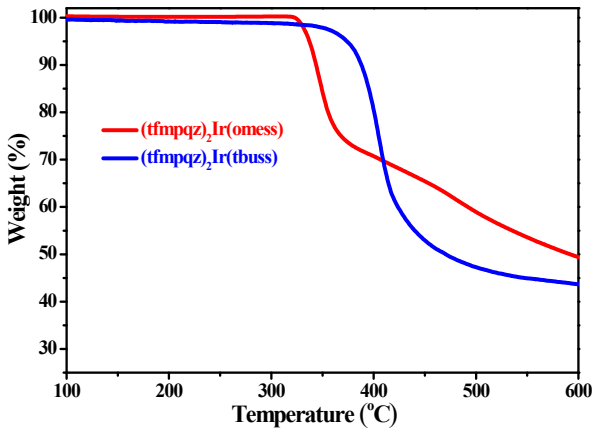

Fig. S1 TGA curves of $(tfmpqz)_2Ir(omess)$ and $(tfmpqz)_2Ir(tbuss)$ complexes.

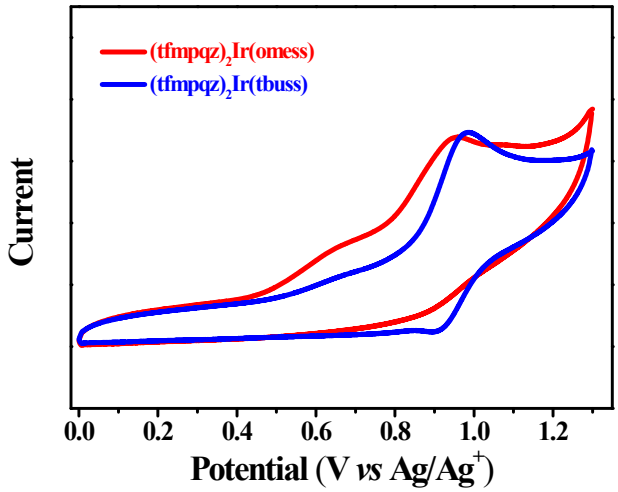

Fig. S2 CV curves of $(tfmpqz)_2Ir(omess)$ and $(tfmpqz)_2Ir(tbuss)$ complexes.

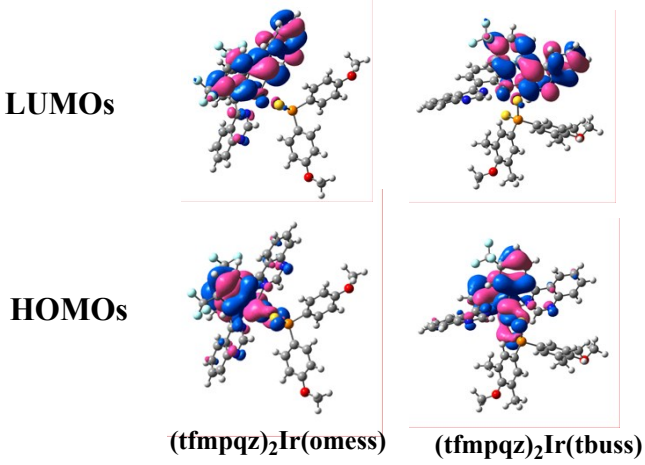

Fig.S3 Theoretical HOMO/LUMO electron distributions of two complexes.

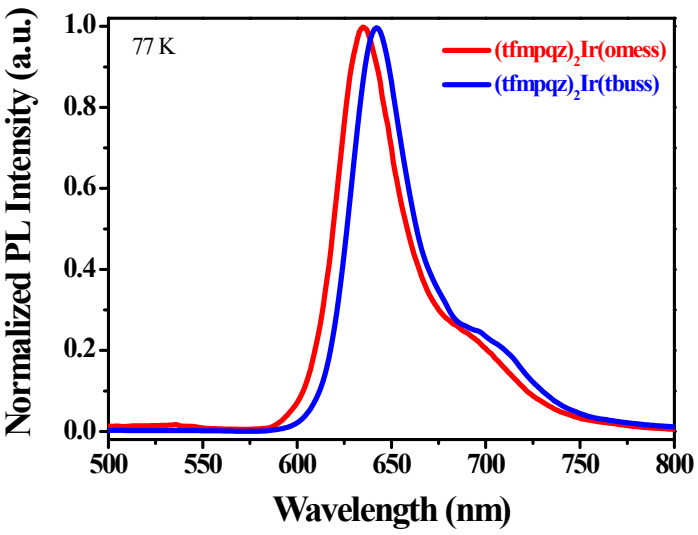

Fig.S4 the PL emissions of two complexes measured at 77 K.

