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Anchoring a Sulfonate Group to an Electron-transporting Molecule via an Alkyl Chain and Its Use as the Counter-anion in a Phosphorescent Cationic Iridium Complex

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Abstract

We report an electron-transporting anion prepared by anchoring a sulfonate group onto an electron-transporting molecule via a flexible alkyl chain and its use as the counter-anion in a cationic iridium complex. The flexible alkyl chain improves the solubility of the bulky anion in water or in polar organic solvent. The anion exhibits similar photophysical and electrochemical properties to the parent electron-transporting molecule. Within the complex, the anion does not disturb the the phosphorescence of the cation in the solid film. Solution-processed small-molecule organic light-emitting diodes (OLEDs) using the complex as the dopant show superior performances over the reference device using the conventional complex with a PF_6^-

counter-anion. It is revealed that anchoring anionic groups to optoelectronically active molecules via flexible alkyl chains is a feasible approach to develop optoelectronically active anions for assembling ion pairs with advanced optoelectronic properties.

Key words: cationic iridium complexes; phosphorescence; counter anion; Electron-transporting; organic light emitting diodes

1. Introduction

Phosphorescent cationic iridium complexes have received tremendous research interest during the past decade for their applications in a wide variety of fields, such in photo-catalysis,^[1, 2] biological imaging,^[1, 3] ion-sensing [4] and as electroluminescent devices.^[5, 6] In organic electroluminescence, they were initially used as emitting materials in light-emitting electrochemical cells,^[5,7] by virtue of their intrinsic ionic nature and phosphorescent properties. With high phosphorescent efficiencies, tunable emission color and good solubility in polar solvent, these cationic iridium complexes have also been utilized as phosphorescent dopants in solution-processed organic light-emitting diodes (OLEDs), which have achieved comparable performances to the neutral iridium complexes.^[6, 8-17] Their potential as sublimable phosphorescent emitters for vacuum-evaporated OLEDs has also been demonstrated.^[18-21] The prototype cationic iridium complex, with a form of $[Ir(ppy)_2(bpy)]PF_6$, uses 2-phenylpyridine (Hppy) as the cyclometalating ligand (CAN), 2,2'-bipyridine (bpy) as the ancillary ligand (NAN) and PF_6^- as the

counter-anion.^[22] In 2005, plummer et al. for the first time employed $[Ir(ppy)_2(bpy)]PF_6$ as the phosphorescent dopant in solution-processed OLEDs, which afforded yellow electroluminescence with a peak current efficiency of 22 cd A⁻¹.^[8] Over the past decade, a huge number of phosphorescent cationic iridium complexes have been developed and interest on their applications in OLEDs is arising.^[6, 8-21]

Typical phosphorescent cationic iridium complexes contain two functional parts, *i.e.*, phosphorescent cations, with a general formula of $[Ir(CAN)_2(NAN)]^+$, and the counter-anions. Previous studies have been focused on $[Ir(CAN)_2(NAN)]^+$, while limited attention has been paid to the counter-anions.^[5, 6] This is because $[Ir(CAN)_2(NAN)]^+$ determines essentially the emission property of the whole complex. The small counter-anions, such as optoelectronically innocent PF₆⁻ and BF₄⁻, can migrate under electrical fields, which enables the fabrication of LECs.^[5-7] However, anion-migrations under electrical fields are not favored for OLED operations. Therefore, tailoring the counter-anions is critically important for improving the performances of cationic iridium complexes in OLEDs.

Managements of counter-anions in cationic iridium complexes for optoelectronics applications have seldom been explored. Mauro et al. and Wu et al. employed phosphorescent iridium-based anions as the counter-anions for the cationic complexes.^[23, 24] The resultant luminescent ion-pairs (soft salts) feature the low-energy emission from either the cations or the anions in solid state, owing to the energy transfer between the cations and anions. These soft-salt complexes showed moderate performances in OLEDs.^[24, 25] Guo et al. also developed iridium-based soft

