Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Luminescent Biscarbene Iridium(III) Complexes as Living Cell Imaging Reagents

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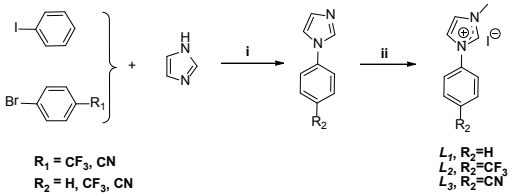
Experimental

Materials. The phosphate buffer solution (PBS, pH 7.4) for the measurement of the UV-Vis absorption and emission spectra was purchased from Sangon Inc. Anhydrous DMF (from Acros) and tetrabutylammonium hexafluorophosphate ($TBAPF_6$, from Fluka) were used for the electrochemical characterization without further treatment. Iodobenzene (J&K Chemical Ltd.), 1-bromo-4-isocyanobenzene (J&K Chemical Ltd.), 1-bromo-4-(trifluoromethyl)benzene (J&K Chemical Ltd.), 1H-imidazole (Sinopharm Chemical Reagent Co., Ltd.), 5-methoxypicolinic acid (**pic**, Fastsyn Inc.), 2,2'-bipyridine (**bpy**, aladdin Inc.), Dimethylformamide (DMF, Sinopharm Chemical Reagent Co., Ltd.), 2-ethyoxylethanol (Sinopharm Chemical Reagent Co., Ltd.) were used as received. The chloro(1,5-cyclooctadiene)iridium(I) dimer ($[IrCl(COD)]_2$) were synthesized according to the published procedure.[1]

Synthesis and characterization



Scheme S1. The synthetic route for imidazolium-based carbene ligand precursors ***L*₁**, ***L*₂** and ***L*₃**. i: CuI, L-proline, K_2CO_3, DMSO, 90 °C. ii: CH_3I, THF, 40 °C.

General procedures for imidazolium-based carbene ligand precursors (*L*)

The synthesis of ***L*₁**, ***L*₂** and ***L*₃** involves two steps which are illustrated in the Scheme S1. The synthesis of aryl-imidazole intermediates is a literature method using the Ullmann coupling reaction.[2] For the ligand synthesis, after purification by silica gel column chromatography, an extra amount of CH_3I (4 eq.) was added to the THF solution of the intermediate at 40 °C. After 24 hours, a large amount precipitate appeared in the solution. The target product of ***L*** was obtained by filtration and washing with THF.

***L*₁**. (Overall Yield: 83%, referred to 1H-imidazole) ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 10.40 (s, 1 H), 7.45 (m, 3 H), 7.69 (t, *J*=1.6 Hz, 1 H), 7.55 (m, 3 H), 4.26 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 135.72, 134.33, 130.63, 130.48, 124.71, 122.17, 120.81, 37.68.

***L*₂**. (Overall Yield: 78%, referred to 1H-imidazole) ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm: 9.87 (s, 1 H), 8.36 (t, *J*=2 Hz, 1 H), 8.00 (m, 4 H), 7.96 (t, *J*=2 Hz, 1 H), 3.93 (s, 3 H). ^{19}F NMR (376 MHz, DMSO-d_6) δ ppm: -62.39 (s).

***L*₃**. (Overall Yield: 75%, referred to 1H-imidazole) ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm: 9.90 (s, 1 H), 8.40 (t, *J*=2 Hz, 1 H), 8.20 (td, *J*=2 Hz, 8.8 Hz, 2 H), 8.00 (m, 3 H), 3.96 (s, 3

H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 137.95, 136.58, 134.43, 124.68, 122.49, 120.72, 117.76, 112.22, 36.31.

