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Supporting Information

Sulfur atom contained ligands induced rapid room temperature synthesis of red iridium(III) complexes with Ir-S-P-S structures for 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). 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 and refined by full-matrix least-squares on *F*2.[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. 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, F, S and P 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.

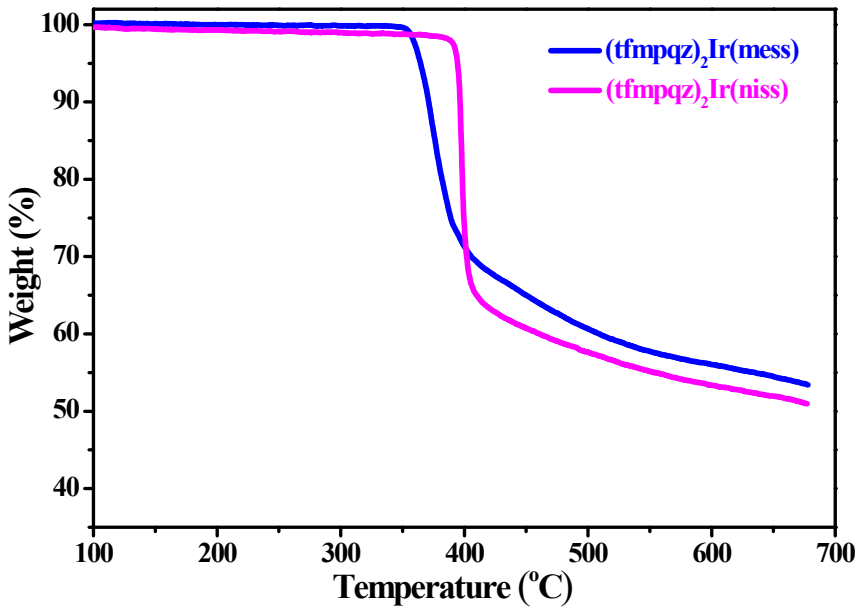

Fig. S1 TGA curves of $(tfmpqz)_2Ir(mess)$ and $(tfmpqz)_2Ir(niss)$ complexes.

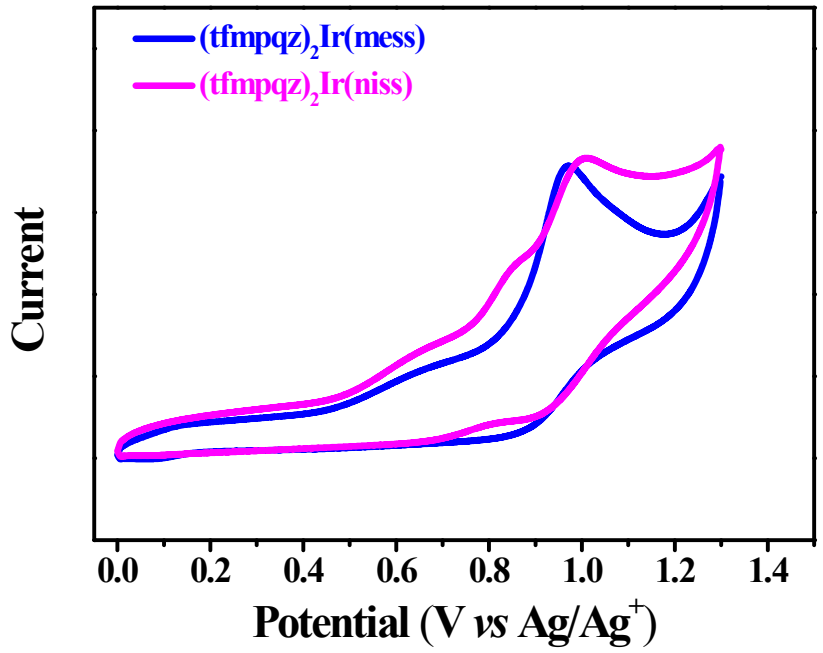

Fig. S2 CV curves of $(tfmpqz)_2Ir(mess)$ and $(tfmpqz)_2Ir(niss)$ complexes.