complexes and used them to make light-emitting or electrochromic switch devices.^[26] Ma et al. used bulky tetraphenylborate anions to replace PF_6^- in the complexes and by tailoring the tetraphenylborate anions with fluorine, they tuned successfully the volatility of the complexes to enable the fabrication of vacuum-evaporated OLEDs.^{[20,} ^{27]} We recently demonstrated a concept that functionalizing the counter-anions with optoelectronic properties such as electron-transporting properties to improve the optoelectronic performances of the complexes in devices.^[16] The key point for this molecular design is to anchor anionic groups (such as sulfonate) onto electron-transporting molecules to prepare electron-transporting counter-anions. It is noted that anchoring a sulfonate group directly onto an electron-deficient electron-transporting molecule via conventional electrophilic substitution reactions sounds difficult. A sulfonate-containing starting material was thus used to develop the electron-transporting counter-anion in our previous work.^[16] A more versatile molecular design should be demonstrated for the development of optoelectronically active anions.

Here, we report an electron-transporting anion, OXD-7-OBu-SO₃⁻ (Scheme 1), which is prepared via anchoring an anionic sulfonate group to an electron-transporting molecule, 1,3-bis(5-(4-(tert-butyl)phenyl)-1,3,4-oxadiazol-2-yl)benzene (OXD-7),^[28-30] through a flexible alkyl chain, and its use as the counter-anion in a blue-green-emitting cationic iridium complex (Complex 1 in Scheme 2). Anchoring an anionic group via a flexible alkyl chain is more versatile for the design and synthesis of electron-transporting anions and moreover, improves the solubility of the

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anions in water or in polar organic solvent. The improved solubility of the anion facilitates the anion-exchange reactions in polar media for the synthesis of the complex (Scheme 2). In addition, the flexible alkyl chain of the anion renders the complex with improved solubility, which benefits the fabrication of OLEDs via a solution-process. The photophysical and electrochemical properties of $OXD-7-OBu-SO_3^{-}K^{+}$ and complex 1 have been comprehensively investigated. Complex 1 has been adopted as the dopant in solution-processed small-molecule OLEDs, which show superior performances, with more than doubled efficiencies, compared to the reference device incorporating the conventional complex with a $PF_6^$ counter-anion.



Scheme 1. Synthetic route to $OXD-7-OBu-SO_3^-K^+$.



Scheme 2. Synthetic route to complex 1.

2. Results and discussion

2.1. Synthesis

Scheme 1 depicts the synthetic route to OXD-7-OBu-SO $_{3}^{-}K^{+}$. In previous studies, OXD-7 was usually synthesized through the cyclization of N'-benzoylbenzohydrazide derivatives under a harsh reaction condition with refluxing POCl₃.^[28] In the present study, we utilized an iodine-assisted cyclization of a N'-benzylidenebenzohydrazide derivative under a mild reaction condition to synthesize the OXD-7 core (Scheme 1). This cyclization reaction affords the product with a high yield and more importantly, few by-products, simplifies purification produces which the of the $OXD-7-OBu-SO_3^{-}K^{+}$ salt.

As shown in Scheme 1, the sulfonate group is anchored to the OXD-7 core via a butoxy chain, which requires a hydroxyl group attached to the OXD-7 core. Dimethyl

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5-hydroxyisophthalate was thus used as the starting material to prepare the N'-benzylidenebenzohydrazide derivative, compound 2 (Scheme 1). However, cyclization of compound 2 with the iodine-assisted cyclization reaction failed to produce the desired hydroxyl-anchored OXD-7. The hydroxyl group thus reacted first with 1,4-butane sultone to produce the sulfonate-containing N'-benzylidenebenzohydrazide derivative, compound 3 (Scheme 1), which was successfully cyclized via the iodine-assisted cyclization reaction to afford OXD-7-OBu-SO₃⁻K⁺ with a high yield of 75%.

Scheme 2 depicts the synthesis of complex 1. The phosphorescent cation, $[Ir(ppy)_2(pzpy)]^+$, where pzpy is 2-(1*H*-pyrazol-1-yl)pyridine, is an efficient blue-green phosphorescent emitter.^[31] The cleavage of the chloro-bridged iridium dimer $[Ir(ppy)_2Cl]_2$ with pzpy leads to the formation of $[Ir(ppy)(pzpy)]^+Cl^-$. The anion-exchange reaction between $[Ir(ppy)(pzpy)]^+Cl^-$ and OXD-7-OBu-SO₃⁻K⁺ was performed in water/methanol solution. After the anion-exchange, complex 1 precipitated from the solution and was further purified by recrystallization from organic solvent.