General procedures for neutral biscarbene iridium(III) complexes

A mixture of $[IrCl(COD)]_2$ (2 mmol) and NaOMe (9.2 mmol) in 2-ethoxyethanol (50 mL) was stirred for 3 hours at 40 °C. After cooling to room temperature, imidazolium-based carbene ligand precursor (***L***) (8 mmol) was added to the solution. The solution was stirred for another 24 hours at 140 °C. After cooling to room temperature, extra nonionic water was added to the solution and a large amount of precipitate appeared. After filtration and washing with nonionic water, the dichloro-bridged dimer ($[Ir(\boldsymbol{L})_2(\mu\text{–}Cl)]_2$) was obtained without further purification. The obtained $[Ir(\boldsymbol{L})_2(\mu\text{–}Cl)]_2$ was dissolved into 50 mL DMF, **pic** (4.2 mmol) and K_2CO_3 (42 mmol) were added, then the solution was stirred for 24 hours at 140 °C. The solvent was removed by roto-evaporation. The residue was chromatographied on a silica gel column with dichloromethane/methanol/triethylamine (various ratios based on the complex properties) as eluent to give the pure products.

1. (Overall Yield: 48%, referred to $[IrCl(COD)]_2$) ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm: 8.02 (t, *J*=1.6 Hz, 2 H), 1.93 (d, *J*=8.8 Hz, 1 H), 7.60 (dd, *J*=2.4 Hz, 8.4 Hz, 1 H), 7.38 (m, 3 H), 7.31 (m, 2 H), 6.79 (m, 2 H), 6.52 (m, 2 H), 6.31 (d, *J*=7.2 Hz, 1 H), 6.21 (d, *J*=7.2 Hz, 1 H), 3.76 (s, 3 H), 3.69 (s, 3 H), 3.01 (s, 3 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 173.83, 172.98, 171.81, 158.51, 147.70, 147.11, 144.64, 137.77, 137.66, 137.33, 132.90, 130.10, 127.97, 124.77, 124.31, 122.49, 122.32, 120.78, 120.66, 120.26, 115.65, 115.19, 111.41, 110.93, 55.89, 34.63, 34.16. TOF-MS: calculated $[M+Na]^+$ 680.1377, observed$[M+Na]^+$ 680.1348.

2. (Overall Yield: 42%, referred to $[IrCl(COD)]_2$) ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm: 8.20 (s, 2 H), 7.96 (d, *J*=8.4 Hz, 1 H), 7.67 (dd, *J*=2.4 Hz, 8.4 Hz, 1 H), 7.55 (m, 4 H), 7.27 (d, *J*=2.4 Hz, 1 H), 7.17 (m, 2 H), 6.49 (s, 1 H), 6.39 (s, 1 H), 3.78 (s, 3 H), 3.72 (s, 3 H), 3.05 (s, 3 H). ^{19}F NMR (376 MHz, DMSO-d_6) δ ppm: -61.46 (s), -61.54 (s). TOF-MS: calculated $[M+H]^+$ 794.1306, observed$[M+H]^+$ 794.1290.

3. (Overall Yield: 53%, referred to $[IrCl(COD)]_2$) ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm: 8.21 (t, *J*=2 Hz, 2 H), 7.96 (d, *J*= 8.8, 1 H), 7.68 (dd, *J*= 2.4 Hz, 8.8 Hz, 1 H), 7.55 (m, 4 H), 7.32 (m, 3 H), 6.51 (d, *J*= 2 Hz, 1 H), 6.34 (d, *J*=1.6 Hz, 1 H), 3.79 (s, 3 H), 3.73 (s, 3 H), 3.06 (s, 3 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 173.34, 172.42, 171.86, 158.81, 151.85, 151.40, 143.99, 139.81, 139.60, 137.96, 133.87, 131.18, 128.38, 126.76, 126.57, 123.97, 123.80, 121.07, 119.73, 119.53, 116.62, 116.10, 112.13, 111.73, 107.03, 106.69, 56.07, 34.78, 34.44. TOF-MS: calculated $[M+H]^+$ 708.1463, observed$[M+H]^+$ 708.1430.

General procedures for cationic biscarbene iridium (III) complexes

A mixture of $[Ir(\boldsymbol{L})_2(\mu\text{–}Cl)]_2$ and 2,2'-bipyridine (2.2 eq.) in CH_3OH/CH_2Cl_2 (50 mL, v:v=4:1) was stirred for 24 hours at boiling temperature. The solvent was removed by roto-evaporation. The pure products of cationic biscarbene iridium(III) complexes were

obtained by chromatography and re-crystallization.

