Supporting Information

A series of red iridium(III) complexes using flexible dithiocarbamate derivatives as ancillary ligands for highly efficient phosphorescent 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 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 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.[1]

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 [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.

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.[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 CH_2Cl_2 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 ITO-coated 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.

Table S1. The crystallographic data of $(4tfmpiq)_2Ir(dipdtc)$, $(4tfmpiq)_2Ir(dpdtc)$ and $(4tfmpiq)_2Ir(^tBuCzdtc)$.

	$(4tfmpiq)_2Ir(dipdtc)$	$(4tfmpiq)_2Ir(dpdtc)$	$(4tfmpiq)_2Ir(^tBuCzdtc)$
Formula	$C_{39}H_{32}F_6IrN_3S_2$	$C_{45}H_{28}F_6IrN_3S_2$	$C_{53}H_{42}F_6IrN_3S_2$
Formula weight	912.99	981.02	1091.21
T (K)	296(2)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	*C2/c*	*P2(1)/c*	*P*-1
a (Å)	26.026(4)	15.5226(15)	11.30(2)
b (Å)	12.9400(14)	12.6925(12)	15.22(3)
c (Å)	22.386(3)	20.610(2)	16.31(3)
α (deg)	90	90	79.22(3)
β (deg)	97.214(4)	97.559(2)	79.11(3)
γ (deg)	90	90	82.46(3)
V (Å^3)	7479.4(16)	4025.3(7)	2692(8)
Z	8	4	2
ρ_{calcd} (g/cm^3)	1.622	1.619	1.346
μ (Mo Kα) (mm^{-1})	3.744	3.485	2.613
F (000)	3600	1928	1088
Range of transm factors (deg)	1.577-25.009	1.323-25.009	1.289-25.009
Reflns collected	20676	22112	13597
Unique(R_{int})	6595(0.0458)	7096(0.0292)	9302(0.0805)
R_1^a, wR_2^b [I > 2s(I)]	0.0466, 0.1200	0.0303, 0.0775	0.0803, 0.1988
R_1^a, wR_2^b (all data)	0.0743, 0.1376	0.0360, 0.0813	0.1274, 0.2324
GOF on F^2	1.021	1.033	0.969
CCDC	1832335	1832373	1832374

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

Table S2. Selected bond lengths and angles of (4tfmpiq)$_2$Ir(dipdtc), (4tfmpiq)$_2$Ir(dpdtc) and (4tfmpiq)$_2$Ir(^{t}BuCzdtc).

	(4tfmpiq)$_2$Ir(dipdtc)	(4tfmpiq)$_2$Ir(dpdtc)	(4tfmpiq)$_2$Ir(^{t}BuCzdtc)
Selected Bonds	Bond length (Å)	Bond length (Å)	Bond length (Å)
Ir-C(1)	2.014(7)	2.006(4)	2.049(13)
Ir-C(2)	1.991(7)	2.008(7)	2.087(14)
Ir-N(1)	2.049(6)	2.060(4)	2.074(10)
Ir-N(2)	2.042(6)	2.047(4)	2.130(11)
Ir-S(1)	2.458(2)	2.4822(11)	2.521(4)
Ir-S(2)	2.4442(19)	2.4665(12)	2.504(4)
S(1)-C(3)	1.746(8)	1.708(5)	1.761(11)
S(2)-C(3)	1.714(8)	1.716(4)	1.748(11)
C(3)-N(3)	1.315(10)	1.339(5)	1.420(13)
Selected angles	(°)	(°)	(°)
C(1)-Ir-N(1)	79.6(3)	79.14(15)	78.7(4)
C(2)-Ir-N(2)	79.3(3)	78.94(16)	78.6(5)
S(1)-Ir-S(2)	71.46(7)	71.27(4)	71.30(13)
S(2)-C(3)-S(1)	111.6(4)	114.7(2)	113.2(6)
C(3)-S(2)-Ir	88.6(3)	87.11(15)	88.1(4)
C(3)-S(1)-Ir	87.5(3)	86.77(15)	87.3(4)
N(3)-C(3)-S(1)	123.4(6)	123.4(3)	121.7(8)

Table S3. The electronic cloud density distribution.

