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A multifunctional ionic iridium complex for field-effect and light-emitting device

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We synthesized a new ionic iridium complex with interesting multifunction of both insulativity and light emission. With this material as gate dielectric, we have fabricated a multifunctional device which behaves as a normal transistor at low gate voltage and a light emitting device when the voltage is over 4 V. The emission brightness can be tuned by V_{GS} and V_{DS} separately. This device can potentially be applied in overvoltage alarm system.

Light-emitting complexes are of great interest as the rapid development of organic electronics.[1-5]Among these various compounds, ionic iridium complexes have caught much attention due to their high luminescent efficiency.[6-9] They are generally used in light-emitting electrochemical cells (LECs) which can work effectively at quite low voltage because of their operation mechanism.[10-12] Ionic compounds can not only be applied in LECs, but also in transistors where they serve as insulators to induce working voltage.[13,14] Therefore, iridium ionic complexes used as emitting materials in LECs have potential to be employed as dielectric materials in transistors as well, leading to realization of the fabrication of multifunctional devices. In this manuscript we synthesized a new ionic iridium complex and successfully fabricated a multifunctional device with it.

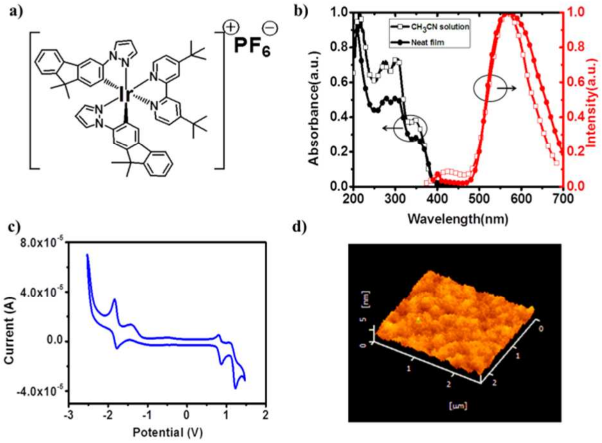

Fig. 1(a) Chemical structure of the ionic iridium complex [Ir(dmfpz)$_2$(dtb-bpy)]PF$_6$; (b) the absorption and photo luminescent (PL) spectra of the ionic complex in dilute CH$_3$CN solution and thin film; (c) cyclic voltammetry curves of iridium complex; (d) the atomic force microscopy (AFM) image of the ionic iridium complex dielectric layer.

The ionic iridium light-emitting complex [Ir(dmfpz)$_2$(dtb-bpy)]PF$_6$, shown in Fig. 1a, contains two kinds of ligands, 1-(9, 9-dimethyl-fluorene-2-yl)-1*H*-pyrazole (dmfpz) and 4,4'-Bis(tert-butyl)-2,2-bipyridine (dtb-bpy). These ligands have steric hindrance which enhance luminescent efficiency and improve stability.[15,16] Synthesis of the material are shown in Electronic Supplementary Information. Fig.1b exhibits the absorption and photo luminescent (PL) spectra of the ionic complex in dilute CH$_3$CN solution and thin film. The absorption spectra are typical for iridium complexes, with the absorption under 350 nm ascribing to 1π-π* transitions from ligands and the absorption above 350 nm corresponding to excitations to MLCT (metal to-ligand charge-transfer) and LLCT (ligand-to-ligand charge-transfer).[17] The PL spectra give a wide broad peak without refined structures, which belongs to MLCT and LLCT transitions. The electrochemical behaviour of this complex is investigated by cyclic voltammetry (Fig.1c). The oxidation potential of complex is 0.83 V, while the reduction potential is -1.81 V, indicating the HOMO and LUMO levels of this complex to be -5.57 eV and –2.93 eV and the level gap is 2.64 eV. The atomic force microscopy (AFM) image (Fig.1d) demonstrates the thin film of ionic iridium complex is smooth and homogeneous with the RMS of only 0.65 nm.

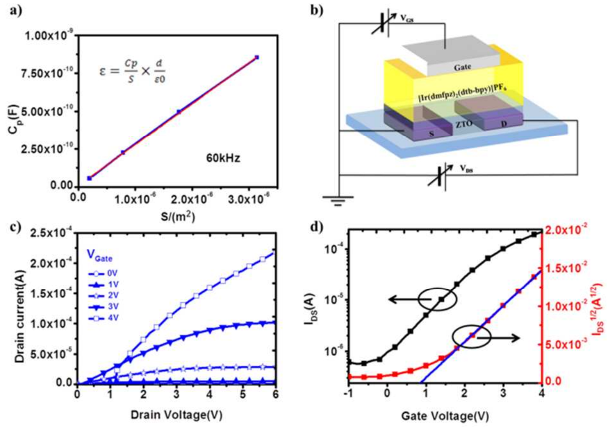

Fig.2(a) The capacitance information of iridium complex from which the dielectric constant is calculated by the expression inset (d: the thickness of film;ε_0:permittivity of vacuum); (b) sketch of the device; (c) the output curves of the device; (d) the transfer curves of the device.

