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Supporting Information (SI)

Rapid room temperature synthesis of red iridium(III) complexes with Ir-S-P-S structures for efficient 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 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 sample (*fac*-Ir(ppy)$_3$) and the unknown 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 room temperature. 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 using the program SHELXS-97.[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.

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}.

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 2,6DCzPPy was co-evaporated to form emitting layer from two separate sources. 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.

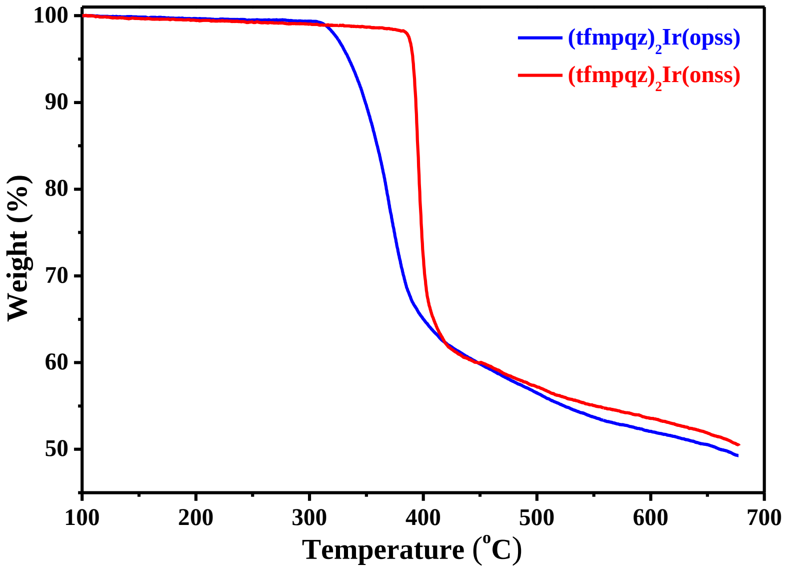

Fig. S1 TGA curves of $(tfmpqz)_2Ir(opss)$ and $(tfmpqz)_2Ir(onss)$ complexes.

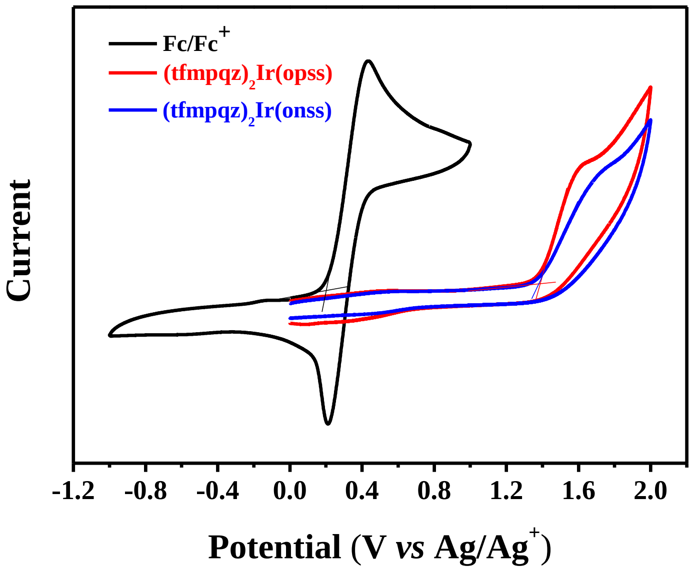

Fig. S2 CV curves of $(tfmpqz)_2Ir(opss)$ and $(tfmpqz)_2Ir(onss)$ complexes.