4. (Overall Yield: 40%, referred to $[IrCl(COD)]_2$) ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm: 8.80 (d, J=8.0 Hz, 2 H), 8.20 (m, 2 H), 8.08 (m, 4 H), 7.60 (m, 2 H), 7.46 (dd, J=0.8 Hz, 7.6 Hz, 2 H), 7.36 (d, J=2.4 Hz, 2 H), 6.92 (m, 2 H), 6.68 (m, 2 H), 6.32 (dd, J=1.2 Hz, 7.2 Hz, 2 H), 2.93 (s, 6 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 169.53, 156.53, 150.99, 147.02, 138.75, 137.11, 134.28, 128.39, 126.11, 125.13, 123.59, 122.52, 116.10, 112.45, 34.88. TOF-MS: calculated $[M\text{-}Cl]^+$ 661.1819, observed$[M\text{-}Cl]^+$ 661.1799.

5. (Overall Yield: 33%, referred to $[IrCl(COD)]_2$) ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm: 8.86 (d, J=8.0 Hz, 2 H), 8.25 (m, 4 H), 8.00 (m, 2 H), 7.71 (d, J=8 Hz, 2 H), 7.64 (m, 2 H), 7.51 (d, J= 2 Hz, 2 H), 7.34 (m, 2 H), 6.46 (d, J=2 Hz, 2 H), 2.97 (s, 6 H). ^{19}F NMR (376 MHz, DMSO-d_6) δ ppm: -61.49 (s). T OF-MS: calculated $[M\text{-}Cl]^+$ 797.1567, observed$[M\text{-}Cl]^+$ 797.1545.

General experiments. ^{1}H, ^{13}C and ^{19}F NMR spectra were acquired on a VARIAN 400 MHz magnetic resonance spectrophotometer. The UV-Vis absorption spectra and PL spectra were obtained with a Perkin Elmer Lambda 25 UV-Vis spectrophotometer and a HITACHI F-4600 spectrofluorometer, respectively.

X-ray structure determination. A suitable crystal of complex **3** was mounted on a glass fiber and transferred to a Rigaku Mercury CCD area detector at 293 K. The structure was resolved and refined by full-matrix least-squares procedures based on F^2 using SHELXS-97 and SHELXL-97 programs, respectively. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were treated as idealized contributions.

Electrochemical measurements. The cyclic voltammetry (CV) was performed with a PARSTAT 2263 advanced electrochemical system, Princeton Applied Research. Anhydrous DMF was used as the solvent under nitrogen atmosphere and 0.1 mol/L of $TBAPF_6$ as the supporting electrolyte. A platinum wire (1 mm in diameter, the electrode area 0.785 mm^2) sealed in a PTFE rod was used as the working electrode. A piece of platinum wire and a piece of silver wire were used as counter electrode and quasi-reference electrode, respectively. The potentials were referred to ferrocene/ferrocenium (Fc/Fc^+) redox couple. The potential scan rate in all the experiments was kept at 100 mV s^{-1}.

DFT and TD-DFT calculations. The Gaussian 03 suite of programs[3] was used for DFT and TD-DFT calculations. The ground state optimization of the biscarbene iridium (III) complexes was performed using B3LYP density functional theory. The LANL2DZ basis set was selected to treat iridium atom and the 6-31G basis set for other atoms. The vertical excitation energies of the low-lying singlet and triplet excited states of **1-5** were obtained by TD-DFT calculations based on the ground-state geometry.

Cell culture. HeLa and A549 cells were cultured in Dulbecco's Modified Eagle Medium (DMEM, Hyclone) supplemented with 10% fetal bovine serum (FBS, Hyclone) and 1% penicillin/streptomycin (pen/strep, Hyclone) in 10 cm culture dishes (Fisher) at 37 °C in an

atmosphere containing 95% air and 5% CO_2 (v/v).

