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Rubing Bai, Pei Wang, Xianwen Meng, Lei He

PII: S0143-7208(20)30831-7

DOI: https://doi.org/10.1016/j.dyepig.2020.108586

Reference: DYPI 108586

To appear in: Dyes and Pigments

Received Date: 2 April 2020

Revised Date: 25 May 2020

Accepted Date: 25 May 2020

Please cite this article as: Bai R, Wang P, Meng X, He L, Sky-blue-emitting cationic iridium complexes with oxadiazole/triazine-type counter-anions and their use for efficient solution-processed organic light-emitting diodes, *Dyes and Pigments* (2020), doi: https://doi.org/10.1016/j.dyepig.2020.108586.

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Author statement

Rubing Bai performed the measurements, analyzed the data and prepared the manuscript draft, Pei Wang synthesized the compounds, Xianwen Meng fabricated and characterized the devices, and Lei He conducted conceptualization, supervised the project and revised the manuscript.

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Sky-blue-emitting Cationic Iridium Complexes with Oxadiazole/Triazine-type Counter-anions and Their Use for Efficient Solution-processed Organic Light-emitting Diodes

Rubing Bai, Pei Wang, Xianwen Meng, and Lei He*

College of Chemistry, Key Laboratory of Pesticide and Chemical Biology of Ministry of Education, Hubei International Scientific and Technological Cooperation Base of

Pesticide and Green Synthesis, Central China Normal University, Wuhan 430079,

People's Republic of China.

E-mail: helei@mail.ccnu.edu.cn

Abstract

Counter-anion control has emerged as a facile approach to tune the properties of cationic iridium complexes for optoelectronic applications. Here we report cationic sky-blue-emitting iridium complexes with electron-deficient oxadiazole/triazine-type counter-anions and their use for highly efficient solution-processed organic light-emitting diodes (OLEDs). A sky-blue-emitting complex $[Ir(meoppy)_2(dmapzpy)]^+$ (meoppy is 4-methoxy-2-phenylpyridine and dmapzpy is 4-dimethylamino-2-(1*H*-pyrazol-1-yl)pyridine) has been developed as the phosphorescent cation. Hexafluorophosphate $(PF_{6}^{-}),$ 3,5-bis(5-(4-(tert-butyl)phenyl)-1,3,4-oxadiazol-2-yl)benzenesulfonate (OXD-7-SO₃⁻), 4-(4,6-diphenyl-1,3,5-triazin-2-yl)benzenesulfonate $(TRZ-p-SO_3^{-})$ and 3-(4,6-diphenyl-1,3,5-triazin-2-yl)benzenesulfonate $(TRZ-m-SO_3)$ have been

developed as the counter-anions in complexes R, 1, 2 and 3, respectively. In doped films, the complexes afford similar sky-blue emission peaked at around 472 nm with high phosphorescent efficiencies of around 0.80. Solution-processed, double-layer OLEDs using the complexes as dopants afford sky-blue electroluminescence peaked at around 476 nm. The devices using complexes 1-3 show largely enhanced performances compared to the device using the reference complex R, owing to the improved carrier-recombination balance imparted by the electron-trapping effects of the oxadiazole/triazine type counter-anions. The devices based on complexes 2 and 3 exhibit higher performances than that based on complex 1, because of the stronger electron-trapping effects of TRZ-p-SO₃⁻ and TRZ-m-SO₃⁻ compared to OXD-7-SO₃⁻. The double-layer device using complex 3 shows a peak current efficiency of 29.4 cd A⁻¹ and an external quantum efficiency of 12.4%, which are the highest for blue OLEDs using cationic iridium complexes reported so far.

Key words: iridium complex; cationic; counter anion; phosphorescence; organic light emitting diode

1. Introduction

Phosphorescent cationic iridium complexes have been extensively researched in the past decades, because of their attractive features such as easy preparation, high phosphorescent efficiencies at room temperature, tunable emission color across the entire visible spectrum, rich electrochemical properties, and good solubility in polar solvents. They have been widely applied as functional agents in biological imaging or sensing [1, 2], photo-catalysis [3], and light emitting devices [4-6]. In particular, they have been demonstrated to be suitable dopants for solution-processed organic light-emitting diodes (OLEDs) [4, 7-26], which, with high performances and low fabrication cost, have emerged as promising devices for display or lighting applications [27, 28].

Phosphorescent cationic iridium complexes have a general form of $[Ir(C^{\wedge}N)_2(N^{\wedge}N)]^+A^-$, with $[Ir(C^{\wedge}N)_2(N^{\wedge}N)]^+$ as the phosphorescent cation $(C^{\wedge}N)^+$ is the cyclometalating ligand and N^{\wedge}N is the ancillary ligand) and A⁻ as the counter-anion $(A^{-} is usually PF_{6})$ [29]. In the past decade, huge efforts have been devoted to tuning the emission properties of $[Ir(C^{\wedge}N)_2(N^{\wedge}N)]^+$ through judicious control of both $C^{\wedge}N$ and N[^]N ligands [4, 6-16, 18, 21-24, 26], but only limited attention has been paid to A⁻ [17, 19, 20, 25, 30-32]. The PF_6^- anion is electrochemically and thermally stable but it does not afford any optoelectronic properties such as light-emitting or carrier-transporting properties. Moreover, when the complexes are used as dopants in OLEDs, the small PF_6^- anions migrate and redistribute within the emissive layer under an external electrical field, which is undesired for the operation of OLED device. Bulky anions. such tetraphenylborate fluorine as and its or trifluoromethyl-substituted derivatives [5, 30], have been employed as counter-anions in cationic iridium complexes, which successfully enhance the volatility of the complexes for vacuum-evaporation devices. These bulky anions however are still optoelectronically inactive, which cannot largely enhance the performances of the complexes in OLEDs.

In cationic iridium complexes, $[Ir(C^N)_2(N^N)]^+$ and A⁻ are closely bound together by strong coulombic attraction between them. Therefore, they are in close proximity yet can be independently tuned, which opens an avenue to tune the overall optoelectronic property of the complex through counter-anion control [33, 34]. For OLEDs, the performances are determined by carrier transport/recombination balance in the emissive layers, which is largely affected by carrier-trapping/transporting on the dopants [35-38]. Therefore, rendering the counter-anions of cationic iridium complexes with carrier-trapping/transporting properties represents a facile approach to tune the carrier transport/recombination balance in OLEDs using the complexes as dopants [20, 25, 32]. To this end, suitable carrier trapping/transporting counter-anions need to be developed. Because blue-emitting cationic iridium complexes have shown much lower performances than green, yellow and orange-red-emitting ones in OLEDs [4, 5], carrier-trapping/transporting counter-anions with high triplet energies (*E*_T) suitable for blue-emitting complexes are in demand.