2.2. Photophysical characterizations





Figure 1. a) Absorption and PL spectra of OXD-7-OBu-SO₃K in CH₃OH (1×10^{-5} M) (excitation for PL: 280 nm); ε denotes the molar extinction coefficient. b) Absorption and PL spectra of complex 1 and [Ir(ppy)₂(pzpy)]PF₆ (R) in CH₃CN (1×10^{-5} M) (excitation for PL: 380 nm). c) PL spectra of complex 1 in CH₃CN under different excitation wavelengths. d) PL spectra of complex 1 in the 2 wt. % doped PMMA film under different excitation wavelengths.

of $[Ir(ppy)_2(pzpy)]PF_6(R)$ were also shown.								
Absorption		Emission at room temperature	Electrochemi-					
λ [nm]	CH ₃ CN ^b	2% in PMMA ^c	cal data [V]					
$(\varepsilon [\times 10^4$								

Table 1. Photophysical and electrochemical data of complex 1. For comparison, data

	$(-5, 10^4)$										
	$(\epsilon [\times 10] M^{-1} \text{ cm}^{-1}])^{a}$	PL	$\Phi_{\rm em}$	K _r , K _{nr}	-	PL	$\Phi_{\rm em}$	K _r , K _{nr}	Eo	d K	E _{red} ^e
	wi chi j)	[nm]	(τ[µs])	$[10^5 \mathrm{s}^{-1}]$		[nm]	(τ[μs])	$[10^5 \mathrm{s}^{-1}]$			
1	410 (0.30)	477,	0.19	1.3,		477,	0.77	2.6,	0.7	6	-2.25,
	380 (0.49)	505	(1.47)	5.5		504	(2.93)	0.8			-2.39
	284 (7.67)										
R	410 (0.29)	475,	0.23	1.5,		476,	0.80	2.5,	0.8	51	-2.18
f	380 (0.48)	503	(1.56)	4.9		504	(3.20)	0.6			
	253 (4.98)										

^a In CH₃CN solution (2×10^{-5} M). ^b In degassed CH₃CN solution (1×10^{-5} M). ^c Films coated on quartz substrates. ^d Onset oxidation potentials. ^e Peak reduction potentials. ^f

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Most data were quoted from reference ^[31], except that the Φ in PMMA was measured with the absolute PLQY measurement system and the electrochemical data were measured in DMF solution (see experimental).

Fig. 1a depicts the absorption and PL spectra of OXD-7-OBu-SO₃K in methanol solution. OXD-7-OBu-SO₃K absorbs strongly in the ultra-violet region below 350 nm and emits intense light peaked at 352 nm. As shown in Fig. 1a, the light emission of OXD-7-OBu-SO₃K resembles that of OXD-7. Fig. 1b depicts the absorption and PL spectra of complex 1 in CH₃CN solution. Detailed photophysical properties have been summarized in Table 1. For comparison, those of the reference complex with a $PF_6^$ counter anion, $[Ir(ppy)_2(pzpy)]PF_6$, are also shown. As shown in Fig. 1b, complex 1 shows strong absorption bands in the ultra-violet region below 350 nm, which arise from both the $[Ir(ppy)_2(pzpy)]^+$ cation and the OXD-7-OBu-SO₃⁻ anion. Complex 1 also shows relatively weak absorption bands extending from 350 nm to the visible region. These weak absorption bands also appear in the absorption spectrum of $[Ir(ppy)_2(pzpy)]PF_6$ (Fig. 1b) and are assigned to the metal-to-ligand charge-transfer ³MLCT, ³LLCT (MLCT), ligand-to-ligand charge-transfer (LLCT), and ligand-centered ${}^{3}\pi$ - π^{*} transitions in the $[Ir(ppy)_{2}(pzpy)]^{+}$ cation.^[31]

As shown in Fig. 1b, in the CH₃CN solution, complex 1 emits blue-green light peaked at 477 nm under the excitation wavelength of 380 nm. This blue-green light emission resembles that from $[Ir(ppy)_2(pzpy)]PF_6$, as revealed by the almost overlapped emission spectra of complex 1 and $[Ir(ppy)_2(pzpy)]PF_6$ (Fig. 1b). On the other hand, only the $[Ir(ppy)_2(pzpy)]^+$ cation was excited at 380 nm excitation.