Complex	Orbital	Energy/eV (Calculated)	Energy/eV (Experimental)	Composition (%)		
				Main Ligands	Ir	Ancillary Ligands

$(4tfmpiq)_2Ir(dipdtc)$	HOMO	-5.43	-5.23	43.42	47.37	9.21
	LUMO	-2.23	-2.86	94.00	3.70	2.30
$(4tfmpiq)_2Ir(dpdtc)$	HOMO	-5.46	-5.28	46.10	46.65	7.24
	LUMO	-2.22	-2.89	92.98	4.45	2.56
$(4tfmpiq)_2Ir(^tBudpdtc)$	HOMO	-5.45	-5.27	46.53	45.66	7.81
	LUMO	-2.17	-2.88	93.00	4.37	2.64
$(4tfmpiq)_2Ir(Czdtc)$	HOMO	-5.57	-5.40	47.96	44.72	7.32
	LUMO	-2.24	-2.97	92.98	4.31	2.72
$(4tfmpiq)_2Ir(^tBuCzdtc)$	HOMO	-5.55	-5.38	46.72	46.48	6.80
	LUMO	-2.30	-2.96	92.38	3.67	3.95

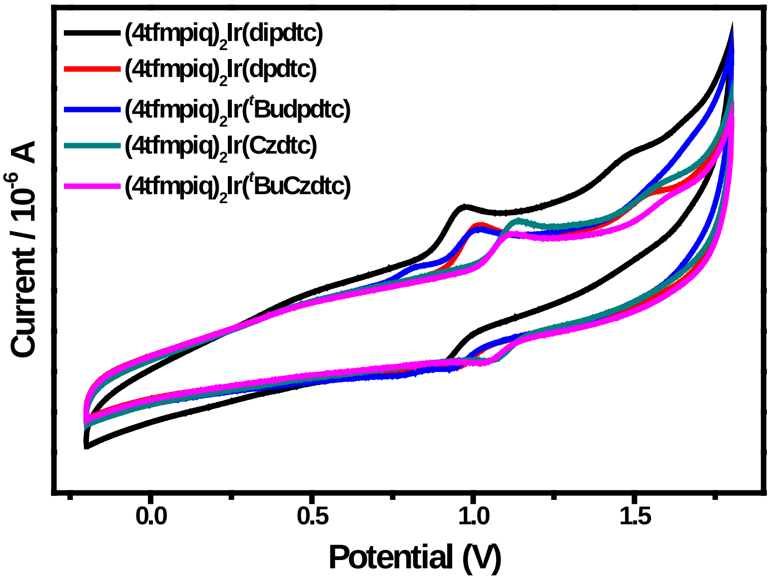

Fig. S1. Cyclic voltammograms of complexes the iridium(III) complexes.

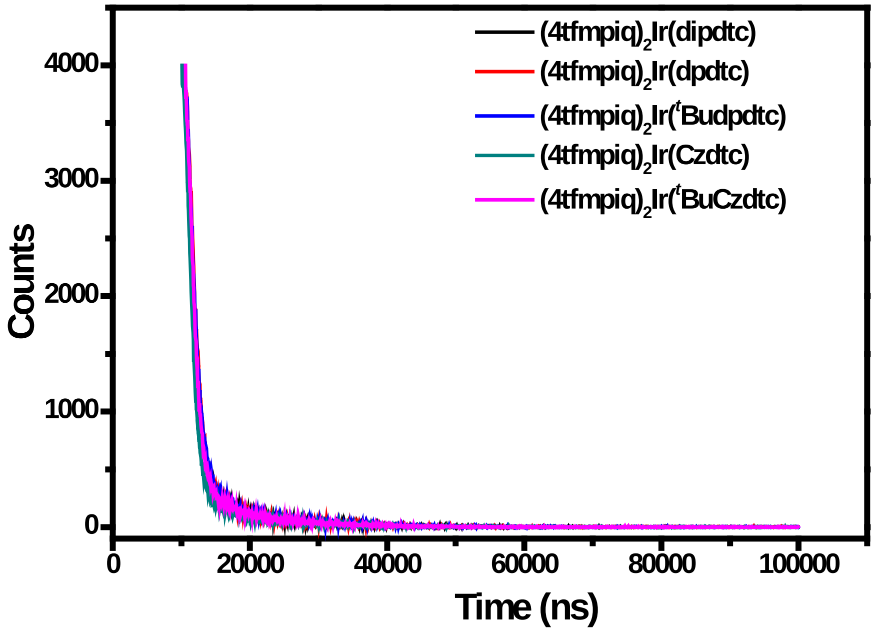

Fig. S2. The lifetime curves of the iridium(III) complexes in degassed CH_2Cl_2 solution.

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