Here we report electron-deficient oxadiazole/triazine-type counter-anions for sky-blue-emitting cationic iridium complexes and the use of the complexes in solution-processed OLEDs. A highly efficient, fluorine-free, sky-blue-emitting cationic iridium complex, $[Ir(meoppy)_2(dmapzpy)]^+$, has been developed as the phosphorescent cation (meoppy is 4-methoxy-2-phenylpyridine and dmapzpy is 4-dimethylamino-2-(1*H*-pyrazol-1-yl)pyridine) (Chart 1). Previously reported 3,5-bis(5-(4-(tert-butyl)phenyl)-1,3,4-oxadiazol-2-yl)benzenesulfonate (OXD-7-SO₃⁻) ($E_T = 2.7$ eV) has been used as the counter-anion for complex 1 [20]. Two

4-(4,6-diphenyl-1,3,5-triazin-2-yl)benzenesulfonate triazine-type anions. (TRZ-p-SO₃⁻) and 3-(4,6-diphenyl-1,3,5-triazin-2-yl)benzenesulfonate (TRZ-m-SO₃⁻) $(E_{\rm T} = 3.0 \text{ eV})$, have been developed as counter-anions for complexes 2 and 3, respectively (Chart 1). The high triplet energies of these counter-anions prevent back energy-transfer from the phosphorescent cation to the counter-anion, which helps to maintain high luminescent efficiencies of the complexes. For comparison, $[Ir(meoppy)_2(dmapzpy)]^+PF_6^-$ (complex R) has also been prepared. In solution and thin films, the complexes afford similar sky-blue emission peaked at 472 nm. Varying the counter-anion does not alter the emission characteristics of $[Ir(meoppy)_2(dmapzpy)]^+$. energy-transfer efficient from An occurs the oxadiazole/triazine-type counter-anions to $[Ir(meoppy)_2(dmapzpy)]^+$ in doped films. Electrochemical measurements have revealed that the two triazine-based anions show stronger electron-accepting capability than OXD-7-SO₃⁻. Solution-processed, double-layer OLEDs using the complexes as dopants afford similar sky-blue electroluminescence (EL) with an emission peak at 476 nm. Nevertheless, the devices using complexes 1-3 as dopants show largely enhanced performances compared to the reference device using complex R, owing to the electron-trapping effects of the oxadiazole/triazine-type anions that improve the carrier-recombination balance. In particular, the device using complex 3 with a triazine-based counter-anion shows the highest performance, affording a peak current efficiency of 29.4 cd A⁻¹ and an external quantum efficiency (EQE) of 12.4%, which is the highest for blue OLEDs (including solution-processed and vacuum-evaporated devices) based on cationic



iridium complexes reported so far [8, 16, 21, 23, 24, 26, 30, 39-44].

Chart 1. Chemical structures of the counter-anions and the complexes.

2. Results and Discussion

2.1. Synthesis and structural characterizations



Scheme 1. Synthesis of TRZ-p-SO₃Na and TRZ-m-SO₃Na.



Scheme 2. Synthesis of complexes R and 1-3.

Scheme 1 outlines the synthetic routes to TRZ-p-SO₃Na and TRZ-m-SO₃Na. OXD-7-SO₃Na was prepared according a reported procedure to [20]. 1,3-bis(5-(4-(tert-butyl)phenyl)-1,3,4-oxadiazol-2-yl)benzene (OXD-7) and 2,4,6-triphenyl-1,3,5-triazine (TRZ) were selected as the cores of the counter-anions because of their electron-deficiency for trapping or transporting electrons and high triplet energies (2.7 and 3.0 eV, respectively) [45-47]. The synthesis of TRZ-p-SO₃Na and TRZ-m-SO₃Na started from bromine substituted benzenesulfonyl chloride, which, upon esterification with neopentyl alcohol, palladium catalyzed boronation reaction and palladium catalyzed C-C coupling reaction, leads to the triazine-based neopentyl benzenesulfonate (TRZ-p-NeOSO₂ and TRZ-m-NeOSO₂). TRZ-p-SO₃Na and TRZ-m-SO₃Na were then readily prepared by iodolysis of TRZ-p-NeOSO₂ and

TRZ-m-NeOSO₂ in acetone, respectively, in the presence of NaI. TRZ-p-SO₃Na and TRZ-m-SO₃Na were isolated from the reaction mixture by filtration with high yields (>90%) and high purity.

Scheme 2 outlines the synthetic the complexes. Here routes to 4-methoxyl-2-phenylpyridine (meoppy) was selected as the cyclometalating ligand, because fluorine-free meoppy with a high-triplet energy is a suitable candidate for constructing blue-emitting cationic iridium complexes [24, 48]; 4-dimethylamino-2-(1H-pyrazol-1-yl)pyridine (dmapzpy) was employed as the ancillary ligand to ensure the generation of efficient blue emission from the meoppy-centered triplet state [24, 49]. The $[Ir(meoppy)_2(dmapzpy)]^+$ cation was readily prepared by cleaving the chloro-bridged iridium dimer [Ir(meoppy)₂Cl]₂ with dmapzpy. Complexes R and 1-3 were then readily prepared by anion-exchange reactions between $[Ir(meoppy)_2(dmapzpy)]^+Cl^-$ and NH_4PF_6 , OXD-7-SO₃Na, TRZ-p-SO₃Na or TRZ-m-SO₃Na in CH₃OH/H₂O solution. The complexes were purified by column chromatography or recrystallization and their structures were characterized by NMR spectroscopy, high-resolution mass spectrometry and elemental analysis.

2.2. Photophysical characterizations



Figure 1. Absorption and/or PL spectra of a) OXD-7-SO₃Na, TRZ-p-SO₃Na and TRZ-m-SO₃Na in CH₃OH solution and b) complexes R and 1-3 in CH₃CN solution. The PL spectra of the complexes were measured under excitation at 380 nm. TRZ-p-SO₃Na and TRZ-m-SO₃Na afforded no PL spectra because they were non-emissive in the solution.