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Therefore, the blue-green light emission of complex 1 originates from the $[Ir(ppy)_2(pzpy)]^+$ cation. In the degassed CH₃CN solution, complex 1 affords a PLQY of 0.19 and an excited-state lifetime (τ) of 1.43 µs, both of which are a little lower than those (PLQY=0.23, τ =1.56 µs) of $[Ir(ppy)_2(pzpy)]PF_6$. From the PLQY and τ , the radiative (K_r) and non-radiative (K_{nr}) rates of complex 1 were calculated. As shown in Table 1, complex 1 exhibits a little lower K_r and a considerably higher K_{nr} than $[Ir(ppy)_2(pzpy)]PF_6$ in CH₃CN solution, which accounts for the lower PLQY of complex 1. It is known that the luminescence of iridium complex is sensitive to the local environment of the complex. For complex 1, the bulky OXD-7-OBu-SO₃⁻ anion seems to induce additional non-radiative deactivation for the phosphorescent $[Ir(ppy)_2(pzpy)]^+$ cation in the fluid solution, presumably due to the interaction between the iridium complex cation and the polar sulfonate group.^[32]

Fig. 1c depicts the PL spectra of complex 1 in CH_3CN solution under different excitation below 350 nm at which both the $[Ir(ppy)_2(pzpy)]^+$ cation and the $OXD-7-OBu-SO_3^-$ anion were excited. As shown in Fig. 1c, complex 1 emits intense ultra-violet light centered at 352 nm, which arises from the $OXD-7-OBu-SO_3^-$ anion, as well as the low-energy blue-green light, which comes from the $[Ir(ppy)_2(pzpy)]^+$ cation. The strong emission from $OXD-7-OBu-SO_3^-$ anion indicates the incomplete energy transfer from $OXD-7-OBu-SO_3^-$ to $[Ir(ppy)_2(pzpy)]^+$ in the dilute fluid solution.^[23, 24, 26]

As shown in Fig. 1d, in the 2 wt.% doped poly(methylmethacrylate) (PMMA) film, complex 1 always exhibits predominant blue-green light emission from the

 $[Ir(ppy)_2(pzpy)]^+$ cation, independent of the excitation wavelength. This reveals that in the solid state, the energy is efficiently transferred from OXD-7-OBu-SO₃⁻ to $[Ir(ppy)_2(pzpy)]^+$. This efficient energy transfer in the diluted PMMA film indicates that $[Ir(ppy)_2(pzpy)]^+$ and OXD-7-OBu-SO₃⁻ are closely bound together via the electrostatic force between them in the solid film. Under the excitation at 380 nm, complex 1 in the PMMA film only gives blue-green light emission from the $[Ir(ppy)_2(pzpy)]^+$ cation, with a PLQY of 0.77 and a τ value of 2.93 µs, which are similar to those (0.80 and 3.2 µs, respectively) of $[Ir(ppy)_2(pzpy)]PF_6$. As shown in Table 1, the large increase of PLQY from the solution to the PMMA film is mainly ascribed to the remarkable decrease of K_{nr} . The comparable PLQY and τ values between complex 1 and $[Ir(ppy)_2(pzpy)]PF_6$ indicate that the OXD-7-OBu-SO₃⁻ anion hardly disturbs the phosphorescence of the cation in the film, which reveals the advantage of binding the phosphorescent emitter and the electron-transporting molecule together via electrostatic force.

2.3. Electrochemical characterizations



Figure 2. Cyclic voltammograms of OXD-7-OBu-SO₃⁻K⁺, OXD-7, complex 1 and $[Ir(ppy)_2(pzpy)]PF_6$ (R) in DMF solution. The small peaks around -1.5 V come from some unknown impurities in the electrolytes.