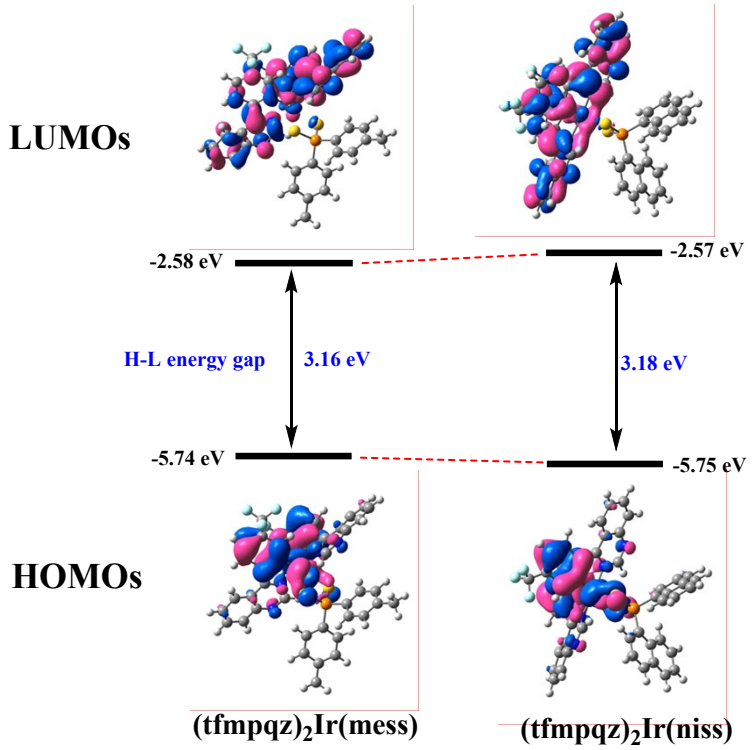

Fig. S3 Theoretical HOMO/LUMO energy levels and electron distributions of $(tfmpqz)_2Ir(mess)$ and $(tfmpqz)_2Ir(niss)$ complexes.

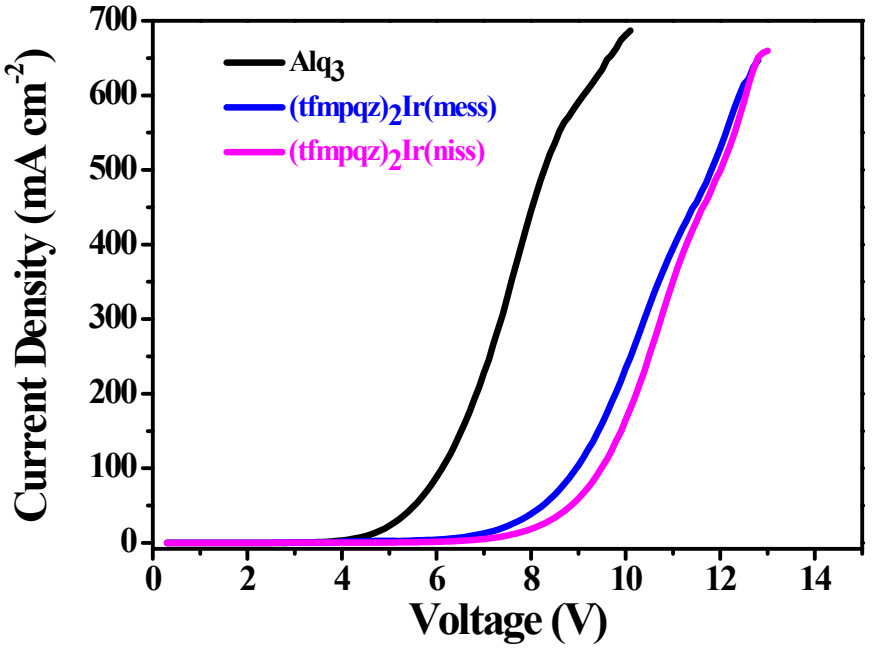

Fig. S4 *J*-V characteristics of electron-only devices.