Table 1. Photophysical and electrochemical data of complexes R and 1-3.

Absorption	PL in CH ₃ CN ^b			PL i	PL in PMMA film ^c			Electrochemical	
λ [nm]							Da	nta ^d	
(ε [×10 ⁴	λ	$\Phi_{\rm p}$	k _r , k _{nr}	λ	$\Phi_{\rm p}$	k _r , k _{nr}	Eox	E _{red}	
$M^{-1} cm^{-1}])^{a}$	[nm]	(τ [μs])	$[10^5 \text{ s}^{-1}]$	[nm]	(τ [μs])	$[10^5 \text{ s}^{-1}]$	[V]	[V]	

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R	260 (5.45), 380 (0.53), 410 (0.27)	472, 496	0.28 (1.50)	1.9, 4.8	470, 497	0.80 (2.43)	3.3, 0.8	0.75 ^{qr}	-2.52 ^{ir}
1	269 (8.45), 379 (0.54), 412 (0.26)	473, 497	0.28 (1.39)	2.0, 5.2	471, 499	0.82 (2.51)	3.3, 0.7	0.72 ^{qr}	-2.36, ^r -2.55 ^{ir}
2	259 (7.16), 380 (0.56), 411 (0.29)	472, 496	0.25 (1.44)	1.7, 5.2	471, 499	0.79 (2.38)	3.3, 0.9	0.73 ^{qr}	-2.09, ^r -2.53 ^{ir}
3	264 (8.67), 380 (0.55), 409 (0.30)	472, 496	0.23 (1.25)	1.8, 6.2	471, 499	0.80 (2.38)	3.4, 0.8	0.72 ^{qr}	-2.13, ^r -2.57 ^{ir}

^a In CH₃CN solution (10⁻⁵ M). ϵ denotes molar extinction coefficient. ^b In degassed CH₃CN (10⁻⁵ M) solution. ^c 2 wt.% doped PMMA films on quartz substrates. ^d Potentials were quoted versus Fc⁺/Fc (Fc is ferrocene); r, qr and ir denote reversible, quasi-reversible and irreversible processes, respectively; for irreversible processes, onset potentials were quoted.

Fig.1a depicts the absorption and/or PL spectra of TRZ-p-SO₃Na and TRZ-m-SO₃Na in CH₃OH solution. For comparison, those of OXD-7-SO₃Na were also shown [20]. TRZ-p-SO₃Na and TRZ-m-SO₃Na exhibit strong absorption bands in the ultra-violet region with the absorption onsets at around 320 nm, which correspond to the absorption from the 2,4,6-triphenyl-1,3,5-triazine core. From the absorption onsets, the optical bandgaps of TRZ-p-SO₃Na and TRZ-m-SO₃Na were calculated at 3.9 eV, which are larger than that (3.7 eV) of OXD-7-SO₃Na. While OXD-7-SO₃Na are almost non-emissive in CH₃OH solution.

Fig. 1b shows the absorption and photoluminescence (PL) spectra of complexes R and 1-3 in CH₃CN solution and Table 1 compiles detailed photophysical

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characteristics. Complex R exhibits strong absorption bands in the ultra-violet region below 350 nm, which are ascribed to ligand-centered ${}^{1}\pi$ - π^{*} transitions in [Ir(meoppy)₂(dmapzpy)]⁺, and weak absorption bands that extend to the visible region, which are assigned to metal-to-ligand charge-transfer (1 MLCT), ligand-to-ligand charge-transfer (1 LLCT), 3 MLCT, 3 LLCT and ligand-centered ${}^{3}\pi$ - π^{*} transitions [50-52]. The strong spin-orbital coupling on the heavy iridium atom makes the spin-forbidden triplet transitions partially permitted [50, 51]. As shown in Fig. 1b, complexes 1-3 show almost the same weak absorption bands above 350 nm, which should come from the [Ir(meoppy)₂(dmapzpy)]⁺ cation. Complexes 1-3 show much stronger absorption bands than complex R below 350 nm in the ultra-violet region, which should result from the superposition of absorption of [Ir(meoppy)₂(dmapzpy)]⁺ and the counter-anion.

As shown in Fig. 1b, complexes R shows sky-blue emission peaked at 472 and 496 nm in degassed CH₃CN solution. The structured emission spectrum indicates that the emissive excited-state contains notable ligand-centered ${}^{1}\pi$ - π * character. The sky-blue emission from complex R is very similar to that afforded by an analogous complex [Ir(buoppy)₂(dmapzpy)]PF₆ (buoppy is 4-butoxy-2-phenylpyridine) [24], of which the emission has been assigned to the ${}^{3}MLCT$ (Ir \rightarrow buoppy)/ ${}^{3}\pi$ - π * (buoppy-centered) state. Because the only difference between complex R and [Ir(buoppy)₂(dmapzpy)]PF₆ is the length of alkyl chain anchored to the cyclometalating ligand, the emission of complex R should have similar excited-state character to [Ir(buoppy)₂(dmapzpy)]PF₆, *i.e.*, its emission should arise from the

³MLCT (Ir \rightarrow meoppy)/ ³ π - π * (meoppy-centered) state. The use of highly electron-rich dmapzpy ancillary ligand ensures the generation of highly efficient sky-blue emission from the cyclometalating ligand with a high ³ π - π * triplet energy such as buoppy and meoppy [24, 48]. In degassed CH₃CN solution, complex R affords a luminescent efficiency (Φ) of 0.28 and an excited-state lifetime (τ) of 1.50 µs, from which the radiative (k_r) and non-radiative (k_{nr}) decay rates were calculated at $1.9 \times 10^5 \text{ s}^{-1}$ and $4.8 \times 10^5 \text{ s}^{-1}$, respectively.