The dielectric constant of the iridium complex film is measured to be 3.06 (Fig.2a). The device structure is shown in Fig.2b. Firstly, a zinc tin oxide (ZTO, a kind of n-type material with high optical transmittance and high mobility[18]) layer is deposited by spin-coating on a glass substrate with source and drain electrodes (ITO) on it, and then the gate dielectric film of $[Ir(dmfpz)_2(dtb\text{-}bpy)]PF_6$ is formed also by spin-coating. Finally, the gate electrode film of silver is deposited by thermal evaporation in vacuum. Details of fabrication process are presented in Electronic Supplementary Information.

Figure 2c shows the output characteristics of this top-gate-structured transistor. When the V_{GS} is lower than 4 V, the device exhibits normal n-type characteristics with the source electrode grounded. Fig.2d displays the transfer curves of the device. From this diagram we estimate on/off current ratio to be 250, electron mobility to be 48.3 $cm^2 V^{-1} s^{-1}$, while the threshold voltage V_T to be only 0.85 V. The low working voltage is attributed to the high capacitance of the electrical double layers (EDLs) formed at the gate-electrolyte and semiconductor-electrolyte interfaces and the large concentration of electrons on the surface of the semiconductor.[13,14]

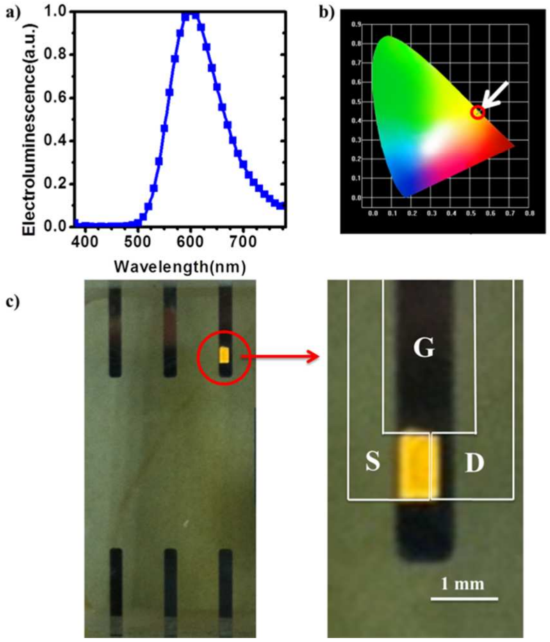

Fig.3 (a) Electroluminescent (EL) spectra of the device; (b)the CIE coordinates of the light emitted; (c) the photo of a working device (V_{GS}=5 V, V_{DS}=1V).

When the gate voltage becomes higher (over 4 V), the device acts as a controllable light-emitting electrochemical cell (LEC) rather than a transistor. Fig.3a shows the electroluminescent (EL) spectra of the device. The EL peak is at 600 nm. The red-shift of EL comparing with PL is because when applying a positive gate voltage to the device, an electric field will be formed, which polarizes the ionic complex and decreases the energy level of the excited states as a result.[19,20] The device gives orange light with the CIE coordinates of (0.55, 0.45) (Fig.3b). Fig.3c depicts the emission photos of this device. The emission is visible in ambient light through the source and drain ITO electrodes and the glass substrate. It is obvious that the device behaves like a LEC under a high gate voltage. However, different from a traditional LEC, this device has three electrodes rather than two, thus, we investigated functions of these three electrodes (gate, source and drain electrodes).

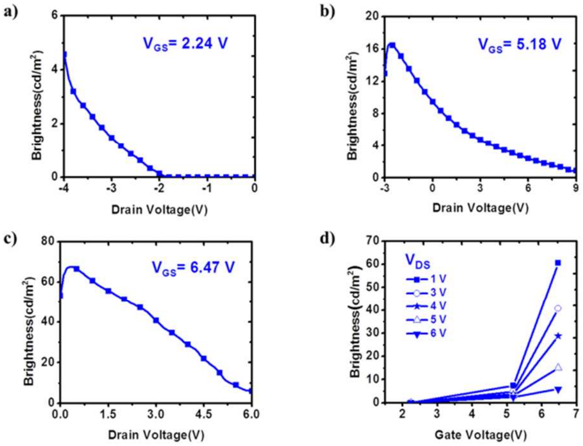

Fig.4 The control of brightness via V_{GS} or V_{DS}: (a) (b) (c) the control of brightness via V_{DS}; (d) the control of brightness via V_{GS}.

Fig.4a, 4b and 4c display the emission brightness at different gate voltages. From Figure 4a, we can find that, under V_{GS}=6.47 V and V_{DS}=0.3 V, the highest brightness is 67.7 cd m^{-2}. The changes of brightness versus the drain voltage are obvious in Fig.4(a-c), and this verified that at a settled gate voltage, the emission can be modulated by the drain voltage. The initial increase of brightness can be explained by the response time of the device. Moreover, from the three curves in Fig.4(a-c), it is clear that the gate voltage can also modulate the brightness. As summarized in Fig.4d, with the increase of the gate voltage, stronger emission can be observed from the device.