The electrochemical properties of OXD-7-OBu-SO₃K and complex 1 were investigated via cyclic voltammetry in DMF solution. Fig. 2 shows the cyclic voltammograms. For comparison, those of OXD-7 and $[Ir(ppy)_2(pzpy)]PF_6$ (R) were also shown. The redox potentials were summarized in Table 1. Similar to OXD-7, OXD-7-OBu-SO₃K exhibits a reversible reduction in the solution, with a reduction potential at -2.43 V, which is close to that (-2.30 V) of OXD-7. From the reduction potential, the LUMO level of OXD-7-OBu-SO₃K was calculated to be -2.3 eV. Because of the electron-deficient characteristic of the OXD-7 core, the oxidation of OXD-7-OBu-SO₃K was not detected within the electrochemical window of DMF. From the optical band gap, the HOMO level of OXD-7-OBu-SO₃K was calculated to be -5.9 eV.

As shown in Fig. 2, complex 1 exhibits an irreversible oxidation in the DMF solution. This oxidation resembles that of $[Ir(ppy)_2(pzpy)]PF_6$ which occurs on the $[Ir(ppy)_2(pzpy)]^+$ cation. On the other hand, complex 1 shows a complicated reduction, which involves the reductions of $[Ir(ppy)_2(pzpy)]^+$ and OXD-7-OBu-SO₃⁻.



2.4. OLED devices

Figure 3. EL spectra of devices I, II and III under 10 V.



Figure 4. Energy level diagram for the OLEDs (unit for energy level: eV).

OLEDs were fabricated with complex 1 as the phosphorescent dopant via a solution process. The device structure is ITO/PEDOT: PSS (40 nm)/H2: complex (40 nm)/TPBI (40 nm)/LiF (1 nm)/Al (100 nm). Here H2 is a carbazole-based dendrimer,^[33, 34] which is used as the hole-transporting host, and TPBI is 1,3,5-tris(1-phenyl-1*H*-benzimidazol-2-yl)benzene, which is used as the electron-transporting/hole-blocking material. It is noted that the triplet energy (2.9 eV) of H2 is higher than that (2.6 eV) of $[Ir(ppy)_2(pzpy)]^+$ and thus, the back energy $[Ir(ppy)_2(pzpy)]^+$ transfer from to H2 is suppressed. For comparison. $[Ir(ppy)_2(pzpy)]PF_6$ was also used as the dopant (10 wt.%) in H2 to fabricate the reference OLED (Device I). The doping concentration of complex 1 in H2 was varied from 10 wt.% (device II) to 20 wt. % (device III). Fig. 3 depicts the EL spectra of devices I, II and III at 10 V. EL spectra of the devices under different voltages are shown in the supporting information (Fig. S1). As shown in Fig. 3, all the devices give blue-green light emission, which originates from the phosphorescent $[Ir(ppy)_2(pzpy)]^+$ cation, with the major emission peaks at 484 nm and Commission Internationale de L'Eclairage (CIE) coordinates around (0.21, 0.47).

It is noted from Fig. 3 that there exists a small emission band around 410 nm in the EL spectrum of device I at 10 V. Further increasing the operating voltage from 10 V to 14 V, as shown in Fig. S1a, enhances the relative intensity of this emission band to the emission from the $[Ir(ppy)_2(pzpy)]^+$ cation. On the contrary, devices II and III do not show any emission band around 410 nm under low or high driving voltages (Fig. S1b-c). Clearly, the OXD-7-OBu-SO₃⁻ anion in complex 1 helps to diminish the

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small emission band around 410 nm. In general, the residual high-energy emission bands in the EL spectra of OLEDs come from the host, due to the incomplete energy transfer from the host to the dopant under electrical excitation. The PL spectra of the emissive layers of devices I, II and III indicate that the energy transfer from the H2 host to complexes R or 1 is incomplete under photoexcitation (Fig. S2). The energy level diagram of devices I–III, as shown in Fig. 4, indicates that the [Ir(ppy)₂(pzpy)]⁺ cation behaves as an electron trap in the emissive layer, which should help to suppress the emission from the host under electrical excitation, because excitons can form directly on [Ir(ppy)₂(pzpy)]⁺ via electron-trapping.^[9, 35] The considerable emission from the host in the EL spectra of device I indicates that the electron-trapping and the resultant direct exciton formation on $[Ir(ppy)_2(pzpy)]^+$ in the [H2: 10% complex R] emissive layer is relatively weak. In contrast, the disappearance of the emission from the host in the EL spectra of devices II and III indicates that the electron-trapping and the resultant direct exciton formation on $[Ir(ppy)_2(pzpy)]^+$ in the [H2: 10% or 20% complex 1] emissive layers is relatively strong. It is thus shown that the OXD-7-OBu-SO₃⁻ anion in complex 1 facilitates the electron-trapping and direct exciton formation on the $[Ir(ppy)_2(pzpy)]^+$ cation, because it promotes the electron-injection into the emissive layer and the electron-transport within the emissive layer.