In degassed CH₃CN solution, complexes 1-3 show almost identical PL spectra to complex R, when only the $[Ir(meoppy)_2(dmapzpy)]^+$ cation is excited at the excitation wavelength of 380 nm. Moreover, complexes 1-3 also afford similar experimental Φ (0.23-0.28) and τ (1.25-1.44 µs) and calculated k_r (1.7-2.0×10⁵ s⁻¹) and k_{nr} $(5.2-6.2\times10^5 \text{ s}^{-1})$ values to complex R (Table 1). These results indicate that the oxadiazole/triazine type counter anions do not largely affect the emission of $[Ir(meoppy)_2(dmapzpy)]^+$ in solution. At the excitation of 300 nm where both the $[Ir(meoppy)_2(dmapzpy)]^+$ cation and the counter-anion were excited, complex 1 exhibits ultraviolet emission peaked at 352 nm from the OXD-7-SO₃⁻ anion and sky-blue emission from the $[Ir(meoppy)_2(dmapzpy)]^+$ cation (Fig. S1a), which indicates incomplete OXD-7-SO₃⁻ an energy transfer from to $[Ir(meoppy)_2(dmapzpy)]^+$, because of the fluctuation of distance between them in fluid solution. At the excitation of 300 nm, complexes 2 and 3 only show sky-blue emission from [Ir(meoppy)₂(dmapzpy)]⁺ (Fig. S1b and c), because the triazine-based counter-anions are nearly non-emissive.

The emission properties of complexes R and 1-3 were also measured in the 2 wt.% doped poly(methylmethacrylate) PMMA films. Fig. S2 depicts the PL spectra in the doped films and detailed emission characteristics were summarized in Table 1. In the doped film, complex R affords sky-blue emission peaked at 472 and 496 nm (Fig. S2a), with a high Φ value of 0.80 and a τ value of 2.43 µs at the excitation of 380 nm. The k_r and k_{nr} values were calculated at 3.3×10^5 and 8×10^4 s⁻¹, respectively. The remarkable increase of Φ in going from solution to doped film largely results from the suppressed non-radiative deactivation in the rigid solid film. In the doped films, complexes 1-3 show almost identical sky-blue emission to complex R (Fig. S2b-d), with emission peaks at around 472 and 496 nm at the excitation of 380 nm. Moreover, complexes 1-3 show very similar experimental Φ (0.79–0.82) and τ (2.38–2.51 µs) and calculated k_r (3.3–3.4×10⁵ s⁻¹) and k_{nr} (7–9×10⁴ s⁻¹) values to complex R (Table 1). It is thus further confirmed that the electron-deficient oxadiazole/triazine type counter-anions do not largely disturb the emission of $[Ir(meoppy)_2(dmapzpy)]^+$. The similar photophysical properties of complexes 2 and 3 indicate that varying the position (para- or meta-) of the sulfonate group on the 2,4,6-triphenyl-1,3,5-triazine core does not largely affect the interaction between the phosphorescent cation and the counter-anion. The high Φ values indicate that the counter-anions do not quench the phosphorescence from the $[Ir(meoppy)_2(dmapzpy)]^+$ cation, because of their high triplet energies that prevent back energy-transfer [53].

At the excitation of 300 nm where both cation and counter-anion are excited, complex 1 exhibits predominant sky-blue emission from the $[Ir(meoppy)_2(dmapzpy)]^+$

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cation and negligible emission from the OXD-7-SO₃⁻ anion (Fig. S2b), which indicates complete energy-transfer $OXD-7-SO_3^$ almost from an to $[Ir(meoppy)_2(dmapzpy)]^+$ within the single complex in the highly diluted film. The efficient energy-transfer indicates that $OXD-7-SO_3^-$ and $[Ir(meoppy)_2(dmapzpy)]^+$ are located quite close to each other in the rigid film owing to the strong coulombic attraction between them. The close proximity between the cation and electron-trapping/transporting counter-anion benefits the use of the complexes in light-emitting devices. At the excitation of 300 nm, complexes 2 and 3 also show dominant sky-blue emission from the [Ir(meoppy)₂(dmapzpy)]⁺ cation. The emission from the triazine-based counter-anions were not observed because of their non-emissive characteristics.



2.3. Electrochemical measurements



Figure 2. Cyclic voltammograms of a) OXD-7-SO₃Na, TRZ-p-SO₃Na and TRZ-m-SO₃Na and b) complexes R and 1-3 in *N*,*N*-dimethylformamide (DMF) solution.

The electrochemical properties of the counter-anions and the complexes were characterized by cyclic voltammetry in solution. Fig. 2a shows the cyclic voltammograms of TRZ-p-SO₃Na and TRZ-m-SO₃Na. For comparison, the cyclic voltammogram of OXD-7-SO₃Na was also shown [20]. In DMF solution, TRZ-p-SO₃Na and TRZ-m-SO₃Na both show reversible reduction processes (Fig. 2a), with the reduction potentials at -2.05 and -2.09 V, respectively. The reversible reductions indicate that TRZ-p-SO₃⁻ and TRZ-m-SO₃⁻ have good electrochemical stability for accepting electrons. The reduction potentials of TRZ-p-SO₃Na and TRZ-m-SO₃Na are anodically shifted compared to that (-2.15 V) of OXD-7-SO₃Na, which indicates that the triazine-type counter-anions are more electron-deficient than the oxadiazole-type counter-anion. From the reduction potentials, the LUMO levels of

TRZ-p-SO₃⁻ and TRZ-m-SO₃⁻ were calculated at around -2.8 eV, which lie lower than that (-2.7 eV) of OXD-7-SO₃⁻, indicating that TRZ-p-SO₃⁻ and TRZ-m-SO₃⁻ have stronger electron-trapping capability than OXD-7-SO₃⁻.

Fig. 2b shows the cyclic voltammograms of the complexes. In DMF solution, complex R exhibits a quasi-reversible oxidation, with the oxidation potential at around 0.72 V, and an irreversible reduction with the onset reduction potential at around -2.52 V (Fig. 2b). Complexes 1-3 show similar quasi-reversible oxidations and irreversible reductions to complex R (Fig. 2b), which occur on the $[Ir(meoppy)_2(dmapzpy)]^+$ cation. As shown in Fig. 2b, complexes 1-3 also show reversible reductions that correspond to the reductions of counter-anions.



Figure 3. EL spectra of OLEDs based complexes R and 1-3. Inset shows the device structure.

Solution-processed OLEDs with complexes R and 1-3 as dopants were fabricated.