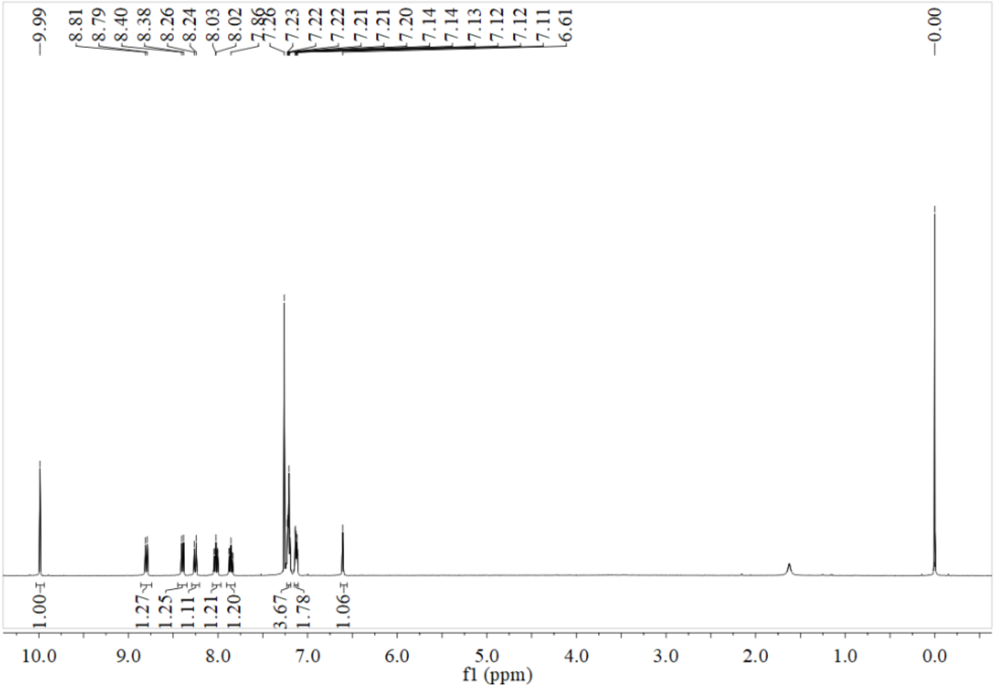

Fig. S3 ^{1}H NMR of (tfmpqz)$_2$Ir(opss) complex.

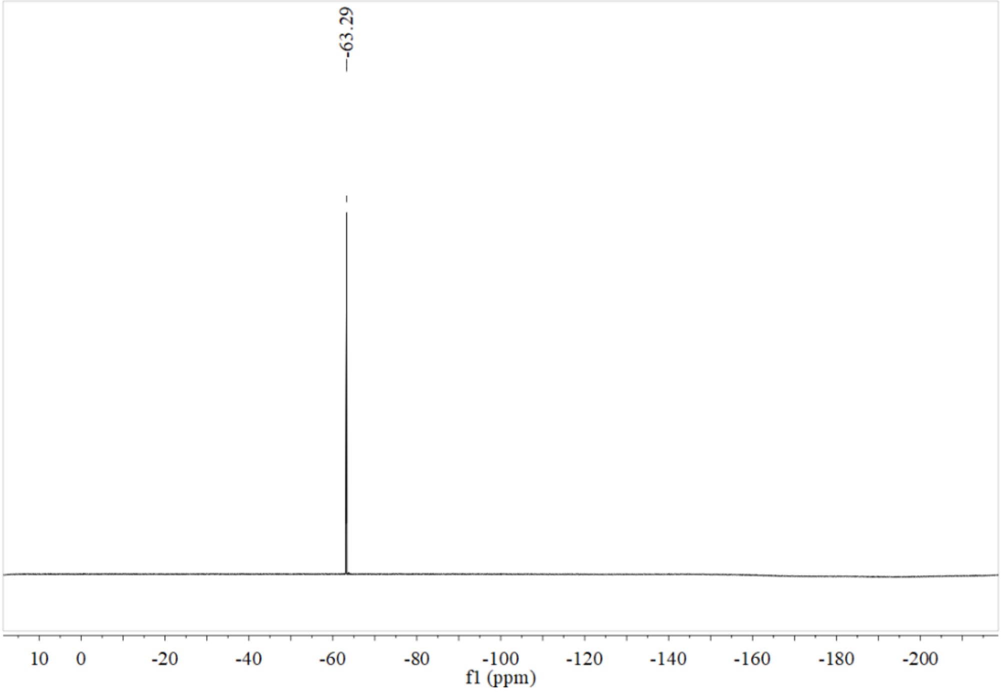

Fig. S4 ^{19}F NMR of (tfmpqz)$_2$Ir(opss) complex.