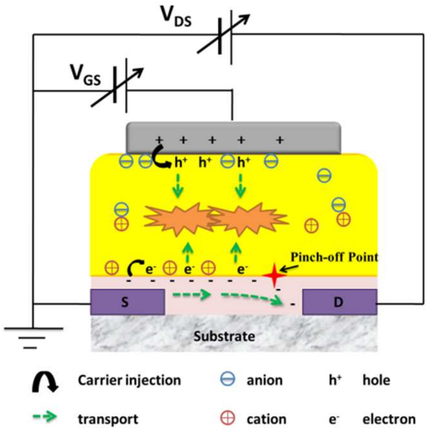

Fig. 5 Schematic representations of the device operation.

We suggest the operation mechanism of this multifunctional device as follows (Fig.5): when a positive voltage is applied to the gate electrode, PF_6^- will migrate towards the gate electrode, forming an electrochemical double layer. Meanwhile, $[Ir(dmfpz)_2(dtb\text{-}bpy)]^+$ left near the semiconductor will induce electrons in the semiconductor layer, forming another electrochemical double layer. In this state, the transistor operates as a normal field-effect transistor with low threshold voltage because of the two electrochemical double layers. With the increase of gate voltage, under the help of gate-source field and electrochemical double layer field, holes will be injected from the gate to the iridium complex while electrons from ZTO layer to iridium complex layer. Holes and electrons will drift to the bulk of the complex layer and recombine to give light emission. Because the recombining region is a parallel layer to the transparent substrate, it will achieve an area emission. At this time, the device acts as a controllable LEC. The drain electrode gives an electric field, forming a pinch-off point, which will influence the emission zone and brightness of the device. Such operation mechanism can also be explained and proved by energy level alignment of this light emission system (Fig.6).

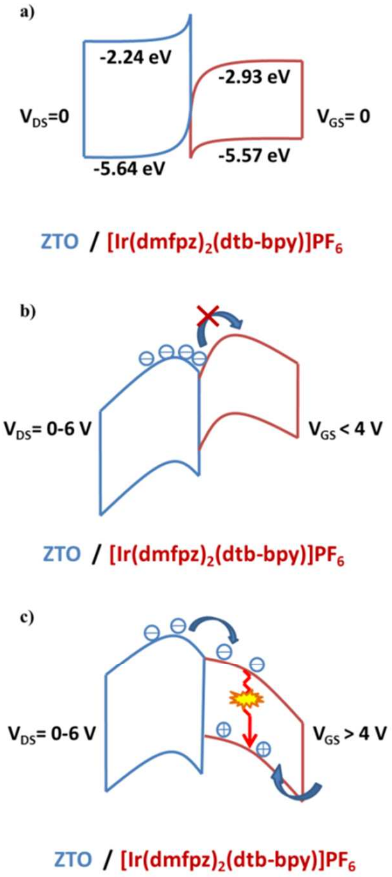

Fig. 6 Energy level diagram of the device in relation to the carrier injection and transport.

From Fig.6, it can be found that when gate voltage is lower than 4 V, electrons can accumulate near the interface of ZTO layer and the dielectric layer ([Ir(dmfpz)$_2$(dtb-bpy)]PF$_6$). Under V_{DS} of 6 V and V_{GS} smaller than 4 V, the energy band bending in ZTO is quite large, electron injection to the dielectric layer is forbidden, therefore, the device exhibits field effect rather than light emission characteristic. When gate voltage is higher than 4 V, the energy band bending in the dielectric layer benefits the injection of electrons from ZTO layer and holes from gate electrode to the dielectric layer and results in the light emission in the dielectric layer of the device.

The iridium complex layer plays an important role in the device performance. The film thickness may be one of the influential elements. When the gate voltage is lower than 4 V, the device is a kind of electrolyte-gated transistor. All the applied gate potential is dropped over EDLs and the capacitance of the electrolyte is essentially independent on its thickness, indicating the transistor performance is insensitive to the thickness of the iridium complex film.[14] When the gate voltage is over 4 V, the device behaves as a controllable LEC. Reports have stated that LECs are not quite sensitive to the thickness of light emitting layers.[21,22] However, as for LECs based on transition mental complexes, some device characteristics were found to be influenced by the thickness of active layers.[23] Therefore, the relationship between the film thickness and the device performance needs to be further investigated in our future research.

Conclusions

In summary, we have synthesized a multifunctional ionic iridium complex. With this complex, we have successfully fabricated a device behaving as a transistor or an emission device at different voltages. The emission brightness can be controlled by both V_{GS} and V_{DS} separately. The versatility of this complex is quite interesting and has potential to be used in overvoltage alarm devices.

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Notes and references

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