The device structure is indium-tin-oxide (ITO) /PEDOT: PSS (40 nm)/26DCzPPy: x % complex (50 nm)/TmPyPB (40 nm)/LiF (1 nm)/Al (100 nm) (Inset in Fig. 3), with poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) as the anode buffer layer, 2,6-bis(3-(carbazol-9-yl)phenyl)pyridine (26DCzPPy) as the host for the complex in the emissive layer and 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB) as the electron-transporting/hole-blocking layer. The emissive layer was deposited from a solution-process. The doping concentrations of complexes R and 1-3 in the emissive layers were set at 10 wt.%, 13 wt.%, 13 wt.% and 15 wt.%, respectively. The doping concentrations of [Ir(meoppy)₂(dmapzpy)]⁺ in the emissive layers were all at 8.5 wt.%.

Fig. 3 depicts the EL spectra of OLEDs. The devices all showed sky-blue emission with the emission peak at around 476 nm and Commission Internationale de L'Eclairage (CIE) coordinates at around (0.18, 0.42). The EL arose from the $[Ir(meoppy)_2(dmapzpy)]^+$ cation and the counter-anions and the host did not contribute to the emission. The PL spectra of the emissive layers show dominant emission from the $[Ir(meoppy)_2(dmapzpy)]^+$ cation and very weak ultra-violet emission from the counter-anions or the host (Fig. S3), which indicates almost complete energy-transfer from the counter-anions and the host to the $[Ir(meoppy)_2(dmapzpy)]^+$ cation.



Figure 4. Current-density and brightness versus voltage curves for OLEDs based on complexes R and 1-3.

	V	n	FOF	R	ΕL λ	CIE
	• on	Ic,max	LQL _{max}	$D_{\rm max}$		CIL
	$(V)^{a}$	$(\operatorname{cd} \operatorname{A}^{-1})^{b}$	(%) ^c	$(cd m^{-2})^{d}$	(nm)	(x,y)
R	4.0	24.0	9.9	5400	476, 506	(0.18, 0.42)
1	4.1	26.2	11.0	5600	476, 504	(0.18, 0.42)
2	4.2	29.2	12.3	7100	476, 504	(0.17, 0.42)
3	4.2	29.4	12.4	8500	476, 504	(0.17, 0.42)

Table 2. Summary of performances for OLEDs based on complexes R and 1-3.

^a Voltage to reach 1 cd m2. ^b Maximum current efficiency. ^c Maximum external quantum efficiency. ^d Maximum brightness.

Fig. 4 depicts the current-density and brightness versus voltage curves of the OLEDs and Table 2 summarizes the performances of OLEDs. The devices based on complexes 1-3 showed lower current-density than the devices based on complex R, which implies that complexes 1-3 behave as stronger charge-trappers than complex R [35]. From the energy-level diagrams of the OLEDs (Fig. S4), the $[Ir(meoppy)_2(dmapzpy)]^+$ cation behaves as a hole trapper in the emissive layer because of its shallower highest occupied molecular orbital (HOMO) level than that

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of the host. The three electron-deficient counter-anions, with deeper lowest unoccupied molecular orbital (LUMO) levels than that of the host, behave as strong electron-trappers, when the counter-anions cannot form electron-transporting channels within the emissive layers at low doping levels (4.5-6.5 wt.%) [7, 35]. The lowered current densities for the devices based on complexes 1-3 compared to the device based on complex R agree with the electron-trapping effects of the oxadiazole/triazine type counter-anions. The slightly higher turn-on voltages for the devices based on complexes 1-3 compared to the device based on complex R also consist with the electron-trapping effects of the oxadiazole/triazine type counter-anions in the emissive layers [7]. It is noted that the device based on complex 2 showed lower current density then the device based on complex 3, which implies that TRZ-p-SO₃⁻ has a stronger electron-trapping effect than TRZ-m-SO₃⁻. It is thus suggested that changing the anchoring position of sulfonate at the phenyl ring (meta- or para-position with triazine) electron-trapping capability respect to the tunes the of the 2,4,6-triphenyl-1,3,5-triazine core. Substitution of sulfonate at the *para* position exerts a stronger electron-withdrawing inductive effect to the triazine as compared to substitution at the *meta* position, which partially explains the stronger electron-trapping effect of TRZ-p-SO₃⁻.

As shown in Table 2, the device based on complex R afforded a peak current efficiency of 24 cd A^{-1} and a peak EQE of 9.9%. The devices based on complexes 1-3 showed largely enhanced performances, with peak current efficiency/EQE of 26.2 cd $A^{-1}/11\%$, 29.2 cd $A^{-1}/12\%$ and 29.4 cd $A^{-1}/12.4\%$, respectively. The higher device

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performances for the devices based on complexes 1-3 indicate improved carrier recombination balance in the emissive layers, which can be ascribed to more balanced electron/hole transport and facilitated direct electron-hole recombination on the complexes imparted by the electron-trapping effects of the counter-anions in complexes 1-3. Similar effects have been observed in neutral iridium complexes carrying electron-trapping oxadiazole or triazole type units [54, 55]. The devices based on complexes 2 and 3 showed higher performances than complex 1, which indicates that the triazine type counter-anions can improve the device performances to a larger extent owing their stronger electron-trapping effects than the oxadiazole type counter-anion. It is worth noting that the device based complex 3 is the most efficient blue OLED using cationic iridium complexes as dopants reported so far (Table S1) [8, 16, 21, 23, 24, 26, 30, 39-44]. The devices showed decreased efficiencies at high brightness (Fig. S5), owing the triplet-triplet or triplet-polaron quenching at high current densities [56, 57]. The devices based on complexes 2 and 3 still showed high current efficiencies of 27.0 and 27.2 cd A^{-1} , respectively, at a practically high brightness of 1000 cd m⁻².

3. Conclusion

Sky-blue-emitting cationic iridium complexes with electron-deficient oxadiazole/triazine type counter-anions, $[Ir(meoppy)_2(dmapzpy)]^+[OXD-7-SO_3^-]$ (1), $[Ir(meoppy)_2(dmapzpy)]^+[TRZ-p-SO_3^-]$ (2) and $[Ir(meoppy)_2(dmapzpy)]^+[TRZ-m-SO_3^-]$ (3), have been designed and synthesized.