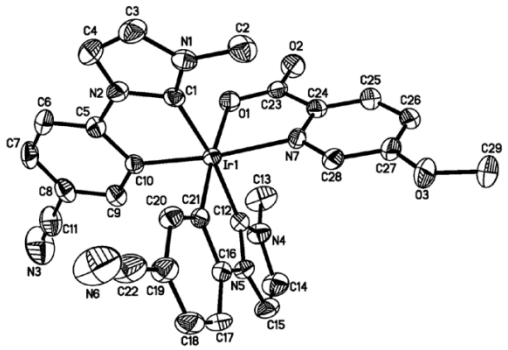
Cytotoxicity assay. The cytotoxicity of these biscarbene iridum(III) complexes was measured using the 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay in HeLa and A549 cell lines. Cells were seeded into a 96-well cell-culture plate at 10^4/well and incubated for 24 hours at 37 °C. The cells were washed three times with PBS and subsequently incubated with fresh DMEM containing various concentrations of iridium (III) complexes (in DMSO/culture medium, 1/99, v/v) for 24 hours at 37 °C. Then MTT (5 mg/ml, 20 μl/well) was added. After incubation for 4 hours, DMSO (150 μl/well) was added and incubated at 37 °C for 10 min. Finally, the absorbance of each sample at 490 nm was measured using a microplate reader (Perkin Elmer, Victor X4). The data represent the mean ± standard deviation of three independent experiments. Data were analyzed using SigmaPlot10.0 and SPSS16.0.

Lipophilicity. The lipophilicity (log $P_{o/w}$) was measured according to the literature method.[4] Equal amounts of *n*-octanol and phosphate-buffered saline (PBS) were thoroughly mixed on the oscillator for 24 hours. The mixture was then kept still for a further 24 hours, during which period of time the mutually saturated water and oil phases are separated. Excess amount of complexes **1-5** was individually dissolved in *n*-octanol saturated PBS. The iridium(III) saturated solutions were then centrifuged to yield clear solution (concentration denoted as C_o). The saturated solution was then mixed with an equal amount of *n*-octanol (saturated with PBS) and shaken on oscillator for another 24 hours. After separation, the final concentration of **1-5** in water phase as denoted as C_w. Both C_o and C_w were measured by emission spectra area from 380 to 700 nm at the excitation light of λ_{ex}=360 nm. The lipophilicity of **1-5** was calculated according to the equation: log $P_{o/w}$= log $[(C_o - C_w)/C_w]$.

Luminescence imaging. HeLa cells were seeded on 35 mm cell culture dishes with glass coverslips (22 mm) (FluoroDish, FD35-100) and incubated for 24 hours at 37 °C under a 5% CO_2 atmosphere. Then the culture medium was removed and fresh DMEM (with 1% pen/strep and 10% FBS) containing 20 μM iridium (III) complexes (in DMSO/culture medium, 1/99, v/v) was added to the cell culture dishes. After incubation for 2 hours at 37 °C, the medium containing the excess iridium (III) complexes was removed and the cells were washed gently with PBS (1 mL×3), which was followed by carrying out the imaging experiments on Nikon A1R confocal laser scanning microscope. Luminescence was collected at 570-620 nm for the HeLa cells incubated with **1** and **4** while 500-550 nm for **2**, **3** and **5** (excitation light: 403 nm laser).

Flow Cytometry. The same incubation procedure (described above for imaging) was used to prepare samples for flow cytometry. The cells were washed with PBS and trypsinized. The final volume of 1 mL of PBS solution was then ready for the cytometrical analyzed by a FACSCalibure flow cytometer (BD. Co., excitation at 375 nm). The emission was measured using a long-pass filter at 502 nm. 9000-10000 cells for each sample were analyzed.

A



B

Selected bond distances (Å)	
Ir1-C1$_{carbene}$	2.031(5)
Ir1-C10$_{phenyl}$	2.030(5)
Ir1-C21$_{phenyl}$	2.012(5)
Ir1-C12$_{carbene}$	2.033(5)
Ir1-N7	2.144(4)
Ir1-O1	2.144(3)
Selected bond angles (deg)	
C1-Ir1-C10	78.95(19)
C21-Ir1-C12	79.24(19)
O1-Ir1-N7	76.99(14)
C21-Ir1-C1	92.08(18)
C1-Ir1-C12	170.30(19)

Figure S1. The data of crystal structure of complex **3**. (A) ORTEP diagram, hydrogen atoms and solvents are omitted for clarity; (B) Selected bond distances (Å) and angles (deg).

Table S1. Crystallographic data of complex **3**.