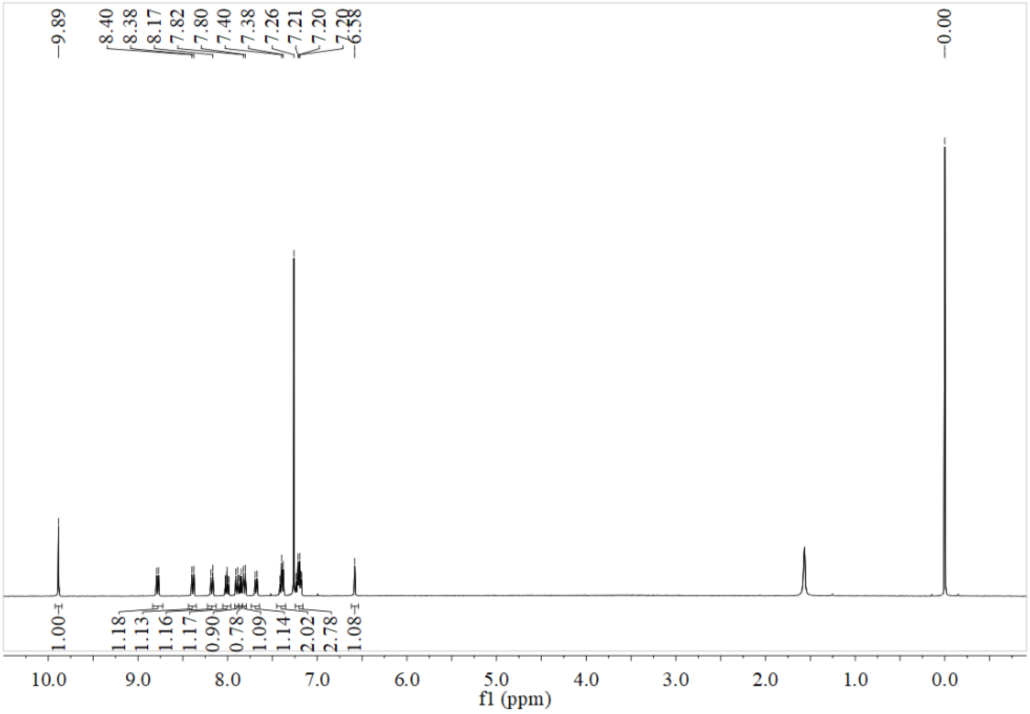

Fig. S5 ^{1}H NMR of (tfmpqz)$_2$Ir(onss) complex.