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The counter-anions were found not to affect the emission of the phosphorescent $[Ir(meoppy)_2(dmapzpy)]^+$ cation and in films, they transferred efficiently the energy to the $[Ir(meoppy)_2(dmapzpy)]^+$ cation. When the complexes were used as dopants in solution-processed OLEDs, the counter-anions behaved as electron-trappers which improved the carrier-recombination balance in the emissive layers, leading to largely enhanced device performances compared to the reference complex with a PF₆⁻ counter-anion. The sky-blue device using complex 3 showed a peak EQE of 12.4%, which is the highest for blue OLEDs using cationic iridium complexes as dopants reported so far. The work has revealed that the oxadiazole/triazine type anions with high triplet energy and electron-trapping effects are promising counter-anions for blue-emitting cationic iridium complexes for advanced optoelectronic applications. In particular, the triazine-type anions with high-triplet energy of 3.0 eV can be suitable counter-anions for deep blue-emitting cationic iridium complexes.

4. Experimental Section

General information. High-resolution mass spectrometry, NMR spectra and elemental analysis were measured on a BRUKER 400/500 NMR spectrometer, a LTQ-ORBITRAP-ETD mass spectrometer and an EA3000 elemental analyzer, respectively. PL and absorption spectra were recorded on a Macy UV-1800 UV-vis spectrophotometer and a Gangdong F-320 fluorospectrophotometer, respectively. PL transient lifetimes and photoluminescent efficiencies in thin films were measured with a transient spectrofluorometer equipped with an integrating sphere (Edinburgh

Instruments, FLS1000). The photoluminescent efficiencies in degassed solution were measured versus quinine sulfate ($\Phi_p = 0.545$ in 1 M H₂SO₄). Cyclic voltammetry was performed in degassed solution (10^{-3} M) at a scan rate of 100 mV s⁻¹ with a LK1100 voltammetric analyzer. A glass-carbon working electrode, a silver-wire pseudo-reference electrode and a platinum-wire counter-electrode were used for the measurements. The supporting electrolyte and the internal standard were tetrabutylammonium hexafluorophosphate (0.1 M) and ferrocene, respectively.

Materials. All reactants and solvents were purchased from commercial sources and used as received. $[Ir(meoppy)_2Cl]_2$ was synthesized by reacting 4-methoxyl-2-phenylpyridine (meoppy) with $IrCl_3.nH_2O$ in refluxed 2-ethoxyethanol: H_2O (3: 1) under nitrogen atmosphere according to reported procedures [58, 59]. 4-dimethylamino-2-(1*H*-pyrazol-1-yl)pyridine (dmapzpy) was prepared according to a reported procedure [24].

Synthesis of neopentyl 4-bromobenzenesulfonate (Br-Ph-p-NeOSO₂). 4-bromobenzene-1-sulfonyl chloride (5.1 g, 20 mmol) was dissolved in 1,2-dichloroethane (15 mL) and the solution was cooled in an ice bath. To the solution, pyridine (3.1 g, 40 mmol) and 2,2-dimethyl-1-propanol (2.2 g, 25 mmol) dissolved in 1,2-dichloroethane (15 mL) were added dropwise under a nitrogen atmosphere. The mixture was stirred at room temperature for 12 h and then diethyl ether was added. The mixture was filtered. The filtrate was washed with HCl solution and water and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum and the solid was recrystallized from ethanol, affording a white solid (3.8 g, 12.4 mmol). Yield: 62%. ¹H NMR (500 MHz, CDCl₃, δ[ppm]): 7.77 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 3.69 (s, 2H), 0.91 (s, 9H). HRMS (ESI, m/z): 307.0007 [M+H]⁺ (calc. 306.9998).

4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) **Synthesis** neopentyl of benzenesulfonate (PinB-Ph-p-NeOSO₂). Br-Ph-p-NeOSO₂ (1.5 g, 5 mmol), bis(pinacolato)diboron (1.9 g, 7.5 mmol), [1,1'-bis(diphenylphosphino)ferrocene] dichloropalladium(II) (184 mg, 0.25 mmol) and CH₃COOK (1.5 g, 15 mmol) were suspended in dioxane (15 mL). The mixture was stirred at 100 \Box under a nitrogen atmosphere for 12 h. After being cooled to room temperature, the mixture was extracted with ethyl acetate. The organic phase was washed with water and then dried over anhydrous Na₂SO₄. The solvent was removed under vacuum and the residual was purified by column chromatography on silica gel with petroleum ether/CH₂Cl₂ (10: 1) as the eluent, affording a white solid (1.4 g, 3.9 mmol). Yield: 78%. ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3, \delta[\text{ppm}])$: 7.98 (d, J = 8.0 Hz, 2H), 7.89 (d, J = 8.0 Hz, 2H), 3.67 (s, 2H), 1.37 (s, 12H), 0.90 (s, 9H). HRMS (ESI, m/z): 355.1756 $[M+H]^+$ (calc. 355.1745).

Synthesis of neopentyl 4-(4,6-diphenyl-1,3,5-triazin-2-yl)benzenesulfonate $(TRZ-p-NeOSO_2)$. PinB-Ph-p-NeOSO₂ (2.5 g, 7.1 mmol), 2-chloro-4,6-diphenyl-1,3,5-triazine (2.1 g, 7.9 mmol), Pd(PPh₃)₄ (413 mg, 0.36 mmol) and K₂CO₃ (5 g, 36 mmol) were suspended in toluene: ethanol: water (40/20/40 mL). The mixture was stirred at 80 \Box under a nitrogen atmosphere for 24 h. After being cooled to room temperature, the mixture was extracted with CH₂Cl₂ (50

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mL×2). The organic phase was washed with water and then dried by anhydrous Na₂SO₄. The solvent was removed under vacuum and the residual was purified by column chromatography on silica gel with petroleum ether/CH₂Cl₂ (10: 1) as the eluent, affording a white solid (2.6 g, 5.7 mmol). Yield: 80%. ¹H NMR (500 MHz, CDCl₃, δ [ppm]): 8.95 (d, J = 8.4 Hz, 2H), 8.78 (d, J = 7.2 Hz, 4H), 8.12 (d, J = 8.4 Hz, 2H), 7.63 (m, 6H), 3.76 (s, 2H), 0.93 (s, 9H). HRMS (ESI, m/z): 460.1701 [M+H]⁺ (calc. 460.1689).