	Complex **3**
empirical formula	C29 H22 Ir N7 O3,0.75(N C2 H3)
crystal system	Monoclinic
Space group	P 21/n
Crystal size (mm)	0.60×0.40×0.20
a, Å	9.3412(7)
b, Å	17.4760(13)
c, Å	17.6846(14)
α, deg	90
β, deg	91.040(2)
γ, deg	90
V, Å^3	2886.5(4)
Z	4
calculated density, mg/m^3	1.702
absorption coefficient, mm^{-1}	4.672
F(000)	1450
final R indices [I>2σ(i)]	0.0342
wR2 [I>2σ(i)]	0.0776
R1 (all data)	0.0389
wR2(all data)	0.0798
GOF on F^2	1.121

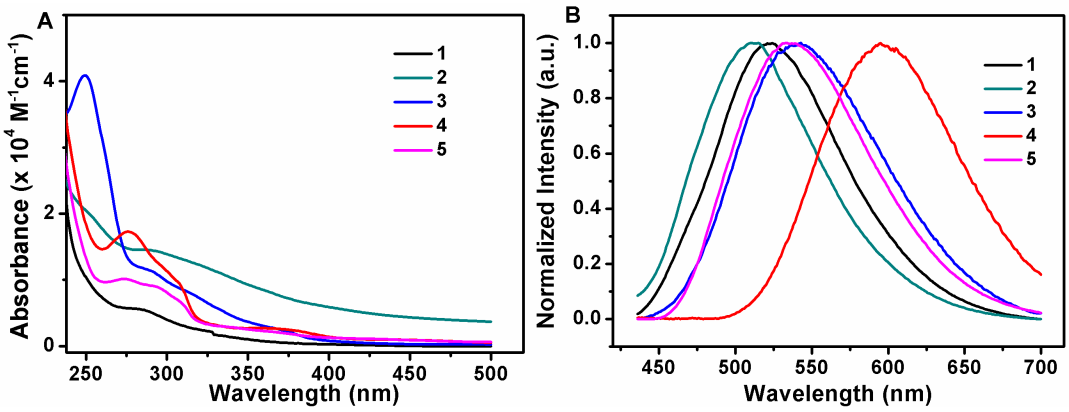


Figure S2. Absorption (A) and normalized emission (B) spectra of complexes **1-5** in DMSO/PBS solution (pH 7.4, 1/99, v/v). (40 μM for absorption and emission spectra.)

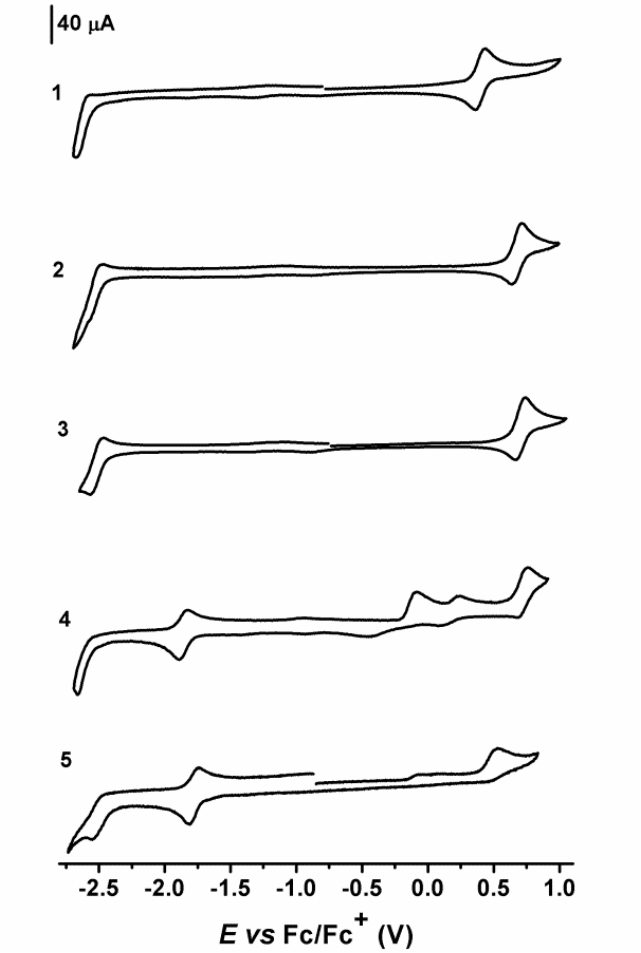


Figure S3. Cyclic voltammograms of complexes **1-5** in DMF with 0.1 M $TBAPF_6$. Concentration: 2 mM, scan rate: 100 mV/s.