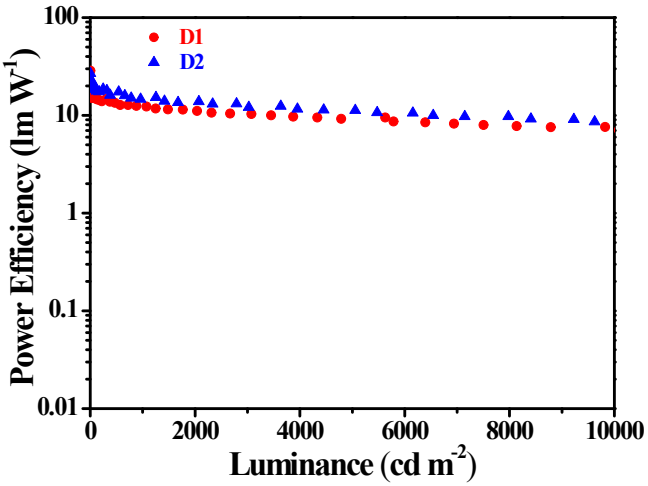

Fig.S5 Power efficiency (η_p) *versus* luminance characteristics of two devices.

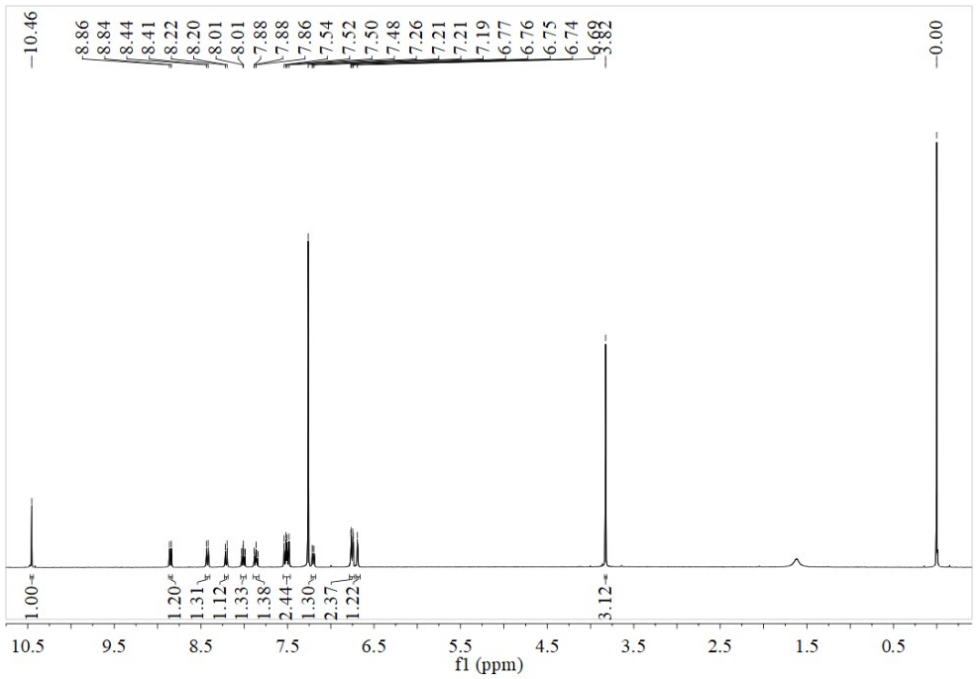

Fig. S6 ^{1}H NMR of $(tfmpqz)_2Ir(omess)$ complex.