Synthesis of sodium 4-(4,6-diphenyl-1,3,5-triazin-2-yl)benzenesulfonate (*TRZ-p-SO*₃*Na*). TRZ-p-NeOSO₂ (1.0 g, 2.2 mmol) and NaI (3.3 g, 21.8 mmol) were dissolved in acetone (40 mL). The mixture was stirred at 80 \Box under a nitrogen atmosphere in a sealed pressure tube for 12 h. The mixture was cooled to room temperature and then filtered. The solid was washed with acetone (10 mL), affording a white solid (0.85 g, 2.0 mmol). Yield: 91%. ¹H NMR (400 MHz, DMSO-*d*₆, δ [ppm]): 8.81-8.70 (m, 6H), 7.88 (d, J = 8.2 Hz, 2H), 7.78-7.64 (m, 6H). HRMS (ESI, m/z): 388.0763 [M–Na]⁻ (calc. 388.0761).

Synthesis of neopentyl 3-bromobenzenesulfonate (Br-Ph-m-NeOSO₂). The synthesis of Br-Ph-m-NeOSO₂ was similar to that of Br-Ph-p-NeOSO₂, except that 3-bromobenzene-1-sulfonyl chloride replaced 4-bromobenzene-1-sulfonyl chloride. Yield: 60%. ¹H NMR (400 MHz, CDCl₃, δ [ppm]) 8.06 (s, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.45 (t, J = 7.9 Hz, 1H), 3.71 (s, 2H), 0.92 (s, 9H). HRMS (ESI, *m/z*): 307.0010 [M+H]⁺ (calc. 306.9998).

Synthesis of neopentyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)

*benzenesulfonate (PinB-Ph-m-NeOSO*₂). The synthesis of PinB-Ph-m-NeOSO₂ was similar to that of PinB-Ph-p-NeOSO₂, except that Br-Ph-m-NeOSO₂ replaced Br-Ph-p-NeOSO₂. Yield: 70%. ¹H NMR (500 MHz, CDCl₃, δ [ppm]): 8.34 (s, 1H), 8.05 (d, J = 7.4 Hz, 1H), 7.97 (d, J = 7.7 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 3.69 (s, 2H), 1.36 (s, 12H), 0.91(s, 9H). HRMS (ESI, *m/z*): 355.1754 [M+H]⁺ (calc. 355.1745).

Synthesis of neopentyl 3-(4,6-diphenyl-1,3,5-triazin-2-yl)benzenesulfonate (*TRZ-m-NeOSO*₂). The synthesis of TRZ-m-NeOSO₂ was similar to that of TRZ-p-NeOSO₂, except that PinB-Ph-m-NeOSO₂ replaced PinB-Ph-p-NeOSO₂. Yield: 85%.¹H NMR (500 MHz, CDCl₃, δ [ppm]): 9.28 (s, 1H), 9.06 (d, J = 7.8 Hz, 1H), 8.78 (d, J = 7.8 Hz, 4H), 8.14 (d, J = 7.8 Hz, 1H), 7.80 (t, J = 8.0 Hz, 1H), 7.69 – 7.56 (m, 6H), 3.80 (s, 2H), 0.95 (s, 9H). HRMS (ESI, m/z): 460.1699 [M+H]⁺ (calc. 460.1689).

Synthesis of sodium 3-(4,6-diphenyl-1,3,5-triazin-2-yl)benzenesulfonate (*TRZ-m-SO₃Na*). The synthesis of TRZ-m-SO₃Na was similar to that of TRZ-p-SO₃Na, except that TRZ-m-NeOSO₂ replaced TRZ-p-NeOSO₂. Yield: 93%. ¹H NMR (500 MHz, DMSO- d_6 , δ [ppm]): 8.96 (s, 1H), 8.75 (d, J = 7.5 Hz, 4H), 8.71 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 7.5 Hz, 1H), 7.77 – 7.67 (m, 6H), 7.64 (t, J = 7.5 Hz, 1H). HRMS (ESI, m/z): 388.0760 [M–Na]⁻ (calc. 388.0761).

Synthesis of $[Ir(meoppy)_2(dmapzpy)]^+Cl^-$.

 $[Ir(meoppy)_2Cl]_2$ (1.8 g, 1.5 mmol) and dmapzpy (0.56 g, 3.0 mmol) were dissolved in ethanol/1,2-dichloroetahne (30: 30 mL). The mixture was refluxed under a nitrogen atmosphere for 12 h. The solvent was removed under vacuum and the residual was purified by column chromatography on silica gel with CH_2Cl_2/CH_3OH (60: 1) as the eluent, affording a yellow solid (1.9 g, 2.4 mmol). Yield: 80%.

Synthesis of $[Ir(meoppy)_2(dmapzpy)]^+PF_6^-$ (complex R).

 $[Ir(meoppy)_2(dmapzpy)]^+CI^-$ (0.50 g, 0.64 mmol) were dissolved in CH₃OH/H₂O (30/30 mL). To the solution, NH₄PF₆ (0.65 g, 4.0 mmol) were added under stirring. The mixture was stirred at room temperature for 1 h. The precipitate was collected and purified by column chromatography on silica gel with CH₂Cl₂ as the eluent, affording a yellow solid (0.47 g, 0.53 mmol). Yield: 83%. ¹H NMR (400 MHz, CDCl₃, δ [ppm]): 8.81(d, J=2.8Hz, 1H), 7.60–7.53 (m, 3H), 7.42 (d, J= 6.7 Hz, 1H), 7.33 (t, J= 3.4 Hz, 2H), 7.20–7.16 (m, 2H), 7.11 (d, J= 2.0 Hz, 1H), 7.00–6.93 (m, 2H), 6.88–6.84(m, 2H), 6.66–6.61 (m, 3H), 6.38 (t, J = 6.8 Hz, 2H), 6.32 (dd, J= 6.8,2.5 Hz, 1H), 3.97-3.94 (m, 6H), 3.16 (s, 6H). HRMS (ESI, m/z): 749.2234 [M–PF₆]⁺ (calc. 749.2211). Anal. found: C, 45.78; H, 3.76; N, 9.33. Anal. calcd for C₃₄H₃₂F₆IrN₆O₂P: C, 45.69; H, 3.61; N, 9.40.

Synthesis of $[Ir(meoppy)_2(dmapzpy)]^+[OXD-7-SO_3^-]$ (complex 1).