Table S2. Photophysical and electrochemical properties of complexes **1-5**.

Complex/solvent		ε (10^3 M^{-1} cm^{-1})[a]	Emission[a]		Redox potentials[c]	
		max @ λ (nm)	λ_{max} (nm)	Φ[b]	E^{ox}(V)	E^{red}(V)
1	DMSO/PBS	(5.57@284, 2.27@325)	(523)	(0.1114)	0.43[d]	-2.60[e]
	CH_3CN	46.0@233, 14.8@282, 7.2@323	546	0.14		
2	DMSO/PBS	(19.77@253, 14.54@288, 8.61@358)	(511)	(0.0180)	0.71[d]	-2.55[e]
	CH_3CN	44.9@237, 14.0@286, 3.4@349	406, 422, 510	0.02		
3	DMSO/PBS	(40.87@249, 11.57@288, 7.96@315, 3.35@355)	(543)	(0.0090)	0.74[d]	-2.56[d]
	CH_3CN	53.7@247, 14.5@289, 3.8@355	514	0.02		
4	DMSO/PBS	(17.30@276, 12.89@293, 9.35@308, 2.64@367)	(595)	(0.0065)	0.75[e]	-1.89[d]
	CH_3CN	46.0@231, 40.1@241, 21.0@278, 10.5@306	600	0.04		-2.67[e]
5	DMSO/PBS	(10.14@273, 9.00@293, 6.57@309, 2.31@359)	(532)	(0.1087)	0.53[e]	-1.81[d]
	CH_3CN	26.8@232, 17.1@246, 11.1@274, 6.7@305	546	0.69		-2.54[e]

[a] Values in bracket are obtained in DMSO/PBS solution (pH 7.4, 1/99, v/v); [b] The quantum efficiencies were calculated by using *fac*-$Ir(ppy)_3$ (0.90)[5] and $Ru(bpy)_3Cl_2$ (Φ=0.028)[6] as references for acetonitrile (deaerated) and DMSO/PBS solutions, respectively; [c] Measured in DMF with complex concentration of 2 mM, all the potential values referenced to Fc/Fc^+; [d] reversible wave; [e] irreversible wave.

Table S3. Frontier orbitals of **1-5** obtained for the optimized structures of the ground state.

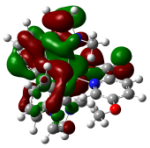
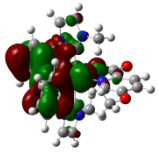
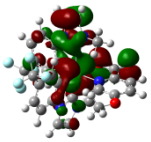
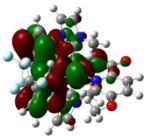
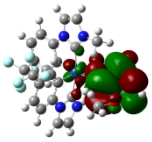
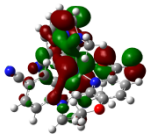
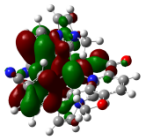
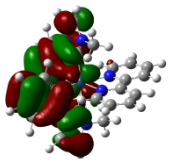
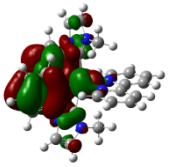
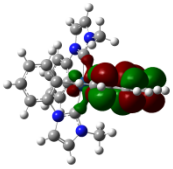
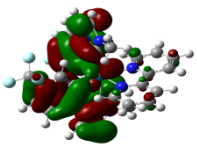
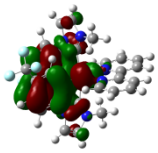
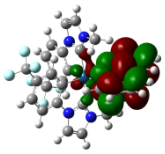
Complex	HOMO-1	HOMO	LUMO
1			
2			
3			
4			
5			

Table S4. Calculated transition wavelength, oscillator strength (*f*) and molecular orbitals involved in the lowest-energy transition of **1-5**