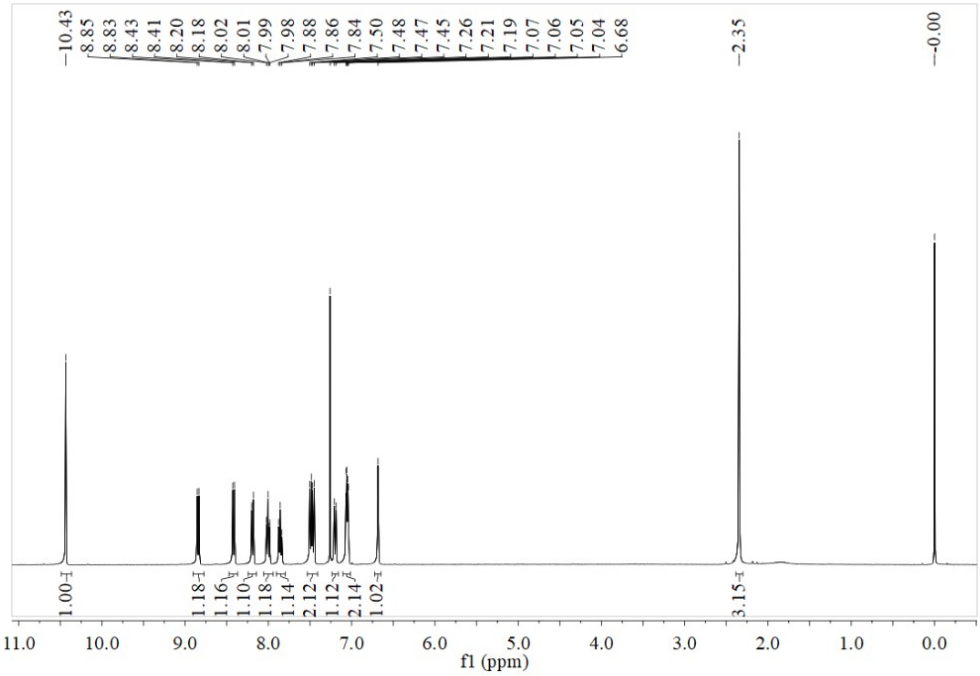

Fig. S5 ^{1}H NMR of $(tfmpqz)_2Ir(mess)$ complex.

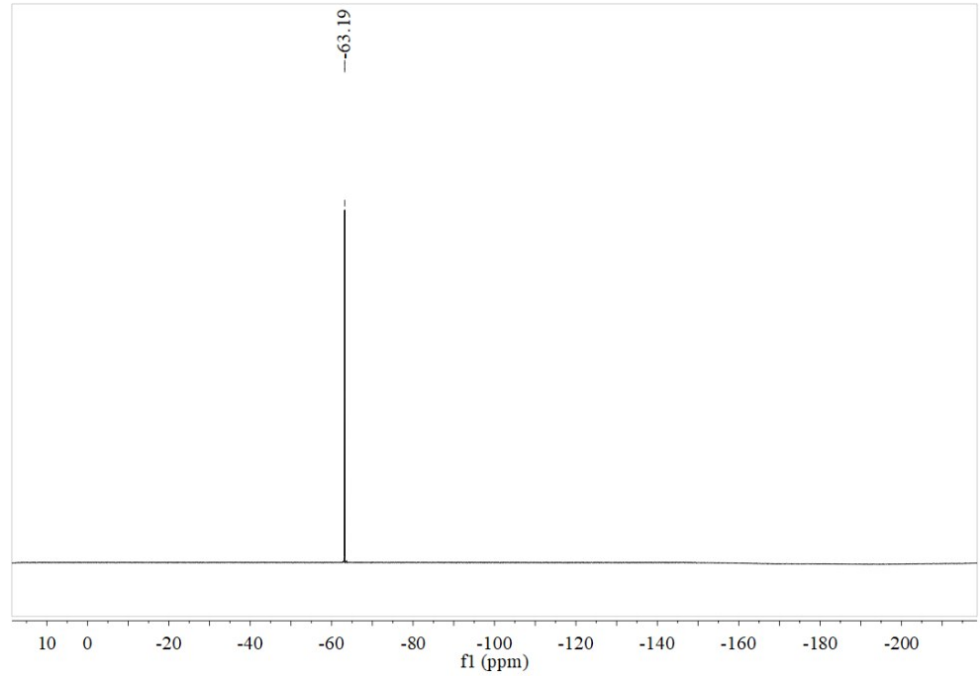

Fig. S6 ^{19}F NMR of $(tfmpqz)_2Ir(mess)$ complex.