[Ir(meoppy)₂(dmapzpy)]⁺Cl⁻ (235 mg, 0.3 mmol) was dissolved in methanol/H₂O (45/15 mL). To the solution, OXD-7-SO₃Na (174 mg, 0.3 mmol) dissolved in methanol/H₂O (15/5 mL) was added dropwise under stirring. The mixture was stirred at room temperature for 1 h and then concentrated. The precipitate was collected and recrystallized from CH₃OH/H₂O, affording a yellow solid (282 mg, 0.22 mmol). Yield: 73%. ¹H NMR (500 MHz, DMSO-*d*₆, δ[ppm]): 9.35 (s, 1H), 8.72 (s, 1H), 8.51 (s, 2H), 8.12 (d, J = 8.1 Hz, 4H), 7.91 (t, J = 6.7 Hz, 2H), 7.76 (s, 2H), 7.68 (d, J = 8.1

Hz, 4H), 7.57 (d, J = 6.6 Hz, 1H), 7.46 (s, 1H), 7.42 (d, J = 6.7 Hz, 1H), 7.18 (s, 1H), 7.06 (d, J = 6.8 Hz, 1H), 6.98 – 6.91 (m, 2H), 6.90 – 6.79 (m, 5H), 6.72 (d, J = 6.6 Hz, 1H), 6.30 (d, J = 7.5 Hz, 1H), 6.25 (d, J = 7.5 Hz, 1H), 3.98 (s, 6H), 3.11 (s, 6H), 1.35 (s, 18H). HRMS (ESI, m/z): 749.2237 [Ir(meoppy)₂(dmapzpy)]⁺ (calc. 749.2211); 557.1875 [OXD-7-SO₃⁻] (calc. 557.1864). Anal. found: C, 58.98; H, 4.99; N, 10.69. Anal. calcd for $C_{64}H_{61}IrN_{10}O_7S$: C, 58.83; H, 4.71; N, 10.72.

Synthesis of $[Ir(meoppy)_2(dmapzpy)]^+[TRZ-p-SO_3^-]$ (complex 2).

The synthesis of complex2 followed a procedure similar to that for complex 1, except that TRZ-p-SO₃Na replaced OXD-7-SO₃Na. Yield: 81%. ¹H NMR (500 MHz, DMSO-*d*₆, δ [ppm]): 9.35 (d, J = 2.4 Hz, 1H), 8.80 – 8.70 (m, 6H), 7.96–7.84 (m, 4H), 7.79–7.62 (m, 8H), 7.56 (d, J = 6.6 Hz, 1H), 7.46 (s, 1H), 7.42 (d, J = 6.4 Hz, 1H), 7.19 (d, J = 2.0 Hz, 1H), 7.06 (d, J = 6.7 Hz, 1H), 6.98–6.93 (m, 2H), 6.90–6.79 (m, 5H), 6.76-6.70 (m, 1H), 6.30 (d, J = 7.2 Hz, 1H), 6.25 (d, J = 7.2 Hz, 1H), 3.98 (s, 6H), 3.11 (s, 6H). HRMS (ESI, m/z): 749.2228 [Ir(meoppy)₂(dmapzpy)]⁺ (calc. 749.2211); 388.0772 [TRZ-p-SO₃⁻⁻] (calc. 388.0761). Anal. found: C, 58.21; H, 4.23; N, 11.01. Anal. calcd for C₅₅H₄₆IrN₉O₅S: C, 58.08; H, 4.08; N, 11.08.

Synthesis of $[Ir(meoppy)_2(dmapzpy)]^+[TRZ-m-SO_3^-]$ (complex 3).

The synthesis of complex 3 followed a procedure similar to that for complex 1, except that TRZ-m-SO₃Na replaced OXD-7-SO₃Na. Yield: 86%. ¹H NMR (400 MHz, DMSO- d_6

, δ[ppm]): 9.35 (d, J= 1.4 Hz, 1H), 8.95 (s, 1H), 8.75 (d, J = 7.2 Hz, 4H), 8.71 (d, J = 8.0 Hz, 1H), 7.96-7.88 (m, 3H), 7.80 – 7.60 (m, 9H), 7.56 (d, J = 6.2 Hz, 1H), 7.47 (s,

1H), 7.42 (d, J = 6.8 Hz, 1H), 7.19 (s, 1H), 7.05 (d, J = 6.8 Hz, 1H), 6.99-6.91 (m, 2H), 6.90 – 6.80 (m, 5H), 6.76-6.71 (m, 1H), 6.30 (d, J = 7.2 Hz, 1H), 6.25 (d, J = 7.6 Hz, 1H), 6H), 3.11 6H). HRMS (ESI, m/z): 749.2233 3.97 (s. (s. $[Ir(meoppy)_2(dmapzpy)]^+$ (calc. 749.2211); 388.0775 $[TRZ-m-SO_3^-]$ (calc. 388.0761). Anal. found: C, 58.34; H, 4.19; N, 10.99. Anal. calcd for C₅₅H₄₆IrN₉O₅S: C, 58.08; H, 4.08; N, 11.08.

OLEDs. ITO-coated glass substrates (17 Ω/\Box) were sufficiently cleaned in acetone and ethanol, and then in detergent and deionized water. The ITO substrates were exposed under UV-zone for 10 min before use. The PEDOT: PSS layer was deposited onto the ITO substrate by spin-coating and heated at 150 °C for 10 min. The emissive layer was then deposited onto the PEDOT: PSS layer by spin-coating from 1,2-dichloroethane solution (8 mg mL⁻¹) at 2000 r min⁻¹ and then baked at 80 °C on a hotplate for 30 min in a nitrogen-filled glove box. The film-coated substrate was transferred into a high-vacuum chamber ($<5\times10^{-4}$ Pa) and TmPyPB, LiF and Al layers were consecutively deposited by thermal evaporation at 1–2, 0.1 and 5 Å s⁻¹, respectively. The devices were measured in the glove box without exposure to air. The current density-voltage-brightness characteristics were recorded by a Keithley 2400 source meter and a calibrated silicon photodiode. The EL spectra were recorded by an OPT-2000 fiber spectrometer. The forward viewing external quantum efficiency was calculated by assuming a Lambertian emission pattern.

Acknowledgements

We thank the National Natural Science Foundation of China (Grant No.

51773074), the program of introducing talents of discipline to universities of china

(111 program, B17019), and the self-determined research funds of CCNU from the

colleges' basic research and operation of MOE for financial support.

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Highlights

- Oxadiazole/triazine type counter-anions were developed for sky-blue cationic Ir • complex
- The complex using the counter-anion showed higher performance than that using • PF₆ in OLED
- Double-layer solution-processed sky-blue OLED afforded an efficiency of 29.4 • $cd A^{-1}$

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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