Complex	State	λ_{max} [nm]	*f*	Assignments
1	T_1	475.25	0	HOMO→LUMO(69.66%)
	S_1	436.77	0.0026	HOMO→LUMO(70.03%)
2	T_1	434.95	0	HOMO→LUMO(65.97%) HOMO-1→ LUMO(18.49%)
	S_1	409.81	0.0024	HOMO→LUMO(69.97%)
3	T_1	433.87	0	HOMO→LUMO(64.16%) HOMO-1→ LUMO(22.00%)
	S_1	429.08	0.0028	HOMO→LUMO(69.78%)
4	T_1	620.48	0	HOMO→LUMO(70.13%)
	S_1	615.27	0	HOMO→LUMO(70.09%)
5	T_1	560.24	0	HOMO→LUMO(69.78%)
	S_1	556.24	0	HOMO→LUMO(70.13%)

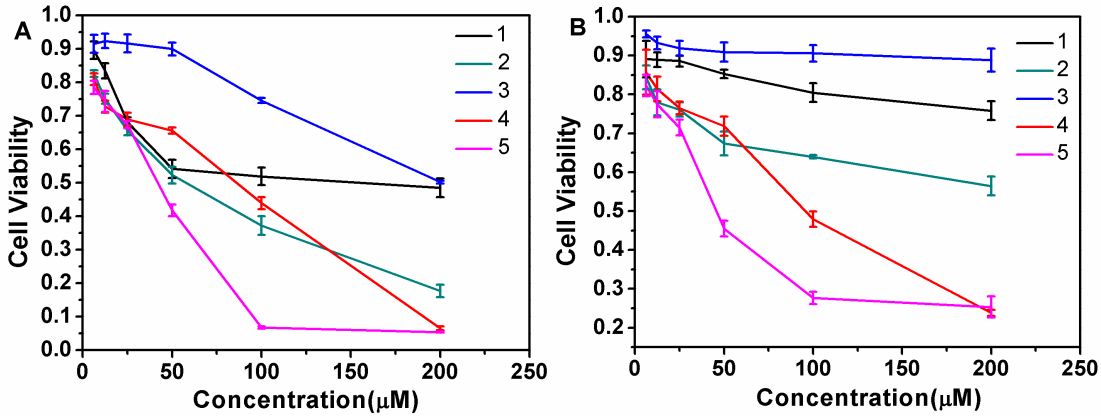


Figure S4. The cell viability values estimated by MTT assay versus incubation concentrations of complexes **1-5**. HeLa (A) and A549 (B) cell lines were cultured in the presence of 5-200 μM complexes at 37 °C for 24 hours. The data represent the mean ±standard deviation of three independent experiments.