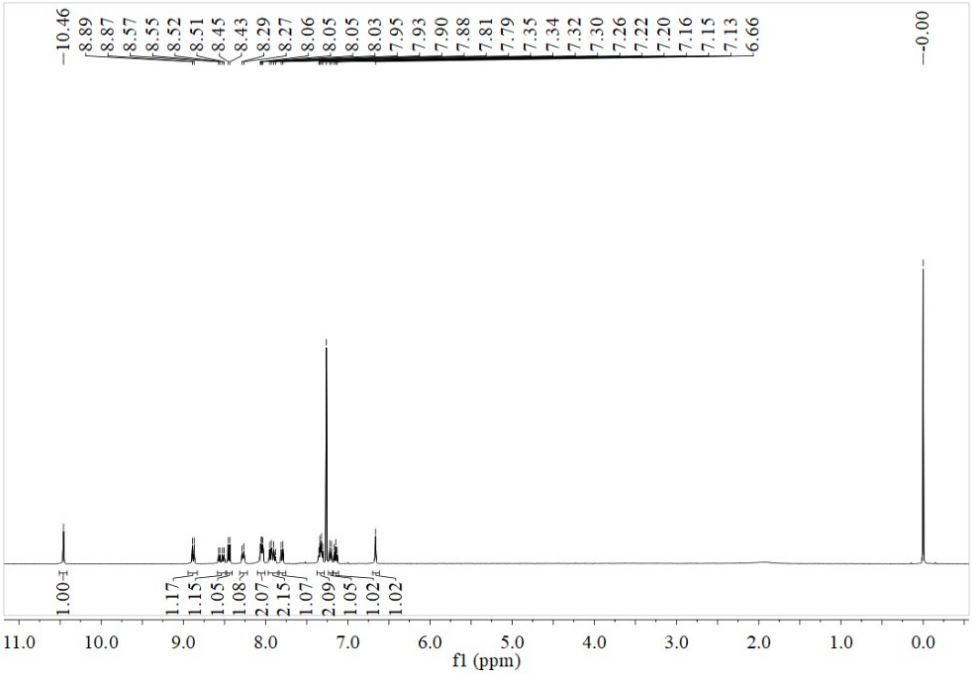

Fig. S7 ^{1}H NMR of $(tfmpqz)_2Ir(niss)$ complex.