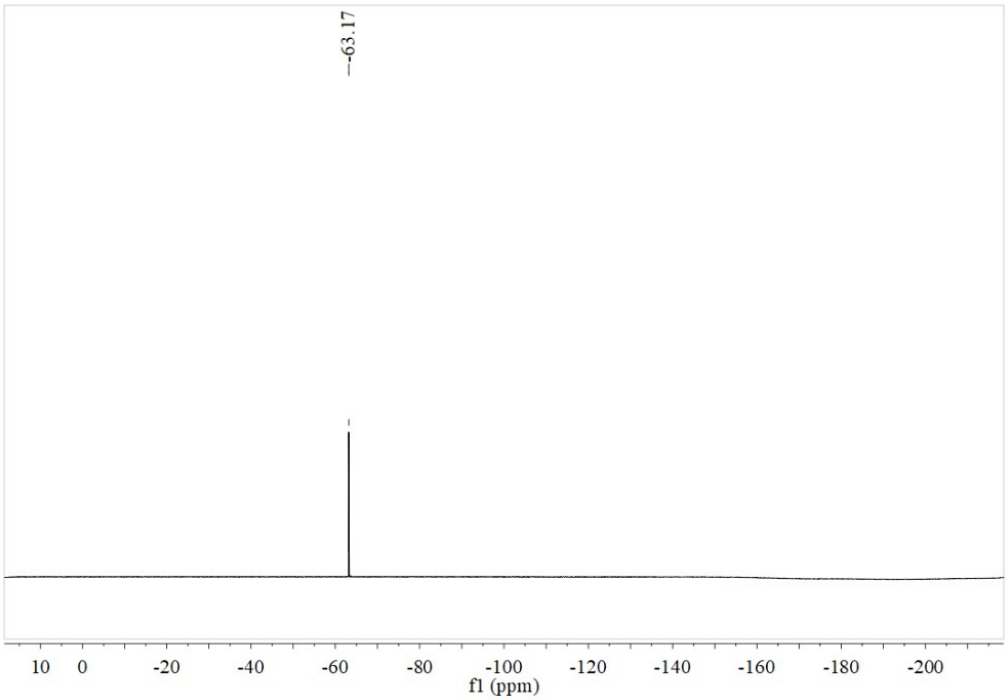

Fig. S7 ^{19}F NMR of $(tfmpqz)_2Ir(omess)$ complex.

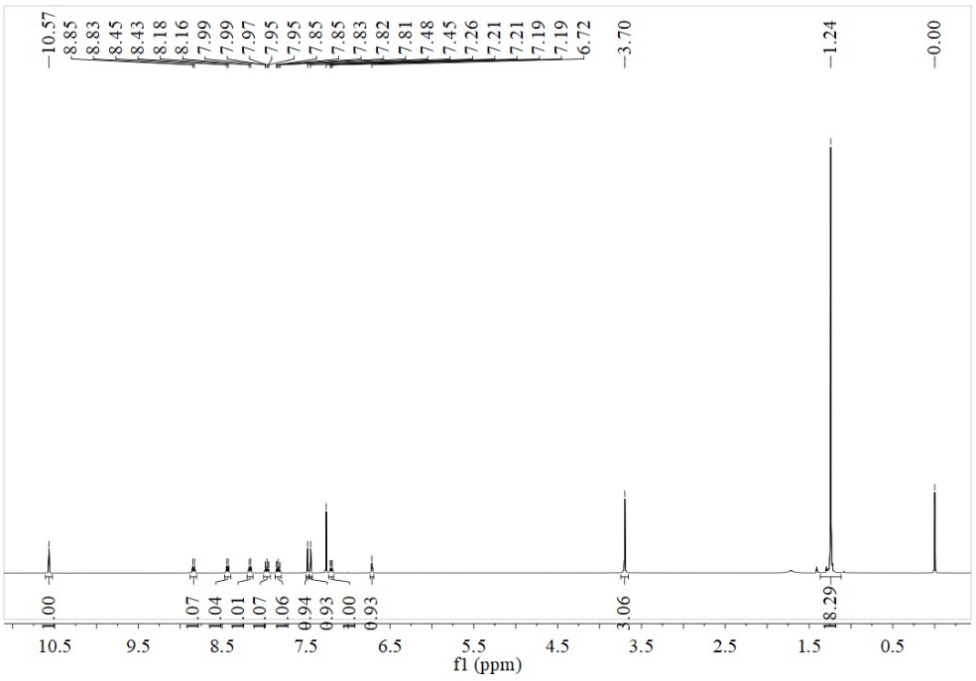

Fig. S8 ^{1}H NMR of $(tfmpqz)_2Ir(tbuss)$ complex.