Figure 5. Current density (solid symbols) and brightness (open symbols) *versus* voltage curves for devices I, II and III.

 Table 2. Device characteristics for devices I-IV. Complex R denotes

 [Ir(ppy)₂(pzpy)]PF₆.

Device	Emissive layer ^a	V _{on} B _m		$\eta_{c, m}$	EQE _m	CIE	
		(V) ^b	$(cd m^{-2})^{c}$	$(cd A^{-1})^{d}$	(%) ^e	(x, y)	
Ι	H2: 10% complex R	7.9	11900	10.4	4.0	(0.21, 0.47)	
II	H2: 10% complex 1	7.4	10300	21.6	8.1	(0.22, 0.49)	
III	H2: 20% complex 1	7.3	12800	21.0	7.9	(0.22, 0.49)	

^a Weight percentages for the doping. ^b Voltage to reach 1 cd m⁻². ^c Maximum brightness. ^d Maximum current efficiency. ^e Maximum external quantum efficiency.

Fig. 5 shows the current-density and brightness versus voltage curves for devices I–III. Detailed electrical characteristics were summarized in Table 2. Device II with 10 wt. % complex 1 as the dopant shows a lower current density than device I with 10 wt.% $[Ir(ppy)_2(pzpy)]PF_6$ as the dopant. As shown in Fig. 4, the OXD-7-OBu-SO₃⁻ anion has a much deeper HOMO level than H2. As a result, OXD-7-OBu-SO₃⁻ could

hinder the hole transport in the emissive layer via charge scattering,^[10] which leads to the lower current density of device II than that of device I. As shown in Fig. 5, device III with 20 wt.% complex 1 as the dopant shows a higher current density than device II. The OXD-7-OBu-SO₃⁻ anion facilitates the electron-transport in the emissive layer, although it could hinder the hole transport at the same time. The net result of these two conflicting effects is that the current density increase from device II to device III. As shown in Fig. 5, in the low-voltage region (<15V), device III shows a little higher current density then device I, owing to the facilitation of electron-transport by OXD-7-OBu-SO₃⁻. Nevertheless, in the high-voltage region, device III still shows lower current density than device I.

A notable enhancement on device performance can be observed upon going from device I, to device II and to device III, as shown in Table 2. Specifically, the efficiencies of devices II and III (21.6 and 21.0 cd A^{-1} , respectively) are more than doubled compared to that $(10.4 \text{ cd } \text{A}^{-1})$ of device I. Because H2 only transports holes in the emissive layer, carrier transport and recombination are unbalanced in device I. For devices II and III, the OXD-7-OBu-SO₃⁻ anion facilitates the electron-transport in the emissive layer, which improves the electron-hole recombination balance, leading to enhanced device efficiencies. Therefore, using electron-transporting counter anions in cationic iridium complexes is an effective avenue to enhance the performances of the complexes small-molecule through facilitation in OLEDs of electron-injection/transport in the emissive layer.

3. Conclusions

An electron-transporting anion, OXD-7-OBu-SO₃, was prepared via anchoring a sulfonate group onto the electron-transporting molecule OXD-7 through a flexible alkyl chain. OXD-7-OBu-SO₃ exhibited similar photophysical and electrochemical properties to OXD-7. A blue-green-emitting cationic iridium complex was prepared by using OXD-7-OBu-SO₃ as the counter-anion. OXD-7-OBu-SO₃ did not disturb the phosphorescence of the iridium-based cation in the solid film. Solution-processed small-molecule OLEDs incorporating the complex as the dopant afforded remarkably enhanced performances, with more than doubled efficiencies, compared to the reference device using the complex with a PF_6^- counter anion. It is believed that anchoring anionic groups via flexible alkyl chains can also be used to prepare other optoelectronically active anions for advanced optoelectronic materials.