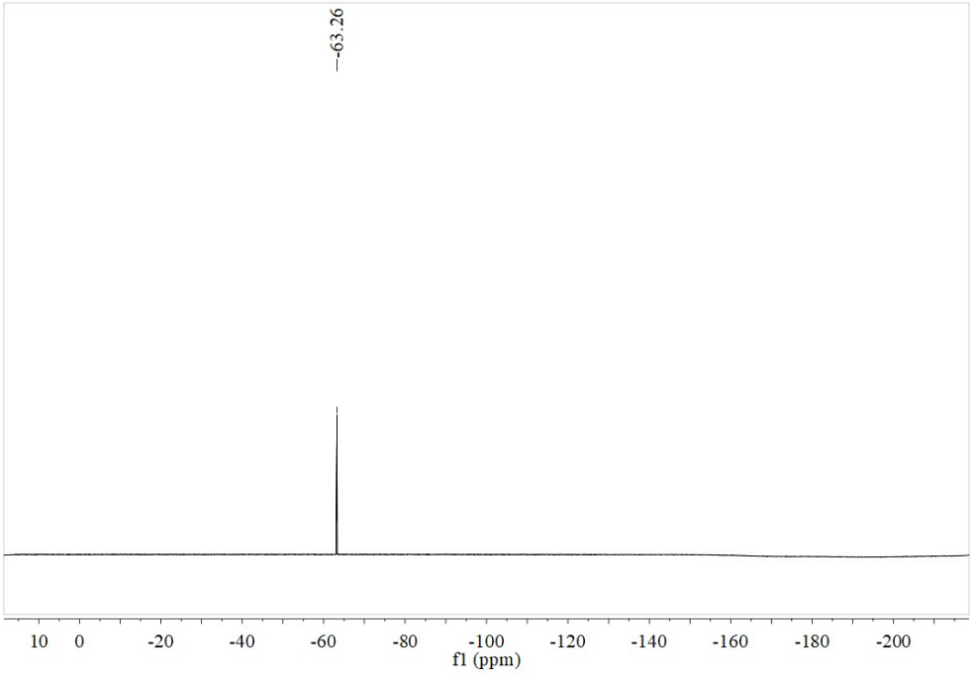

Fig. S8 ^{19}F NMR of $(tfmpqz)_2Ir(niss)$ complex.

Table S1. Crystal information of $(tfmpqz)_2Ir(mess)$ and $(tfmpqz)_2Ir(niss)$ complexes.

	$(tfmpqz)_2Ir(mess)$	$(tfmpqz)_2Ir(niss)$
Formula	$C_{44}H_{30}F_6IrN_4PS_2$	$C_{50}H_{30}F_6IrN_4PS_2$
Formula weight	1016.01	1089.12
T (K)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic
Space group	*P*-1	P_{2c}
a (Å)	8.691 (4)	24.7841 (9)
b (Å)	12.924 (6)	20.5732 (8)
c (Å)	18.497 (9)	8.1565 (3)
α (deg)	94.765(8)	90
β (deg)	102.429(8)	90
γ (deg)	92.407(7)	90
V (Å^3)	2017.9(17)	4158.9 (3)
Z	2	2
ρ_{calcd} (g/cm^3)	1.672	1.752
μ (Mo Kα) (mm^{-1})	3.517	3.421
F (000)	1000	2164
Range of transm factors (deg)	1.584-25.010	2.573-25.008
Reflns collected	11195	28080
Unique(R_{int})	7068 (0.0266)	7035 (0.0474)
R_1^a, wR_2^b [I > 2s(I)]	0.0316, 0.0719	0.0323, 0.0832
R_1^a, wR_2^b (all data)	0.0397, 0.0750	0.0380, 0.0865
GOF on F^2	1.019	1.031
CCDC No.	1867798	1867804

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

Table S2. Selected bond lengths and angels of $(tfmpqz)_2Ir(mess)$ and $(tfmpqz)_2Ir(niss)$ complexes.

$(tfmpqz)_2Ir(mess)$		$(tfmpqz)_2Ir(niss)$	
selected bonds and angels			
C33-Ir1	2.007 (5)	C6-Ir1	1.995 (8)

C20-Ir1	2.013 (4)	C21-Ir1	2.006 (8)
Ir1-N3	2.051 (3)	Ir1-N1	2.023 (7)
Ir1-N2	2.054 (3)	Ir1-N3	2.039 (7)
Ir1-S2	2.525 (4)	Ir1-S2	2.524 (2)
Ir1-S1	2.539 (5)	Ir1-S1	2.529 (2)
C33-Ir1-N3	78.89 (6)	C6-Ir1-N1	79.3 (3)
C20-Ir1-N2	79.23 (5)	C21-Ir1-N3	79.7 (3)
S2-Ir1-S1	79.65 (5)	S2-Ir1-S1	80.07 (7)

Table S3. HOMO and LUMO electron cloud density distributions of each fragment of $(tfmpqz)_2Ir(mess)$ and $(tfmpqz)_2Ir(niss)$ complexes.

Complexes	Orbit	Composition(%)		
		tfmpqz	Ir atom	ancillary ligand
$(tfmpqz)_2Ir(mess)$	HOMO	44.79	49.15	6.06
	LUMO	90.64	4.70	4.66
$(tfmpqz)_2Ir(niss)$	HOMO	42.58	47.69	9.73
	LUMO	92.56	4.72	2.71

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