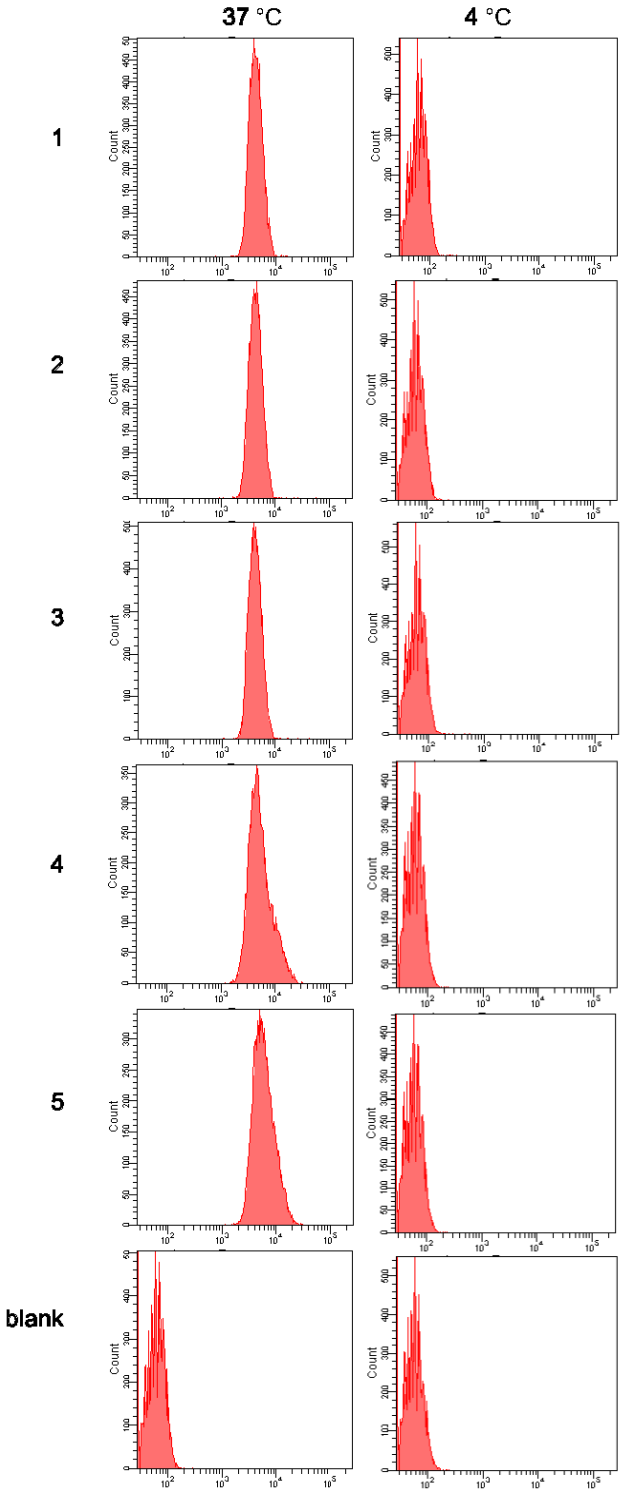


Figure S5. Flow cytometry results of HeLa cells incubated with blank medium and complexes **1**-**5**.

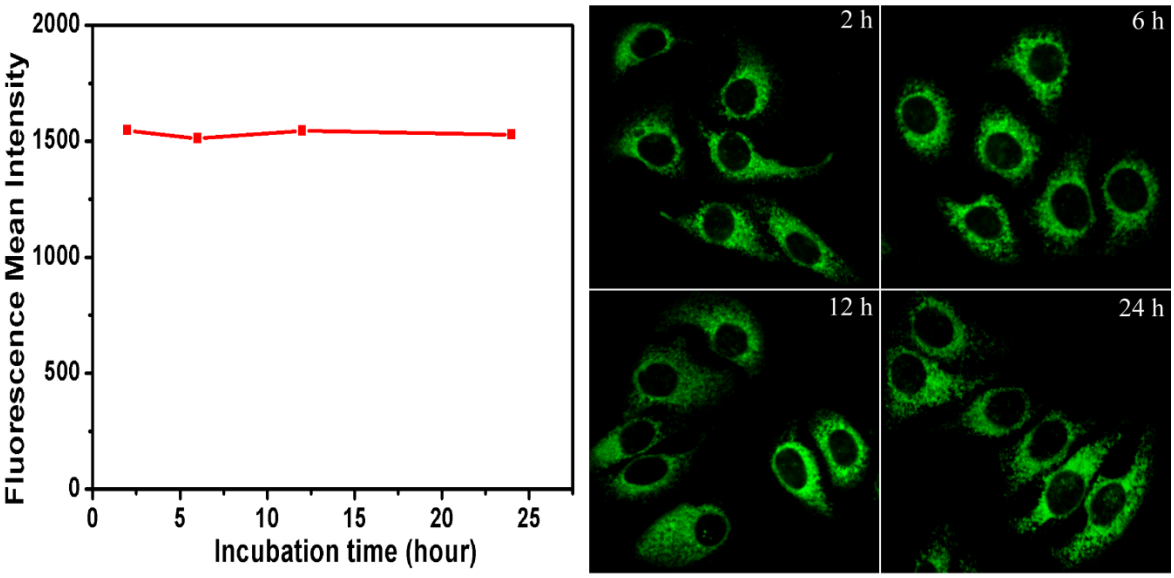


Figure S6. The stability study of complex **5** in HeLa cells. Left: the plot of the fluorescence mean intensity vs incubation time; right: fluorescence images of HeLa cells incubated with complex **5** for different incubation time at 37 °C. Note: The fluorescence intensity during the incubation time ranging from 2 hours to 24 hours remained unchanged within the experimental error, which demonstrated that these carbene iridium complexes are stable in the cells.

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