Experimental

General information. All reactants and solvents, unless otherwise stated, were purchased from commercial sources and used as received. ¹H-NMR spectra were recorded on a Bruker 500 NMR spectrometer with Si(CH₃)₄ as the internal standard. Mass spectrometry was performed with a LTQ-ORBITRAP-ETD mass spectrometer. Elemental analysis was determined on an EA3000 elemental analyzer (Eurovector, Italy). Absorption spectra were recorded with a UV-vis spectrophotometer (Shimadzu UV-2450). PL spectra were recorded with a fluorospectrophotometer (Hitachi F-4600). The PL transient lifetimes were measured on a transient spectrofluorimeter Accepted Manuscript

(Edinburgh Instruments, FLSP920) with a time-correlated single-photon counting technique. The PLQY of the complex (excited at 390 nm) was measured in degassed CH₃CN solution with quinine sulfate ($\Phi_p = 0.545$ in 1 M H₂SO₄) as the standard.^[36] The PLQYs in thin films were measured on an absolute PLQY measurement system (Hamamatsu C11347) equipped with an integrating sphere. Cyclic voltammetry was performed on a LK1100 voltammetric analyzer in DMF solutions (10^{-3} M) at a scan rate of 100 mV/s, with a glass-carbon working electrode, a Ag wire pseudo-reference electrode and a Pt wire counter electrode. Tetrabutylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte and ferrocene was selected as the internal standard. The solutions were degassed with argon before measurements.

Synthesis of OXD-7-OBu-SO₃⁻K⁺

The 5-hydroxyisophthalohydrazide (1) intermediate was synthesized according to a reported procedure.^[37]

Synthesis of $(N'^{I}E,N^{3}E)-N'^{I},N^{3}-bis(4-(tert-butyl)benzylidene)-5-hydroxyisophthalohydrazide (2). To compound 1 (630 mg, 3 mmol) dissolved in ethanol (20 mL) was added 4-tertbutylbenzaldehyde (704 µL, 6.6 mmol). The reaction mixture was refluxed overnight under a nitrogen atmosphere and then cooled to room temperature. The precipitate was collected and recrystallized from ethanol, yielding a white powder (1.2 g, 2.4 mmol). Yield: 80%. ¹H-NMR (400 MHz, DMSO, <math>\delta$ [ppm]) δ 11.89 (s, 2H), 10.18 (s, 1H), 8.45 (s, 2H), 7.90 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 4H), 7.50 (m, 6H), 1.31 (s, 18H). HRMS (ESI, m/z): 497.25116 [M-H]⁻ (calc. 497.25581).

Synthesis of potassium 4-(3,5-bis((*E*)-2-(4-(tert-butyl)benzylidene)hydrazinecarbonyl) phenoxy)butane-1-sulfonate (3). Compound 2 (1.2 g, 2.4 mmol) and KOH (209 mg, 3.74 mmol) were dissolved in ethanol (40 mL). The reaction mixture was stirred for 0.5 h, To the solution, 1,4-butane sultone (288 μ L, 2.9 mmol) dissolved in ethanol (5 mL) was added. The reaction mixture was refluxed 10 h under a nitrogen atmosphere and then cooled to room temperature. The precipitate was collected and recrystallized from ethanol, yielding a white powder (1.2 g, 1.8 mmol). Yield: 75%. ¹H-NMR (500 MHz, DMSO, δ [ppm]) δ 11.96 (s, 2H), 8.52 (s, 2H), 8.03 (s, 1H), 7.71–7.64 (m, 6H), 7.50 (d, J = 8.0 Hz, 4H), 4.19–4.12 (m, 2H), 2.58–2.52 (m, 2H), 1.93–1.70 (m, 4H), 1.31 (s, 18H). HRMS (ESI, m/z): 633.26917 [M – K]⁻ (calc. 633.27523).