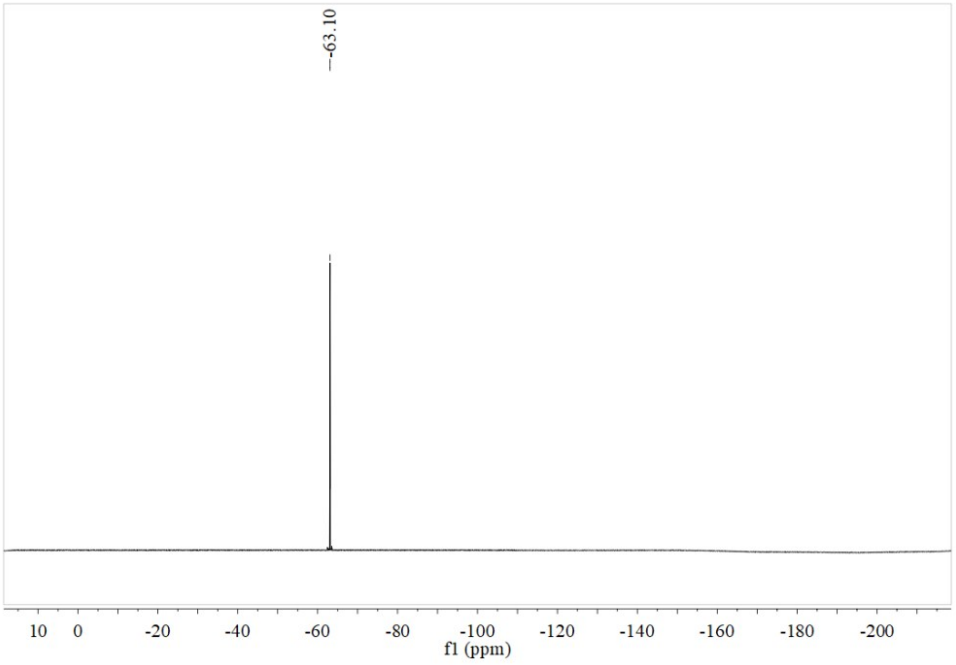

Fig. S9 ^{19}F NMR of $(tfmpqz)_2Ir(tbuss)$ complex.

Table S1. Crystal information of $(tfmpqz)_2Ir(omess)$ complex.

	$(tfmpqz)_2Ir(omess)$
Formula	$C_{44}H_{30}F_6IrN_4O_2PS_2$
Formula weight	1048.01
T (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*P* 21/n
a (Å)	8.2405(7)
b (Å)	23.652(2)
c (Å)	20.2737 (18)
α (deg)	90
β (deg)	93.404 (2)
γ (deg)	90
V (Å^3)	3944.4(6)
Z	4
ρ_{calcd} (g/cm^3)	1.765
μ (Mo Kα) (mm^{-1})	3.605
F (000)	2064
Range of transm factors (deg)	2.189-25.006
Reflns collected	23111
Unique(R_{int})	6944 (0.0474)
$R_1{}^a$, $wR_2{}^b$ [I > 2s(I)]	0.0436, 0.0918
$R_1{}^a$, $wR_2{}^b$ (all data)	0.0771, 0.0971
GOF on F^2	0.996
CCDC No.	1867812

$R_1{}^a = \Sigma||F_o| - |F_c||/\Sigma F_o|$. $wR_2{}^b = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)]^{1/2}$

Table S2. Selected bond lengths of $(tfmpqz)_2Ir(omess)$ complex.

C6 - Ir1	2.002 (6)	P1 - S2	2.018 (2)	C21 - Ir1 - N3	78.6 (2)
C21 - Ir1	2.004 (6)	C35 - P1	1.811 (6)	C6 - Ir1 - N2	79.2 (2)
Ir1 - N3	2.038 (5)	C42 - P1	1.814 (7)	S2 - Ir1 - S1	79.37 (5)
Ir1 - N2	2.040 (5)	C31 - O1	1.426 (8)	S2 - P1- S1	105.73 (10)
Ir1 - S2	2.5105 (16)	C32 - O1	1.368 (8)	C35 - P1- C42	105.6 (3)
Ir1 - S1	2.5350 (16)	C38 - O2	1.413 (10)	C32 - O1 - C31	118.8 (6)
P1 - S1	2.024 (2)	C39 - O2	1.403 (9)	C39 - O2 - C38	117.9 (7)

Table S3. HOMO and LUMO electron cloud density distributions of each fragment of both Ir(III) complexes.

Complexes	Orbit	Composition(%)		
		tfmpqz	Ir atom	ancillary ligand
$(tfmpqz)_2Ir(omess)$	HOMO	44.62	49.01	6.37
	LUMO	91.08	4.68	4.24
$(tfmpqz)_2Ir(tbuss)$	HOMO	43.18	48.81	8.01
	LUMO	91.37	4.71	3.92

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