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Supporting Information

Efficient Phosphorescent red iridium(III) complexes containing four-membered Ir-S-C-S ring backbone and large hindered spacers for high-performance OLEDs

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#Lu and #Li have the same contributions to this paper.

Materials and Measurements. All reagents and chemicals were purchased from commercial sources and used without further purification. ¹H NMR spectra were measured on a Bruker AM 400 spectrometer. Mass spectrometry (MS) spectra were obtained on an electrospray ionization (ESI) mass spectrometer (LCQ fleet, Thermo Fisher Scientific) for ligands and high-resolution electrospray mass spectra (HRMS) was measured on G6500 from Agilent for complexes. Elemental analyses for C, H, and N were performed on an Elementar Vario MICRO analyzer. TG-DSC 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-920 fluorescence spectrometer in degassed CH₂Cl₂ 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.¹

X-ray Crystallography. The single crystals of complexes were carried out on a Bruker SMART CCD diffractometer using monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at room temperature. Cell parameters were retrieved using SMART software and refined using SAINT ² 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 ³ supplied by Bruker. The structures were solved by direct methods and refined by full-matrix least-squares on *F*2 using the program SHELXS-97.⁴ 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-AgNO₃ (0.1 M) in CH₂Cl₂ 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.⁵ The basis set of 6-31G(d, p) was used for C, H, N, O, and F atoms while the LanL2DZ basis set was employed for Ir atoms.⁶ The solvent effect of CH₂Cl₂ was taken into consideration using conductor like polarizable continuum model (C-PCM).⁷

OLEDs fabrication and measurement. All OLEDs were fabricated on the pre-patterned ITOcoated glass substrate with a sheet resistance of 15 Ω /sq. The deposition rate for organic compounds is 1-2 Å/s. The phosphor and the host TCTA or 2,6DCzPPy were 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 and then by evaporation of Al metal with a rate of 3 Å/s. 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.

	(4tfmpq) ₂ Ir('Budpdtc) (4tfmpq) ₂ Ir('BuCzdt			
Formula	$C_{51}H_{42}F_6IrN_5S_2$	$C_{51}H_{40}F_6IrN_5S_2$		
Formula weight	1095.21	1093.20		
T (K)	296(2)	296(2)		
Wavelength (Å)	0.71073	0.71073		
Crystal system	Triclinic	Monoclinic		
Space group	<i>P</i> -1	C2/c		
<i>a</i> (Å)	8.2104(6)	45.967(7)		
<i>b</i> (Å)	14.8349(11)	18.658(3)		
c (Å)	20.6198(15)	21.437(3)		
α (deg)	74.7250(10)	90.00		
β (deg)	79.5860(10)	91.993(2)		
γ (deg)	77.3990(10)	90.00		
$V(Å^3)$	2344.1(3)	18374(5)		
Z	2	16		
$ ho_{ m calcd} ({ m g/cm^3})$	1.552	1.581		
μ (Mo K α) (mm ⁻¹)	3.002	3.064		
F (000)	1092	8704		
Range of transm	1 569-25 010	0.886-25.010		
factors (deg)	1.507 25.010			
Reflns collected	13231	66875		
Unique(R _{int})	8220(0.0267) 16161(0.0804			
$R_{I^{a}}, wR_{2^{b}}[I > 2s(I)]$	0.0469, 0.1150	0.0454, 0.1105		
R_1^a , wR_2^b (all data)	0.0570, 0.1225	0.0878, 0.1388		

Table S1. The crystallographic data of (4tfmpq)₂Ir('Budpdtc) and (4tfmpq)₂Ir('BuCzdtc).

GOF on F^2	1.054	1.059
CCDC	1832350	1832348

 $R_{I^{a}} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma F_{o}|. \ wR_{2^{b}} = [\Sigma w(F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w(F_{o}^{2})]^{1/2}.$

Table S2. Selected bond lengths and angles of $(4tfmpq)_2 Ir(^tBudpdtc)$ and $(4tfmpq)_2 Ir(^tBuCzdtc)$.

Bond length	(4tfmpq) ₂ Ir('Budpdtc)	(4tfmpq) ₂ Ir('BuCzdtc)		
Selected Bonds	Bond length (Å)	Bond length (Å)		
Ir-C(1)	2.002(7)	2.029(7)		
Ir-C(2)	2.009(7)	1.994(7)		
Ir-N(1)	2.034(6)	2.052(7)		
Ir-N(2)	2.054(6)	2.034(6)		
Ir-S(1)	2.4524(19)	2.4660(19)		
Ir-S(2)	2.4689(18)	2.4201(19)		
S(1)-C(3)	1.699(7)	1.704(7)		
S(2)-C(3)	1.710(7)	1.710(7)		
C(3)-N(3)	1.358(9)	1.361(9)		
Selected angles	(°)	(°)		
C(1)-Ir-N(1)	79.0(3)	78.4(3)		
C(2)-Ir-N(2)	78.3(3)	78.5(3)		
S(1)-Ir-S(2)	71.60(6)	70.86(6)		
S(2)-C(3)-S(1)	115.2(4)	112.2(4)		
C(3)-S(2)-Ir	86.2(2)	89.2(3)		
C(3)-S(1)-Ir	87.0(2)	87.8(2)		
N(3)-C(3)-S(1)	122.8(5)	125.3(5)		

Complex	Orbital	Energy/eV (Calculated)	Energy/eV (Experimental)	Composition (%)		
				4tfmpqz	Ir	Ancillary Ligands
(4tfmpq) ₂ Ir('Budpdtc)	НОМО	-5.67	-5.49	43.26	47.54	9.20
	LUMO	-2.58	-3.21	91.79	4.11	4.10
(4tfmpq) ₂ Ir('BuCzdtc)	НОМО	-5.78	-5.58	43.85	47.92	8.23
	LUMO	-2.67	-3.21	93.82	3.40	2.78

Table S3. The electronic cloud density distribution.



Fig. S1 The TG curve of the iridium complexes.



Fig. S2. Cyclic voltammograms of complexes the iridium(III) complexes.



Fig. S3 The selected lifetime curves of the iridium(III) complexes in degassed CH_2Cl_2 solution (up: the curves from original data; down: the fitted curves).



Fig. S4 Current efficiency versus luminance of $(4tfmpq)_2 Ir({}^tBudpdtc)$ based devices with different doped concentrations: (a) single emitting layer, (b) double emitting layer.



Fig. S5 Current efficiency versus luminance curves of (4tfmpq)₂Ir(^{*i*}BuCzdtc) based devices with different doped concentrations: (a) single emitting layer, (b) double emitting layer.

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