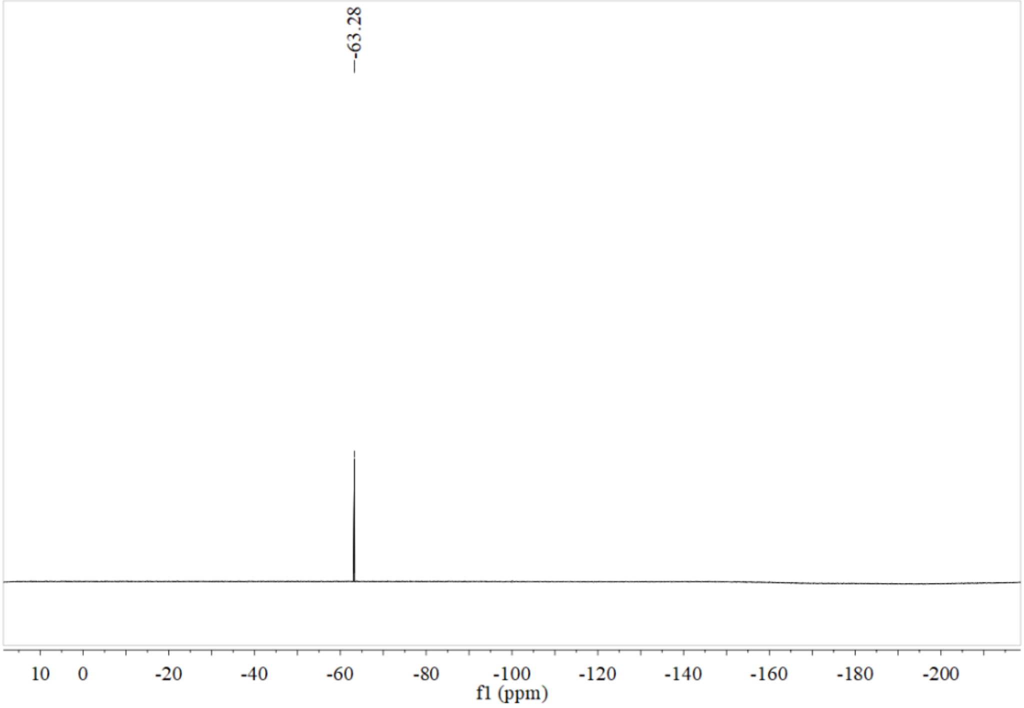

Fig. S6 ^{19}F NMR of (tfmpqz)$_2$Ir(onss) complex.

Table S1. Crystal information of (tfmpqz)$_2$Ir(onss) complex.

	(tfmpqz)$_2$Ir(onss)
Formula	$C_{50}H_{30}F_6IrN_4O_2PS_2$
Formula weight	1120.07
T (K)	193(2)
Wavelength (Å)	1.34139
Crystal system	Monoclinic
Space group	P 21/n
a (Å)	21.161(3)
b (Å)	8.4097(10)
c (Å)	26.306(3)
α (deg)	90
β (deg)	110.612(4)
γ (deg)	90
V (Å^3)	4381.7(9)
Z	4
ρ_{calcd} (g/cm^3)	1.698
μ (Mo Kα) (mm^{-1})	5.131
F (000)	2208
Range of transm factors (deg)	2.888-53.496
Reflns collected	7883
Unique(R_{int})	7883(0.1412)
$R_1{}^a$, $wR_2{}^b$ [I > 2s(I)]	0.0698, 0.1929
$R_1{}^a$, $wR_2{}^b$ (all data)	0.0908, 0.2095
GOF on F^2	1.116
CCDC No.	1887635

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

Table S2. Selected bond lengths of (tfmpqz)$_2$Ir(onss) complex (Å).

C6-Ir1	2.012 (7)	P1-S1	1.975 (3)
C19-Ir1	1.991 (8)	P1-S2	1.975 (3)
Ir1-N3	2.052 (7)	C6-Ir1-N1	79.8 (3)
Ir1-N1	2.062 (7)	C19-Ir1-N3	79.9 (3)
Ir1-S2	2.515 (2)	S2-Ir1-S1	80.37 (7)
Ir1-S1	2.528 (2)	S1-P1-S2	110.95 (15)
O1-P1	1.574 (7)	C41-O1-P1	132.1 (6)
O2-P1	1.594 (6)	C31-O2-P1	126.8 (6)

Table S3. Electrochemical data of two complexes.

Complex	E_{ox} (V)[a]	E (Fc/Fc$^+$)	E_g^{opt} (eV)[b]	E_{HOMO} (eV)[c]	E_{LUMO} (eV)[d]
(tfmpqz)$_2$Ir(opss)	1.38	0.20	2.06	-5.98	-3.92
(tfmpqz)$_2$Ir(onss)	1.37	0.20	2.06	-5.97	-3.91

[a] Oxidation potentials measured by cyclic voltammetry. [b] Calculated from the absorption band edge of the solution, $E_g^{\mathrm{opt}} = 1240/\lambda_{\mathrm{edge.}}$ [c] Calculated from empirical equation: $E_{\mathrm{HOMO}} = -[E_{\mathrm{ox}} - E\ (\mathrm{Fc/Fc^+}) + 4.8]$ eV. [d] Calculated from $E_{\mathrm{LUMO}} = E_g^{\mathrm{opt}} + E_{\mathrm{HOMO.}}$

References:

1. *SAINT-Plus*, version 6.02, Bruker Analytical X-ray System, Madison, WI, 1999.
2. Sheldrick, G. M. *SADABS An empirical absorption correction program*, Bruker Analytical X-ray Systems, Madison, WI, 1996.
3. Sheldrick, G. M. *SHELXTL-97*. Universität of Göttingen, Göttingen, Germany, 1997.