Synthesis of potassium 5-(3,5-bis(5-(4-(tert-butyl)phenyl)-1,3,4-oxadiazol-2-yl)phenyl)pentane-1-sulfonate (OXD-7-OBu-SO₃⁻K⁺). Compound 3 (1.2 g, 1.8 mmol), potassium carbonate (1.3 g, 9 mmol) and iodine (1.4 g, 5.4 mmol) were suspended in dry DMSO (10 mL). The reaction mixture was stirred at 100 °C under nitrogen atmosphere for 5 h and then cooled to room temperature. To the brown suspension, a solution of K₂S₂O₃ (5%) was added dropwise until the brown color disappeared. Saturated KCl solution was further added to the suspension to promote the precipitation of product. The precipitate was collected and purified by column chromatography on silica gel (200–300 mesh) with CH₂Cl₂/methanol (10: 1) as the eluent, yielding a white powder (901 mg, 1.35 mmol). Yield: 75%. ¹H-NMR (400 MHz, DMSO, δ [ppm]) δ 8.33 (t, *J* = 1.4 Hz, 1H), 8.17 – 8.10 (m, 4H), 7.85 (d, *J* = 1.4 Hz, 2H), 7.72 – 7.63 (m, 4H), 4.23 (t, *J* = 6.0 Hz, 2H), 2.57–2.52 (m, 2H), 1.95–1.75

(m, 4H), 1.35 (s, 18H). HRMS (ESI, *m/z*): 629.24164 [M–K]⁻ (calc. 629.24393).

Synthesis of complex 1

 $[Ir(ppy)_2(pzpy)]^+Cl^-$ was synthesized according to a reported procedure ^[31] and purified through column chromatograph before use. [Ir(ppy)₂(pzpy)]⁺Cl⁻ (204 mg, 0.3 mmol) was dissolved in deionized water/CH₃OH (10/10 mL). To the solution, OXD-7-OBu-SO₃K (200 mg, 0.3 mmol) dissolved in deionized water/CH₃OH (10/10 mL) was added dropwise under stirring. The mixture was further stirred at room temperature for 1 h and then filtered. The precipitate was collected, dried under vacuum and recrystallized from CH₂Cl₂/hexane, yielding a yellow powder (241 mg, 0.19 mmol). Yield: 63%. ¹H-NMR (500 MHz, DMSO, δ [ppm]) δ 9.32 (d, J = 3.0 Hz, 1H), 8.54 (d, J = 8.5 Hz, 1H), 8.37 – 8.31 (m, 2H), 8.27 (dd, J = 8.0, 3.1 Hz, 2H), 8.18 -8.11 (m, 4H), 8.00 - 7.94 (m, 2H), 7.93 - 7.82 (m, 4H), 7.77 (d, J = 6.0 Hz, 1H), 7.20 (d. J = 6.0 Hz, 1H), 7.70 - 7.63 (m, 5H), 7.56 - 7.51 (m, 1H), 7.29 (d, J = 2.0 Hz, 1) 1H), 7.27–7.17 (m, 2H), 7.05–6.95 (m, 2H), 6.93 – 6.82 (m, 3H), 6.19 (t, J = 8.0 Hz, 2H), 4.23 (t, J = 6.5 Hz, 2H), 2.55–2.51 (m, 2H), 1.95–1.75 (m, 4H), 1.35 (s, 18H). HRMS (ESI, *m/z*): 629.24408 [OXD-7-OBu-SO₃]⁻ (calc. 629.24393); 646.1598 $[Ir(ppy)_2(pzpy)]^+$ (calc. 646.1577). Anal. Calcd. (%) for $C_{64}H_{60}IrN_9O_6S$: C, 60.27; H, 4.74; N, 9.88. Found: C, 61.95; H, 4.85; N, 9.77.

Fabrication and characterization of OLEDs

ITO substrates (15 Ω/\Box) were cleaned in detergent and then in deionized water, and treated with UV-zone before use. The PEDOT: PSS layer was spin coated onto the ITO substrate in air and baked at 200 °C for 10 minutes. The PEDOT: PSS-coated

substrate was transferred into a nitrogen-filled glove box, in which the emissive layer was spin coated on top of PEDOT: PSS from 1, 2-dichloroethane solution. The film was then baked at 80 °C for 30 minutes to remove the residual solvent. The film-coated substrate was then transferred into a vacuum chamber, where the TPBI, LiF and Al layers were consecutively evaporated at evaporation rates of 1–2, 0.1–0.2 and 2–3 Å/s, respectively. The devices were characterized with Keithley 4200 semiconductor characterization systems. The EL spectra were collected with a Photo Research PR705 spectrophotometer in ambient conditions.

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